The Use of Tulsion-6812, Tulsion-63 and Amberlyst-16w in the Production of Biodiesel

Miriam Velle Osborg
Environmental Physics
PREFACE

The background of this thesis is a wish to test the usability of Tulsion-63, Tulsion-6812, and Amberlyst-16w in biodiesel production under a range of conditions. This master thesis is the result of a lab project at the Norwegian University of Life Sciences, Department of Mathematical Sciences and Technology.

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

Signature:

Ås, May 13th, 2016

Miriam Velle Osborg
ACKNOWLEDGEMENTS

During the last year, my advisor Professor Dr. Jorge Mario Marchetti has spent much of his time supervising this project and me. His support has been an absolute necessity for the progress of this project, and Dr. Marchetti has been an unreplaceable resource of experience and knowledge for the duration of my study on the master thesis.

I give my thanks to Mangesh Avhad for his time, advice, and assistance, during the lab work and with modelling in Aspen. I also express my gratitude to Alexander Hykkerud and Marcos Sánchez for the advice and time invested in assisting me in the early stages of the lab work.

I would like to show my gratitude to the Norwegian University of Life Sciences Department of Mathematical Sciences and Technology for providing financial support and an excellent study environment. I also give my thanks to the Thermax Inc., Chemical Division USA office for delivering the catalysts for my project.

Final thanks goes to my friends and family, to my friend Magnhild Skattebu, and to my fiancé Hans Emil Glestad for help and support during the whole process.

Thank you all so much

Miriam Velle Osborg
ABSTRACT

Biodiesel, a renewable fuel of a vegetal origin is continuously getting more pronounced. Fossil fuels are finite resources and a contributing factor to environmental change [1], making biodiesel an important environmental friendly alternative. In the process of making biodiesel competitive with the price of fossil fuels, the use of a heterogeneous catalyst is a measure worth considering. Heterogeneous catalysts have the advantages of being able to reduce product rinsing and obtain reusability. This leads to the purpose of this study, presenting a screening of operation variables effects on the catalysed alcoholysis processes. Acetic acid and ethanol was used in an esterification reaction with three different heterogeneous catalysts. In the conclusions, it is stated that Tulsion-6812 and Tulsion-63 needs further study on catalyst rinsing. Due to severe leaching, they are not preferable in the matter tested in this study. Untreated Amberlyst-16w had no leaching, and the parameters tested provided a trend of higher conversions with higher temperatures. Further, it spent shorter time spent until reaching equilibrium with higher catalyst amount. The reaction yielded faster reaction rates with low molar ratios, although higher final conversions with higher molar ratios were obtained. The Amberlyst-16w catalyst is also proved to be reutilized four times.

SAMANDRAG

Biodiesel er eit drivstoff med opphav frå vegetabiliske oljer, som stadig vekker større interesse. Fossile drivstoff er ein avgrensa ressurs som også bidrege til klimaendringar[1], dette gjer biodisel til eit viktig miljøvenleg alternativ. For å gjere biodiesel meir konkurransedyktig er val av katalysator viktig. Heterogene katalysatorar har fordelar som å vere gjenbrukbare og kan til dømes filtrerast ut av produkta etter bruk, som igjen reduserer naudsynt reinsing av produkta. I dette studiet har tre heterogene katalysatorar vorte testa. Eddiksyre og etanol var reaktantar i esterifiseringsreaksjonen. Tulsion-6812 og -63 fungerer dårlig som heterogene katalysatorar i prosessane testa i dette studiet. Ubehandla Amberlyst-16w hadde ingen lekkasje, og har følgande trendar; å gi høgre konversjon med høgare temperaturar, raskare nå likepunktet med høgre katalysatormengde og raskare reaksjonshastighet ved lågare molar rate men nå høgre sluttkonversjonar med høgre. Amberlyst-16w viste seg gjenbrukbar minst fire gongar.
CONTENTS

List of Figures .............................................................................................................. VII
List of Tables ................................................................................................................ IX

1 Introduction .............................................................................................................. 1

2 Theory ....................................................................................................................... 2

2.1 Biodiesel Basics ................................................................................................. 2

2.2 Catalyst ............................................................................................................... 6

2.2.1 Homogeneous Catalysts ............................................................................... 7

2.2.2 Heterogeneous Catalysts ............................................................................ 9

2.2.3 Tulsion-63 MP Dry ................................................................................... 10

2.2.4 Tulsion-6812 ........................................................................................... 11

2.2.5 Amberlyst-16w ......................................................................................... 11

2.3 Reactants ............................................................................................................. 13

2.4 Industrial Perspective ......................................................................................... 13

2.5 Environmental Aspect ....................................................................................... 15

2.6 Diesel Engine ..................................................................................................... 17

2.7 Properties of Fossil Diesel and Biodiesel .......................................................... 17

2.8 Advantages with Biodiesel ............................................................................... 20

2.9 Disadvantages with Biodiesel .......................................................................... 20

2.10 Industrial Production of biodiesel .................................................................. 20

2.10.1 Reactors ...................................................................................................... 22

2.10.2 Reaction Rates ........................................................................................... 23

2.10.3 Conversions ............................................................................................... 24

2.11 Reaction Mechanisms ...................................................................................... 25

2.11.1 Acid Transesterification Mechanism ......................................................... 25

2.11.2 Esterification Mechanism ......................................................................... 27

2.12 Titration ............................................................................................................. 28

2.13 Developing a Kinetic Model ............................................................................ 29

3 Materials and Methods ......................................................................................... 32

3.1 Materials ............................................................................................................. 32

3.2 Equipment .......................................................................................................... 33

3.3 Methods .............................................................................................................. 35

3.3.1 Running the Batch Reactor ......................................................................... 35

3.3.2 Catalyst Pre-treatment ............................................................................... 36
3.3.3 Catalysts Leaching Tests ................................................................. 36
3.3.4 Reaction Experiments ................................................................. 36
3.3.5 Reuse Test .............................................................................. 37
3.3.6 Determination of Biodiesel Conversion ................................. 37
3.3.7 Kinetic Modelling in Aspen ......................................................... 38
4 Results and Discussion ................................................................. 39
  4.1 Tulsion-63 .......................................................................... 39
    4.1.1 Reactions with Tulsion-63 ................................................. 42
  4.2 Tulsion-6812 .................................................................. 42
    4.2.1 Tulsion-63 and Tulsion 6812 .......................................... 47
  4.3 Amberlyst-16w ................................................................. 48
    4.3.1 Weight Change of the Catalyst ......................................... 52
    4.3.2 Un-treated Amberlyst-16w Compared to Dried Amberlyst-16w  54
    4.3.3 Effect of Catalyst Amount ........................................... 58
    4.3.4 Effect of Molar Ratio .................................................... 59
    4.3.5 Effect of Temperature .................................................. 60
    4.3.6 Reuse of Amberlyst-16w ................................................. 62
    4.3.7 Evaluation of Experimental Errors in this Work .............. 64
    4.3.8 Components in the Reaction ......................................... 65
    4.3.9 Non Tested Parameters ................................................. 65
    4.3.10 Kinetics Modelling ...................................................... 66
5 Conclusions .......................................................................... 72
  5.1 Tulsion-6812 and Tulsion-63 ............................................... 72
  5.2 Amberlyst-16w ................................................................. 72
6 Future Work ........................................................................ 73
7 References ........................................................................ 74
8 Appendix ................................................................................ A
  8.1 List of Experiments .............................................................. A
  8.2 The Script Used in Aspen ..................................................... E
  8.3 Results From Modelling in Aspen .......................................... F
    8.3.1 Surface Reaction as Controlling Step ............................ F
    8.3.2 Adsorption as Controlling Step .................................... H
    8.3.3 Desorption as Controlling Step .................................... J
NOMENCLATURE

FA  Fatty Acid
FAE Fatty Acid Ester
FAAE Fatty Acid Alkyl Ester
FAEE Fatty Acid Ethyl Ester
FAME Fatty Acid Methyl Ester
FFA Free Fatty Acid
MG Monoglyceride
DG Diglyceride
TG Triglyceride
N Molar ratio (alcohol: fatty acid)
C Catalyst amount in percentage of fatty acids
T Temperature (°C)
rpm rotations per minute

A Alcohol, type: Ethanol
S Active site on catalyst, type: Amberlyst-16w
FA Fatty acid, type: Acetic Acid
BD Biodiesel
W water
AS Alcohol connected to a catalyst active site
BDS Biodiesel connected to a catalyst active site
LIST OF FIGURES

Figure 1: Example of a mixed TG with different lengths and number of double bounds in the FAs. ... 2
Figure 2: The structure of Glycerol ........................................................................................................ 2
Figure 3: The structure of a FFA which has different lengths, number and placement of bounds. ....... 3
Figure 4: A general transesterification reaction .................................................................................... 4
Figure 5: A general esterification reaction ............................................................................................ 4
Figure 6: Concentrations of component A and component B during an equilibrium reaction............ 5
Figure 7: Potential energy between reactants and products without catalyst (E1) and with catalyst (E2) ........................................................................................................................................... 6
Figure 8: Saponification process, here shown with sodium hydroxide working as a homogeneous base catalyst.......................................................................................................................... 7
Figure 9: A general esterification reaction ........................................................................................... 8
Figure 10: A general hydrolization reaction, shown for MG ................................................................. 9
Figure 11: Human population in the world given in millions .............................................................. 14
Figure 12: Consumed petroleum fuels, given in units of million barrels per day. .............................. 14
Figure 13: Global production of biodiesel given in thousands barrels per day from 2002 to 2012 ..... 22
Figure 14: A general mechanism for transesterification reaction for a homogeneous acid catalyst ... 26
Figure 15: A qualitative plot of conversion during a transesterification reaction.............................. 27
Figure 16: A general mechanism of an esterification reaction for a homogeneous acid catalyst ...... 28
Figure 17: The colour of the liquid with acid content ........................................................................... 29
Figure 18: The colour of the liquid with neutral content (light pink).................................................... 29
Figure 19: The colour of the liquid with base content ......................................................................... 29
Figure 20: Illustration of the three reaction steps, here illustrated with a chosen reaction model. ..... 30
Figure 21: Tulsion-63 in the container .................................................................................................. 32
Figure 22: Tulsion-6812 in the container .............................................................................................. 32
Figure 23: Amberlyst-16w direct from the container .......................................................................... 32
Figure 24: The glass batch reactor used with magnetic stirrer, needle to take samples, cooling device on the top, and device to measure the temperature. The reactor could be opened at the middle. ....... 34
Figure 25: The warm water bath, heating water to a given temperature and sending it through the outer container to heat the content of the inner .............................................................................. 34
Figure 26: The batch reactor under operation with 400 mL volume in the reactor, 200rpm stirring ... 35
Figure 27: T-63 and 96% ethanol before stirring, T=ambient.............................................................. 41
Figure 28: T-63 and 96% ethanol after 120 minutes stirring, T=ambient............................................. 41
Figure 29: T-63 remains after 120 minutes stirring in 96% ethanol ........................................ 41
Figure 30: T-63 rinsed in absolute ethanol after a leaching test with absolute ethanol on filter paper. 41
Figure 31: T-6812 initially after addition of rectified ethanol to the untreated catalyst, T=ambient ... 44
Figure 32: T-6812 after stirring with magnetic stirrer in rectified ethanol for 120 min, T=ambient .... 44
Figure 33: T-6812 remaining after 120 minutes of reaction with rectified ethanol ........................... 44
Figure 34: T-6812 rinsed in ethanol after leaching test with absolute ethanol on filter paper .......... 45
Figure 35: T-6812 used in reaction with absolute ethanol, which has laid over a week on aluminium foil, corroding through the foil ................................................................. 45
Figure 36: Conversion over time for reaction with Tulsion-6812 with acetic acid and ethanol with N=10, C=2, T=65 ................................................................. 46
Figure 37: Untreated Amberlyst -16w right after addition of absolute ethanol to the beaker ........... 49
Figure 38: Untreated Amberlyst-16w and absolute ethanol after 120 minutes mechanical stirring .... 49
Figure 39: Remaining Amberlyst -16w after filtering out the liquid ............................................. 49
Figure 40: Dried catalyst right after addition of absolute ethanol to the beaker ............................. 50
Figure 41: Dried catalyst and absolute ethanol after 120 minutes stirring in the beaker ............... 50
Figure 42: Amberlyst-16w after filtering out the liquid ............................................................... 50
Figure 43: Dried Amberlyst-16w right after addition of ethanol 96% to the beaker ..................... 51
Figure 44: Dried Amberlyst-16w after stirring with ethanol 96% for 120 minutes in the beaker ...... 51
Figure 45: Amberlyst-16w after filtering out the liquid, after 120 minutes stirring ....................... 51
Figure 46: Weight of untreated Amberlyst-16w over time when exposed to air ............................ 52
Figure 47: Weight gain of dried catalyst due to air exposure over time, with a visually drawn trend line ................................................................................................................. 53
Figure 48: A picture of the catalyst straight from the container is shown to the left, to the right is the untreated catalyst after air exposure for over three days ........................................ 54
Figure 49: Dried catalyst compared to catalyst directly from the container, N=6, C=5%, T=60°C and stirring at 200rpm ........................................................................................................ 55
Figure 50: Dried catalyst and untreated catalyst with similar number of beads used in both reactions compared to acetic acid with N=6, T=60°C and stirring at 200rpm ........................................ 56
Figure 51: Pictures from microscope showing the untreated catalyst ......................................... 57
Figure 52: Pictures from microscope showing the catalyst dried for 24 hours at 65°C ..................... 57
Figure 53: Effect of catalyst amount, N=6, T=60°C and stirring at 200rpm ................................. 58
Figure 54: Effect of molar ratio tested with C=5%, T=60°C and stirring at 200rpm ....................... 59
Figure 55: Effect of temperature tested with temperatures with N=6, C=5% and stirring at 200rpm . 61
Figure 56: Reuse of catalyst from experiment with N=9, C=5%, T=60 and stirring at 200rpm, all runs are with the same parameters and treatment between runs ........................................... 62
Figure 57: Pictures from the microscope showing the used catalyst to the right comparing with the unused catalyst to the left. ........................................................................................................................................ 63
Figure 58: Surface reaction model with experimental data, T=60°C, C=5%, N= 6 ................................. 67
Figure 59: Surface reaction model with experimental data, T=70°C, C=5%, N= 6 .............................. 67
Figure 60: Surface reaction model with experimental data, T=60°C, C=5%, N= 9 ............................. 68
Figure 61: Surface reaction model with experimental data, T=60°C, C=15%, N= 6 .......................... 68
Figure 62: Adsorption model with experimental data, T=60°C, C=5%, N= 6 ................................. 69
Figure 63: Adsorption model with experimental data, T=70°C, C=5%, N= 6 ................................. 69
Figure 64: Adsorption model with experimental data, T=60°C, C=5%, N= 9 ................................. 69
Figure 65: Adsorption model with experimental data, T=60°C, C=15%, N= 6 ............................... 69
Figure 66: Desorption model with experimental data, T=60°C, C=5%, N= 6 ................................. 70
Figure 67: Desorption model with experimental data, T=70°C, C=5%, N= 6 ................................. 70
Figure 68: Desorption model with experimental data, T=60°C, C=5%, N= 9 ................................. 70
Figure 69: Desorption model with experimental data, T=60°C, C=15%, N= 6 .............................. 70

LIST OF TABLES

Table 1: Different vegetable oils with appurtenant FFA-values [4].......................................................... 3
Table 2: Typical characteristics of T-63 from Thermax [13] ................................................................. 11
Table 3: Typical characteristics T-6812 MP [15] ...................................................................................... 11
Table 4: Typical Characteristics Amberlyst-16w ..................................................................................... 12
Table 5: Properties of diesel and biodiesel fuels ................................................................................... 19
Table 6: Top 10 countries in biodiesel production with amount produced given in billions litres ...... 21
Table 7: Results from leaching tests Tulsion-63 .................................................................................... 40
Table 8: Results from leaching tests Tulsion-6812 ............................................................................... 43
Table 9: Results from leaching tests Amberlyst-16w .............................................................................. 48
1 INTRODUCTION

Biodiesel is being increasingly recognized as an alternative to traditional fuels. The main arguments for the usage of biodiesel are the several environmental benefits, and that the amount of available petroleum is steadily decreasing. Fossil fuels are also finite and a contributing factor to environmental change [1]. Vegetable oil has been a known fuel since the 1930s but has not been a popular alternative due to the low cost of petrol. Biodiesel is a renewable fuel source when produced accordingly. Another advantage is that biodiesel does not demand a significant change in the vehicle [2], compared to other fuel alternatives, although slight motor changes are recommended. Currently production costs of biodiesel are still high compared to those of current fossil diesel fuel [3]. One way to reduce production costs and make biodiesel more competitive compared to traditional diesel, is by reducing the cost of the catalyst, and expand the possibilities of usable feedstocks [1].

The most common catalysts are homogeneous catalyst, predominantly because of their price and fast reaction rates [3]. On the contrary, the cost from aqueous quenching, rinsing of wastewater and loss of catalyst gains to the total cost [3]. Therefore, an alternative is needed. Changing to heterogeneous catalysts may become an excellent way to strongly reduce product rinsing and production costs [1, 3]. Still ongoing research is testing different types of heterogeneous catalysts that can be filtered from the product after use, which in return can avoid expensive rinsing processes [3].

This study will test the three heterogeneous catalysts, Tulsion-68, Tulsion-6813, and Amberlyst-16w, for use in biodiesel production through esterification reaction. All reaction experiments are run with ethanol and acetic acid as reactants in a simple batch reactor. The effects of different molar ratio, amounts of catalysts and temperatures are tested on the reaction. An attempt on writing the kinetics will be given for the catalyst with the best results.
2 THEORY

2.1 BIODIESEL BASICS

Biodiesel is a fuel from a mixture of FAME with methanol, or FAEE when ethanol is involved. These esters are derived from TGs with different FAs attached. See Figure (1).

\[
\begin{align*}
\text{H}_2\text{C} & \text{-} \text{O} \text{-} \text{C} \text{-} \text{CH}_2(\text{CH}_2)_{11}\text{CH}_3 \\
\text{H} & \text{-} \text{O} \text{-} \text{C} \text{-} \text{CH}_2(\text{CH}_2)_{13}\text{CH}_3 \\
\text{H}_2\text{C} & \text{-} \text{O} \text{-} \text{C} \text{-} (\text{CH}_2)_7\text{CH} \equiv \text{CH} (\text{CH}_2)_7\text{CH}_3
\end{align*}
\]

**Figure 1:** An example of a mixed TG with different lengths and number of double bounds in the FAs.

TGs are made up of a Glycerol structure with three FAs instead of the glycerol’s three hydroxyl groups. To illustrate, the structure of Glycerol is shown in Figure (2).

\[
\begin{align*}
\text{H} & \text{-} \text{C} \text{-} \text{C} \text{-} \text{C} \text{-} \text{H} \\
\text{OH} & \text{-} \text{OH} \text{-} \text{OH}
\end{align*}
\]

**Figure 2:** The structure of Glycerol

The different FAs in Figure (1) are defined by the amount of double bounds and the length of the chain. Some examples of compositions of FAs in vegetable oils, are shown in Table (1) [4].
Table 1: Different vegetable oils with appurtenant FFA-values [4]

<table>
<thead>
<tr>
<th>Vegetable oil</th>
<th>FFA-level [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rape seed oil</td>
<td>2.0</td>
</tr>
<tr>
<td>Tall oil</td>
<td>100</td>
</tr>
<tr>
<td>Jatropha oil</td>
<td>14.0</td>
</tr>
<tr>
<td>Acid oil</td>
<td>59.3</td>
</tr>
<tr>
<td>Crude soybean oil</td>
<td>0.4 - 0.7</td>
</tr>
<tr>
<td>Animal fat</td>
<td>5 - 30</td>
</tr>
<tr>
<td>Used cooking oil</td>
<td>2.0 – 7.0</td>
</tr>
<tr>
<td>Waste oil</td>
<td>46.8</td>
</tr>
</tbody>
</table>

Not all FA are bound to glycerol. These are called FFA and an example of these is shown in Figure (3).

![Figure 3: The structure of a FFA which has different lengths, number and placement of bounds.](image)

Esters are commonly produced in the reaction of a carboxylic acid and an alcohol. This is a slow reaction and can use several days to reach equilibrium in the absence of a catalyst, or the reaction will never occur [5]. Therefore, a component with catalytic behaviour is most often used. The exception is when the reaction is taking place with high pressure and/or heat, in a supercritical reaction, when a catalyst might be redundant [2].

To provide a basic understanding of the production of biodiesel, the transesterification reaction is also presented in this study. Most biodiesel is produced by the transesterification of TG from oils using an alkaline catalyst and an alcohol, typically methanol, which is shown in Figure (4) [1]. The transesterification is a reversible reaction of a fat or oil with an alcohol to form FAAE and glycerol.
Figure (4) shows the resulting reaction. The figure fails to illustrate that the TGs are converted stepwise first into DGs, then MGs and in the end glycerol yielding one FAAE in every step of the reaction. When all the TGs in the reaction mixture have yielded three FAAE the conversion is complete.

In this study ethanol and acetic acid were used with the catalyst. This results in a different reaction type called esterification. The transesterification reaction requires a minimum ratio at 3:1 alcohol to FA, for a complete conversion of alcohol to oil [6]. The esterification reaction can complete on lower ratios. This is a one-step reaction and is shown in Figure (5).

The reactions shown in Figure (4) and (5) are equilibrium or two sided reactions. In these types, the reaction can go both ways yielding both product and reactants. When the reaction reaches a point where the reaction rates in each direction is equal, it will have reached its equilibrium point. This results in a total reaction rate of zero. With different measures, the equilibrium point can be shifted to either side. These are important tools in the production of biodiesel.
Le Chatelièr’s principal states that when a changed condition, or stress, is applied to a system in equilibrium, the system will always try to absorb the effect of stress by shifting to a new equilibrium point [7]. To make the reaction yield the highest possible conversion rate of biodiesel, a shift in equilibrium point is desired. Some common methods for shifting an equilibrium is to increase the amount of one of the reactants, remove one of the products, change the temperature, or change the pressure [7]. In this reaction, increasing the amount of alcohol will force more of the acetic acid to react, which will shift the equilibrium to the right yielding more products. Similarly removing glycerol or biodiesel while the reaction is ongoing, shifts the equilibrium to the products. Figure (6) illustrates a reaction with a component A yielding component B before resulting in an equilibrium state over time.

![Figure 6: Concentrations of component A and component B during an equilibrium reaction](image)

This types of reactions with acetic acid and ethanol as reactants, normally takes place at 60-80 °C [1]. Lower temperatures are desirable due to lower heating expenses in industrial production on the contrary this may lower the reaction rate. Below a certain temperature, depending on the catalyst, the reaction might not take place.
2.2 CATALYST

Esterification can take place under ambient conditions where the process may be slow with a low yield. The yield can be increased by elevating temperature, pressure, molar ratio etc., but frequently results in uneconomical processes [2]. Yields of production may also be increased using a catalyst. Catalysts increases the reaction rate without actually interfering with the products by being consumed itself [5]. It can improve a process by accelerating reaction rates or making a reaction possible at lower temperatures [2]. A catalyst reduces the activation energy for a reaction and allows a reaction to use less energy. Figure (7) is an illustration of this concept.

![Figure 7: Potential energy between reactants and products without catalyst (E1) and with catalyst (E2)](image)

Both acid and base catalysts are used in biodiesel production. An acid catalyst function by freeing more H\(^+\) to the mixture and splitting the mono alkyl esters from the remaining Glycerol. A base catalyst will free more OH\(^-\) to the mixture to split the esters. These two types of catalysts are again divided in two groups, called heterogeneous and homogeneous catalysts. A homogenous catalyst is in the same phase as one of the reactants [8]. A heterogeneous catalyst is in a different phase as both of the reactants in the process, resulting in these groups of catalyst having different characteristics and qualities.

Homogeneous catalysts quickly got accepted in the industry given grounds for by their fast reaction rates and low prices, and are commonly used today. Post-production costs from rinsing the products, wastewater, and loss of the catalyst inspired the search for alternatives [3].
The heterogeneous catalysts have advantages like being easier to remove from the products, providing the least expensive rinsing processes, and being easier to handle [9]. Furthermore, heterogeneous catalysts help supressing side reactions favouring a higher purity and selectivity of the products [10]. Still the heterogeneous base catalyst requires refined feedstocks, resulting in feedstocks accounting for 88% of the final production costs. To develop a production process with reduced costs there is a need for a catalyst that can use less refined feedstocks [3, 6].

The alternative to use of catalyst, is the possibility of increasing the reaction rate by using higher temperatures and pressures. A process with these characteristics is called a supercritical process. This process and the use of alternative catalysts are not mentioned further in this report. A report by West et al. [6] showed that solid acid catalysed processes are more economical than the supercritical process, homogeneous acid and alkali catalyst. The process and materials used were sufficiently sized unit blocks for less error when assessing the process. Four processes were run with homogeneous alkali and acid catalyst, heterogeneous acid catalyst and a supercritical process. All four processes produced biodiesels at high quality, though the heterogeneous acid catalyst and the supercritical process were the least complex processes. Manufacturing costs and capital investment were also evaluated, resulting in the heterogeneous acid catalyst as the best process with criteria given [6].

2.2.1 Homogeneous Catalysts

In a homogeneous catalytic process, the catalysts blend in with the reactants. Homogenous catalysts are often cheaper than the heterogeneous, and are frequently used for this reason and those previously mentioned.

Figure 8: Saponification process, here shown with sodium hydroxide working as a homogeneous base catalyst
Homogeneous base catalysts are the fastest of these types of catalyst. Although they are commonly used, they require high quality raw materials. With a need for low FFA numbers and high refinement of the oils used, the result is often the use of expensive reactants, or high costs of refinement of the raw materials. Another drawback is the risk of saponification. The product from Figure (8) becomes increasingly more common with increasing amount of FFA in the feedstock. Saponification is a non-reversible process which lowers the overall yield due to FFA converting into soaps, which will consume catalyst [2] as shown in Figure (8). The saponification also causes problems in the separation step, creating an emulsion between the biodiesel and the glycerol [2]. In addition, the saponification reaction produces water which may function as a catalyst inhibitor.

Acid catalyst can use less refined raw materials due to no risk of saponification from the FFA. These types of catalyst are frequently employed to take advantage of cheaper feedstocks as animal-based oil, or waste cooking oil. On the contrary, homogenous acid catalysts are generally slower than homogeneous base in the transesterification reaction [6].

When using feedstocks with high content of FFA, the commonly used method is esterification reactions with a low cost homogeneous acid catalyst. This reaction is shown in Figure (9).

![Figure 9: A general esterification reaction](image)

Another problem with acid based homogeneous catalysts are the deactivation of the catalyst due to hydrolization from the water. Hydrolization occurs when the water produced in a reaction reacts again with TG, MG, or DG promoting a reverse reaction [11]. The hydrolization reaction is shown for MG in Figure (10).
2.2.2 Heterogeneous Catalysts

In a heterogeneous catalyst, the reactants have to interact with the surface of the catalyst for the catalyst to give the desired effect. This makes the form and mass of the catalyst central, and the weight a better measurement than the volume. An ideal heterogeneous catalysts have the advantages of being reusable and limits the need of product rinsing, compared to homogeneous catalysts. Well-functioning heterogeneous catalysts can easily be removed from the reaction mixture by decantation and filtration [6]. Other advantages are less potential contamination in waste streams due to easier product separation, and reduced equipment corrosion compared to homogeneous acid catalysts. This is due to the fact that the only acidity in the reaction fluid is the acid from potential leaching of the catalyst [2].

Using a satisfactory heterogeneous catalyst may also give the opportunity to use continuous flow processes as long as the decay of the catalyst used allows it [3]. A fixed bed reactor keeps the catalyst inside and eliminates the entire catalyst removal and rinsing step [2]. Criteria’s for a heterogeneous acid catalyst can be listed as follows; environmentally friendly (both in production and in use), high density of active sites, easily recyclable, less discharges, high thermal stability, less separation difficulty, and low cost of separation [4, 9].

A large number of active sites are favourable. A catalyst with high porosity will have increased surface area for reaction with the reactants. The pores do however also need to be adequately large for the stoichiometry of the reactants. If the pores are too small the large
glycerides and alcohols will have problems reaching the active sites of the catalyst. The reusability is also an important factor. Heterogeneous catalysts boast of being reusable. Reusability demands a high stability of the catalyst, a low deactivation factor and a low degree of leaching. A drawback with heterogeneous catalysts is that due to their solid form, diffusion limits the reaction [12].

Heterogeneous base catalysts are, as mentioned, faster in the transesterification reaction than acids. Base catalyst sets higher demands on purification of feedstock to prevent saponification. An acid catalyst is more insensitive to FFA [9], and presents no danger of saponification. A factor that favours heterogeneous acid catalysts when producing biodiesel from low quality feedstocks. The extra cost from the slow reaction rates could be compensated with the reduced cost of being able to use a lower quality feedstock [11].

Heterogeneous acid catalysts also have a tendency to get deactivated by water. The presence of water in bio-oils can reduce biodiesel production significantly. An effective, reusable, low cost heterogeneous catalyst with resistance to water, and satisfactory performances with low temperatures and pressures is needed. Solid catalysts with ordered and large pores could minimise diffusion limitations and moderate strong acid sites to overcome the presence of impurities mainly from FFA in feedstocks [12].

2.2.3 Tulsion-63 MP Dry

Tulsion-63 is a strong acid exchange resin catalyst with large pores, using nuclear sulfonic acid as functional groups. The high surface area accesses a high number of functional groups for the reaction, which again results in a higher yield [13]. The catalyst is made of a macroreticular polymeric material which is based on cross-linked styrene di-vinyl benzene copolymers [14].
Table 2: Typical characteristics of T-63 from Thermax [13].

<table>
<thead>
<tr>
<th>Typical Characteristics Tulsion-63</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Type</strong></td>
</tr>
<tr>
<td><strong>Matrix structure</strong></td>
</tr>
<tr>
<td><strong>Functional group</strong></td>
</tr>
<tr>
<td><strong>Physical form</strong></td>
</tr>
<tr>
<td><strong>Particle size</strong></td>
</tr>
<tr>
<td><strong>Moisture content</strong></td>
</tr>
<tr>
<td><strong>Thermal stability</strong></td>
</tr>
</tbody>
</table>

2.2.4 Tulsion-6812

Similar to Tulsion-63 is also a strong acid exchange resin. Large pores help rapid diffusion of the reactants into the active sites, which increases the total reaction rate [15]. In general, Tulsion-6812 is similar to Tulsion-63, having matrix structure as one of the main differences.

Table 3: Typical characteristics T-6812 MP [15]

<table>
<thead>
<tr>
<th>Typical Characteristics Tulsion-6812 MP</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Type</strong></td>
</tr>
<tr>
<td><strong>Matrix structure</strong></td>
</tr>
<tr>
<td><strong>Functional group</strong></td>
</tr>
<tr>
<td><strong>Physical form</strong></td>
</tr>
<tr>
<td><strong>Particle size</strong></td>
</tr>
</tbody>
</table>

2.2.5 Amberlyst-16w

Amberlyst-16w is also in the ion exchange family, the Amberlyst catalysts typically have large pores [3]. Where Amberlyst-16w is in the lower spectra with pore size closer to medium. Typically, Amberlyst catalysts consists of cross linked poly-esterens with functional
groups added. The name of the polymer used in Amberlyst-16w is not known. The functional
groups are sulfuric acid, which are the active sites for the reaction. The spherical beads are the
size of 200-800 microns [2]. More data of Amberlyst-16w is found in Table (4) based on
information by Dow [16, 17].

Table 4: Typical Characteristics Amberlyst-16w

<table>
<thead>
<tr>
<th>Typical Characteristics Amberlyst-16w</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
</tr>
<tr>
<td>Matrix structure</td>
</tr>
<tr>
<td>Functional group</td>
</tr>
<tr>
<td>Concentration of active sites</td>
</tr>
<tr>
<td>Harmonic mean size</td>
</tr>
<tr>
<td>Physical form</td>
</tr>
<tr>
<td>Particle surface</td>
</tr>
<tr>
<td>Average pore diameter</td>
</tr>
<tr>
<td>Moisture content</td>
</tr>
<tr>
<td>Thermal stability</td>
</tr>
</tbody>
</table>

The mesoporous structure provides space for higher percentage of active sites but with
big reactants, it may hinder mass transfer. On this issue, bigger pores will give a higher mass
transfer [3]. In addition, producing water as a secondary product will make the water cover the
active sites and block them for adsorption of organic molecules. A way to minimize this and
maintain the activity is by having a solid catalyst with many acid sites [3]. Giving an advantage
for catalysts like Amberlyst-16w.

Amberlyst-16w was tested in an earlier study by Tesser et al. [18]. In this study, the
catalyst was dried at 100°C for 24 hours in a ventilated oven before use. The esterification
reaction was run with methanol and oleic acid as reactants [18].

Amberlyst-16w has also been tested for esterification purposes by Ösbay et al. [19],
where the aim of the study was to compare activities of different strong acidic ion-exchange
resins for FFA esterification. The reaction was done with waste cooking oil as FFA and
methanol as the alcohol [19]. From our knowledge, no article has been written on Amberlyst-16w with acetic acid and ethanol, or with the catalyst without untreated pre-treatment.

2.3 Reactants

The choice of reactants forms the reactions. The choice of feedstock is as already mentioned important for the transesterification and esterification processes, and the type of FFA is central when choosing catalyst and process. The feedstock used in this research is acetic acid. Acetic acid is one of the smaller fatty acids having less problems with mass transfer due to the size of pores compared to reactants.

Similarly, the choice of alcohol will affect the reaction. Ethanol provides the opportunity to produce a truly bio based FAE. Methanol is typically produced from non-renewable natural gas, while ethanol is available from fermentation of sugar canes [2]. The use of alcohol might vary according to availability and price. Heavier alcohols are generally costlier. Methanol is commonly used on these premises [2].

Ethanol has some technical challenges. Alcohols with longer carbon chains decreases the solubility and hinders rapid reactions, resulting in more time consuming reactions with longer carbon chain lengths [2].

2.4 Industrial Perspective

With the demand for fuel increasing and the traditional fossil fuels sources being drained by years of consumption, alternative fuels sources are being tested. Population growth and the ongoing industrialization of the world causes an increasing demand for energy resources [20]. Diesel and Gasoline are still the main driving force in the industrial world, linking it together by shipping, land and air transport [3, 20]. This is crucial for the world economy, opening up for trade inside and outside country borders. In 2013 the transport sector used 62% of all oil consumed worldwide, of which 96% came from fossil fuels alone [21]. Accessibility, usability and price of biodiesel compared to petroleum, are important factors when attempting to make biodiesel competitive in this market. Figure (11) and Figure (12) illustrates this by showing
human population growth over the past years [22], and the increase of petroleum fuel consumption [23].

Figure 11: Human population in the world given in millions

Figure 12: Consumed petroleum fuels, given in units of million barrels per day.

Many biodiesel companies need state support to run their business. Processing cost could be reduced through simplified operations and eliminating waste streams [1]. Catalysts neutralization after the reaction has taken place may be a difficult and costly production step.
With the increasing cost of product purification caused by use of homogeneous catalysts, heterogeneous catalyst may be an attractive solution to eliminating waste streams.

Biodiesel is also costly to produce due to high feedstock prices. Ramadhas et al. [24] recommended that for most catalysts, the acid values of feedstocks should be less than 4.0 mg KOH/g before performing alkaline transesterification. Compared to Gerpen [25] that stated that the acid value of a feedstock has to be 2.0 mg KOH/g. Reasoned by availability and price of the catalyst, industrial biodiesel production processes still mostly employ NaOH and KOH [4]. Most commonly used catalysts are in need of high quality raw materials, which is expensive since the cost of feedstock increase when FFA content decrease.

Nonetheless, the use of heterogeneous catalysts in biodiesel production has reduced the negative effects related to the use of low quality feedstocks [3]. Heterogeneous acid catalysts have the ability of having both decent conversions and purity of products with a lower cost of refining feedstocks. Feedstock alternatives that may participate to the competitiveness of biodiesel, are feedstocks like used cooking oil, animal tallow and microalgae to give some examples [3]. The goal is to develop high activity catalysts that can achieve greater yields in shorter time, from affordable feedstocks with less need for refining the product [3, 11].

A mix of biodiesel and traditional fuel is becoming more common. This may be a simpler way to decrease the use of fossil fuels without the necessity of changing any parts of the vehicle. Biodiesel and blends with petroleum based diesel fuel can be used in diesel engines without any significant changes on the engine [26].

2.5 ENVIRONMENTAL ASPECT

More than 85% of the total energy supply in the world still comes from non-renewable energy sources [20]. Even with increasing amounts of renewable energy being produced this number have not yet decreased significantly.

Most countries have different plans and projects on how to reduce the consumption of non-renewable energies. Alternatives such as hydroelectric energy, solar energy, wind energy and bioenergy production are now common alternatives to non-environmental friendly energy sources [20]. Finding alternative fuel sources is a more challenging issue. There is a demand
for a type of fuel that fit the criterions of low cost, high energy density that is safe to use. Types of fuel that may fit these criterions are biodiesel, biogas, electricity and hydrogen. Making these fuel sources meet these demands and to compete with the fossil fuels, demands time and research. In the EU Comissions Climate Meeting 2016, the commission pledged to make energy more secure, affordable and sustainable [27]. Due to biodiesel’s environmental benefits this may be a contributing factor for making biodiesel more attractive as a biofuel.

When considering the active natural carbon cycle with a span of 10 years, the carbon dioxide emitted from an engine running on petroleum are not in the cycle. The carbons emitted from biodiesel fuel are in the carbon cycle. The combustion into carbon dioxide returns to the cycle as bioenergy sources by photosynthesis, which again can be used to produce new fuels [11].

Biodiesel is “readily biodegradable”. Biodegradation can restore a fuel spill over soil in 4-6 weeks before it supports plant germination. When mixed with petroleum the biodiesel appears to increase biodegradation with up to 100% [2]. Toxicity testing shows that biodiesel is significantly less toxic then diesel. Still ingesting or skin contact is not recommended [2]. This also simplifies the transportation and emplacement due to minimal environmental pollution risks, and safety issues in handling the fuel.

The renewability of biodiesel depends on the raw materials used, like the type of alcohol and fatty acids. Methanol is mostly produced from syngas reaction with source from natural gas, making it unrenewable. Ethanol is mainly produced by fermentation of sugar, making it renewable through the photosynthesis.

The use of edible vegetable oils for biodiesel production is one of the non-environmental friendly parts of biodiesel. Being able to use oil types from waste materials, wood or algae, and other non-food competitive resources may strengthen the arguments for developing the use of biodiesel. Therefore, general attention has been drawn to the use of bioethanol and biodiesel produced from second generation of raw materials [20]. Reasoned with their ability to handle feedstocks with higher acidity, heterogeneous acid catalysts are becoming more important.

As mentioned, biodiesel is frequently used in B20 blends composing 20 % biodiesel and 80% traditional fuels. Compared to a 100 % traditional fuel, B20 can reduce air toxics with 20 – 40%. It is asserted that 90% of air toxics can be eliminated by using B100 [26].
A challenge for diesel engines is the NOx emissions. These emissions are associated with elevated gas temperatures, where Nitrogen from the combustion air get oxidized. Higher combustion temperatures, especially over longer time intervals, increases NOx emissions [2]. At this point, the amount of NOx gas emissions increases with use of biodiesel fuel. Particulate emissions are a second difficult challenge. The heterogeneous fuel-air mixture in the cylinder during the diesel combustion contributes to formation of soot particles. These are formed at high temperatures in the combustion chamber. Biodiesel’s low volatility causes a portion of the fuel not to get combusted but rather coat the cylinder walls as liquid before being released in the exhaust process as increased emissions [2].

One must also take into account where production occurs. Production of agricultural raw materials may result in higher total emissions of CO₂ then other materials. The use of areas to feedstock, otherwise left to nature will affect the total CO₂ distributions, factors that do not occur as an issue with fossil fuels. It is therefore important to look at the whole life cycle when evaluating the environmental impact of biodiesel [2].

2.6 DIESEL ENGINE

Before explaining the properties of fossil diesel and biodiesel a short introduction on the diesel engine is presented to give a background to these properties importance. A diesel engine uses compression to ignite. Air enters the cylinder before getting compressed, gaining high temperature and pressure. In this state, fuel is sprayed in to the cylinder and evaporates quickly due to high temperatures. The fuel goes through a series of chemical reactions when mixing with the air, resulting in self-ignition [2]. The ignition pushes the movable part of the cylinder back out and drives the motor. The power of the engine is controlled by variation of the volume of fuel injected to the cylinder [2].

2.7 PROPERTIES OF FOSSIL DIESEL AND BIODIESEL

A diesel engine compresses and combusts the fuel to exhort more of the energy than by combustion alone. Several characteristics are important for determining how well the engine will perform with a certain fuel. Some of the most significant properties are pour point, cloud
point, volatility, viscosity, cetane number and heating value among others. Their explanation are as follows:

*Cetane number:* is a measure of ignition quality and is similar to the octane scale used for gasoline. A high cetane number results in a short ignition delay resulting in more complete combustion of the fuel. Using a fuel with lower cetane number than the one recommended for a specific engine can result in lower power output of the fuel, less complete combustion and greater wear on the engine itself [2].

*Kinematic viscosity:* a measure of a fluid’s resistance to flow, due to friction between the molecules of the fluid. This is measured by applying a controlled shear rate to a liquid and measure the resulting shear stress [26]. The higher viscosity the greater effect of atomization of a fuel upon injection in combustion cylinder and in the end higher formation of engine deposits [2].

*Cloud point:* the temperature where a cloud of crystals first appears in a liquid when the liquid gets cooled down under controlled conditions [26].

*Pour point:* the temperature where the liquid fuel can no longer be poured due to gel formation [26].

*Flash point:* the lowest temperature where a fuel can form an ignitable mixture. Meaning having enough vapour to give a flammable mixture [2].

*Lower heating value:* the heat given from the combustion of the material [2]. This determines the maximum power, where the lower heating value is found when heat of vaporization is subtracted from the higher heating value. This value will depend on the feedstock used, purity, and factors as time of the year [2].

*Lubricity:* the ability of the fluid to work as a lubricant. Diesel engines uses the fuel itself to lubricate vital engine parts as fuel pumps and injectors [2]. Biodiesel improves lubricity and decreases wearing of fuel pumps and engine parts [26].

To compare these values for petroleum fuel and biodiesel Table (5) is made to illustrate this. This table is based on the results from Joshi and Pegg [26].
### Table 5: Properties of diesel and biodiesel fuels

<table>
<thead>
<tr>
<th>Fuel property</th>
<th>Diesel</th>
<th>Biodiesel</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fuel standard</strong></td>
<td>ASTM D975</td>
<td>ASTM PS 121</td>
</tr>
<tr>
<td><strong>Fuel composition</strong></td>
<td>C10 – C21 HC</td>
<td>C12 – C22 FAME</td>
</tr>
<tr>
<td><strong>Lower heating value [MJ/m^3]</strong></td>
<td>36.6*10^3</td>
<td>32.6*10^3</td>
</tr>
<tr>
<td><strong>Kinematic viscosity at 40°C [mm^2/s]</strong></td>
<td>1.3 – 4.1</td>
<td>1.9 – 6.0</td>
</tr>
<tr>
<td><strong>Specific gravity at 15.5°C</strong></td>
<td>0.85</td>
<td>0.88</td>
</tr>
<tr>
<td><strong>Density at 15 °C [kg/m^3]</strong></td>
<td>848</td>
<td>878</td>
</tr>
<tr>
<td><strong>Carbon (wt. %)</strong></td>
<td>87</td>
<td>77</td>
</tr>
<tr>
<td><strong>Hydrogen (wt. %)</strong></td>
<td>13</td>
<td>12</td>
</tr>
<tr>
<td><strong>Oxygen (wt. %)</strong></td>
<td>0</td>
<td>11</td>
</tr>
<tr>
<td><strong>Sulfur (wt. %)</strong></td>
<td>0.05 (max)</td>
<td>0.0 – 0.0024</td>
</tr>
<tr>
<td><strong>Boiling point [°C]</strong></td>
<td>188 – 343</td>
<td>182 – 338</td>
</tr>
<tr>
<td><strong>Flash point [°C]</strong></td>
<td>60 – 80</td>
<td>100 – 170</td>
</tr>
<tr>
<td><strong>Cloud point [°C]</strong></td>
<td>(-15) – 5</td>
<td>(-3) – 12</td>
</tr>
<tr>
<td><strong>Pour point [°C]</strong></td>
<td>(-35) – (-15)</td>
<td>(-15) – 10</td>
</tr>
<tr>
<td><strong>Cetane number</strong></td>
<td>40 – 55</td>
<td>48 – 65</td>
</tr>
<tr>
<td><strong>Stoichiometric air/fuel ratio (wt./wt.)</strong></td>
<td>15</td>
<td>13.8</td>
</tr>
</tbody>
</table>
Both pour point and cloud point decreases with decreasing concentration of biodiesel in the blend [26]. Most of the other biodiesel properties may also be alternated by adding certain chemicals to the fuel [2].

2.8 ADVANTAGES WITH BIODIESEL

Biodiesel has less air pollutants per nett energy than traditional diesel and is also nontoxic and biodegradable [1, 2, 26]. Biodiesel is produced from renewable sources with estimated 40-90% more energy than the energy invested in production and have a clean combustion behaviour [26]. The fuel reduces most regulated exhaust emissions, with exception of NOx emissions. Biodiesel has safer handling and storage than traditional fuel, due to higher flash point. Higher lubricity reduces wear of the motor [2]. Finally biodiesel provides an alternative reducing our dependency on petroleum [2].

2.9 DISADVANTAGES WITH BIODIESEL

One of the more important disadvantage is the feedstocks competing with the food industry. On the emission side there is an increase in nitrogen oxide (NOx) emissions [26]. In cold temperatures the fuel thickens and may even freeze. Decreasing the CP value has the best potential to improve these properties for biofuels and biofuel blends [2], while another alternative is adding cold flow improvers [2].

2.10 INDUSTRIAL PRODUCTION OF BIODIESEL

Biodiesel is produced in different extent all over the world. To give a short overview, data is presented for the 10 countries with the highest production in 2008 [28].
Table 6: Top 10 countries in biodiesel production with amount produced given in billions litres

<table>
<thead>
<tr>
<th>Countries</th>
<th>Major Feedstock</th>
<th>2004</th>
<th>2005</th>
<th>2006</th>
<th>2007</th>
<th>2008</th>
</tr>
</thead>
<tbody>
<tr>
<td>Germany</td>
<td>Rapeseed</td>
<td>1.18</td>
<td>1.9</td>
<td>3.02</td>
<td>3.28</td>
<td>3.2</td>
</tr>
<tr>
<td>USA</td>
<td>Soybean</td>
<td>0.11</td>
<td>0.36</td>
<td>0.99</td>
<td>1.93</td>
<td>2.69</td>
</tr>
<tr>
<td>France</td>
<td>Rapeseed</td>
<td>0.4</td>
<td>0.56</td>
<td>0.84</td>
<td>0.99</td>
<td>2.06</td>
</tr>
<tr>
<td>Brazil</td>
<td>Soybean</td>
<td>-</td>
<td>-</td>
<td>0.07</td>
<td>-</td>
<td>1.2</td>
</tr>
<tr>
<td>Argentina</td>
<td>Soybean</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.2</td>
</tr>
<tr>
<td>Italy</td>
<td>Oil seeds</td>
<td>0.36</td>
<td>0.45</td>
<td>0.51</td>
<td>0.41</td>
<td>0.68</td>
</tr>
<tr>
<td>Thailand</td>
<td>Oil palm</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.40</td>
</tr>
<tr>
<td>Poland</td>
<td>Rapeseed</td>
<td>-</td>
<td>0.11</td>
<td>0.13</td>
<td>0.09</td>
<td>0.31</td>
</tr>
<tr>
<td>Spain</td>
<td>Oil seeds</td>
<td>0.01</td>
<td>0.08</td>
<td>0.11</td>
<td>0.19</td>
<td>0.24</td>
</tr>
<tr>
<td>Austria</td>
<td>Oil seeds</td>
<td>0.06</td>
<td>0.1</td>
<td>0.14</td>
<td>0.3</td>
<td>0.24</td>
</tr>
</tbody>
</table>

The global trade of biodiesel remains modest, with countries predominantly producing for their own consumption. Due to some countries being more favourable to grow the FAs the trade of biodiesel is assumed to rise. It is believed factors like labour costs, availability of land and climate might uneven the trend.

The technologies used in the production process produces two groups of biodiesel; first and second order biodiesel. First order biodiesel may compete with food supply through the use of oil seed plants for FA and sugar or starch to produce ethanol [28]. Second order biodiesel uses more complex feedstock sources, which again demands advanced technologies to convert the lignocellulosic biomass. Second order biodiesel has the opportunity to grow both first and second order feedstocks on the same field, providing a greater variety on the feedstocks available. Still cellulosic biomasses are more difficult to break down making the production line and technology more expensive [28].

To illustrate the increase in biodiesel production, Figure (13) shows the development of the total amount of produced biodiesel from 2002 to 2012. The values are given in thousand barrels per day and collected from the U.S. Energy Information Administration [29]. There is a steep increase in the amount of biodiesel produced between 2005 and 2010, before the production stabilized between 2010 and 2012.
2.10.1 Reactors

To understand the production of biodiesel and how the catalysts described in this thesis is used in the different reactors, a short curriculum on the different main types of reactors is necessary. The different reactors are made for different uses and all have their pros and cons.

2.10.1.1 Batch Reactor

The Batch reactor is a commonly used reactor for science and lab work. This reactor has no flow in or out of the reactor, neither inflow of reactants or outflow of products while the reaction is ongoing. It has a container, a stirring device and heating device and can be made in the size needed. This results in the operator having a better control of the process, and with the content of the reactor in all the same conversion state it is easier to run tests. Using a batch reactor helps to maintain a constant temperature and pressure in the reactor [8]. The batch reactor is not commonly used in industry, mainly because of the need to turn the system completely off, empty and clean the reactor between every run.
2.10.1.2 Continuously Stirred Tank Reactor (CSTR)

This reactor is visibly similar to the Batch reactor, but has a flow through the reactor. It has an inlet and an outlet flow and perfect stirring making the conversion in the outlet stream the same as the conversion elsewhere in the reactor. This puts demands on the size compared to the flowrate in order to get the desired conversions [8]. The CSTR is still commonly used due to the ability to produce large volumes, fulfilling the demands of a producer.

2.10.1.3 Plug Flow Reactor (PFR)

Plug flow consists of a cylindrical pipe or tube. The reactants and the catalyst are added in the inlet and are consumed as they flow down the length of the reactor. When we model the tubular reactor we assume that the concentration varies continuously in the axial direction through the reactor [8]. Typically used for high volume production due to low labour costs. A packed bed flow reactor is similar to a plug flow reactor besides the fact that the solid catalyst is kept inside the chamber in the reactor, allowing reactants to flow through.

2.10.2 Reaction Rates

The reaction rate is the rate of which a reactant is being consumed to form a product. It is defined by Fogler as the number of moles reacting per unit time per unit volume [8]. The reaction rate tells us the speed of the reaction, a factor that may help determine if a reaction is profitable under given circumstances. This can be described with factors such as; temperature, pressure, molar ratio, type of catalyst and catalyst ratio [8]. If the components A and B are used to produce the products C and D in a one-way reaction, as in Equation (1). The resulting reaction rate expression can be shown in Equation (2) described with the reaction rate constant \( k \) and the concentrations of the reactants as shown.

\[
A + B \rightarrow C + D \tag{1}
\]

\[
r_{\text{reaction rate}} = kC_A C_B \tag{2}
\]
If the reaction is a two sided as in Equation (3), the reaction rate will also have a negative term as in Equation (4).

\[ A + B \leftrightarrow C + D \]  
\[ r_{\text{reaction rate}} = k_1 C_A C_B - k_2 C_C C_D \]  

The value of \( k_i \) is specific for each reaction, and will in most circumstances have a strong temperature dependency. The temperature dependency can be written with the Arrhenius equation as shown in Equation (5).

\[ k(T) = B e^{-\frac{E}{RT}} \]  

Where \( B \) is a factor, \( E \) is activation energy, \( R \) is the gas constant and \( T \) is the temperature measured in Kelvin (K).

2.10.3 Conversions

The conversion is a measure of how much of the reactants has reacted and formed the desired product at a given time [8]. The number of moles of \( A \) at a given time \( (N_A) \) can be calculated with Equation (2).

\[ N_A = N_{A0} - N_{A0} X = N_{A0} (1 - X) \]  

Where \( N_{A0} \) is initially amount of \( A \), given in moles and \( X \) is the conversion at this time.
Solving for X provides an equation for conversion given as Equation (7).

\[ X = \frac{N_{A0} - N_A}{N_{A0}} = 1 - \frac{N_A}{N_{A0}} \]  \hspace{1cm} (7)

Where \( N_{A0} \) is initially amount of A, given in moles and \( N_A \) is the number of moles of A at a given time.

2.11 REACTION MECHANISMS

The mechanisms for biodiesel production are different due to the reaction type, catalyst used and reactor used. The main differences are transesterification method compared to the esterification method.

2.11.1 Acid Transesterification Mechanism

The mechanism for Acid transesterification for a homogeneous catalyst will be similar for both MG, DG and TG. For TG the process will repeat itself each time yielding one FAAE a total of three times before completing the process. For MG this process only takes place once before the final products are yielded. The mechanism is explained in Figure (14) for MG to simplify. This mechanism is based on the study of Schuchardt et al. [30].
Figure 14: A general mechanism for transesterification reaction for a homogeneous acid catalyst

Conversion of TG, DG and MG to FAAE, when TG is the reactant and FAAE is the product is illustrated. A qualitative plot of conversion in an ongoing transesterification reaction is illustrated in Figure (15). DG and MG are intermediates in the transesterification reaction as shown.
2.11.2 Esterification Mechanism

An acid catalyst can also esterify FFA which only happens in one repetition of the reaction. The process starts with FFA reciving a proton from the acid catalyst before the protonated FA reacts with alcohol to yield nucleophilic attacked FA. The proton will then wander through the molecule to another hydroxyl group giving a new nucleophilic attacked FA. This results in a water molecule splitting of the nucleophilic attacked FA and a proton splitting of the carbonated FAAE yielding one FAAE and one proton returning to the catalyst. The mechanism is shown in Figure (16) and is based on the study of Clark [31].

**Figure 15:** A qualitative plot of conversion during a transesterification reaction.
Figure 16: A general mechanism of an esterification reaction for a homogeneous acid catalyst

2.12 TITRATION

A sample with a neutral content and phenolphthalein provides the light pink colour of the control sample shown in Figure (18) after addition of a known amount 0.12M NaOH. If a colour change happens immediately after adding the phenolphthalein to the beakers the catalyst is determined to leach base and will have a pink colour as in Figure (19). With no colour change after addition of NaOH to the beakers the catalysts are determined to leach acid as shown in Figure (17). The amount of NaOH necessary to give the neutral light pink colour, as shown in Figure (18), will represent the acidity of the content.
To provide greater insight into the function of a catalyst a kinetic model is necessary. By use of experimental data correlation, using the least square method to evaluate the parameter values, the model is found [18]. Equation (8) shows the calculation of the root mean square.

\[ RMS = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (a_{i}^{exp} - a_{i}^{calc})^2} \]  

(8)

Where \( a_{i}^{exp} \) is the aciditie value from experimental data, \( a_{i}^{calc} \) is the calculated acidity from the kinetic model and \( N \) is the number of data, experimental or calculated.

The principal is to start by choosing a model and then choosing the limiting factor. For a heterogeneous catalyst the reaction has three steps where one of them is the limiting factor. Inside each step all of the reactions are elementary. The first step is the adsorption where the reactant gets adsorbed to the active sites of the catalyst. The second step is the surface reaction, and the third is the desorption where the product detaches from the active site. These steps are illustrated in Figure (20).
After a reactant gets adsorbed onto the surface, it can react in a variety of ways, depending on factors like molecular or atomic adsorption, if it is a single or dual site reaction, and the type of reaction [8]. A number of models may be found for one reaction and many of these needs to be tested to find the best fitting model with the most fitting parameters.

The reaction rate is found by calculating reaction rates for all the elementary reactions within each step to and then solve for the controlling step. The reaction constants $k_i$ and their dependency on temperature and activation energy is given through the Arrhenius equation shown in Equation (1) [18].

To correlate the kinetic data the decrease of FA is measured. The relation between reaction rate and biodiesel can be shown with equation (5) due to the 1:1 ratio between FAs being consumed and production of biodiesel.

To give an example equation (10) is written when the reaction shown as Equation (9) is given;

$$A + B \leftrightarrow D + E$$ (9)
\[-r_A = \frac{dc_A}{dt} = k_1 \left( C_A C_B - \frac{c_D c_E}{K} \right) \]  

(10)

Where $k_1$ is the reaction constant, $K$ is given in Equation (11) and $C_A, C_B, C_D, \text{ and } C_E$ are concentrations of the compounds in the given reaction.

\[K_i = \frac{k_i}{k_{-i}}\]  

(11)

Where $k_i$ is the reaction rate for reaction $i = 1, 2, 3$ in the direction of the products, and $k_{-i}$ is the reaction rates for $i=1,2,3$ in the direction of the reactants.

Several mechanisms could be proposed, using the limiting step methodology. All of them will be tested against the experimental data to find the best fit. In order to find the reaction rate, when a mechanism is proposed, a limiting reaction step is chosen, either PSSH or the equilibrium method can be used to find the kinetic expression for the surface reaction rate for that controlling step [8]. The equilibrium method is used in this study to solve for the controlling elementary reaction while setting the other reactions in equilibrium, meaning the reaction rates are zero [8].
3 MATERIALS AND METHODS

3.1 MATERIALS

The catalysts used are Tulsion-63, Tulsion-6812 and Amberlyst-16. Tulsion-63 and Tulsion-6812 was delivered by Thermax. Pictures of the catalysts directly from the box are shown in Figure (21) and (22). The properties of the catalysts are stated in Table (2) and (3).

![Figure 21: Tulsion-63 in the container](image1)

![Figure 22: Tulsion-6812 in the container](image2)

Amberlyst-16w is delivered from Rohm and Haas Company, DOW. Figure (23) is a picture the catalyst taken from the container. Properties of the catalyst were given in Table (3).

![Figure 23: Amberlyst-16w direct from the container.](image3)
The three catalysts are heterogeneous acid based catalysts in spherical solid form. The most used chemicals are listed as; ethanol 96% and absolute ethanol with purity 99.9% which both were delivered from Kemetyl Norge AS. The acetic acid had an ACS reagent given as equal or higher than 99.7%. Diethyl ether, that was used with ethanol 96% for enlarging samples for titration, with a purity level of 99.7%. Potassium hydroxide, used with absolute ethanol to make titration liquid, which had a purity above or equal to 85%. Phenolphthalein was used as a colour indicator. The acetic acid, diethyl ether, potassium hydroxide and the phenolphthalein were all delivered by Sigma Aldrich.

3.2  EQUIPMENT

The equipment for the reactions was a 500mL glass batch reactor delivered from Quark Glass. Mixing of the reaction fluid was performed by a magnetic stirrer delivered from VWR. Figure (24) is a picture of the reactor with the needed additional equipment; a condenser with a plug attached to the top to prevent alcohol from escaping, and a temperature measurement connected to the plate with magnetic stirrer. When taking samples from the batch reactor a syringe with a long needle on the side of the reactor was used. A water bath from VWR (North American Cat. No. 89202-916) with temperature control, is used to heat the reactor by circulating warm water around the inner chamber of the reactor.

Drying in the oven was the last step after rinsing, or a separate pre-treatment technique. An oven cabinet delivered from Termaks is mainly used. The oven was holding 65°C the whole duration of the drying time. An external device was used when measuring the oven temperature. The thermometer Tenma 72-7715 was with an error at 0.1°C [32]. The catalyst was left in the oven for 24 hours or longer to become completely dry.

Because of problems with electricity, another oven was also used for drying catalysts. This oven was set to use 60 minutes to heat up to 65°C before holding the temperature for 24 hours. The oven had an error at ±1°C and was delivered from Nabertherm.
The microscope used was a Portable Stand Alone LCD Digital Microscope. The microscope can take pictures with a total magnification on 500X. Pictures were taken up to this degree of magnification, without the scale or magnification on each step. The resulting pictures are therefore given without associated magnification.
3.3 METHODS

3.3.1 Running the Batch Reactor

Acetic acid and ethanol were placed in the reactor and heated up with stirring until reaching the reaction temperature. A known amount of catalyst was added and the stirring resumed. Sample at time zero was taken and the clock started.

The zero sample was taken to determine the initial composition of the reaction mixture. At the beginning samples were taken every 15 minutes, then every 30 minutes, every hour, every second hour and finally every third hour until the experiment was finalized. The stirring was stopped for 4-6 seconds to allow the catalyst to set on the bottom before collecting the sample. This was done to avoid the collection of some of the finer particles of the catalyst in the sample. The sampling under these circumstances are assumed to not cause a drop in the reaction rate nor change the temperature in the batch reactor significantly. To avoid further progression of the reaction after sampling, the sample in the glass container was submerged in an ice/water bath to stop the reaction by cooling it down to 0°C.

Experiments were carried out at various temperatures, molar ratios, catalyst amounts and pre-treatments. Temperatures tested were at 40°C, 50°C, 60°C, and 70°C. Catalyst amounts were tested at 5%, 10%, and 15% of the amount of acetic acid. Molar ratios for acetic acid and ethanol were tested with 1:3, 1:6, 1:9, and 1:10. The stirring speed was always set to 200 rpm.

Figure 26: The batch reactor under operation with 400 mL volume in the reactor, 200rpm stirring
### 3.3.2 Catalyst Pre-treatment

A variation of rinsing methods and different ways of drying were used on Tulsion-6812 and Tulsion-63, in order to reduce the leaching and to keep the structure of the beads more stable. The methods used were rinsing with absolute ethanol with magnetic stirring, or with manual stirring for 20 seconds every 15 minutes. The duration of time in the rinsing liquid tested was 90 or 120 minutes. The same rinsing methods were also used with rectified ethanol, acetone, and distillate water. After rinsing the catalyst was dried in an oven.

On Amberlyst-16w the catalyst was used directly from the box as Amberlyst-16w, or dried in the oven at 65°C for 24 hours before use. The catalyst were covered with parafilm to prevent air-pollution before use, and added directly to the reactor.

### 3.3.3 Catalysts Leaching Tests

To test for acid or base leaching each of the catalysts, with none or different pre-treatments, were added to beakers with rectified ethanol, absolute ethanol, acetone, or distillate water. The beakers were then set to stir with magnetic stirring, or manual stirring for 20 seconds every 15 minutes. The tests were run at room temperature and ambient pressure. Two drops of Phenolphthalein were added as an indicator. Drops of 0.12M KOH were added until colour change in the beakers to determine the amount of leached acid.

### 3.3.4 Reaction Experiments

To find the reactions dependency of molar ratio between alcohol and fatty acid, catalyst amount and temperature as well as the effect of pre-treatment experiments, tests where one of these factors differ from the baseline were run. The baseline experiment was with molar ratio 6, temperature at 60°C, catalyst amount at 5% and no pre-treatment of the catalyst. Variations form the base line were done for each variable individually in an upper and/or lower range. When the baseline values were taken into account a minimum of three different values were tested for each factor.
3.3.5 Reuse Test

To know the reusability of Amberlyst-16w, a reusability test was run to see the degree of decay of the catalyst. Used catalyst from an earlier run was reused under the same conditions. Some samples were taken to show the tendency of the reaction and to observe approximately when the final conversion was reached.

After the first experiment the catalyst was filtered out of the reactor content, using a six mL syringe filled four times with the reaction liquid to wash out the remaining beads. Remaining catalyst after four washes was declared lost. The catalyst was allowed to drain of the liquid in the filter for 15 minutes. Without further treatment the catalyst was used again in the same percentage of catalyst amount repeating the experiment. The catalyst is covered with film after measuring the weight of remaining catalyst to prevent air exposure during the preparations. After another run the catalyst was again removed from the batch reactor with the same method, and a new experiment could begin. This continued until the final conversion of the reaction got too low or did not drop significantly after a certain amount of runs.

If the experiment could not be started right away the catalyst was left in the reaction liquid at ambient temperatures without stirring until a new reaction was started. The longest time the catalyst lay in reactor liquid without use was 12 hours.

3.3.6 Determination of Biodiesel Conversion

During the reaction when FFA is consumed the PH values will increase since the products are close to neutral. This provides the possibility to determine biodiesel conversion by titration. The reaction ratio is 1:1 with FFA consumed and to FAME produced, so the increase in PH values were due to the amount of biodiesel formed. In order to see the colour change a 20-50 mg sample was taken and dissolved in a 10 mL 1:1 mix of rectified ethanol and diethyl ether. A few drops of phenolphthalein were added using the same principle as in the leaching tests. When adding a known amount of KOH until a colour change, Equation (7) gives the original acid fraction.
\[ \text{Acid value} = \frac{V_{\text{KOH}}(\text{mL}) \cdot C_{\text{KOH}}(\text{M}) \cdot M_{\text{KOH}}(\text{g mol}^{-1})}{\text{Sample weight (g)}} \]  

(12)

Where \( V_{\text{KOH}} \) is volume added of potassium hydroxide given in millilitres, \( C_{\text{KOH}} \) is the concentration and \( M_{\text{KOH}} \) is the molar mass, and \( \text{Sample weight} \) is the weight of sample added to the titration.

The degree of conversion was calculated based on the zero point samples. To reduce errors, the zero point samples was titrated four times in order to reduce system errors, the other samples were titrated two times.

3.3.7 Kinetic Modelling in Aspen

When modelling the kinetics of a reaction, different models are presented. By choosing a controlling step and applying the equilibrium method, different reaction rates will be proposed and compared towards the experimental data. Fitting the experimental data in Aspen, with the model will allow different values on the models constants, until values that provides a best possible fit to the experimental data are found. Excel was used to see how the different parameters in the kinetic expression detected best matches the data. This is done by plotting the data from Aspen and the experimental data in the same excel sheet.
4 RESULTS AND DISCUSSION

The aim for this assignment was to do a parameter screening of a heterogeneous catalyst. Three catalysts were tested by different means before continuing the parameter screening with Amberlyst-16w. The tests were done with mainly acetic acid and ethanol. Acetic acid was chosen for being a small and light molecule, being capable for rapid reaction rates due to less stoichiometric difficulties. Ethanol was chosen due to being less toxic than methanol, as well as being more renewable.

A short list of the experiments taken for this study is listed in the appendix.

4.1 TULSION-63

The results from the leaching tests with both rinsed and non-treated catalyst is displayed in Table (6). All experiments were conducted with a range between 1.3 g and 3 g om catalyst and 25 mL of the various liquids are used. Temperatures and air conditions were ambient. The control sample showed that one drop of KOH was needed to give colour change in the liquids used with no solvents from the catalyst. If a significantly bigger amount of KOH was needed to give colour change, the catalyst was determined to leach in those conditions.
### Table 7: Results from leaching tests Tulsion-63

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Rectified ethanol</td>
<td>None</td>
<td>2.009</td>
<td>Magnetic</td>
<td>120</td>
<td>500</td>
<td>Yes</td>
</tr>
<tr>
<td>Absolute ethanol</td>
<td>None</td>
<td>3.035</td>
<td>Manual</td>
<td>90</td>
<td>560</td>
<td>Yes</td>
</tr>
<tr>
<td>Absolute ethanol</td>
<td>Drying</td>
<td>3.065</td>
<td>Magnetic</td>
<td>120</td>
<td>514</td>
<td>Yes</td>
</tr>
<tr>
<td>Absolute ethanol</td>
<td>Rinsed in absolute ethanol and dried</td>
<td>2.518</td>
<td>Magnetic</td>
<td>120</td>
<td>114</td>
<td>Yes</td>
</tr>
<tr>
<td>Distillate water</td>
<td>Dried</td>
<td>3.005</td>
<td>Magnetic</td>
<td>120</td>
<td>557</td>
<td>Yes</td>
</tr>
<tr>
<td>Distillate water</td>
<td>None</td>
<td>1.470</td>
<td>Manual</td>
<td>120</td>
<td>300</td>
<td>Yes</td>
</tr>
<tr>
<td>Distillate water</td>
<td>Rinsed in distillate water and dried</td>
<td>1.398</td>
<td>Manual</td>
<td>120</td>
<td>29</td>
<td>Yes</td>
</tr>
<tr>
<td>Acetone</td>
<td>None</td>
<td>3.018</td>
<td>Manual</td>
<td>120</td>
<td>700</td>
<td>Yes</td>
</tr>
<tr>
<td>Acetone</td>
<td>Rinsed in Acetone and dried</td>
<td>3.038</td>
<td>Manual</td>
<td>120</td>
<td>143</td>
<td>Yes</td>
</tr>
<tr>
<td>Acetone</td>
<td>None</td>
<td>2.964</td>
<td>Magnetic</td>
<td>120</td>
<td>643</td>
<td>Yes</td>
</tr>
<tr>
<td>Acetone</td>
<td>Rinsed with magnetic stirrer in Acetone and dried</td>
<td>2.993</td>
<td>Magnetic</td>
<td>120</td>
<td>100</td>
<td>Yes</td>
</tr>
</tbody>
</table>

From Table (7), it can be seen that Tulsion-63 has significant leaching with all the reactants. This is undesirable for removal and reuse of catalyst as well as rinsing of the product.
Figure (27) is a picture of the initial state after addition of catalyst to rectified ethanol. It is visible that the liquid state is clear. While stirring the catalysts there was a visible colour change in the liquid phase and a visible fragmentation of the catalyst as shown in Figure (28). The remains of catalyst after removal of the fluid is shown in Figure (29), confirming the fragmentation of catalyst.

The catalyst was soluble in 96% ethanol as well as absolute ethanol, distillate water and Acetone. The results were the same with manual stirring. When adding the catalyst to the liquid there was a crackling sound for approximately the first 25 minutes. When adding T-63 to distillate water the crackling sound was louder and lasted for approximately 60 minutes. Some of the beads flew out of the water in the first period of time, and you could see the beads jumping in the liquid in connection to the cracking sound.
Figure (30) illustrates the fragmentation of catalyst after stirring with absolute ethanol for 120 minutes. From a visual observation there is less degree of fragmentation than with rectified ethanol. On the contrary, from the results given in Table (7) the degree of leaching is similar.

4.1.1 Reactions with Tulsion-63

Explained by the significant leaching and dissolving of the catalyst, further reaction testing was stopped after two inconclusive tests. The correct conversions were not found due to leaching of the catalyst influencing the results. Further testing was run with Tulsion-6812 which had the least fragmentation.

Patil et al. [14] ran a reaction on Tulsion-63 with acetic acid and iso-amyl-alcohol yielding conversions at 90% and a reusable catalyst. The pre-treatment procedure used was washing the catalyst with methanol and water to separate the impurities. The catalyst was then kept in a vacuum oven at 348K so that it was completely dry before usage.

When interpreting the results of Patil et al. [14] and comparing them to the results obtained, it seems like the fragmentation and solvation problems are reduced. However, when making the model for the reaction, Patil et al. [14] used a Pseudo-homogeneous model representing the reaction system, which may indicate fragmentation and dissolving of catalyst as a problem even after the pre-treatment. A possible explanation for less dissolving may be the longer carbon chain of the iso-amyl-alcohol, making iso-amyl-alcohols less polar than ethanol [33].

4.2 Tulsion-6812

The results from the leaching tests with both rinsed and not pre-treated catalyst are displayed in Table (8). All experiments were run with 2.0 to 3.2 grams of catalyst and 25 mL of the various liquids used, as with Tulsion-63. Temperature and air conditions are ambient for all of the experiments. One drop of KOH was needed to give colour change in the rinsing liquids used, without leaching from the catalyst.
Table 8: Results from leaching tests Tulsion-6812

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Rectified ethanol</td>
<td>None</td>
<td>2.015</td>
<td>Magnetic</td>
<td>120</td>
<td>400</td>
<td>Yes</td>
</tr>
<tr>
<td>Absolute ethanol</td>
<td>None</td>
<td>2.979</td>
<td>Manual</td>
<td>90</td>
<td>460</td>
<td>Yes</td>
</tr>
<tr>
<td>Absolute ethanol</td>
<td>Drying</td>
<td>3.133</td>
<td>Magnetic</td>
<td>120</td>
<td>500</td>
<td>Yes</td>
</tr>
<tr>
<td>Absolute ethanol</td>
<td>Rinsing in absolute ethanol and dried</td>
<td>2.765</td>
<td>Magnetic</td>
<td>120</td>
<td>71.9</td>
<td>Yes</td>
</tr>
<tr>
<td>Distillate water</td>
<td>Dried</td>
<td>3.141</td>
<td>Magnetic</td>
<td>120</td>
<td>572</td>
<td>Yes</td>
</tr>
<tr>
<td>Distillate water</td>
<td>None</td>
<td>2.995</td>
<td>Manual</td>
<td>120</td>
<td>614</td>
<td>Yes</td>
</tr>
<tr>
<td>Distillate water</td>
<td>Rinsed in distillate water and dried</td>
<td>3.006</td>
<td>Manual</td>
<td>120</td>
<td>29</td>
<td>Yes</td>
</tr>
<tr>
<td>Acetone</td>
<td>None</td>
<td>2.992</td>
<td>Manual</td>
<td>120</td>
<td>700</td>
<td>Yes</td>
</tr>
<tr>
<td>Acetone</td>
<td>Rinsed in Acetone and dried</td>
<td>2.823</td>
<td>Manual</td>
<td>120</td>
<td>100</td>
<td>Yes</td>
</tr>
<tr>
<td>Acetone</td>
<td>None</td>
<td>2.992</td>
<td>Magnetic</td>
<td>120</td>
<td>700</td>
<td>Yes</td>
</tr>
<tr>
<td>Acetone</td>
<td>Rinsed with magnetic stirrer in Acetone and dried</td>
<td>2.760</td>
<td>Magnetic</td>
<td>120</td>
<td>72</td>
<td>Yes</td>
</tr>
</tbody>
</table>

From Table (8), Tulsion-6812 had significant leaching with all the reactants. No pre-treatment method was found to reduce the leaching without fragmenting the catalyst significantly. In this study the catalyst`s properties after use was closer to a pseudo homogeneous catalyst than a heterogeneous catalyst.
Figure (31) is a picture taken at initial state after addition of rectified ethanol to the untreated catalyst, T=ambient. When the reaction was running there was a visible colour change in the liquid phase and a fragmentation of the catalyst. This is shown in Figure (32). Figure (33) shows the remaining catalyst after removal of the liquid. The catalyst was soluble in 96% ethanol as well as absolute ethanol, distillate water and acetone with magnetic stirring. The results were the same with manual stirring.

In contact with the liquids, especially with distillate water, the observations were the same as for T-63, with the loud cracking and springing of the beads. However, the noise was reduced and the visible movement of the beads were less.
Figure (34) illustrates fragmentation of catalyst, pre-treated with absolute ethanol, after a leaching test with absolute ethanol. In Figure (35) dried catalyst has been left in a glass container that was covered with a sheet of aluminium foil. The acidic active sites of the catalyst, leaching acid, had corroded through the foil completely.

Some screening tests of Tulsion-6812 were run to see the final conversion of the reaction. The final conversions found were not valid and are therefore not presented in this thesis. The titles of experiments run can be found in the appendix.

Tulsion-6812 was tested in different biodiesel conversion reactions in the 500mL batch reactor as well, a list of these experiments are given as follows;

- Acetic acid and ethanol, 10:1 ratio, 2 % of catalyst, 65°C, and ambient pressure
- Acetic acid and ethanol. 6:1 ratio, 5 % catalyst, 65°C, and ambient pressure
- Acetic acid and ethanol. 6:1 ratio, 2 % catalyst, 65°C, and ambient pressure
- Oleic acid and ethanol. 6:1 ratio, 2% catalyst, 65°C, and ambient pressure
The results from these biodiesel conversion experiments for the Tulsion catalysts, and the ones listed in the appendix 1 for the Tulsion catalysts, where not all valid. The calculated final conversion fluctuated greatly, incorrectly giving both positive and negative conversions. Tulsion-6812 as Tulsion-63, are hydrophilic, which easily got dissolves in contact with other hydrophobic components. This freed acid to the liquid, from the active sites of the catalyst. When taking samples, the acidity values may have been influenced, resulting in fluctuating or negative conversions.

**Figure 36**: Conversion over time for reaction with Tulsion-6812 with acetic acid and ethanol with N=10, C=2, T=65

A graph of one of the more reliable datasets, with a visual trend curve, is shown in Figure (36). The results are taken from a run with 200rpm stirring, N=10 and C=2% with a temperature on 65°C. This is a batch reactor experiment taken for four hours with acetic acid and ethanol as reactants and Tulsion-6812 as catalyst. There can be seen a rapid reaction rate before the reaction rate starts slowing down at around 180 minutes.
4.2.1 Tulsion-63 and Tulsion 6812

Tulsion-63 and T-6812, both had significant leaching of acid. The fact that the catalysts, water and ethanol are all polar substances, makes the catalyst more soluble and the heterogeneous catalyst comes closer to homogeneous. This results in a semi heterogeneous catalyst after the uses attempted in this study.

The solubility was shown in the colour change of the ethanol phase, by observing the change in the catalysts appearances, and the results of the leaching tests. As used in this study, the effect of the catalysts may disappear with the leached acid, making reuse of the catalyst difficult. This might explain the low leaching number in the distillate water pre-treated experiment in Table (6) for Tulsion-63 and Table (7) for Tulsion-6812. The leached acid of the catalyst follow the products of the reaction demanding another rinsing step besides filtering out the still heterogeneous part of the catalyst.

With the catalysts being hydrophilic it would dissolve in other polar substances. Hydroxyl groups as the ones in ethanol, distillate water and acetone are all polar so the catalyst would easier dissolve. Alcohols with longer carbon chains are less polar due to the carbon chain trend getting stronger, making the alcohol heavier and obstructing solubility with polar substances [33].

The interaction with other polar liquids reacts with the sulfonic acid groups in the catalysts. Excess water dissociates active sites by introducing and breaking the bounds between the acid groups, and poisoning the catalyst by forming hydrogen bounds within the network [3, 11]. This may be the reason for the cracking sound from the catalyst in contact with water, and why the beads jump in the liquid in the first time period.

No satisfactory pre-treatment was found to prevent leaching or reduce the leaching significantly without severely fragmenting the catalyst. Patil et al. [14] showed a pre-treatment and a reaction that resulted in 89.65% conversion with unused catalyst, 85.20% conversion on first reuse of catalyst and 79.29% on second reuse. The conditions of the reaction were a temperature at 110°C, molar ratio 2:1, catalyst loading five gm, ambient pressure, and stirring speed 1000 rpm [14]. These are extensions of reaction parameters that have not been tested in this work. This was due to the limitations of the reactants in the process and because of catalyst tendency of leaching and fragmentation.
The highest conversions in the experiments of Patil et al. [14] were found at 130°C, molar ratio 1:1 and high stirring speed. It was shown that increasing the temperature was favourable for the acceleration of the forward reaction, resulting in a yield of approximately 90% conversion (the equilibrium point for the process) earlier with higher temperatures. Not being able to use higher temperatures due to the limitations of the reactants used, may not be favouring the catalyst. With the terms used in this research the highest reliable conversion for Tulsion-6812 was found to be 27.3% after a reaction time of four hours.

4.3 AMBERLYST-16W

The results from leaching tests with both rinsed and not pre-treated catalyst is displayed in Table (9). Approximately 12.5 mL of liquid was used with between 0.5g and 1.0g of catalyst. Temperature and air conditions were ambient as for the Tulsion catalysts. Between 0.0250g and 0.0350g was needed to give a colour change in the various liquids, this higher amount was due to a decay of 0.12M KOH. The sample with distillate water once gave a base result, meaning there was close to zero leaching in distillate water and a slight basicity in the distillate water added.

Table 9: Results from leaching tests Amberlyst-16w

<table>
<thead>
<tr>
<th>Liquids tested</th>
<th>Pre-treatment of catalyst</th>
<th>Mass of catalyst [g]</th>
<th>Stirring</th>
<th>Time [min]</th>
<th>Amount of KOH [g]</th>
<th>Leaching</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absolute ethanol</td>
<td>None</td>
<td>0.987</td>
<td>Magnetic</td>
<td>120</td>
<td>0.0210</td>
<td>No</td>
</tr>
<tr>
<td>Absolute ethanol</td>
<td>Dried</td>
<td>0.703</td>
<td>Magnetic</td>
<td>120</td>
<td>0.0499</td>
<td>Yes</td>
</tr>
<tr>
<td>Rectified ethanol</td>
<td>None</td>
<td>0.992</td>
<td>Magnetic</td>
<td>120</td>
<td>0.0322</td>
<td>No</td>
</tr>
<tr>
<td>Rectified ethanol</td>
<td>Dried</td>
<td>0.634</td>
<td>Magnetic</td>
<td>120</td>
<td>0.0478</td>
<td>Yes</td>
</tr>
<tr>
<td>Distillate water</td>
<td>None</td>
<td>0.990</td>
<td>Magnetic</td>
<td>120</td>
<td>0.0062</td>
<td>No</td>
</tr>
</tbody>
</table>

From Table (9) Amberlyst-16w has no leaching or close to no leaching with all the liquids tested. When drying is used as a pre-treatment method, around 54% of the weight of
catalyst is lost due to loss of moisture content. The weights in this table are the weights of catalyst measured after drying right before addition of catalyst to the reactor. When using the dried catalyst there was a small increase in amount of KOH added to get a neutral solution, enough to determine that the catalyst was leaching. This leaching was minor compared to the leaching from Tulsion-6812 and Tulsion-63. To illustrate the visual difference between untreated catalyst and dried catalyst. Pictures were taken of both catalyst treatments.

**Figure 37:** Untreated Amberlyst -16w right after addition of absolute ethanol to the beaker  
**Figure 38:** Untreated Amberlyst-16w and absolute ethanol after 120 minutes mechanical stirring  
**Figure 39:** Remaining Amberlyst -16w after filtering out the liquid

Figure (37) is a picture of the beaker right after addition of catalyst to the absolute ethanol. The beaker after 120 minutes stirring is shown in Figure (38). There was no visible color change due to solubility of the catalyst and Figure (39) shows no breaking of the catalyst when the liquid was filtered out. These can be compared to the Figures (40-42).
Figure (40) shows the pre-treated catalyst right after addition of absolute ethanol to the beaker. In Figure (41) the catalyst an rinsing liquid can be seen after 120 minutes mechanical stirring in ambient conditions, a colour change can be observed in the liquid. Some fragmentation of the catalyst can be seen in Figure (42) where the pictures were taken after the liquid was filtered out of the catalyst.

Compared to the Figure (38) with the untreated catalyst, a significant increase of visible fragmentation of catalyst can be seen in Figure (41). The increased fragmentation from drying the catalyst speaks against the reusability of the catalyst, compared to the untreated catalyst. Limiting the characteristics of being heterogeneous.
Figures (43), (44) and (45) shows how the dried catalyst works with an addition of water through the use of ethanol 96%, in comparison with absolute ethanol. The picture in Figure (43) was taken right after the addition of ethanol 96% to the beaker, while Figure (44) documents the state after 120 minutes stirring. Figure (45) is documenting the state of the catalyst after removal of the liquid. In Figure (45) both the complete beads of the catalyst and the crushed catalyst resulting in the sand like texture can be observed. The trend is confirmed by the results in Table (9). From the experimental data it gives the impression that the catalyst is more sensitive to water content after drying.

In the study of Ösbay et al. [19] Amberlyst-16w was washed with methanol at 105°C before it was dried in the oven at 110°C for 12 hours. Rinsing of Amberlyst-16w was not attempted in this study to be able to see how the catalyst works without pre-treatment.
4.3.1 Weight Change of the Catalyst

When measuring the weight of catalyst on the scale, the numbers are changing rapidly without settling. To know how much air exposure influences the catalyst, tests were run with dried catalyst and catalyst directly from the container.

4.3.1.1 Weight Loss of Non-Dried Catalyst

Amberlyst-16w straight from the box contains between 52% and 58% moisture [17]. After observing distinct weight loss when measuring catalyst amount, an experiment was run to determine the extent. The initial catalyst weight was noted as 3.004g and the catalyst was kept in the room at ambient conditions with a new measurement of the weight taken in increasing intervals. The results from this experiment are displayed in Figure (46).

Figure 46: Weight of untreated Amberlyst-16w over time when exposed to air
During the first 120 minutes 24.2\% of the total weight of the catalyst was lost. When the weight had stabilized after three days of air exposure, 41.0\% of the catalyst weight was lost. It was assumed that the catalyst request to be in balance with the moisture content in the room.

4.3.1.2 Weight change of dried catalyst

To examine how the catalyst got polluted by drawing moisture from the air, an experiment was conducted to see the mass gain over time. An amount of catalyst was dried in an oven at 65°C for 24 hours. After drying it was weighed and left in the lab for air exposure under ambient conditions. The results are displayed in Figure (47).

![Figure 47: Weight gain of dried catalyst due to air exposure over time, with a visually drawn trend line](image)

The graph shows a rapid weight gain for the first 420 minutes after exposing the dried Amberlyst-16w to air. After 420 minutes the weight started to stabilize. However, the time duration for the catalyst weight to stabilize completely was between three and four weeks. Resulting in a catalyst weight gain of 0.1273g, which was an increase of 17.8\% of the starting weight of dried catalyst. In shorter exposure intervals it was found that after 10 minutes the catalyst had gained 4.8 mg, or 0.7\%. The change of weight is slower with the dried catalyst then with the experiment concerning when using catalyst directly from the container.
When the catalyst was taken directly from the container it will lose weight till it reaches a certain point of balance with the moisture of the surroundings. Similarly, the dried catalyst will gain mass until it reaches a similar equilibrium with the surroundings.

The visual appearance of the dried and not dried catalyst also changed when it was exposed to air over a longer period of time. There is a clear difference between Amberlyst-16 when exposed to air over a considerable time and Amberlyst-16 straight from the container. This can be illustrated in Figure (48).

![Figure 48: A picture of the catalyst straight from the container is shown to the left, to the right is the untreated catalyst after air exposure for over three days.](image)

Shown by Figure (48) there is a decrease in size of the catalyst after being exposed to the air. There was also a significant colour change from a brown to a darker brown colour, and with decreasing moisture content the beads no longer cling together as Amberlyst-16w taken directly from the box.

4.3.2 Non-treated Amberlyst-16w Compared to Dried Amberlyst-16w

With Amberlyst-16w, drying was tested as a pre-treatment. In the two articles found testing Amberlyst-16w the catalyst is rinsed before being dried in the oven to all moisture is removed. This treatment, as shown, resulted in increased amount of the catalyst visually dissolving in the liquid. There was also a slight increase in leaching when pre-treating the
catalyst. To see the yield of conversion of dried catalyst compared to untreated catalyst an experiment was run.

![Figure 49: Dried catalyst compared to catalyst directly from the container, N=6, C=5%, T= 60°C and stirring at 200rpm](image)

The reaction rate for the first 120 minutes were similar, then for the continuation of the experiment. The dried catalyst had a faster reaction rate and gave the highest yield after 1680 min.

In order to run with the same number of beads, both batches of catalysts were measured directly from the box. One of the batches was dried in the oven, while the other was added directly from the container. Amberlyst-16w lost approximately half of the weight when drying due to an original moisture content of 52%. The results from the dried catalyst were compared to the run under the same temperature and molar ratio but with 10% catalyst. The results are displayed in Figure (50).
Figure 50: Dried catalyst and untreated catalyst with similar number of beads used in both reactions compared to acetic acid with N=6, T=60°C and stirring at 200rpm

Figure (50) shows the dried and non-treated catalyst with the similar number of beads of both catalysts on a reaction with N=6, C=5%, stirring at 200rpm and T=60°C. The reactions are similar with a slightly faster reaction rate with the wet catalyst.

From the trends given in Figure (50), drying the catalyst has no significant benefit. The same final conversion, within the errors of the sample measurements, was reached. This was when an assumed similar numerical amount of catalyst compared to amount of acetic acid, was used.

Drying the catalyst means loosing between 52% and 58% of the mass [16, 17]. When using the same amount of catalyst from the box or pre-treated catalyst, the non treated catalyst will need twice the amount of the pre-dried catalyst. This is an expense for industrial use that must be weighed up against factors like reusability and the final conversion gained. From Figure (50) the same amount of catalyst used with wet catalyst also yields a slightly higher final conversion.
When comparing this data there is a slight advantage to the dried catalyst due to the observation that 53% of the moisture of the catalyst is lost when drying, and not 50%. A moisture content on 50% would had made the numerical bead number for dried catalyst closer to the number of beads of untreated catalyst, in relation to the amount of acetic acid used.

To investigate how drying Amberlyst-16w influences the structure and causes fragmentation of the catalyst, it was studied in a “Portable Stand Alone LCD Digital Microscope”. Samples were taken directly from the container, and from catalyst dried in the oven at 65°C for 24 hours. The pictures, taken by Dr. Marchetti, are shown in Figure (51) and (52). The pictures were taken with 500x magnifying as the maximum magnifying. A precise scale of the pictures taken was not possible to provide.

Figure 51: Pictures from microscope showing the untreated catalyst

Figure 52: Pictures from microscope showing the catalyst dried for 24 hours at 65°C

Figure (51) shows untreated Amberlyst-16w, and Figure (52) shows dried catalyst. One can observe a slight colour change, and a reduction in size. No significant sign of damage from drying can be observed on the beads in the pictures taken.
4.3.3 Effect of Catalyst Amount

Catalyst amount in relation to the amount of acetic acid, were tested to provide a broad picture of the catalyst. Amounts lower than 5% were not tested due to time limitations.

![Figure 53: Effect of catalyst amount, N=6, T= 60°C and stirring at 200rpm](image)

Figure (53) displays the variation of the conversion in response to the effect of the amount of catalyst while keeping the temperature constant at 60°C, N= 6 and the speed at 200 rpm. Figure (53) shows a clear tendency of faster reaction rates when higher amounts of catalyst was used. However, the difference between 10 and 15 is not as notorious as with 5-10 %. A reason for this might be saturation of the system due to the amount of catalyst present in the reactor. It is also worth noticing that the final conversion reached by 10 and 15 % catalyst is the same. This is since the catalyst amount does not participate in rising the equilibrium point of the reaction but the reaction rate. In the 5% catalyst run the final conversion is not reached at the point the reactor is stopped. Observing the slope of the graph indicates that it will reach the same point given adequate time.
With a higher catalyst amount the reactions reached the equilibrium point faster, without shifting the equilibrium point. The equilibrium point is achieved in shorter time with a higher catalyst amount.

The trends from the study of Ösbay et al. [19] are not directly comparable to the results from this study since the parameters tested for catalyst amounts are not in the same range. Ösbay et al. tested 1- and 2% catalyst amount [19]. The trend, which can be observed from the catalyst amount plots are still similar to those found in this study, but with lower final conversions.

4.3.4 Effect of Molar Ratio

Molar ratios tested are 3, 6, 9, and 10. Even leaps between values tested were used to better see the trend in the results. Molar ratio 10 was tested to make a better basis for comparing with the dried catalyst.

Figure 54: Effect of molar ratio tested with C=5%, T= 60℃ and stirring at 200rpm
The experiments from Figure (54) were all run with 200rpm stirring, T= 60°C and N=6. From Figure (54) it is observed that lower molar ratios yield higher conversions in the first 840 minutes. After this point there was a change in the trend with higher molar ratios continuing the curve trend and yielding higher conversions. While reactions with lower molar ratios stabilizes on their equilibriums at lower values than the still increasing values for the higher molar ratios.

This change in trend has been evaluated by Marchetti [20], the author points out that until a certain point reactions with higher molar ratios has slower reaction rates then with lower molar ratios. After the changing point the opposite trend is showed. It is argued that the reason for this is explained by both kinetics and the dissolution effect. With high molar ratios the dissolution has the strongest effect and the reaction is slow. On the contrary the final conversion is calculated by the amount of acetic acid converted to biodiesel. A higher amount of reactants limits the equilibrium point less and allows a higher final conversion [20]. Supporting this is Schuchardt et al.’s [30] argument saying that an excess of alcohol favours the formation of products while an excessive amount aggravates the recovery of the other reactant.

Having a larger ratio between alcohol and acetic acid provides more available alcohol to the reaction, securing that all of acetic acid has the opportunity to react. However, large alcohol numbers compared to FAs makes a dissolution problem that may result in a slower rate. This occurs because the catalyst has fewer FAs compared to alcohol, which makes it more difficult to find one of each. With lower numbers on molar ratios the reaction rate increases but it will reach equilibrium at an earlier stage. The effect of dissolution shall always be compared to the kinetics that might overrun some of the dissolution problems.

4.3.5 Effect of Temperature

The chosen temperature interval for testing of the catalyst was set between 40-70 °C. This is a rather broad interval, with not too heat demanding processes. Another reason for this is the limitations of the reactants used and limitations in the lab especially for higher temperature ranges, and time issues for lower temperature ranges. Generally, ion exchange resins are low in thermal stability. This makes them more applicable for low boiling reactants than reactants with a higher boiling point [3] like the reactants used in this work. The thermal stability of Amberlyst-16w is given in table (5) as 130°C, more than sufficient for a reaction
with ethanol. Deactivation of the catalyst due to high temperatures should not be a problem with this use.

![Figure 55](image_url)

**Figure 55:** Effect of temperature tested with temperatures with N=6, C=5% and stirring at 200rpm

There is a clear trend, shown in Figure (55), of an increasing conversion with increasing temperature. The highest temperature gave a conversion of 88% while the lowest tested temperature gave a conversion at 50.2% when the other reaction parameters were N=6, C=5%, and stirring at 200rpm. Together with the amount of catalyst used, the temperature is the parameter that has the biggest influence on conversion for the reaction with Amberlyst-16w, acetic acid and ethanol.

In the study by Altiokka et al [5] a study of an esterification reaction with acetic acid and amyl alcohol as reactants were performed with the presences of Amberlyst-36. These are similar components to the components in this study and a similar trend is observed with change of temperature [5]. Both reactions being strongly dependent of temperature.

Tesser *et al.* [18] tested Amberlyst-16w with methanol and oleic acid at 100°C this yielded a conversion at approximately 91% conversion. This value is not too far from the final conversion for 70°C at 88% conversion. These are resembled processes supporting the results.
found in this study. The trend of the temperature curves are also similar to the trends found in the study by Özbay et al. [19]

4.3.6 Reuse of Amberlyst-16w

The reuse test was run on the catalyst used for the 9 molar ratio experiment. The catalyst was removed as explained and used directly without further treatment. This was done in this manner to show how the catalyst would perform with other reactor types as well. Packed bed reactors or membrane reactors are reactors where treating the catalyst between each run is difficult.

Figure 56: Reuse of catalyst from experiment with N=9, C=5%, T=60 and stirring at 200rpm, all runs are with the same parameters and treatment between runs

The reuse tests were run to the length of four reuses as displayed in Figure (56). The catalyst had a slower initial reaction rate, which is particularly plain on the graph during the
first 600 minutes. The drop in reaction rate in the start of the reaction is largest from the basis to the first reuse.

Within the experimental error all reuses of the catalysts yields the same final conversion after 1680 minutes. This indicates that the catalyst was not significantly deactivated by the reaction liquid or the reactants used in this work. Making the catalyst reusable up to four times under the conditions tested.

To examine the effect of reuse of the untreated catalyst, a sample from catalyst filtered out after a 28 hour run of the N=9, T=60°C, C=5% experiment is compared to unused catalyst taken directly from the container. The pictures are taken with 500x magnifying as the maximum.

Figure 57: Pictures from the microscope showing the used catalyst to the right comparing with the unused catalyst to the left.

Figure (57) is a microscope-picture of untreated Amberlyst-16w to the left and used catalyst to the right. The used catalyst was collected from the first reaction with N=9, T=60°C, C=5%. There is no visual difference, nor signs of breakage to be observed in Figure (57). This supports the findings of Figure (54) that the final conversion of the catalyst does not decrease in the experiments conducted, and that the catalyst does not get significantly deactivated in use.
4.3.7 Evaluation of Experimental Errors in this Work

When doing the experiments all samples were titrated twice, using the average sample as the result. Some experiments were also repeated to ensure replicability in the results given.

There were some possible sources for errors from evaporation of measured components during the time spent to add the components to the reaction mixture, or to cover them in order to prevent evaporation when preparing the reactor for a run. Another source of error is when sampling from the reactor, parts of the total volume is also removed. When taking small enough samples and not too many, sampling will not affect the reaction by concentration change significantly by changing the volume. Finally, the possibility of change of volume due to evaporation of the reaction liquid during reaction time is a possible source of error.

There were many sources for experimental error in the titration, both when sampling, measuring samples on the weight, and finding the correct point of neutral. Some of the more important experimental errors are mentioned in the following part.

When working with the experiment the temperature in the reactor fluctuated with ±0.2°C. When sampling there was also an error of ±1 minute on the sampling time. This might have impacted on the sample results. Another challenge was the possibility of getting fragmentation of the catalyst in the sample. This was a big problem with the Tulsion catalysts, but not a significant problem with Amberlyst-16w.

Another possibility for errors was the sample analysis. Some important sources to mention was the evaporation of the titration sample when measuring the sample weight. This caused the weight not to follow the evaporation completely, further causing sudden and significant drops in weights, and/or not settling on a number. When measuring values between 0.02g and 0.05g, weight drops at 1mg have an important impact on the result. To limit the errors made, approximately the same time was used before adding the titration mixture to the sample every time. There was also the issue of the amount of titration mixture (di-ethyl-ether and ethanol 96%) added that should be close to 10 mL, as well as the accuracy on concentration value of KOH used as titration liquid. When titrating the liquid, another challenge was to always use the same shade of pink as neutral. To restrict this error, the first colour of pink was used, still resulting in an error of ±2 drops.
It could be noted that the error on the values given from this study might have an error of $\pm (2 - 3)\%$. Replicas have been run on some of the experiments to check the validity of the data found.

4.3.8 Components in the Reaction

Esterification reactions with long chain acids are more difficult compared to esterifying shorter chains like the chains in Acetic acid [3]. Acetic acid is chosen to eliminate this difficulty, and because of the availability.

When using ethanol and acetic acid the highest temperatures, you could run the reaction at ambient pressures and the equipment available was 78°C. With the higher limit at 78°C the chosen temperature range was set to be between 40°C and 70°C. This was also due to more evaporation from the reactor with higher temperatures.

4.3.9 Non Tested Parameters

The effect of the parameters not mentioned in the laboratorial study is for instance the mass transfer resistance. Due to time issues the effect of stirring speed was not tested in this study, and the stirring was kept on 200rpm. Giving no direct information regarding the diffusion limitations of the catalyst besides what could be said from a possible kinetic modelling. The results from Altiokka et al [5] supports earlier results showing that most of the Amberlyst series resins have neglectable internal and external diffusion.

In addition, the acid catalysts generally have slower reaction rates than base catalysts, and require higher temperatures and pressures to reach high conversions over a limited time span [11]. With the limitations of the components in the reaction the ideal parameters for the reaction might not have been tested in this work.
4.3.10 Kinetics Modelling

There are several mechanisms for this reaction. This particular attempt on finding a model is also used on an acid esterification reaction with methanol using Amberlyst-46 as catalyst by Oguzhan Ilgen (2014) [34]. This is a similar process which is the reason why this mechanism was the first take into consideration. The strong dependency of temperature indicates that the total reaction is controlled by the surface reaction [5]. Choosing this step as the controlling step when writing the mechanism for the reaction.

\[ r_1: \quad A + S \xrightarrow{k_1} AS \xleftarrow{k_1^{-1}} \quad \text{Adsorption} \quad (13) \]
\[ r_2: \quad AS + FA \xrightarrow{k_2} BDS + W \xleftarrow{k_2^{-1}} \quad \text{Surface reaction} \quad (14) \]
\[ r_3: \quad BDS \xrightarrow{k_3} BD + S \xleftarrow{k_3^{-1}} \quad \text{Desorption} \quad (15) \]

Writing the reaction rates, with Equation (10), given that every step is a composition of elementary reactions. Simplifying by using the identity in Equation (11).

\[ r_1 = k_1 \left( C_A C_S - \frac{C_{AS}}{K_1} \right) \quad (16) \]
\[ r_2 = k_2 \left( C_{AS} C_{FA} - \frac{C_{BDS} C_W}{K_2} \right) \quad (17) \]
\[ r_3 = k_3 \left( C_{BDS} - \frac{C_{BD} C_S}{K_3} \right) \quad (18) \]

Where \( C_A \) is concentration of alcohol, \( C_S \) is concentration of vacant active sites, \( C_{AS} \) is concentration of active sites connected to alcohol, \( C_{FA} \) is concentration of fatty acids, \( C_{BDS} \) is
concentration of active sites connected to biodiesel, $C_W$ is concentration of water and $C_{BD}$ is concentration of biodiesel.

Choosing surface reaction, given with Equation (17), as the controlling reaction and treating $r_1$ and $r_3$ as in equilibrium yielding Equation (20) when using Equation (19).

$$C_T = C_s + C_{AS} + C_{BDS}$$  \hspace{1cm} (19)

Where $C_T$ is the total amount of catalyst active sites, $C_s$ is the number of available active sites, $C_{AS}$ are the active sites occupied by ethanol and $C_{BDS}$ are the active sites occupied by biodiesel before desorption.

$$r_2 = k_3 \left( \frac{C_T}{1+K_1C_A + \frac{C_{BD}}{K_3}} \right) \left( K_1C_AC_{FA} - \frac{C_{BD}C_W}{K_2K_3} \right)$$  \hspace{1cm} (20)

Where $C_A$ is concentration of alcohol, $C_{FA}$ is concentration of fatty acids, $C_W$ is concentration of water, $C_{BD}$ is concentration of biodiesel, $k_2$ is the reaction rate of the reaction step and $K_i$ is found from the relation described in Equation (11).

Figure 58: Surface reaction model with experimental data, T=60°C, C=5%, N= 6

Figure 59: Surface reaction model with experimental data, T=70°C, C=5%, N= 6
Figure (58-61) shows the chosen model with the surface reaction as the controlling step. In this part the orange line is the mechanism while the blue points are experimental data for the given experiment. The plotted values are for the amount of acetic acid in the sample. Only a selection of the experiments with belonging models are shown in the text. The remaining are displayed in the appendix. The fit between the experimental values and the model is good for low temperatures and the baseline, but not a preferable fit for higher temperatures, molar ratios and particularly higher catalyst amounts. The model with the parameter values found does not follow the trend of the experimental data completely at all of these experiments.

To test the model thoroughly the model was applied with adsorption as the controlling step before desorption was tested. Some of the plots with their best fitting parameter values are presented in the text, while the rest are shown in the Appendix.

Choosing adsorption, given with Equation (16), as the controlling step and treating $r_2$ and $r_3$ as in equilibrium yields Equation (21) when using Equation (19).

$$r_1 = \frac{k_1}{1 + K_3 C_{BD} + \frac{C_{BD} C_W}{K_2 K_3 C_{FA}^2}} \left( C_A - \frac{C_{BD} C_W}{K_1 K_2 K_3 C_{FA}} \right)$$  (21)

Where $C_A$ is concentration of alcohol, $C_{FA}$ is concentration of fatty acids, $C_W$ is concentration of water, $C_{BD}$ is concentration of biodiesel, $k_2$ is the reaction rate of the reaction step and $K_i$ is found from the relation described in Equation (11).
Figure 62: Adsorption model with experimental data, T=60°C, C=5%, N= 6

Figure 63: Adsorption model with experimental data, T=70°C, C=5%, N= 6

Figure 64: Adsorption model with experimental data, T=60°C, C=5%, N= 9

Figure 65: Adsorption model with experimental data, T=60°C, C=15%, N= 6:

Figure (62-65) shows the chosen model with the adsorption reaction as the controlling step. The model did not give preferable fit to the experimental data on both catalyst amount, temperature and molar ratio. This can be seen when studying the trend of the model in Figure (63).

When using the desorption step, given in Equation (18) as the controlling elementary reaction and treating $r_2$ and $r_1$ as in equilibrium, this yields Equation (22) when using Equation (19).
\[ r_3 = k_5 \left( \frac{C_T}{1 + K_1 C_A + \frac{C_A C_{FA} K_1 K_2}{C_W}} \right) \left( \frac{C_A C_{FA} K_1 K_2}{K_2 C_W} - \frac{C_E}{K_3} \right) \]  

(22)

Where \( C_A \) is concentration of alcohol, \( C_{FA} \) is concentration of fatty acids, \( C_W \) is concentration of water, \( C_{BD} \) is concentration of biodiesel, \( k_2 \) is the reaction rate of the reaction step and \( K_i \) is found from the relation described in Equation (11).

The model based on desorption as the controlling step is illustrated when plotted against experimental values in Figure (66-69). From the graphs given, this is the generally least fitting version of the model. This can also be shown by looking at the RMS values calculated the program with Equation (4) Where the adsorption had the best fit in the overall model, from
these results. It can not be known that adsorption is the controlling step from these results when using another model.

Adsorption as controlling step: 3,3184e-001  
Surface reaction as controlling step: 3,4586e-001  
Desorption as controlling step: 3,4032e-001

The calculated RMS value from the program may be misleading due to the issue that a graph that has the wrong trend, still might fit some of the points from the experimental values. This gives these graphs a lower RMS value while still having a non-correct trend curve. From observing the graphs this might be the case for the desorption step in particular. From the observations from the graphs, the models found when adsorption and surface reaction are controlling steps gives a better picture of the trend then the desorption step.

To be able to develop a correct kinetic model, the model needs to be able to interpret all the experimental data. No parameters were found to match with all experiments. Resulting in the conclusion that the model attempted may be wrong. The model does not give a precise function of both temperature, catalyst amount and molar ratio, for any of the three controlling steps tested. A better alternative might be found when testing other models.

The rest of the possible models needs to be attempted to know which is the best model and the controlling step of the reaction. The model tested in this study does not give a good description of the reaction found in the lab.
5 CONCLUSIONS

5.1 TULSION-6812 AND TULSION-63

With the results from this study Tulsion-6812 and Tulsion-63 had too severe leaching to be used as heterogeneous catalysts. With the observed fragmentation of catalysts in polar liquids they are not easily reusable and do not fill the requirements as an ideal heterogeneous catalyst in this work. These catalysts require further study on pre-treatment methods in order to come up with a final conclusion on this part.

5.2 AMBERLYST-16W

From the experiments done, drying the catalyst as a pre-treatment had no positive effect regarding the parameters tested. For the untreated catalyst, the rate of reaction will increase with higher temperatures. The final conversion will increase with increasing catalyst amount within the given time interval. Higher molar ratios will enhance the final conversion by pushing the equilibrium, while lower molar ratios yield higher conversion for shorter reaction time.

The kinetic modelling with the model chosen does not give an ideal fit to the experimental data when using any of the three elementary reactions as the controlling step. More models need to be attempted to know which model is the best for this process.
6 Future Work

The Tulsion catalysts both need further analyses in order to come up with an effective pre-treatment method, to have less severe leaching and fragmentation of the catalyst. Tulsion-63 has earlier been used with iso-amyl alcohol and acetic acid. The pre-treatment used was washing with water and methanol before drying in a vacuum oven at 75°C until the water content was completely removed [14]. In the research by Patil et al. [14] the method used gave acceptable reuse conversions with Tulsion-63, even though a Pseudo homogenous model was still used for the kinetics.

This process can be further optimized with ideal temperature and molar ratio for the reaction. The catalyst amount added can be optimized to the time available to convert a certain amount of fatty acids to biodiesel. All of the experiments have been run at ambient pressure. Pressure is an important factor for the degree of conversion so finding an ideal pressure is part of the total optimization of the process. A further study with higher pressures and temperatures may give a more complete analysis of the catalyst.

Different stirring speeds were not tested in this work, due to time limitations. A higher stirring speed could affect the reaction rates significantly and be an important parameter that should be tested.

Testing with different oils, would give a wider characterization of the catalyst. Oleic acid is similar to many of the FA compositions given in Table (1), so a continuation of this study could be to test the catalyst with ethanol and for instance oleic acid. This is a factor that could be even more central with a polymeric catalyst due to the trend that ion exchange resins behave differently with different reaction mediums [3].

To give a kinetics with a good fit with the experimental data, different models and controlling steps needs to be tested. To be able to know the model with the best fit to the experimental data, not only different reaction pathways but also steps controlling the overall process should be taken into consideration.
7 REFERENCES


## APPENDIX

### 8.1 LIST OF EXPERIMENTS

A list of the experiments performed in this work

<table>
<thead>
<tr>
<th>Exp. Number</th>
<th>Exp. description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Leaching test with T-6812 and rectified ethanol; T=ambient, magnetic stirrer, 120 min</td>
</tr>
<tr>
<td>2</td>
<td>Leaching test with T-63 and rectified ethanol; T=ambient, magnetic stirrer, 120 min</td>
</tr>
<tr>
<td>3</td>
<td>Leaching test with T-6812 and absolute ethanol; T=ambient, manual stirring, 120 min</td>
</tr>
<tr>
<td>4</td>
<td>Leaching test with T-63 and absolute ethanol; T=ambient, manual stirring, 120 min</td>
</tr>
<tr>
<td>5</td>
<td>Leaching test with dried T-6812 and absolute ethanol; T=ambient, magnetic stirrer, 120 min</td>
</tr>
<tr>
<td>6</td>
<td>Leaching test with dried T-6812 and absolute ethanol; T=ambient, magnetic stirrer, 120 min</td>
</tr>
<tr>
<td>7</td>
<td>Leaching test with T-6812 rinsed in absolute ethanol, and absolute ethanol; T=ambient, magnetic stirrer, 120 min</td>
</tr>
<tr>
<td>8</td>
<td>Leaching test with T-63 rinsed in absolute ethanol, and absolute ethanol; T=ambient, magnetic stirrer, 120 min</td>
</tr>
<tr>
<td>9</td>
<td>Leaching test with dried T-6812 and distillate water; T=ambient, magnetic stirrer, 120 min</td>
</tr>
<tr>
<td>10</td>
<td>Leaching test with dried T-63 and distillate water; T=ambient, magnetic stirrer, 120 min</td>
</tr>
<tr>
<td>11</td>
<td>Leaching test with T-6812 and distillate water; T=ambient, manual stirrer, 120min</td>
</tr>
<tr>
<td>12</td>
<td>Leaching test with T-63 and distillate water; T=ambient, manual stirrer, 120min</td>
</tr>
</tbody>
</table>
13 Leaching test with T-6812 rinsed in distillate water and dried, and distillate water; T=ambient, manual stirrer, 120min
14 Leaching test with T-63 rinsed in distillate water and dried, and distillate water; T=ambient, manual stirrer, 120min
15 Leaching test with T-6812 and Acetone; T=ambient, manual stirrer, 120min
16 Leaching test with T-63 and Acetone; T=ambient, manual stirrer, 120min
17 Leaching test with T-6812 rinsed in Acetone and dried, and Acetone; T=ambient, manual stirrer, 120min
18 Leaching test with T-63 rinsed in Acetone and dried, and Acetone; T=ambient, manual stirrer, 120min
19 Leaching test with T-6812 and Acetone; T=ambient, magnetic stirrer, 120min
20 Leaching test with T-63 and Acetone; T=ambient, magnetic stirrer, 120min
21 Leaching test with T-6812 rinsed with magnetic stirrer in Acetone, and Acetone; T=ambient, magnetic stirrer, 120min
22 Leaching test with T-6812 rinsed with magnetic stirrer in Acetone, and Acetone; T=ambient, magnetic stirrer, 120min
23 Final conversion screening, with acetic acid and ethanol; N=6, C=0, T=ambient
24 Final conversion screening, T-6812 with acetic acid and ethanol; N=6, C=2, T=ambient
25 Final conversion screening, T-63 with acetic acid and ethanol; N=6, C=2, T=ambient
26 Final conversion screening, sulfuric acid with acetic acid and ethanol; N=6, C=2, T=ambient
27 Final conversion screening, T-6812 rinsed twice (stirring by hand) with distillate water and dried, with acetic acid and ethanol; N=6, C=2, T=ambient
28 Final conversion screening, T-63 rinsed twice (stirring by hand) with distillate water and dried, with acetic acid and ethanol; N=6, C=2, T=ambient
29 Final conversion screening, T-6812 rinsed twice (stirring by hand) with Acetone, with acetic acid and ethanol; N=6, C=2, T=ambient
30 Final conversion screening, T-63 rinsed twice (stirring by hand) with Acetone, with acetic acid and ethanol; N=6, C=2, T=ambient
31 Acetic acid and absolute ethanol; 180 min, N=6, C=0, T=ambient
32 T-6812 with acetic acid and absolute ethanol; 180 min, N=6, C=2, T=ambient
33 T-63 with acetic acid and absolute ethanol; 180 min, N=6, C=2, T=ambient
Reactor experiment, T-6812 with acetic acid and absolute ethanol; N=10, C=2, T=65

Reactor experiment T-6812 with acetic acid and absolute ethanol; N=6, C=5, T=65

Reactor experiment T-6812 with acetic acid and absolute ethanol; N=6, C=2, T=65

Reactor experiment T-6812 with oleic acid and absolute ethanol; N=6, C=2, T=65

Leaching test with A-16, and absolute ethanol; T=ambient, magnetic stirrer, 120min

Leaching test with dried A-16, and absolute ethanol; T=ambient, magnetic stirrer, 120min

Leaching test with A-16, and rectified ethanol; T=ambient, magnetic stirrer, 120min

Leaching test with dried A-16, and rectified ethanol; T=ambient, magnetic stirrer, 120min

Leaching test with A-16w, and distillate water; T=ambient, magnetic stirrer, 120min

Reactor experiment A-16w with acetic acid and absolute ethanol; N=6, C=5, T=60, time= 1hours (evaporated)

Reactor experiment dried A-16 wet with acetic acid and absolute ethanol; N=6, C=5, T=60, time= 4hours

Reactor experiment A-16w with acetic acid and absolute ethanol; N=6, C=5, T=60, time= 5hours

Reactor experiment long run A-16w with acetic acid and absolute ethanol; N=6, C=5, T=60, time= 2040min

Reactor experiment long run dried A-16w with acetic acid and absolute ethanol; N=6, C=5, T=60, time= 1680min

Reactor experiment long run A-16w with acetic acid and absolute ethanol; N=6, C=10, T=60, time= 1680min

Reactor experiment long run A-16w with acetic acid and absolute ethanol; N=6, C=15, T=60, time= 1680min

Reactor experiment long run A-16w with acetic acid and absolute ethanol; N=6, C=5, T=70, time= 1680min
51 Reactor experiment long run A-16w with acetic acid and absolute ethanol; N=6, C=5, T=50, time= 1680min
52 Reactor experiment long run A-16w with acetic acid and absolute ethanol; N=6, C=5, T=40, time= 1680min
53 Reactor experiment long run A-16w with acetic acid and absolute ethanol; N=3, C=5, T=60, time= 1680min
54 Reactor experiment long run A-16w with acetic acid and absolute ethanol; N=10, C=5, T=60, time= 1680min
55 Reactor experiment long run A-16w with acetic acid and absolute ethanol; N=9, C=5, T=60, time= 1680min
56 Reactor experiment retest A-16w with acetic acid and absolute ethanol; N=6, C=5, T=40
57 Reactor experiment retest A-16w with acetic acid and absolute ethanol; N=6, C=5, T=50
58 Reactor experiment retest A-16w with acetic acid and absolute ethanol; N=6, C=5, T=40
59 Reactor experiment 1. reuse of catalyst from experiment 55, long run A-16w with acetic acid and absolute ethanol; N=9, C=5, T=60, time= 1680min
60 Reactor experiment 2. reuse of catalyst from experiment 55, long run A-16w with acetic acid and absolute ethanol; N=9, C=5, T=60, time= 1680min
61 Reactor experiment 3. reuse of catalyst from experiment 55, long run A-16w with acetic acid and absolute ethanol; N=9, C=5, T=60, time= 1680min
62 Reactor experiment 4. reuse of catalyst from experiment 55, long run A-16w with acetic acid and absolute ethanol; N=9, C=5, T=60, time= 1680min
8.2 THE SCRIPT USED IN ASPEN

The script that was used to write the model tested in Polymath. Here shown with the reaction step as the controlling step of the reaction.

```plaintext
Model rh11
Ca as concentration;
Cf as concentration;
Cm as concentration;
Cw as concentration;
Ce0 as concentration;
Cm0 as concentration;
k11 as setconstant;
k22 as setconstant;
k33 as setconstant;
k44 as setconstant;
k55 as setconstant;
k66 as setconstant;
E1 as energy;
E2 as energy;
E3 as energy;
E4 as energy;
E5 as energy;
E6 as energy;
T as temperature;
R as reallvalue (1.98);
k1 as constant;
k2 as constant;
k3 as constant;
k4 as constant;
k5 as constant;
k6 as constant;
k1=k11*exp(-E1/(R*T));
k2=k22*exp(-E2/(R*T));
k3=k33*exp(-E3/(R*T));
k4=k44*exp(-E4/(R*T));
k5=k55*exp(-E5/(R*T));
k6=k66*exp(-E6/(R*T));
xa as conversion;
m0 as catalyst;
xa=1-Ca/Ca0;
//Ca=Ca0*(1-xa);
Cf=Ca0*xs;
Cm=Cm0-(Ce0*xs);
Cw=Cw0*xs;
xa=((((k1*Cm+Ce0*k3)/(k2))-(2*(k4+Cf+Cw)/(k5)))^((m0/2)+k1*Cm)/(k2)+((k6+Cf)/(k5))))/Ce0;
End
```
8.3 RESULTS FROM MODELLING IN ASPEN

The amount of acetic acid, plotted with the model found. The parameters found for each model are given for every chosen controlling step.

8.3.1 Surface Reaction as Controlling Step

Figure A1: Model with experimental data, T=40°C, C=5%, N=6

Figure A2: Model with experimental data, T=50°C, C=5%, N=6

Figure A3: Model with experimental data, T=60°C, C=5%, N=6

Figure A4: Model with experimental data, T=70°C, C=5%, N=6
Figure A5: Model with experimental data, $T=60^\circ C$, $C=5\%$, $N=3$

Figure A6: Model with experimental data, $T=60^\circ C$, $C=5\%$, $N=9$

Figure A7: Model with experimental data, $T=60^\circ C$, $C=5\%$, $N=10$

Figure A8: Model with experimental data, $T=60^\circ C$, $C=10\%$, $N=6$

Figure A9: Model with experimental data, $T=60^\circ C$, $C=15\%$, $N=6$
Table A1: Parameters when the surface reaction is the controlling step

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>E1</td>
<td>12974.1</td>
<td>k001</td>
<td>8682.5</td>
</tr>
<tr>
<td>E2</td>
<td>17402.5</td>
<td>k002</td>
<td>19856.7</td>
</tr>
<tr>
<td>E3</td>
<td>23153.4</td>
<td>k003</td>
<td>78481.7</td>
</tr>
<tr>
<td>E4</td>
<td>17601.1</td>
<td>k004</td>
<td>962.659</td>
</tr>
<tr>
<td>E5</td>
<td>12468.7</td>
<td>k005</td>
<td>8461.52</td>
</tr>
<tr>
<td>E6</td>
<td>8480.0</td>
<td>k006</td>
<td>105.787</td>
</tr>
</tbody>
</table>

8.3.2 Adsorption as Controlling Step

Figure A10: Adsorption model with experimental data, T= 40°C, C=5%, N=6

Figure A11: Adsorption model with experimental data, T=50°C, C=5%, N=6

Figure A12: Adsorption model with experimental data, T=60°C, C=5%, N=6

Figure A13: Adsorption model with experimental data, T=70°C, C=5%, N=6
Figure A14: Adsorption model with experimental data, $T=60^\circ C$, $C=5\%$, $N=3$

Figure A15: Adsorption model with experimental data, $T=60^\circ C$, $C=5\%$, $N=9$

Figure A16: Adsorption model with experimental data, $T=60^\circ C$, $C=5\%$, $N=10$

Figure A17: Adsorption model with experimental data, $T=60^\circ C$, $C=10\%$, $N=6$

Figure A18: Adsorption model with experimental data, $T=60^\circ C$, $C=15\%$, $N=6$
Table A1: Parameters when the adsorption is the controlling step

<table>
<thead>
<tr>
<th></th>
<th>E1</th>
<th>k001</th>
<th>E2</th>
<th>k002</th>
<th>E3</th>
<th>k003</th>
<th>E4</th>
<th>k004</th>
<th>E5</th>
<th>k005</th>
<th>E6</th>
<th>k006</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>12971.8</td>
<td>11166.1</td>
<td>17378.7</td>
<td>19793.0</td>
<td>23144.2</td>
<td>74208.0</td>
<td>17649.8</td>
<td>1631.14</td>
<td>12408.3</td>
<td>7828.22</td>
<td>8747.2</td>
<td>105,298</td>
</tr>
</tbody>
</table>

8.3.3 Desorption as Controlling Step

**Figure A19**: Desorption model with experimental data, T= 40°C, C=5%, N=6

**Figure A20**: Desorption model with experimental data, T=50°C, C=5%, N=6

**Figure A21**: Desorption model with experimental data, T=60°C, C=5%, N=6

**Figure A22**: Desorption model with experimental data, T=70°C, C=5%, N=6
Figure A23: Desorption model with experimental data, T=60°C, C=5%, N= 3

Figure A24: Desorption model with experimental data, T=60°C, C=5%, N= 9

Figure A25: Desorption model with experimental data, T=60°C, C=5%, N=10

Figure A26: Desorption model with experimental data, T=60°C, C=10%, N= 6

Figure A18: Adsorption model with experimental data, T=60°C, C=15%, N= 6
Table A3: Parameters when the desorption is the controlling step

<table>
<thead>
<tr>
<th></th>
<th>E1</th>
<th>k001</th>
<th>10974.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1</td>
<td>12971.8</td>
<td>k001</td>
<td>10974.0</td>
</tr>
<tr>
<td>E2</td>
<td>17370.7</td>
<td>k002</td>
<td>19222.5</td>
</tr>
<tr>
<td>E3</td>
<td>23092.4</td>
<td>k003</td>
<td>78481.7</td>
</tr>
<tr>
<td>E4</td>
<td>16928.3</td>
<td>k004</td>
<td>1631.14</td>
</tr>
<tr>
<td>E5</td>
<td>12399.2</td>
<td>k005</td>
<td>7829.12</td>
</tr>
<tr>
<td>E6</td>
<td>8737.0</td>
<td>k006</td>
<td>105.782</td>
</tr>
</tbody>
</table>