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Biodiesel by acid-catalyzed transesterification with butanol

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Abstract

Jatropha oil and Rapeseed oil was transesterified with *n*-butanol by the use of H_2SO_4. Before conducting the experiments a review of the effect of alcohol type was preformed. Alcohols from methanol to butanol, branched and straight, were reviewed for the effect on the acid catalyzed transesterification reaction. From the review it was found that propanol and butanol were the best for the acidic transesterification reaction.

Variables such as time, temperature, alcohol amount and catalyst concentration were investigated in the experiments. The variables were compared to the responses yield, viscosity and acid number by employing response surface methodology. All experiments were analyzed with H-NMR and a NMR atlas was constructed. The time needed for a complete acid esterification with transesterification was found equal to the time needed for acid esterification with alkali transesterification. For the acidic transesterification it was found that temperature plays a vital role and needs to be as high as possible, preferably the boiling point of butanol. Catalyst concentration was compromised between acid number and viscosity to 2 % v/v. The amount of alcohol was proven to reach an optimum for rapeseed oil at 7.0 equivalents, whereas 7.5 equivalents were found for jatropha oil.

Acknowledgement

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I would as well express gratitude to Ingvar Eide at Statoil ASA for his help with response surface methodology and his modeling of the results for this thesis.

Adrian N. Bynes

Content

Abbreviations

AV = Acid Value (the same as AN)

AN = Acid Number (the same as AV)

CCD = Central Composite Design

CCFD = Central Composite Face-centered Design

CN = Cetane number

CP = Cloud point

FAAE = Fatty acid alkyl ester

FABE = Fatty acid butyl ester

FAME = Fatty acid methyl ester

FFA = Free Fatty acid

HC = Heat of combustion

NMR = Nuclear magnetic resonance

PP = Pour point

R^2 = the coefficient of multiple determination

R^2_{adj} = Adjusted R^2

R^2_{pre} = R^2 for predictions

RSM = Response surface methodology

VGO = Vegetable oil

% v/v = Volume percentage

% w/w = Weight percentage

1. Introduction

The growing need for energy combined with the declining volume of petroleum reserves has led to increased interest in alternative fuels as biodiesel [1-3]. The European parliament has defined a goal for biodiesel usage of 10% by 2020 [4].

When Rudolph Diesel invented the diesel engine, he initially fueled it with vegetable oil (VGO) [5, 6]. However, the usage of VGO in diesel engines suffers from several drawbacks over time, mainly due to their high viscosity. Some of the problems with VGO in diesel engines are for example carbon deposition, injector plugging and piston sticking amongst others [1, 3, 5-8]. On the other hand, an advantage with biodiesel is comparable properties with diesel and with far lower viscosity than VGO. It can be used blended or sometimes unblended in a diesel engine without modifications [1, 3-5, 9]. Biodiesel is normally defined as fatty acid methyl esters or FAME for short. However, it is useful when other alcohols than methanol are used to introduce fatty acid alky esters (FAAE) [1, 3, 5, 10, 11]. If biodiesel production is to become 100% renewable, ethanol or butanol which both are obtainable through fermentation should be used [4, 7].

There are four main methods to reduce the viscosity of VGO: blending, microemulsion, pyrolysis and transesterification [3, 6, 9]. Blending refers to mixing VGO with diesel to achieve an acceptable viscosity. Microemulsion is a clear fluid consisting of oil and water phases (an alcohol) together with a surfactant. Pyrolysis is decomposition (cracking) of the oil by means of heating or a catalyst without the presence of oxygen to reduce its viscosity [3, 6, 7, 9, 12]. All three methods reduce the viscosity, but blending and microemulsion will continue to give the same engine problems as VGO [6]. The product of pyrolysis may be chemically comparable to fossil fuel but the method is very expensive [6]. The last method is transesterification. It is an efficient and commonly used method for reducing the viscosity of VGO and produce biodiesel [3, 5-9]. It can be done with acidic, alkali or enzymatic catalysts. The acidic and alkali catalysts can be in liquid or solid state, where liquid catalysts are the most common.

The focus of the thesis

The thesis will focus on finding relationships between the variables affecting the one-step acid catalyzed transesterification. An acidic catalyst was chosen due to its ability to handle free fatty acids. Sulfuric acid will be used as it is one of the most common acids for acidic transesterification. The choice of alcohol was n-butanol due to its renewability combined with the prospect for this alcohol coupled with acidic catalysts. All of this will be considered further through chapter 2 and discussed in chapter 5.

2. Background & theory

The general transesterification reaction involves glycerol triesters (oil, triglyceride) changed to alkyl monoesters (FAME/FAAE) [1, 5, 6, 12]. Stoichiometric 3 moles of alcohol are needed per mole of triglyceride [1, 5, 8, 10]. The reaction is normally catalyzed with an alkali, but also acidic and enzymatic catalysts are used [3, 6].

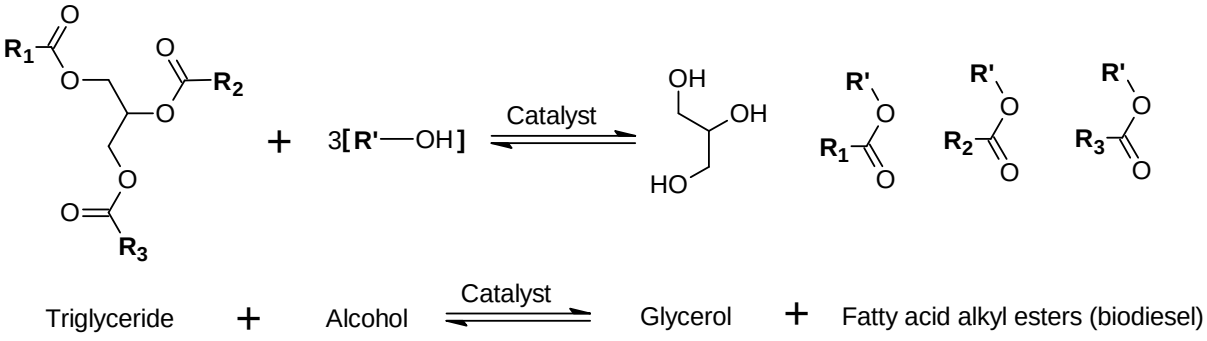


Figure 1: A stoichiometric transesterification reaction [1, 5].

2.1. Catalysts

Enzymatic catalysts have received much attention as they avoid soap formation which is a problem for the most common alkali catalysts when faced with low quality oils. The enzymatic catalyst also reduces wastewater and in general do not have any side reactions. This type of catalyst has a long reaction time and is more expensive than the commonly used alkali catalysts [1, 3]. Catalysts in solid state have also been researched on as they simplify the catalyst regeneration process and separation is easy (filtration); hence generating less wastewater. However, they are also are expensive with long reaction time and with a high alcohol to oil ratio compared to liquid catalysts [1, 3, 12]. The alkali/acidic catalyst description below refers to liquid catalysts.

Alkali catalysts are the most commonly used and the fastest at room temperature [1, 3, 5-7, 12]. Common alkalis are NaOH and KOH among others [5, 6]. When using this type of catalyst it is recommended to use methanol as alcohol due to its reactivity with the alkalis [1, 3, 5, 6]. Indeed several studies have reported troubles when using alcohols with longer chains than ethanol together with an alkali catalyst. The long chained alcohols do not react with an alkali type catalyst [1, 5, 7]. Alkali catalysts acts by eliminating a proton from the alcohol before the anion of the alcohol act upon the oil, therefore it is commonly regarded as a pre-step before the transesterification occurs between the alcohol anion and the oil [1, 6].

Alkali catalysts have several advantages with a lower catalyst and alcohol concentration as well as being non-corrosive towards the reactor compared to other catalyst types [1, 5]. However, when more than 1 % of free fatty acids (FFA) are present, alkali catalysts generate water and soap. This can potentially stop the reaction and make recovery of the product difficult [1, 3, 5, 6, 8, 10].

In non-edible oil, waste frying oil and algae oil a significant volume of FFA is typical. However, these oils are generally less expensive compared to VGO [1, 3, 8, 10, 13]. The cost of VGO is increasing with the growing human population [1, 3, 4, 6]. Already ¾ of the total costs of biodiesel production is associated with the oil [3, 6, 12]. This increases the attention towards waste oil and non-edible oil for biodiesel production. By using an acidic catalyst the FFA is converted to biodiesel by esterification. Acidic catalysts require high temperatures to be completed within a reasonable time [1, 3, 5-7, 10]. Normally acidic catalysts and esterification are used as a pretreatment before conducting transesterification with an alkali catalyst, in a two-step process [3, 5, 13, 14]. Sulfuric acid is mostly used, but also phosphoric acid and hydrochloric acid amongst others are reported [1, 3, 5-7, 10].

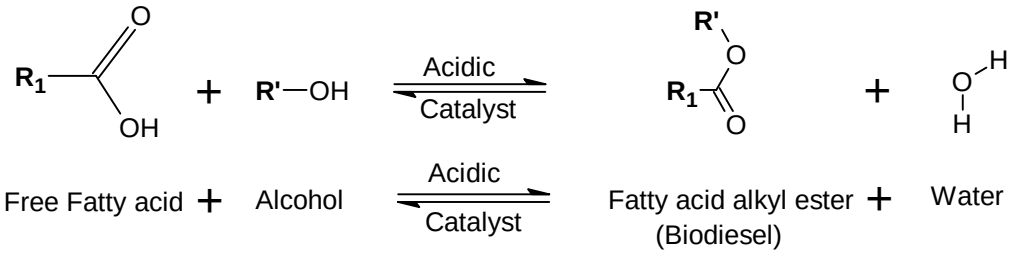


Figure 2: Esterification reaction [12].

2.2. The Feedstock oil

Hoekman et al. [15] found in their review that an increased unsaturation decreased the viscosity and gave far better cold flow properties. Increased poly-unsaturation gave worse oxidative stability, the more unsaturated the more it contributes to instability. Linolenic acid is the most dominant and has an upper limit in the EU standard for biodiesel (EN14214) at 12 % w/w [15, 16]. Viscosity, cold flow and oxidative stability are some of the most important properties for the biodiesel. Viscosity and cold flow will be discussed further in chapter 2.3.2.

Both Jatropha and rapeseed oil have large amounts of oleic acid giving lower viscosity and better cold flow properties. Rapeseed has some linolenic acid below the limit of 12 % while Jatropha have 16 % saturated fatty acid (palmitic) which can worsen its cold flow properties. Despite these adverse properties, Rapeseed is amongst the most commonly used VGO for biodiesel production while Jatropha is amongst the top choices for non-edible oils. For more information on the selection of feedstock oil for biodiesel production the reader is recommended to see the review of Hoekman et al [15].

Rapeseed oil production is increasing rapidly. It is the fourth most produced oilseed in the world and is the dominant feedstock in Europe [15, 17]. It is considered a 1st generation feedstock as it is a VGO [15]. The high production per unit land makes rapeseed on of the most popular choices for biodiesel production [17]. About 40 % of oil can be extracted from the plant and used for biodiesel production. The remains after pressing for oil contain 38-43 % of protein and can be utilized for food production [17]. The main fatty acids in rapeseed oil are oleic acid (64 %), linoleic acid (22.3 %) and linolenic acid (8.4 %) [5, 6, 8, 15]. As rapeseed oil is a VGO it should be sensitive to rising prices in the future. However, it is important to note that the remains after pressing still can be used as food.

Jatropha curcas is a bush or small tree receiving increasing interest as a potential biodiesel source and is considered a 2nd generation feedstock oil [3, 15]. Oil from Jatropha is non-edible due to poisonous substances [1, 3]. The use of Jatropha oil should therefore not affect the price and availability of VGO for food use. The plant can be grown in dry wastelands and sandy soil [3, 14]. Estimates suggest a potential of 200 thousand metric tones each year in India [14]. The seed of *Jatropha curcas* contains approximately 50 % oil and around 14 % FFA [3, 14]. The high content of FFA makes it impossible to use an alkaline catalyst unless the oil is pretreated. The main fatty acids in Jatropha oil are oleic (45 %), linoleic (34.4 %) and palmitic (16 %) [1, 3, 15].

2.3. Impact of the alcohol type

In the following chapter the effect of different alcohols on the reaction and product parameters will be reviewed. Transesterification will only be considered with acidic catalysts.

2.3.1. Reaction parameters

The parameters to be examined are temperature, reaction time, the ratio of alcohol to oil, and the concentration of catalyst.

Temperature

Temperature has a major impact on a chemical reaction in accordance with the Arrhenius equation. Increased temperature tends to increase the reaction rate. The most frequent temperature used is the boiling temperature of the specific alcohol [1, 5, 7, 8, 10]. Using temperature above the boiling temperature of an alcohol will result in vaporization of the alcohol in an open environment [1]. A study done by Nimcevic et al. [7] showed no decrease in the reaction times when the temperature was slightly lower than the boiling point for *n*-propanol. Nevertheless the overwhelming majority of articles examined demonstrated an acceleration of the acid-catalyzed transesterification reaction when elevated temperatures were used [1, 7, 8, 10]. A reported problem with increased temperature is more corrosiveness of sulfuric acid when used as catalyst [1, 7].

Alcohol to oil ratio

For the stoichiometric transesterification reaction, 3 moles of alcohol to 1 mole of oil is required [1, 8, 10]. The transesterification reaction is however a reversible reaction. Alcohol should be added in surplus to push the reaction in the preferred direction [1, 3]. The most frequent ratio used is 6:1 alcohol to oil, but if there is a high content of FFA in the oil a larger ratio is required [1, 3]. 6:1 is reported as the best ratio for methanol by Saravanan et al. [8], whereas increasing ratios are reported with longer chained alcohols. Butanol was suggested to be used with a 7.5:1 alcohol to oil ratio. However, Nimcevic et al. [7] concluded from their experiments that 9:1 was the best ratio for propanol and butanol. They also found that with the use of 6:1 for longer chained alcohols (propanol, butanol) the reaction time was increased with 2 hours. Contradictory, Sanli and Canakci [5] found 6:1 to be recommended as the best and demonstrated only a minor effect on completeness and time for higher ratios on longer chained alcohols. This was supported by Whalen et al. [10]. Even where researches have used the same type of oil (sunflower oil) Sanli and Canakci [5] found a ratio of 6:1 whereas Saravanan et al. [8] found 7.5:1 for butanol to oil ratio.

Catalyst concentration

The acid-catalyzed transesterification reaction is carried out by two subsequent substitution reactions [1, 7]. The acid first reacts with the oil, protonating it, before the protonated oil reacts with the alcohol [1, 6]. Any non-reacted FFA in the oil will react with alcohol and produce water which inhibits the reaction [1, 6]. Nimcevic et al. [7] reported 1.5 % w/w acid to oil was the most favorable concentration. At 2 % w/w to oil there was an insignificant reduction in yield while at 0.5 % w/w to oil the yield was reduced significantly. A reaction time of 3 hours was kept the same for all of the catalyst concentrations in this article [7]. This is in contrast to Wahlen et al. [10] where 3 % w/w to oil was estimated to give the best results. Nimcevic et al. used rapeseed oil while Wahlen et al. used soybean oil.

There are several conflicting results where Saravanan et al. [8] concluded 6 % v/v acid to oil was the most successful. This Compared to 3, 4 and 5 % v/v acid to oil. They found no major increase in yield from 5 to 6 % v/v acid to oil for butanol, but a large effect on specific gravity was observed. Though, for methanol and ethanol Saravanan et al. found a significant impact on yield when increasing the catalyst concentration from 5 to 6 % v/v acid to oil. This is inconsistent to previous thesis on the same topic at my faculty where Ekwunu [1] argued that 2 % v/v was the best in comparison to other concentrations in the range 2-6 % v/v acid to oil. All acids discussed here were H_2SO_4.

Reaction time

The reported reaction time varies. Normally 3 to 4 hours is reported as sufficient time if all other parameters are optimized [1, 7, 8]. There are large variations where Wahlen et al. [10] report as short as 30 minutes for butanol. Sanli and Canakci [5] recommend more than 48 hours for propanol and butanol. For methanol, both Wahlen et al. [10] and Saravanan et al. [8] found that more than 69 hours is needed for a significant yield. Nimcevic et al. [7] terminated the experiment with methanol due to the time it took. Saravanan et al. [8] fixed the reaction time at 5 hours and the extent of completion (percent of yield recovered) favored increasing chain length for the alcohol. The study graded butanol (95%) in favor of ethanol (85%) and at the lower end methanol (75%). Explanation for the increased reaction time with decreased chain length has been suggested by Wahlen et al. [10] as a result of increased miscibility of long chained alcohols with oil, besides the ability for higher temperature. Branched alcohols are shown to display longer reaction time than their straight counterparts. Nimcevic et al. [7] found that *Iso*-propanol and *iso*-butanol added 1 hour to the time for completion compared to *n*-propanol and *n*-butanol. *Tert*-butanol did not react at all. The assumed explanation is that steric interference decrease the reaction rate. All reactions were done at or close to the boiling temperature for the alcohol used.

2.3.2. Product parameters

In this chapter, the alcohol's effect on the product will be reviewed. For certain parameters the results of the oil's distribution of saturated and unsaturated fatty acids is more dominant [15]. This is in particular true for viscosity and cold flow properties.

Cetane number

The cetane number (CN) for biodiesel is generally higher than that for diesel. CN is linked to the time delay before ignition of the fuel, where a high CN will give a short delay [8, 11]. Generally a decrease in nitrogen oxides emissions and average combustion temperature is achieved with an elevated CN [8, 11]. A review by Knothe [11] showed that increased alkyl ester chains and more saturation enhance CN. Saravanan et al. [8] found by reviewing literature that branching of the alkyl chain reduce CN. This is supported by Knothe [11] but the branched chains still have CN equal to methyl esters. If a slight increase in CN is necessary, then longer straight chained alcohols will increase the CN to some minor extent [11].

Energy content

The energy content in a fuel is measured by its heat of combustion (HC) [8]. Generally that content is lower in a biodiesel than in a petroleum based diesel. This is partly counteracted by biodiesel's higher density. This would mean 5-6 % higher fuel consumption when operating on biodiesel compared to petroleum based diesel [8, 15]. Knothe [11] found that HC increase with longer alkyl ester chains. Saravanan et al. [8] measured the HC of Mahua oil transesterified with different alcohols and identified a rise from 42.5 MJ kg^{-1} for methyl-, 43.2 for ethyl- to 44.5 MJ kg^{-1} for butyl ester. They also measured the energy content for diesel no. 2 at 45.6 MJ kg^{-1}.

Viscosity

The main purpose for the transesterification reaction is to reduce the viscosity of the oil. This makes viscosity the single most important property of the biodiesel [5-8]. Correct viscosity for the biodiesel is essential for proper flow through lines, nozzles, and for good atomization [1, 8, 11]. The American standards (ASTM D6751, method D445) permit 1.9-6.0 mm^2s^{-1} for the viscosity of biodiesel. The European standards require 3.5-5.0 mm^2s^{-1} (EN14214) [10, 11, 15, 16]. Rodrigues et al. [2] documents that increasing chain length of either the alcohol or the fatty acid gives higher viscosity. The difference between long and short chains is more apparent when the temperature gets lower [2, 15]. Branching of an alcohol chain was found to lower its viscosity compared to the equivalent straight chained alcohol [2].

Measurements on Mahua oil done by Saravanan et al. [8] found 7.2 mm^2s^{-1} for methyl esters, 6.8 for ethyl esters and 4.7 mm^2s^{-1} for butyl esters, in comparison 2.6 mm^2s^{-1} for diesel no. 2. It should be noted that the reaction for methyl and ethyl esters were not completed. The reaction was stopped before a yield over 95% was accomplished. However, the result for butyl esters is in accordance with the work of Wahlen et al. [10] on soybean oil where 4.5 mm^2s^{-1} was found. This is within the requirements for biodiesel. In addition Lapuerta et al. [4] measured on waste cooking oil the viscosity for methyl esters at 5.16 mm^2s^{-1} and for ethyl esters at 4.92 mm^2s^{-1} for a finished reaction.

Cold Flow properties

The point at which a fuel becomes cloudy due to crystallization is characterized by its cloud point (CP). The pour point (PP) on the other hand is the lowest temperature at which the fuel still flows [11]. If the oil used for transesterification has a large amount of saturated fatty acids then a considerable increase in CP and PP is typical [2, 11, 15]. Wahlen et al. [10] showed that CP decreases for esters derived from n-butanol compared to esters derived from methanol. This is supported by Rodrigues et al. [2]. Yet Rodrigues et al. found that n-butanol hold superior cold flow properties to n-octanol. Therefore no linear correlation has been established between CP and the type of alcohol. The results of Rodrigues et al. [2] showed that the fatty acid composition was more important than the type of alcohol. Branched chain alcohols however are reported to possess significant better cold flow properties than their straight counterparts [2, 10, 11].

Emissions & cost of alcohol

Biodiesel reduces pollution compared to diesel. Carbon dioxide, Carbon monoxide, smoke density, particulate matter, and total hydrocarbon emissions are all reported to decrease substantially [4, 9, 10]. However, the release of nitrogen oxides increases slightly with biodiesel. Even thought its CN is generally higher [4, 8, 11]. Lapuerta et al. [4] investigated the emissions of methyl and ethyl esters and revealed that methyl esters reduce particulate matter emissions more than ethyl esters. This was explained with a higher oxygen content of methyl esters.

The cost of ethanol, *iso*-propanol, and *n*-butanol is approximately 1.5 times higher than methanol. The cost of *n*-propanol is 3 times higher [7]. However, due to announced large scale production of butanol, its price is expected to drop [10].

Acid Value

This product parameter is not reviewed in order to compare alcohols, but it is an important parameter when acidic catalysts and esterification is applied. The Acid value (AV) is defined as milligrams of potassium hydroxide that is required to neutralize the acids in one gram of sample. In some occasions the name acid number (AN) is used [18]. The property can be used as an estimate of the content of free fatty acids in a biodiesel fuel [19]. The AV is useful for monitoring the esterification process and can be used to assign a percentage (esterification) conversion by dividing AV of the biodiesel sample with AV of the starting material [12]. However, AV is most commonly reported in $^{mg\ KOH}/_{g}$ sample [18]. If the AV is too high then depositions in injectors and corrosion of storage tanks may occur [20]. AV can also be used to monitor the degradation state of the produced biodiesel when stored over time, as the AV then increases [20]. The EU standard for biodiesel requires an AV of less than 0.5 $^{mg\ KOH}/_{g}$ sample and is measured by titrating a standardized KOH solution against a solution of the sample dissolved in 2-propanol (various options available in EN 14104:2003) with phenolphthalein as an indicator [16, 18].

2.4. Response surface methodology

Generally there are two approaches for process optimizing: classical (mechanistic) and statistical [21]. The classical approach is the well known one-variable-at-a-time approach where one variable is optimized while the others remain on a fixed level. This method is easily applied, but it has problems with detecting and handling interaction between the variables which can have a large impact on the results. That is where a statistical approach comes into play. Response surface methodology (RSM) is a collection of statistical and experimental methods for planning, modeling, evaluating and analyzing variables for a wanted response [21, 22]. It is important to understand that since it involves a statistical approach the results are to be considered an approximation. Unless stated otherwise the following is based on the response surface methodology book by Myers and Montgomery [22].

A particular characteristic is regarded as the response. Often there are several responses. These responses are affected by some independent variables which can be controlled. Example of responses can be yield, acid value, viscosity and so on. Examples of variables can be time, temperature, catalyst concentration and stirring. These variables have different natural units (Celsius, %, $^{mm2}/_{s}$ etc) however it is convenient to use coded variables (X_1, X_2, X_3) which are dimensionless with zero as mean. For example if the variable X_1 is the coded variable for temperature and the response is viscosity, then a negative response for a positive value of X_1 would mean the viscosity decreases with increasing temperature.

The coded variables for a high value of X_1 will be +1 while for a low value it will be -1, the mean will therefore be zero. The relative impact of the different variables can then be addressed. By considering different variables, their effect and the interaction between these variables (X_1X_2 for X_1 and X_2) RSM is capable of determining which of the variables that is more important for the wanted response (having a larger impact) and how they affect each other. The way this is done is by approximating a response function (the model). The result is plotted graphically in three dimensions and is often accompanied with a two dimensional contour plot as shown in figure 3. RSM can be used for optimizing the response, achieve specific customer specifications, minimizing variation in the response and designing more robust processes (capable of handling different environmental factors while still achieving the same response).

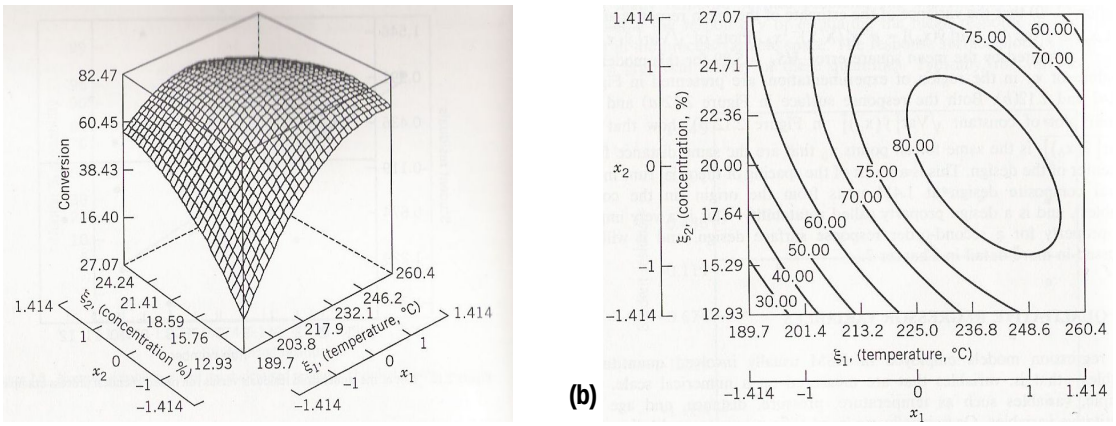


Figure 3: Example of a second-order model response surface plot (a) and its Contour plot (b) [22].

The first-order model in figure 4 is a multiple linear regression model; it does not contain an interaction term. However if $\beta_3 = \beta_{12}$ and $X_3 = X_1X_2$ the model will take into account interaction between coded variable X_1 and X_2. The partial regression coefficient β measures changes in η per unit X. The β is commonly estimated using a method called the least squares. Larger β gives a more significant term (negative or positive). The β for a single variable can be compared to the β for the first variable together with a second variable (the X_1X_2), thereby deciding the effect of interaction. Two single variables with comparable β give two variables which are highly connected, for example reaction time and temperature.

$$\eta = \beta_0 + \beta_1 x_1 + \beta_2 x_2 \ldots\ldots + \beta_k x_k \qquad \eta = \beta_0 + \sum\beta_j x_j + \sum\beta_{jj} x^2_j + \sum\sum\beta_{ij} x_i x_j$$

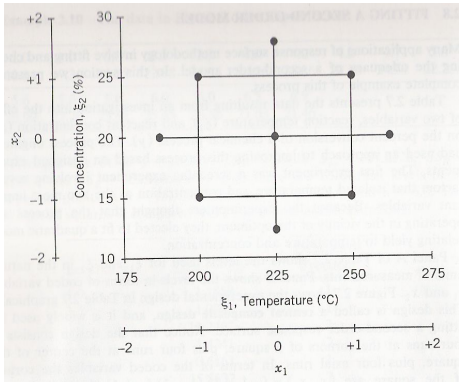
First-order model — Second-order model

Figure 4: The general first-order (without interaction) and second-order models [14, 22].

Further the η estimated by the model should be checked with the measured η to assure the validity and adequacy of the model. The difference between the measured and the modeled η is the residual. A common method to check the validity of a model is by plotting the residuals in a normal probability plot. The residuals should then align along a straight line. The residual procedure can also be used to estimate how well the model explains the response, termed the R^2. The R^2 estimates the variations found in the response with the difference in variables. Addition of a variable X_k to explain the response will always increase R^2, but it is the relative increase compared to other X's that is important. Alternatively $R^2_{adjusted}$ can be used which will decrease if unnecessary terms are added to the model. The R^2 can be assigned a percentage stating how much of the data the model can explain, for example an R^2 of 0.9 implies that 90 % of the real response is covered by the model. The R^2 can also be used when the relationship between variables and responses have been estimated and extrapolated to give an $R^2_{predicted}$. The $R^2_{predicted}$ states how well the model can explain new or extrapolated results.

Often a first-order model is used to check if the chosen variables give a response near the maximum response or the wanted level of response. The variables in the first-order model are often only low – high levels of the variables giving a flat response surface. The experimental planning phase (the design) is viewed geometrical in figure 5. A linear model would often only use the cube, depending on the number and type of variables used to describe the response. If interaction terms (joint effects) are taken into the model the design is called a factorial design. First-order models might not have interaction terms in them; however second-order models are usually based on factorial designs thereby taking interactions into account. This first-order model procedure is usually called a pre-study or screening experiment and the method is called the method of steepest ascent. The first-order model can also be used to identify the most important variables before conducting a more comprehensive study. A first-order model will in most cases be inadequate near the operability region (maximum or wanted response) as the effect of curvature is too significant. A second-order model however gives a curved response surface (figure 3a) and a good approximation of the true response.

(a)



(b)

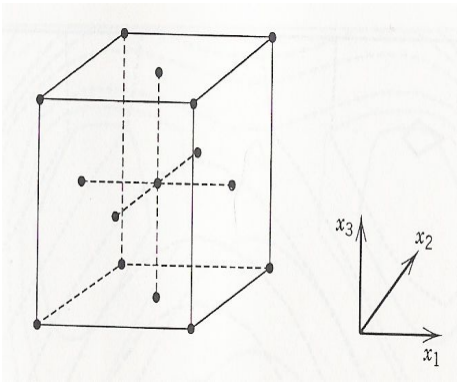


Figure 5: The general central composite design and face-centered design for second-order models [22].

The most common design for a second-order model is the central composite design (CCD) with variations of it. In figure 5a the inner scale is the variables in natural units while the outer scale is the coded units. The points outside the cube is the α points and in figure 5a a general CCD is shown (α outside) with two variables making it two-dimensional. In figure 5b the central composite face-centered design (CCFD) is shown with the α on the cube side and with three variables making the design three-dimensional. Often the point in the center of the cube (X_1, X_2 = 0 in figure 5a) is repeated several times to address the uncertainty in the experiments. The graphical nature of response surface methodology appears by looking at the design (figure 5) and the resulting plots (figure 3). This graphical approach is also the reason for the term response surface methodology [22].

3. Materials & methods

The jatropha oil and rapeseed oil was ordered and delivered by Statoil ASA Rotvoll in Trondheim, Norway. The crude rapeseed oil was labeled degummed. The crude jatropha oil acquired through Statoil ASA was originally delivered by Terasol Energy India. Both *n*-butanol and concentrated sulfuric acid was of analytical grade. The butanol was delivered by VWR International and the acid delivered by Merck KGaA with concentration stated to 95-97 %.

3.1. Procedure & reactor

The reactor setup had a capacity of 5 x 50 mL flasks as indicated by figure 6. The two flasks in front (R1 & R2) were used as reactor flasks, the two flasks on each side were used as mixing flasks for butanol and sulfuric acid. The flasks furthest away was used for temperature measurement, it contained 30 mL of oil (jatropha or rapeseed) and 6 equivalents of alcohol. The temperature measuring device was connected to the heating plate and automatically controlled the temperature. Each flask contained a 2 cm long egg shaped stirring magnet.

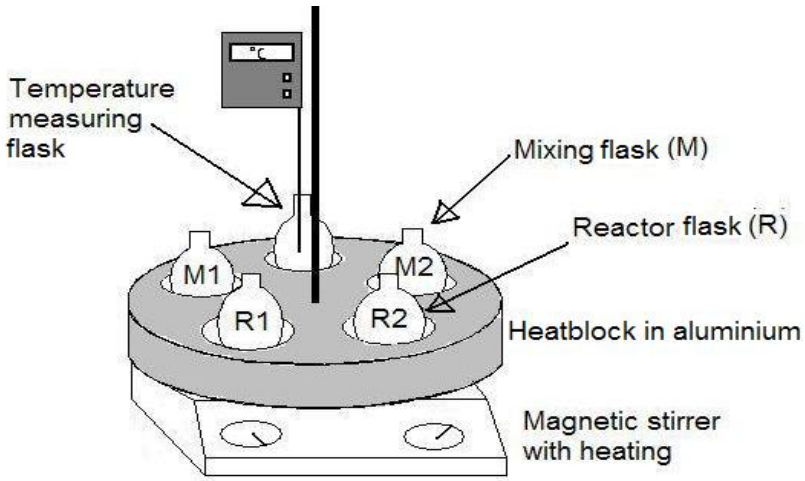


Figure 6: sketch of reactor setup

The procedure that will be described was the same for each and every one of the experiments unless otherwise stated. During the pre-study the oil was measured by volume in a cylinder (50 mL capacity) where the weight of exactly 30 mL of oil had been pre measured. However during the main study the oil was measured with a syringe (10 mL capacity) directly into the round bottom reactor flask (50 mL capacity) and the weight was measured for each experiment. The oil was then transferred to the reactor flask (pre-study) and heated to the given temperature while magnetic stirring was commenced.

The stirring speed was held at the highest stabile speed, a level assuring a homogeneous solution. The stirring speed was held at the same level for all experiments. The magnetic stirrer was not equipped with stirring speed indicators. A similar second round bottom flask (mixing flask) was used to mix butanol and sulfuric acid in the given amounts. The mix was quickly heated in the flask before the mix was poured into the reactor flask. The reactor flask was then allowed to react for the predetermined time. After the given time had passed the reactor flask was sealed with a glass fitting and cooled under tap water. The stirring magnet was removed to avoid plugging the separator funnel.

The cooled product was transferred to a separator funnel (250 mL capacity) and 50 mL of cold tap water was added carefully to avoid emulsions. The funnel was gently tilted back and fourth 3-4 times before settling for 15 minutes and separating away the water phase. This was repeated a total of three times but for the two last times only 5 minutes of settling was necessary. The washed product was further transferred to a flask (100 mL capacity) and connected to a rotary evaporator. The rotary evaporator was rotating at 200 rpm and with a temperature of 50°C in the heating bath. For the first 5 minutes the pressure was set to 80 mbar, after that the device was set to achieve the lowest pressure available. This was in the range of 6 mbar to 12 mbar. After one hour on the rotary evaporator a stirring magnet was added to the flask and it was fitted to a vacuum line connected to an oil pump. Any vapor would be frozen in a cooling unit with liquid nitrogen placed between the vacuum line and the oil pump to avoid damaging the pump. Magnetic stirring was commenced and the product was left connected on the vacuum line for one hour. The vacuum line achieved a pressure in the range of 0.16 mbar to 0.20 mbar. The stirring magnet in the flask was removed and the product was weighted for yield calculations. After this the product was poured into vials (30 mL capacity) for storing before further analysis of the product was started.

3.2. Experiment design

The experiments were done in two steps. First a pre-study (table 1) was done to check that the design was near the maximum response for yield. Then a main study (table 2) was conducted with the entire design. The program used for experiment planning, modeling and generating plots was Modde 8.0 from Umetrics [23]. A central composite face-centered design (CCFD) was used with three responses: yield, viscosity and acid number. For each of the three responses four variables were used: temperature, time, alcohol to oil ratio and catalyst concentration. The program recommends 0,5 as minimum for R^2 (named R2 in plots) and 0,1 as minimum with 0,5 as recommended for $R^2_{prediction}$ (named Q2 in plots) [23]. The design planning and modeling on results with Modde 8.0 was done by Ingvar Eide at Statoil ASA in Trondheim.

Table 1: Experimental design for pre-study

Exp. Nr.	Temp °C	Time h	Alc/TriG (table 3)	Cat % v/v
1	70	1	4	1
2	110	1	4	3
3	70	3	4	3
4	110	3	4	1
5	70	1	8	3
6	110	1	8	1
7	70	3	8	1
8	110	3	8	3
9	90	2	6	2
10	90	2	6	2
11	90	2	6	2
12	90	2	6	2

Table 2: Experimental design for main study

Exp. Nr.	Temp °C	Time h	Alc/TriG (table 3)	Cat % v/v
1	70	1	4	1
2	110	1	4	1
3	70	3	4	1
4	110	3	4	1
5	70	1	8	1
6	110	1	8	1
7	70	3	8	1
8	110	3	8	1
9	70	1	4	3
10	110	1	4	3
11	70	3	4	3
12	110	3	4	3
13	70	1	8	3
14	110	1	8	3
15	70	3	8	3
16	110	3	8	3
17	70	2	6	2
18	110	2	6	2
19	90	1	6	2
20	90	3	6	2
21	90	2	4	2
22	90	2	8	2
23	90	2	6	1
24	90	2	6	3
25	90	2	6	2
26	90	2	6	2
27	90	2	6	2
28	90	2	6	2

Table 3: alcohol equivalents and mL based on average triglyceride mass

Oil		Alcohol	
type	mL	Equiv.	mL
Jatropha	30	4	10,7
Jatropha	30	6	16,0
Jatropha	25	8	17,9
Rapeseed	30	4	11,7
Rapeseed	30	6	17,5
Rapeseed	25	8	19,5

The pre-study (table 1) was done once for jatropha oil whereas the main study (table 2) was done for both jatropha and rapeseed oil giving a total of 68 experiments. The experiments were done in a randomized order but with two and two experiments with equal temperatures at the same time. Catalyst concentration was based on volumetric percentage to the oil. One volumetric percentage (% v/v) has been calculated to two weight percentages (% w/w), 2 % v/v equals 4 % w/w and 3 % v/v equals 6 w/w. The alcohol to oil ratio (Alc/TriG) was based on the molar ratio of alcohol to average triglyceride mass, the latter will be explained in 3.3 analysis of the product but the equivalents are shown in table 3. Note that for 8 alcohol equivalents the volume of oil is reduced (table 3) due to the capacity of the flasks.

3.3. Analysis of the product

The average mass of the triglyceride was determined by multiplying the different fatty acid components with their relative fractions (chapter 2.2) and calculating for a triglyceride molecule based on this average fatty acid. For Jatropha the average triglyceride mass was calculated to 874 $^{g}/_{mol}$ while for rapeseed it was found 864 $^{g}/_{mol}$. The carbon (12*3=36) and hydrogen (1*5=5) of the glycerol part is then subtracted from the triglyceride and divided by 3. Adding the butyl mass (12*4+9=57) to the remaining triglyceride gives the theoretical mass of fatty acid butyl esters for the oil. The theoretical FABE mass is 334.67 $^{g}/_{mol}$ for jatropha and 331.33 $^{g}/_{mol}$ for FABE based on rapeseed.

The number of moles of triglyceride can be found by dividing the measured oil mass on the average triglyceride mass. Each mole of triglyceride gives 3 moles of FABE and this is then multiplied with the theoretical FABE mass to give each experiment's theoretical product mass. Yield can now be calculated by comparing the experimental mass of product to the theoretical mass of product. It should be noted that for the pre-study a pre-measured volume of oil was weighted and calculated for yield, whereas in the main study each experiment was weighted and calculated for yield.

H-NMR-spectrums were measured with tetramethylsilane (TMS) as internal reference on a Varian Mercury 300 MHz. 1 drop off sample was placed in a measuring tube and dissolved with $CDCl_3$ to the required mark for the machine (approximately 0.6 mL). Chemsketch from ACDLABS were used to simulate H-NMR signals for butyl decanoate, butyl 7-decanoate, glycerol and butanol.

Density was measured with an Anton Paar DMA-4500 at 40°C. Viscosity was measured with the rheometer Physica MC200, application US200 version 2.3 and measuring system MK 24 (75mm, 1°). The rheometer was set to measure 6 points between a shear rate of $^{100}/_{s}$ to $^{1000}/_{s}$ and an average was calculated. The viscosity was measured in centipoise and converted to $^{mm^2}/_{s}$ by dividing with $^{g}/_{cm^3}$ from the density measurements.

For the acid value titration the EU standard EN14104 was used as template, but modified as described as follows. A solution of approximately 0.055 M KOH (pellets) in 99 % 2-propanol was prepared. The KOH solution was standardized against approximately 0.050 g benzoic acid in 50 mL 99 % 2-propanol. Bromothymol blue (BTB) was used as indicator and the standardization was repeated minimum 5 times. Each KOH solution was standardized when prepared, and on the start of each day as the concentration decreased slightly with time. The standardized KOH solution was used against a solution of approximately 4 g sample in 50 mL 99 % 2-propanol with 0.15 mL phenolphthalein as indicator for the titrations of samples. Each sample titration was repeated 3 times. In accordance with EN14104 the concentration (standardization) of the KOH solution was calculated with equation 1 and the acid value (titration) was calculated with equation 2 [18].

$$\frac{1000 \times m_0}{122{,}1 \times V_0} \qquad (1)$$

m_0 is the mass (g) of benzoic acid
V_0 is the voume (mL) of KOH used

$$\frac{56{,}1 \times V \times C}{m} \qquad (2)$$

V is the volum (mL) of KOH used
C is the concentration ($^{mol}/_{L}$) of KOH
m is the mass (g) of the sample

4. Results

The results will be presented mainly graphically. Contour plots have been chosen to present the main interactions and effects, while 3 dimensional plots at the end will present the model under more optimized conditions. First the NMR results and pre-study results will be presented.

4.1. NMR atlas

An NMR atlas constructed from the NMR samples is shown is figure 7. Rapeseed and jatropha signals appeared at the same areas, but their signals were not similar. Jatropha had a clear triplet at 2.8 ppm while rapeseed had five signals in a cluster in the same area. The emulsion between biodiesel and water was measured by sampling before the rotary evaporator and checked against a biodiesel sample with water added. As mentioned in chapter 3.3, Chemsketch were used to simulate H-NMR signals for comparison. Butyl decanoate and butyl 7-decenoate can be found at the bottom of the figure, which were both computer simulated. Glycerol and butanol signals at the top were simulated, but for butanol a biodiesel sample with added butanol in it was used in addition. The signals appearing at 0.0 ppm are from tetramethylsilane (TMS) which were used as internal reference.

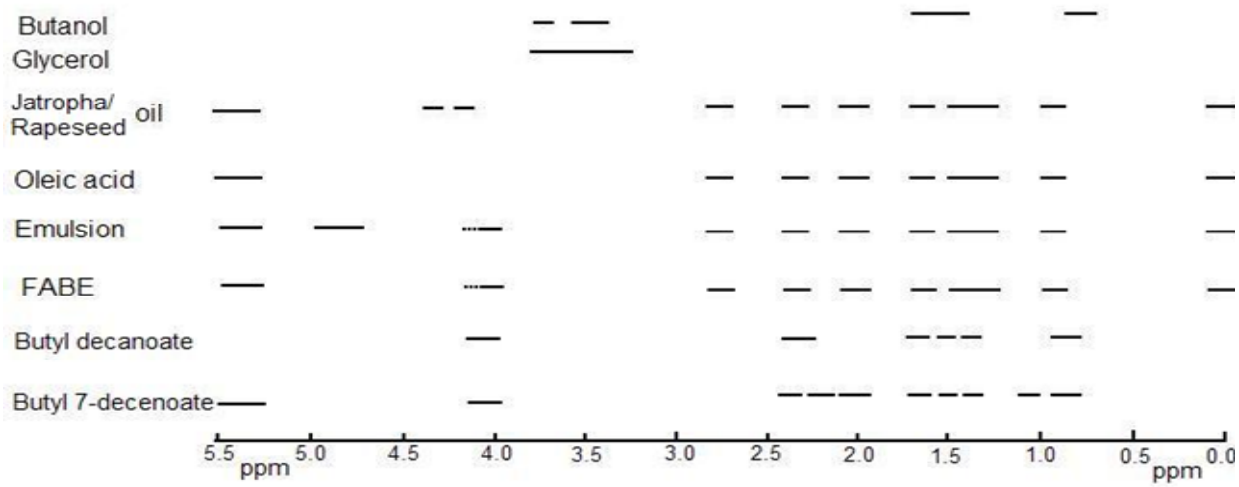


Figure 7: NMR atlas

For most of the samples at 70°C remains of triglycerides were observed, by that meaning two signal peaks appearing between 4.1 to 4.3 ppm. All biodiesel samples at 70°C are summarized in table 4. Sample 13 in the main study is equal to samples 5 in the pre-study as indicated by the parentheses. Reaction conditions not included in the pre-study is not marked with text. Minor traces means that two signal peaks barely observable and not regarded as interferences were found between 4.1 to 4.3 ppm.

Table 4: samples with remains of triglycerides for all experiments

Exp. Nr	Temp °C	Time h	Alc/TriG equiv.	Cat % v/v	Pre-Study	Jatropha Oil	Rapeseed Oil
1	70	1	4	1	Yes	Yes	Yes
3	70	3	4	1	-	Yes	Minor traces
5	70	1	8	1	-	Yes	Yes
7	70	3	8	1	Minor traces	Minor traces	Minor traces
9	70	1	4	3	-	Yes	Yes
11	70	3	4	3	-	Minor traces	None
13 (5)	70	1	8	3	Yes	Yes	Minor traces
15	70	3	8	3	None	None	None
17	70	2	6	2	-	Minor traces	Minor traces

4.2. Pre-study

A normal probability plot of residuals is viewed in figure 8. The R^2 for Yield in the pre-study were 0.41 (41 %), $R^2_{adjusted}$ (now referred to as R^2_{adj}) were 0.073 (7 %) and $R^2_{predicted}$ (R^2_{pre}) were 0.00. The observed (measured) results are along the vertical axis while the results predicted by the RSM model are along the horizontal axis, this will be the same for all of the following normal probability plots.

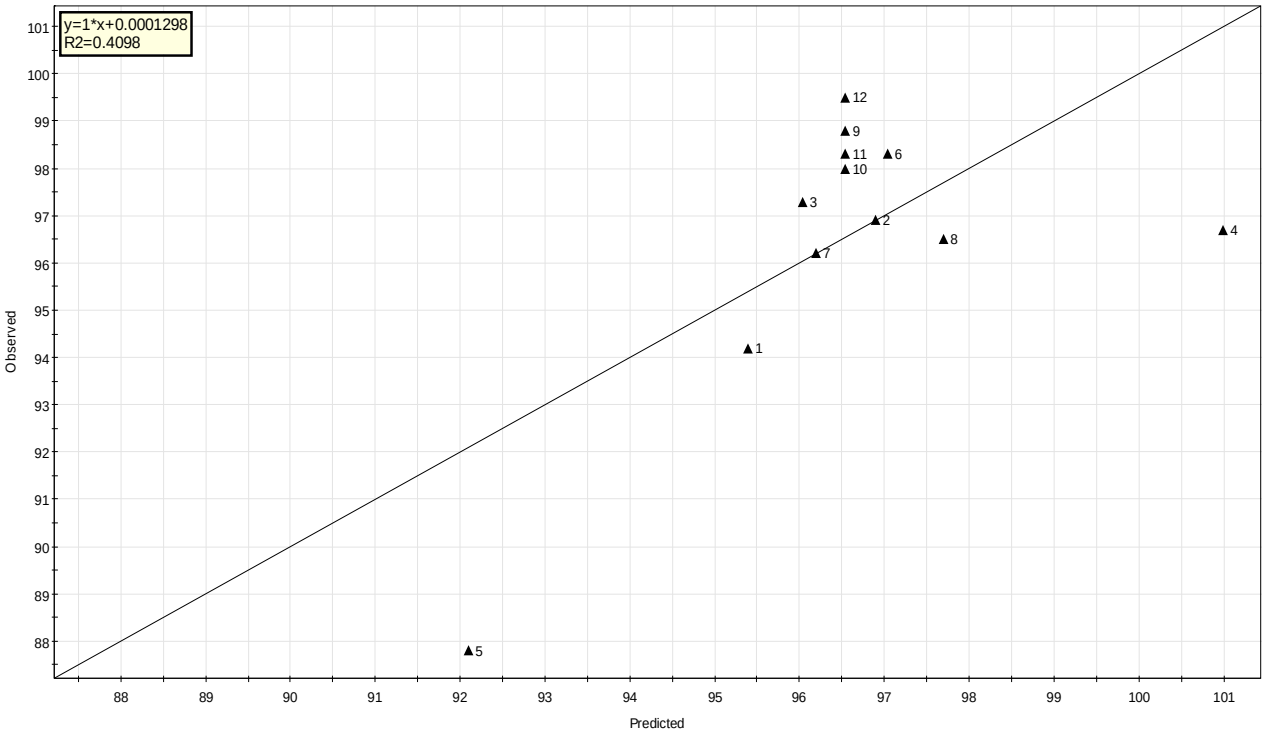


Figure 8: Probability plot of observed versus predicted for yield results.

4.3. Jatropha oil results

The acid number for pure jatropha oil was titrated and calculated to 10.29 $^{mg\ KOH}/_{g}$. Viscosity was measured to 38.8 $^{mm2}/_{s}$. Table 5 summarizes the R' coefficients for the three responses. The more complete experiment details can be found in appendix A1. Figure 9 show a normal probability plot of residuals, the further away from the straight line the higher the absolute value of the residual is.

Table 5: The R^2, R^2_{adj} and R^2_{pre} for yield, viscosity and acid number

Response	R^2	$R^2_{adjusted}$	$R^2_{predicted}$
Yield	0.96	0.92	0.78
Viscosity	0.93	0.86	0.65
Acid number	0.58	0.13	0.00

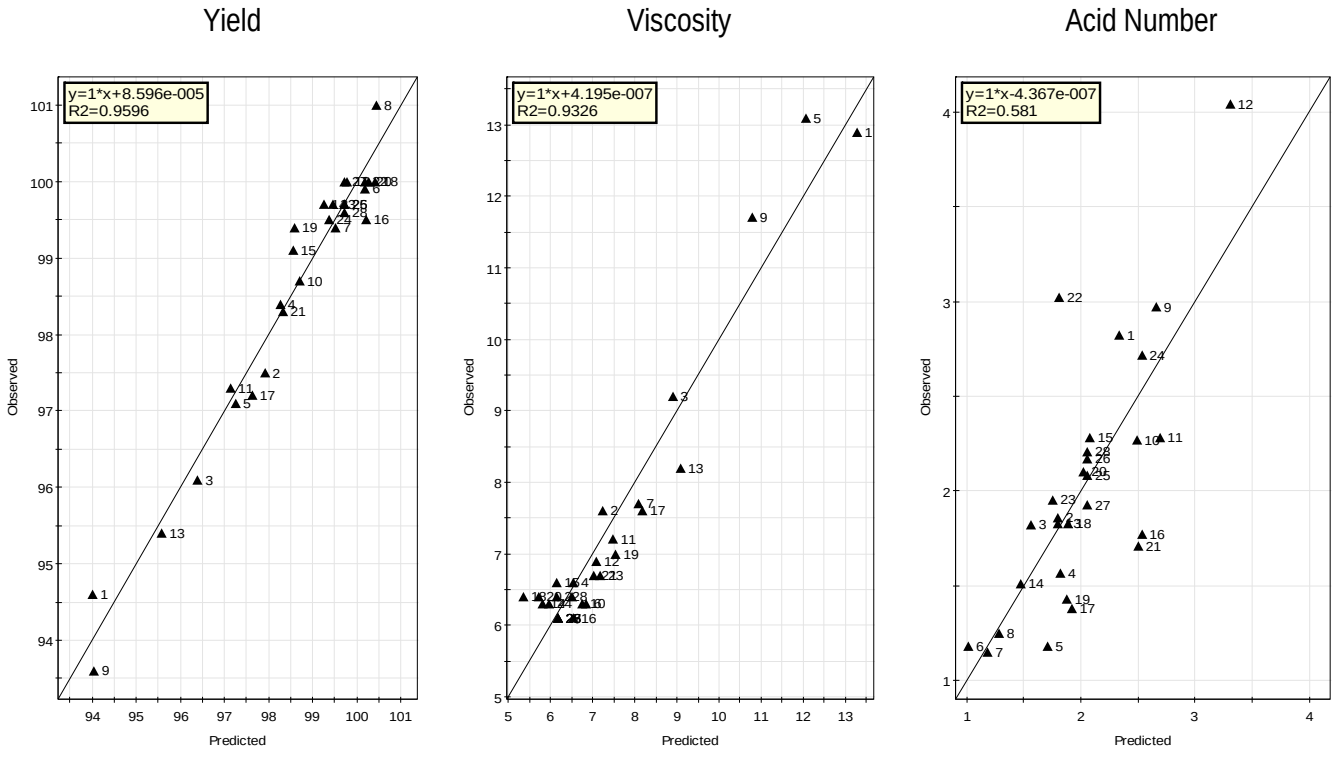


Figure 9: Normal probability plot for the jatropha oil results

In figure 10 the relative impact of the coded variables are shown. The higher the absolute value of the variable is, the larger impact it has on that particular response. The segmented line placed on top of the column shows the uncertainty for that particular variable. Figure 11a-b, 12 and 13a-f shows contour plots for yield, acid number and viscosity respectively. The variables presented in the contour plots are based on the relative impact of the coded variables and are set up against each other in the plots. When variables X and Y are along the axis of a contour plot, the two other variables are at their center value. The center value for temperature is 90°C, for time it is 2 hours, for alcohol equivalents it is 6 and for catalyst concentration it is 2 % v/v.

Figure 14 is a 3D graph (a) and contour plot (b) of yield showing temperature and time on the axis with alcohol equivalents at 7.5 and catalyst concentration at 2 %. Figure 15 is a 3D graph (a) and contour plot (b) of viscosity with the same axes and variable values as with yield.

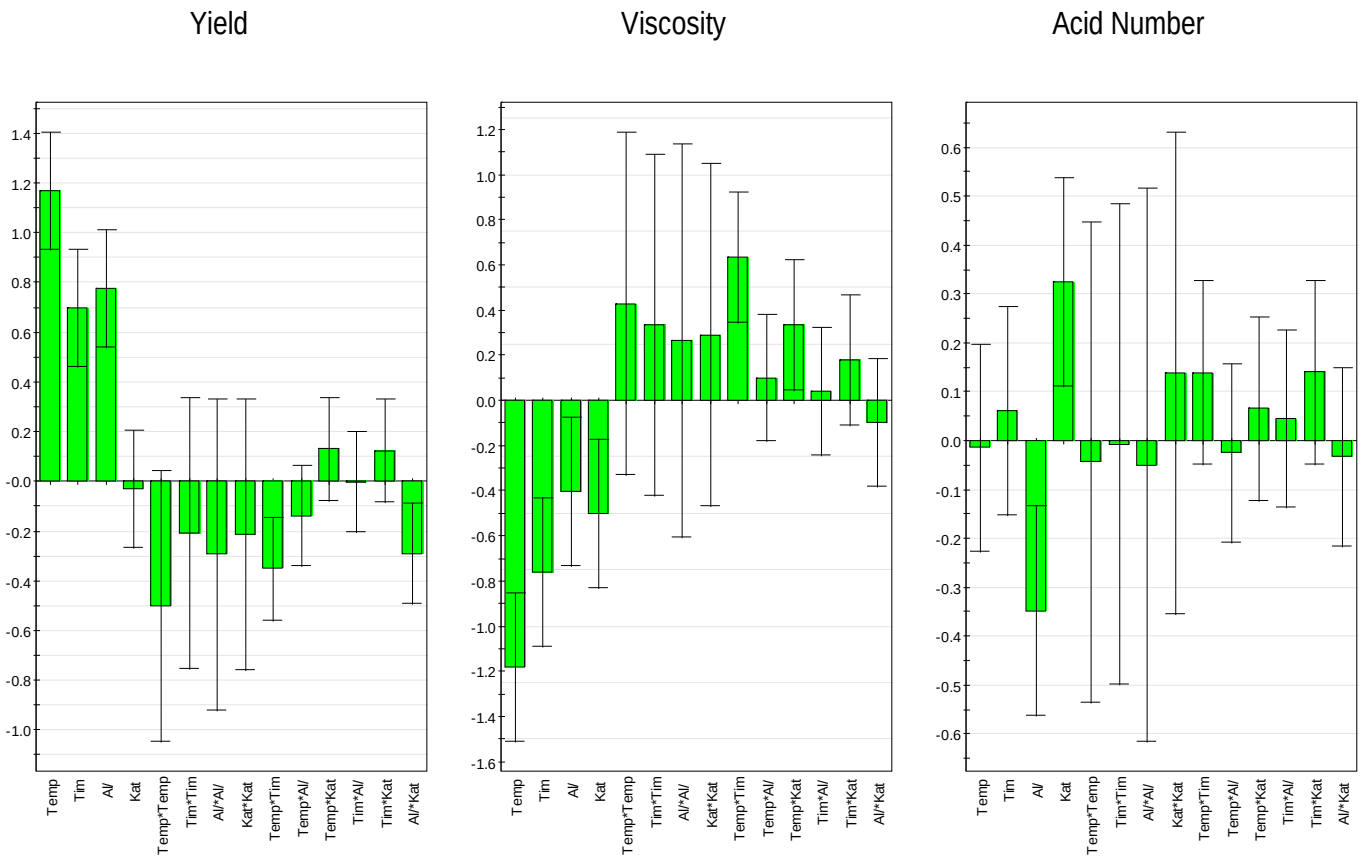


Figure 10: The relative impact of the coded variables

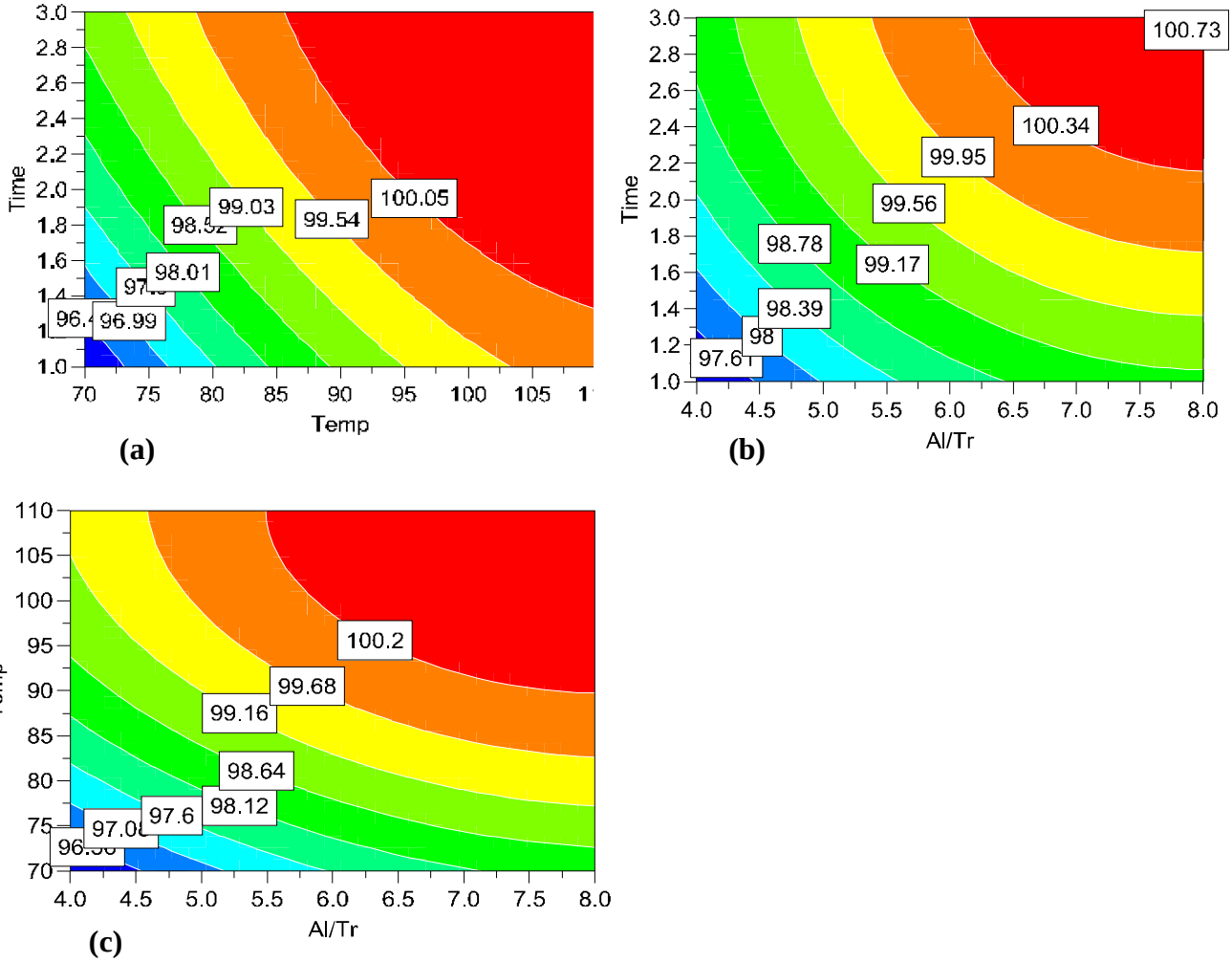


Figure 11: Contour plots for yield, variables not on the axes are held at the center values: 90°C, 2 hours, 6 equiv. and 2 % v/v

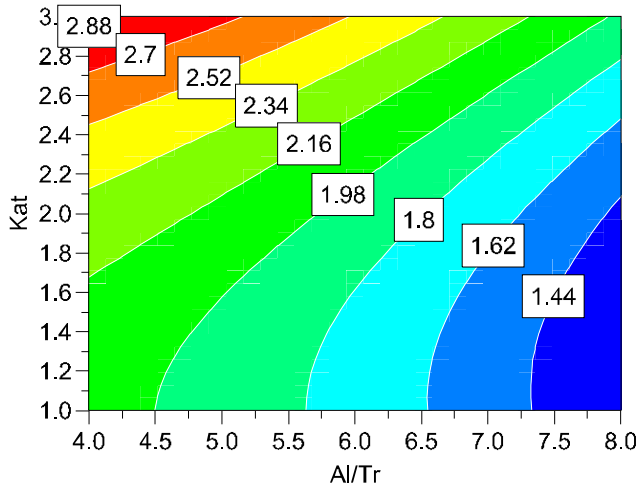


Figure 12: Contour plot for acid value at 90°C and a reaction time of 2 hours

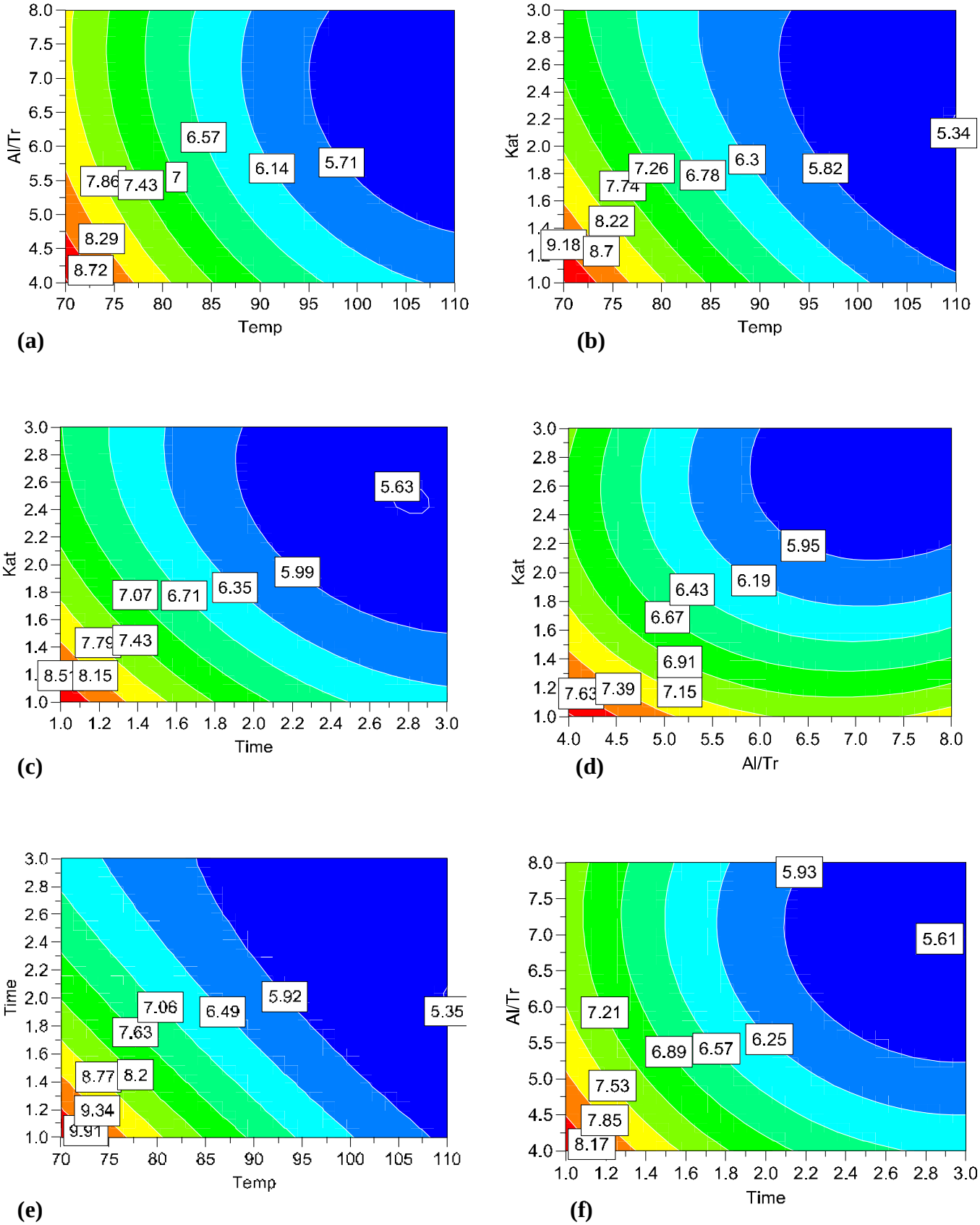


Figure 13: Contour plots for viscosity, variables not on the axes are held at the center values: 90°C, 2 hours, 6 equiv. and 2 % v/v

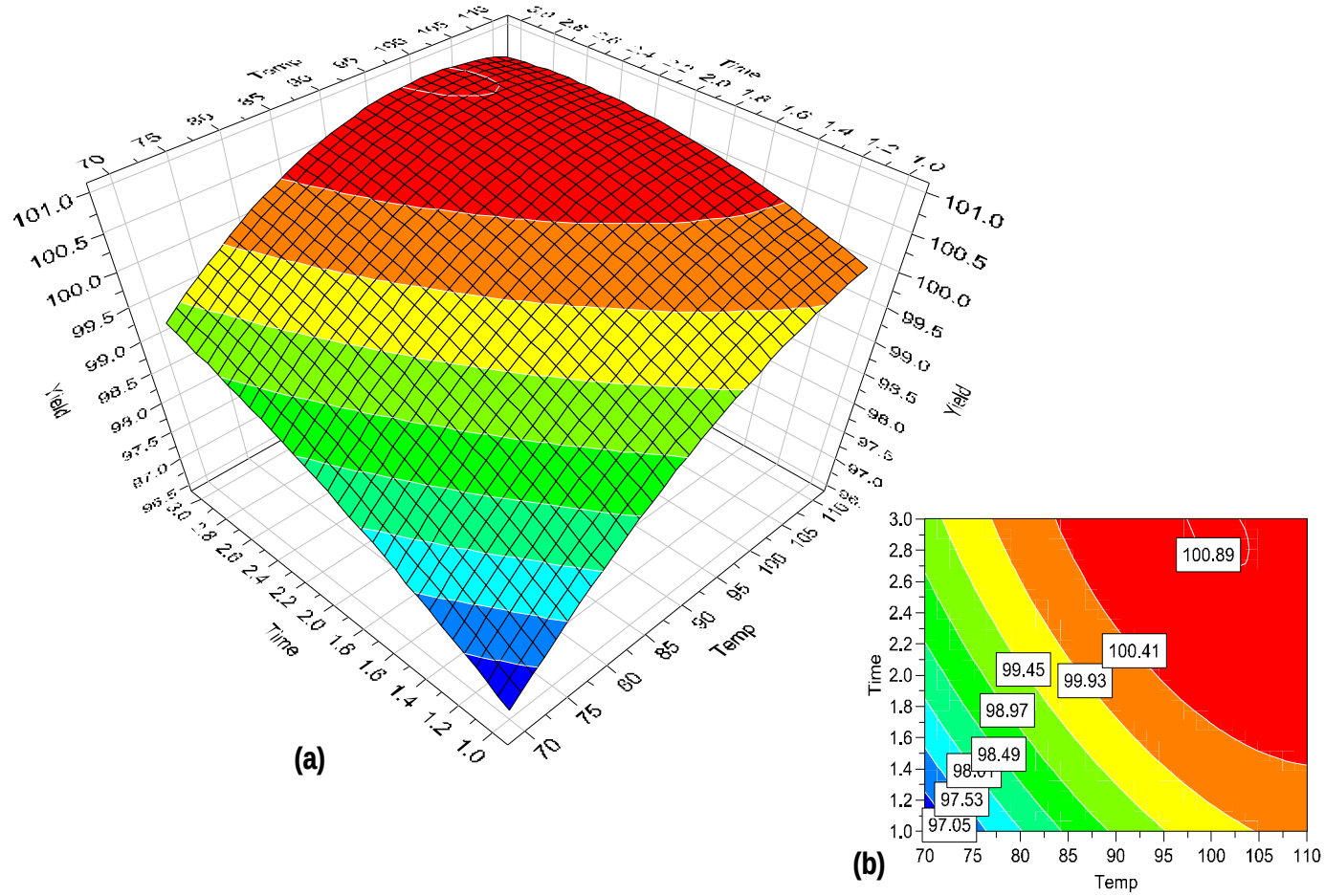


Figure 14: 3D graph (a) of yield and corresponding contour plot (b) with 7.5 equiv. and 2 % v/v

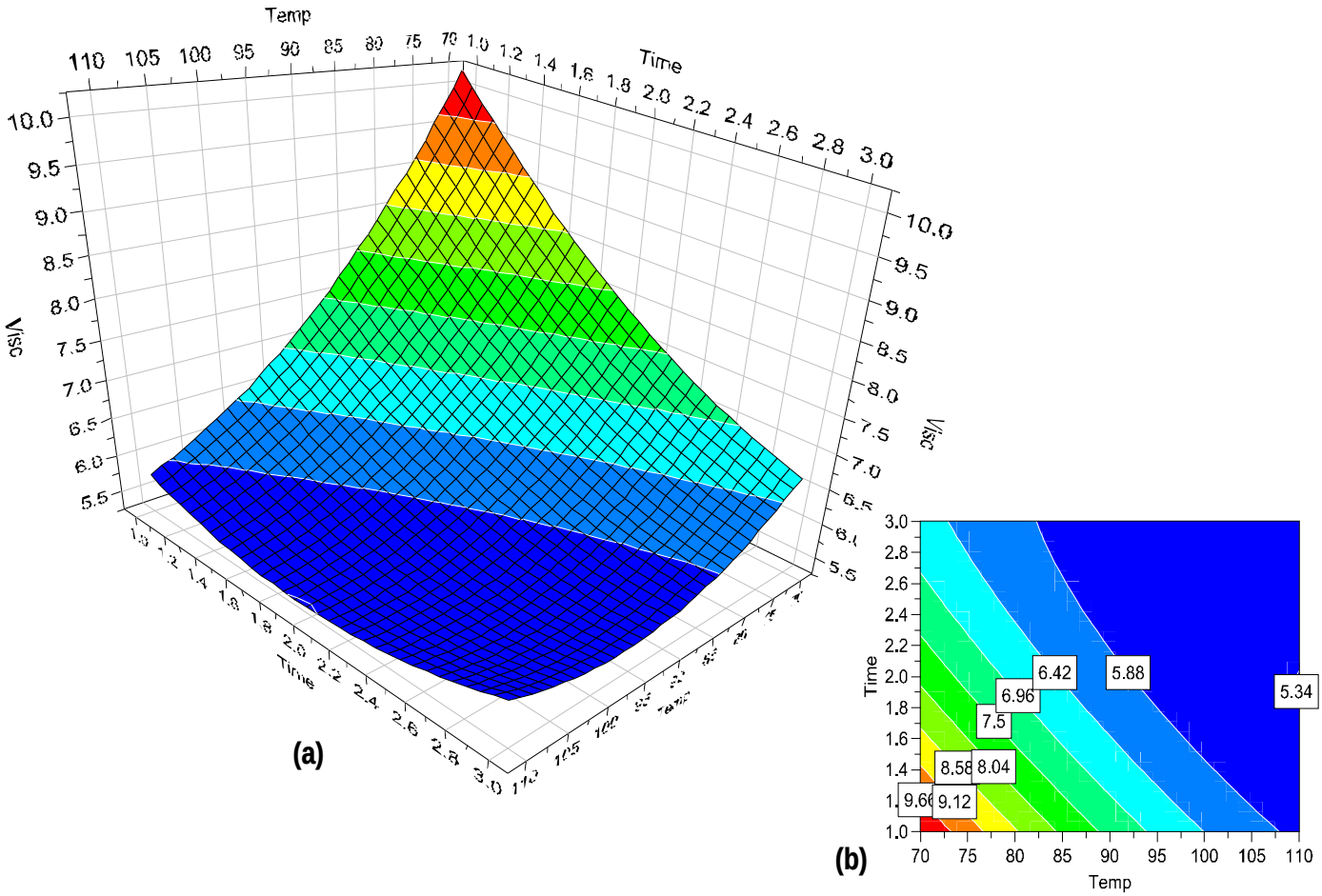


Figure 15: 3D graph (a) of viscosity and corresponding contour plot (b) with 7.5 equiv. and 2 % v/v

4.4. Rapeseed oil results

The acid number for pure rapeseed oil was found to be 2.54 $^{mg\ KOH}/_{g}$. Viscosity was measured to 36.7 $^{mm2}/_{s}$. Table 6 summarizes the R' coefficients for the three responses. The more complete experiment details can be found in appendix A2. Figure 16 show a normal probability plot of residuals for the rapeseed oil model.

Table 6: R^2, R^2_{adj} and R^2_{pre} for yield, viscosity and acid number

Response	R^2	$R^2_{adjusted}$	$R^2_{predicted}$
Yield	0.92	0.83	0.62
Viscosity	0.93	0.85	0.68
Acid number	0.83	0.65	0.45

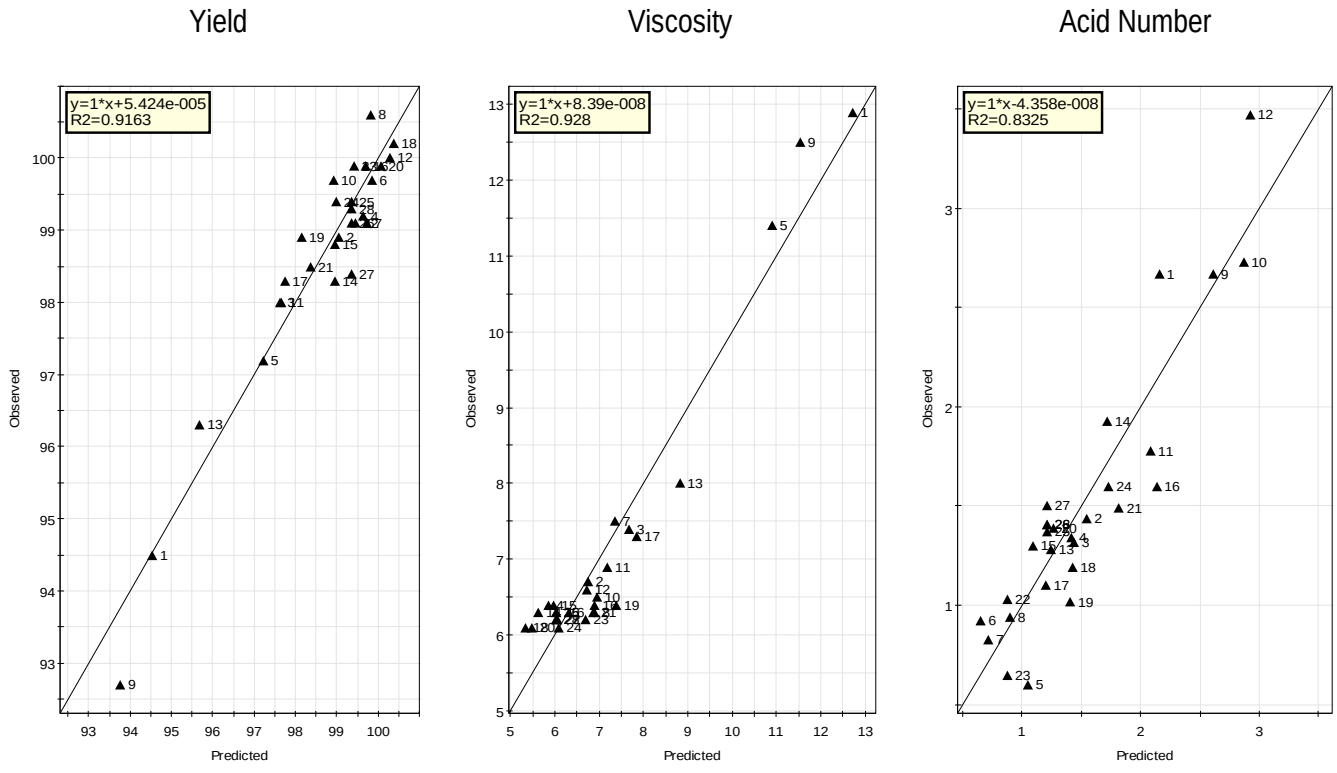


Figure 16: Normal probability plot for the Rapeseed oil results

In figure 17 the relative impact of the coded variables are shown. The role and function is the same as with jatropha oil. Figure 18a-b, 19 and 20a-f shows contour plots for yield, acid number and viscosity respectively. The variables presented in the contour plots are based on the relative impact of the coded variables, and are set up against each other in the plots. When variables X and Y are along the axis of a contour plot, the two other variables are at their center value. The center value for temperature is 90°C, for time it is 2 hours, for alcohol equivalents it is 6 and for catalyst concentration it is 2 % v/v.

Figure 20 is a 3D graph (a) and contour plot (b) of yield showing temperature and time on the axis with alcohol equivalents at 7.0 and catalyst concentration at 2 %. Figure 21 is a 3D graph (a) and contour plot (b) of viscosity with the same axes and variable values as with yield.

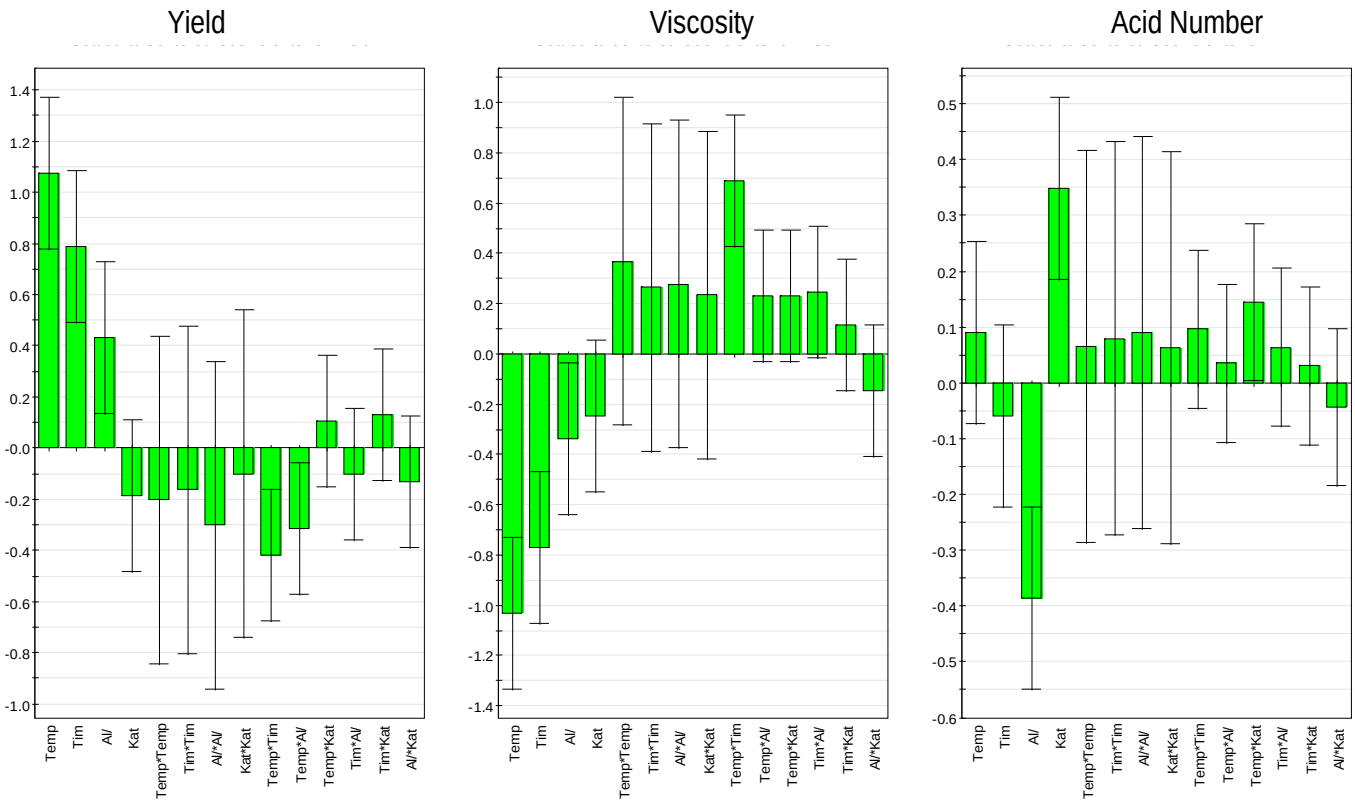
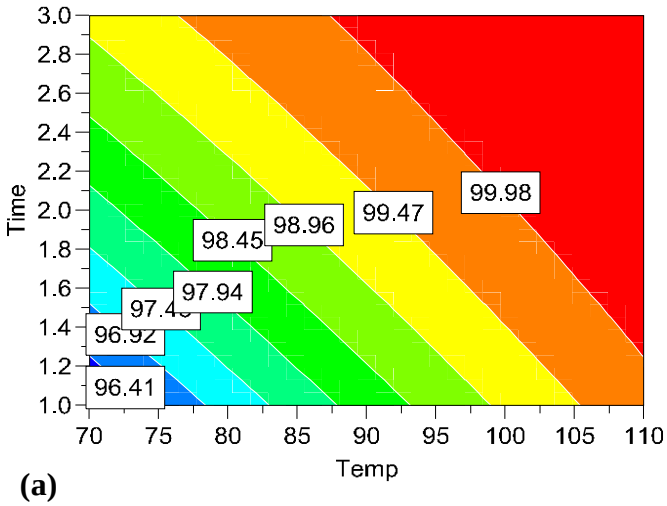
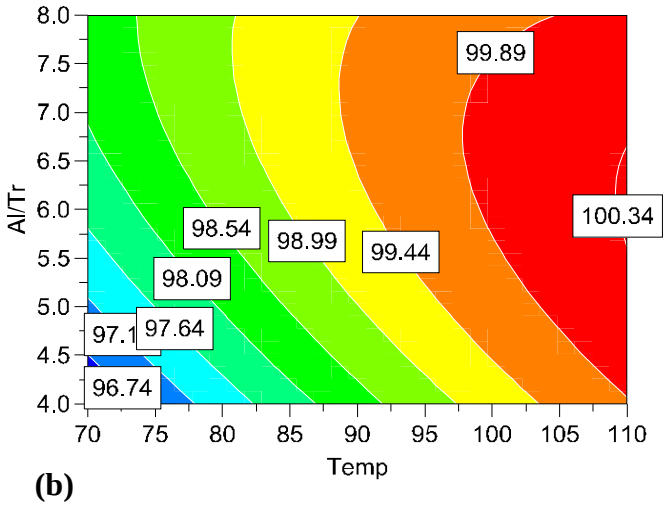


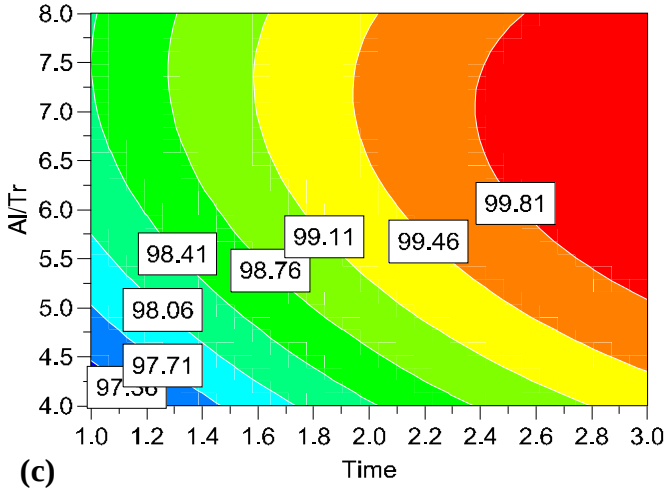
Figure 17: The relative impact of the coded variables



(a)



(b)



(c)

Figure 18: Contour plots for yield, variables not on the axes are held at the center values: 90°C, 2 hours, 6 equiv. and 2 % v/v

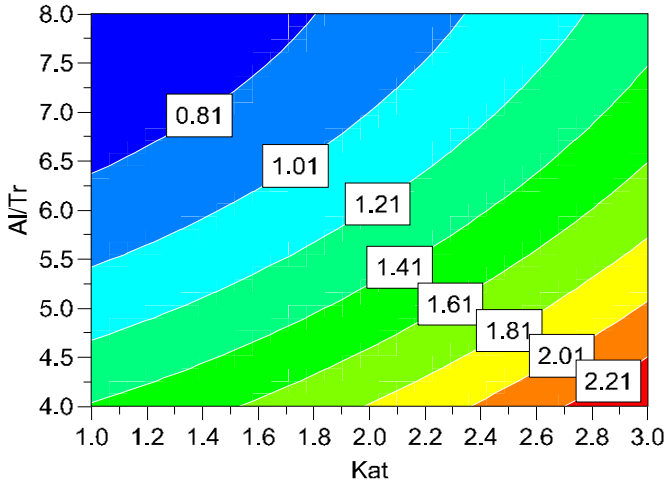


Figure 19: Contour plot for acid value at 90°C and a reaction time of 2 hours

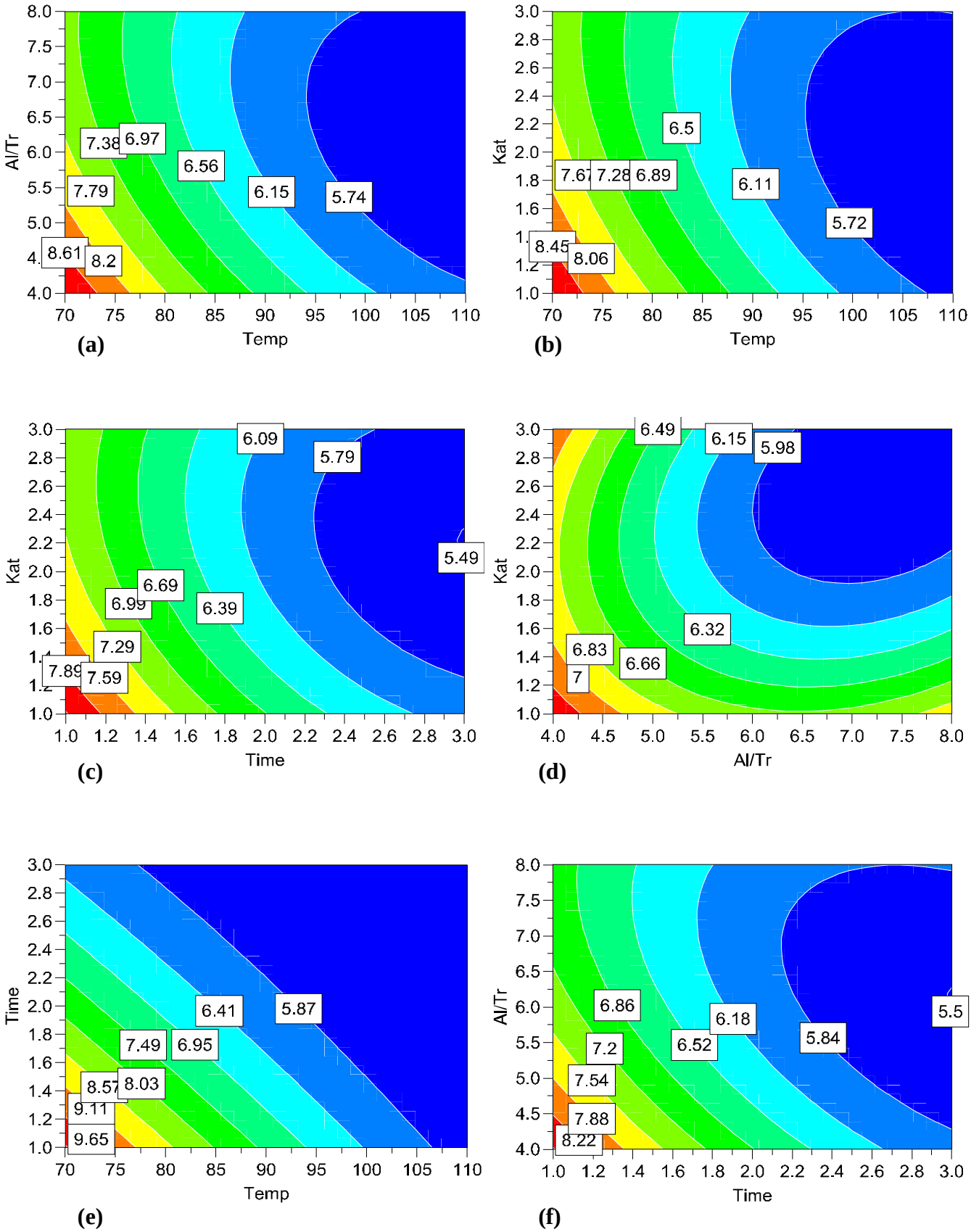


Figure 20: Contour plots for viscosity, variables not on the axes are held at the center values: 90°C, 2 hours, 6 equiv. and 2 % v/v

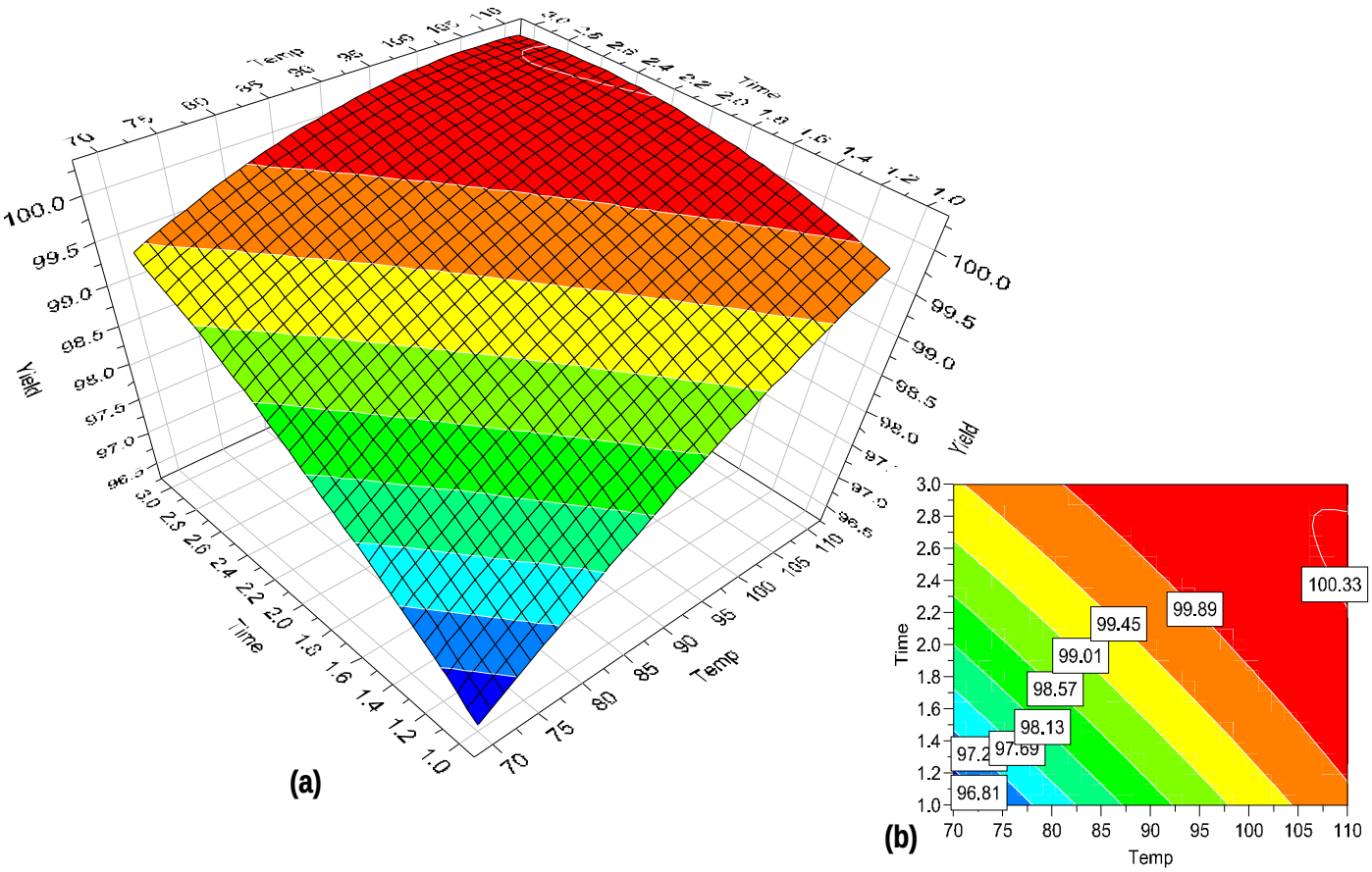


Figure 21: 3D graph (a) of yield and corresponding contour plot (b) with 7.0 equiv. and 2 % v/v

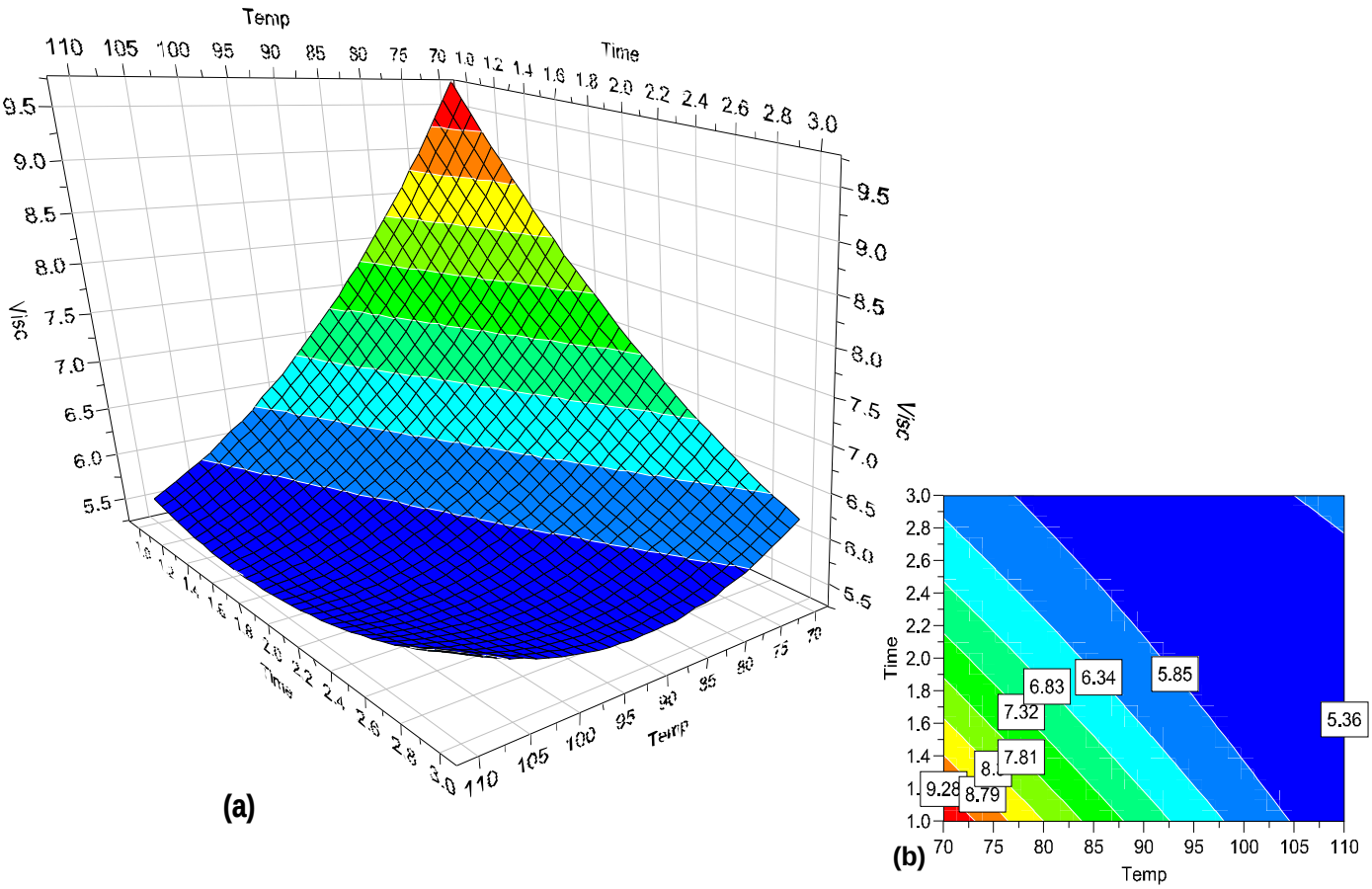


Figure 22: 3D graph (a) of viscosity and corresponding contour plot (b) with 7.0 equiv. and 2 % v/v

5. Discussion

The discussion is split into three parts. The first part (5.1 – 5.3) includes discussions on constraints, the procedure and analysis. The second part (5.4) discusses the model itself and the accuracy of it, while the last part (5.5 – 5.8) discusses the effect of the variables predicted by the model.

5.1. Selection of design constraints

The choice of process fell on the acidic catalyzed transesterification. The capabilities regarding waste oils and non-edible oils where crucial for this choice. The alkali catalyzed process is usually cheaper, faster and require less energy than the acidic counterpart. However, problems with FFA make the alkali catalysts only effective on VGO or oils with less than 1 % FFA. With ¾ of the cost connected to the oil itself for biodiesel production, there are possibilities for major cost reductions within the oil choice and handling. Generally, the waste oils have large amounts of FFA and normally pre-treatment with acid catalyst is necessary before alkali transesterification can proceed. An alternative to pre-treatment will be to do the entire reaction acidic. This would decrease the number of variables as a pre-treatment process would require two sets of variables for the two-step (pre-treatment and transesterification) process. The difficulties involved with transferring from the acidic pre-step to the alkali transesterification would also be avoided with a one-step acidic transesterification. A two-step process involving acidic pre-treatment can easily take close to and exceed 2 hours to finish [3, 14]. For a simpler process with fewer reactors and less equipment the acidic process seems as good as the two-step process. It would apparently not involve more time, as an alkali transesterification on oil with more than 1 % FFA would have to include the acidic pre-treatment.

Chapter 2.3 correlate increased reaction temperature with decreased reaction time for the acid catalyzed transesterification. Longer chained alcohols like propanol and butanol possess higher boiling temperatures than the more commonly used methanol. They are also more soluble in the oil and compared to methanol react far better for the acid catalyzed process. When product parameters like cold flow and viscosity is considered, then this chapter clarifies that the oil itself is mostly affecting these product parameters. To some extent longer chained and especially branched alcohols would improve cold flow properties. Stirring is an important aspect of transesterification. The effect of mass transfer is always a consideration for a chemical system. However, during this thesis stirring was chosen not to be a variable, but was held at a level giving homogeneous solution. Stirring is only effective for the first few minutes of the reaction [1, 5, 13]. Since the minimum time was set to 1 hour, this should not give any significant consequences for the results.

5.2. Procedure & measurements

The common procedure for alkali catalysts is to mix the catalyst with the alcohol before adding it to the heated oil. This procedure was used as it is the most commonly described and is easy to use. However, there is a distinct difference between how acidic and alkali catalysts work. While the alkali catalyst acts upon the alcohol first in a pre-step, the acidic catalyst acts upon the oil first protonating it. The author is not aware of the effect of adding the acid catalyst to either the oil or the alcohol first, and in literature both methods are used with acidic catalysts.

The EN14104 is the European Union standard for measuring the acid number on biodiesel samples. The standard was used as a template but not followed precisely; the main reason for this was the total volume of the sample. The available volume of the sample was not enough for the EN14104 when other parameters were to be measured in addition. Firstly the oil samples were reduced to 4 grams instead of 20 grams and the volume of the solvent was reduced from 100 ml to 50 ml 99 % *iso*-propanol. This reduction in sample solution meant less potassium hydroxide solution and sensitivity, so the concentration of potassium hydroxide was reduced from 0.125 M to 0.055 M. Secondly as a pH meter was not available bromothymol blue was used as indicator for standardizations. And finally the ketone 4-methylpentan-2-one was not obtainable so 99 % *iso*-propanol was used as solvent for benzoic acid instead. The weight of benzoic acid was reduced from 0.15 gram to 0.05 gram improve the accuracy of the volumetric standardization. Considering the now less precise method, each of the samples was titrated 3 times and standardization was done 5 times for the KOH solution.

Within the repeated titrations and standardization, quite good results were obtained with acceptable differences between the repeats. This method would not hold for accurate measurements of samples ready for sale but should give indication on the acid number and the general direction when variables are changed. When indicators like bromothymol blue are used, the accuracy of color change is only as good as the eye observing. The color change was attempted to be equal for each sample making the relationship between samples more precise. Interestingly it was observed that the acid number is very sensitive to biofouling. Sampling of the smallest amount of biofouling within the vials would double the acid number, this was therefore avoided.

For viscosity measurements the European Union standard was not followed. Instead a shear rate scan was conducted with 6 measuring points between $^{100}/_{s}$ to $^{1000}/_{s}$. The scan showed linearity when the shear rate was increased, suggesting Newtonian fluid behavior. The repeated shear rate measurements showed little difference between the center points (90°C, 2 hours, 2 % v/v catalyst and 6 equiv. alcohol) giving low uncertainty in the viscosity measurements. However, the model suggests a far lower viscosity then what was measured; this will be described further in chapter 5.4.

5.3. NMR analysis & atlas

The transesterification from triglyceride to FABE is represented by the two signal peak at 4.5 – 4.1 ppm disappearing and a new signal at 4.0 ppm emerging. This can be seen in the NMR atlas (figure 7, page 24) and the characteristic difference from triglyceride to FABE is supported by Wahlen et al. [10]. On most of the experiments at 70°C remains of triglycerides were observed (table 4, p.25). This is indicated with a dotted line continuing the FABE signal above 4.0 ppm. The only experiment at 70°C without remains of triglycerides is the one where all other variables are maximized. This can indicate that temperatures close to or below 70°C will not be enough for a complete transesterification within the reaction time used in these experiments. Also it can be noted a minor tendency for rapeseed oil to be easier transesterified than jatropha oil. This is shown by comparing the amount of triglyceride remains for rapeseed and jatropha in table 4. Possibly the effect of esterification can play a role here. Jatropha oil have more FFA (higher AN) than rapeseed oil and the water produced during esterification can affect the transesterification. This obliviously does not stop the reaction, but can slow it down slightly.

It is clear that oleic acid (appendix B) is the most abundant fatty acid in both jatropha and rapeseed oil. It can be seen that both oils follow oleic acid as a template; this is also the case for the produced FABE. Butyl 7-decenoate has a signal just below 5.5 ppm which also appears for oleic acid, the oils and the FABE. This signal most likely shows the double bonds as butyl decanoate does not show this type of signal. Butanol have been simulated and added to a sample for testing, in both occasions signals appear around 3.5 ppm. The same goes for glycerol and this shows that NMR can potentially be used to address general impurities. By testing a sample before rotary evaporation and on a finished sample with added water, it is apparent that emulsions would show signals just short of 5.0 ppm. In addition it shows that the produced FABE is clean of these impurities and that the washing and evaporation process was successful. NMR spectrum showing emulsion, butanol and remains of triglycerides signals can be found in appendix B together with an example of the common spectrum for samples.

5.4. Experiment design

The pre-study was only done on the response "yield", for that response a R^2 of 0.41 was achieved (figure 8, p.24). This is under the minimum value of 0.5 stated by the software (chapter 3.2). The pre-study results are therefore considered unreliable, also by looking at figure 8 it is clear that the residuals are not aligned on the straight line. Both jatropha and rapeseed achieved considerable better R^2 of respectively 0.96 and 0.92 (table 5 p.26, table 6 p.31) and thereby giving a far more precise model. The decision to switch to an accurate syringe compared to a volumetric cylinder is apparent. However, some of the increase in R^2 is also due to more experiments and variables. Yet the R^2_{adj} for jatropha and rapeseed is still high clarifying that the full model is significantly more precise, as might have been expected.

The R^2_{pre} (p.26, p.31) is above both the minimum and recommended level for both jatropha and rapeseed, but the model should not be considered an exact understanding of the actual chemical system. The highest R^2_{pre} value is for jatropha yield at 0.78 which means that 22 % of the model can't be explained or supported by the real results (observed). Still the models presented on yield for both jatropha and rapeseed are considered significant and give a good approximation of the real system.

For viscosity both R^2 and R^2_{pre} is in the same range as with yield. However, the predicted viscosity is lower than what was observed. The observed lowest viscosity was 6.1 $^{mm^2}/_s$ while the predicted lowest is 5.3 $^{mm^2}/_s$ (appendix A1 and A2). Yet the model presented is still an approximation, therefore when R^2_{pre} for jatropha and rapeseed are 0.65 and 0.68 respectively $^1/_3$ of the model is uncertain. It might be recommended to treat the models for viscosity with some caution for the assumed best values; the models are nevertheless still of significance and approximate the real results. For acid number the predicted values are below the recommended, but still above the minimum for rapeseed. This can be seen graphically in figure 9 (p.26) and figure 16 (p.31) as there is a spread in the alignment. Therefore the models for acid number should only be treated as indicative.

Figure 10 (p.27) and 17 (p.32) shows the most significant variables for each response. Great caution should be used for the variables more to the right in the figures. The uncertainty shown by the segmented line is larger than the predicted impact shown by the column. The relative importance of each variable can be compared to the contour plots (figures: 11-13 p.28-29 and 18-20 p.33-34). The maximum area for both yield and viscosity is always more towards high temperature than long time, thereby making temperature more significant than time as shown in figure 10 and 17.

Catalyst concentration is shown as insignificant for yield within the time and concentrations used in this thesis. Thereby saying that as long as there is more than 1 % v/v catalyst, the three other variables temperature, time and alcohol equivalents are far more important for yield. For acid number, which is a measurement for esterification, time and temperature is apparently not of importance compared to alcohol and catalyst. An explanation of this is possibly due to the speed of the esterification reaction, which is significantly faster than the transesterification [13]. Indeed even when the temperature is at 70°C the acid number for experiments with maximum alcohol and minimum catalyst still achieve some of the lowest observed acid numbers (table 2 p.21, table 4 p.25, appendix A1 and A2).

5.5. Effect of reaction time

The contour plots for the effect of time shows that the effect is constantly increasing (figures: 11, 13 p.28-29 and 18, 20 p.33-34). Generally more time give higher yield and lower viscosity within the levels chosen for this thesis. The effect of time on yield is on what's called a "rising ridge" and appears to increase too slightly outside the maximum time. However, for an acceptable yield of above 98 %, 2 hours is necessary for both oils. The maximum effect on rapeseed viscosity is slightly beyond 3 hours, while for jatropha the maximum effect appears to be at 3 hours. Maximum effect means the level of the variable (now time) where the variable it is compared against can be altered the most while still achieving the best response.

It is clear from the contour plots that time and temperature interacts. Reduced time for the same response (yield or viscosity) can be achieved with increased temperature. The optimal time based on the 3D graphs for both jatropha and rapeseed appears to be around 2 hours (figures: 14-15 p.30, 21-22 p.35). This is mainly due to viscosity optimization as getting a good yield appears to be easier. The 3D graphs are not on the center values as with the contour plots. Temperature and time is on the axes of the 3D graphs, alcohol equivalents are at 7.5 for jatropha and 7.0 for rapeseed, while catalyst concentration is at 2 % v/v for both oils. The reason for these levels of alcohol and catalyst will be described in 5.7 and 5.8.

Most literature have used yield as indication of completeness. The most common reaction time in literature is 3-4 hours for maximum yield. Here the results state 2 hours for both oils, however, only due to other responses than yield as the yield will be good enough within at that time.

5.6. Effect of temperature

The effect of temperature is the same as with time (figures: 11, 13 p.28-29 and 18, 20 p.33-34). Higher temperature gives higher yield and lower viscosity; it is a constantly increasing effect. Too achieve an acceptable yield of above 98 %, the temperatures needs to be at lest 90°C for both jatropha and rapeseed oil. The maximum effect of temperature on rapeseed yield seems to be beyond the borders of this thesis. The effect is increasing above the highest temperature used in the experiments. However, for jatropha oil the maximum effect on yield for temperature appears to be close to 110°C, the highest temperature used.

When inspecting the contour plots for viscosity, a clear tendency for higher temperature can be seen (figures: 13 p.29, 20 p.34). The increase to outside of the plots seems to be stronger for temperature than for time. This is in agreement with figure 10 (p.27) and 17 (p.32) where temperature is shown to have a larger impact than time. For both jatropha and rapeseed the temperature as close as possible to the boiling point of butanol (117°C) should clearly be the choice.

Time and temperature show strong interaction with each other. By increasing the temperature with 5°C, the time can be reduced with approximately 20 minutes for rapeseed and 25 – 20 minutes for jatropha, while still reaching the same yield and viscosity. This is based on the contour plots for time and temperature (on the axes) on yield and viscosity (figures: 11a, 13e p.28-29 and 18a, 20e p.33-34). These contour plots illustrate the dependency of these to variables on one another. The border lines showing one level of the response to the next are close to straight lines diagonally crossing the plots. The optimal temperature based on the 3D graphs is found to be 110°C for both rapeseed and jatropha (figures: 14-15 p.30, 21-22 p.35). The temperature might even be higher and closer to the boiling point of 117°C for butanol.

Almost all literature uses and recommends the boiling temperature of the alcohol used, including butanol. The results from the model in this thesis maintain this and support the use of the highest temperature available.

5.7. Effect of alcohol ratio

For rapeseed oil the effect of alcohol equivalents on yield reaches a maximum at 7.0 equivalents (figure 18 p.33). Going past this level has a negative and decreasing effect on the yield of rapeseed oil. On jatropha oil an increase in the effect on yield is apparent until the effect reaches a maximum and levels at 7.5 equivalents (figure 11 p.28). The decrease seen for rapeseed yield is not seen on the model for jatropha yield when considering alcohol equivalents.

A high amount of alcohol is necessary for a reduction in the acid number. The lowest level seems to be 7.5 equivalents for jatropha and 7.0 equivalents for rapeseed (figures: 12 p.28, 19 p.33). The esterification and acid number reduction might appear to be more successful for rapeseed compared to jatropha. However, it is important to note that the untreated jatropha oil have an acid number of 10.29 $^{mg\ KOH}/_{g}$ whereas rapeseed starts at 2.54 $^{mg\ KOH}/_{g}$. For the esterification of jatropha oil the reduction in acid number is therefore at 86 % (1 – 1.44/10.29) while the reduction for rapeseed is at 68 %. This reducing effect of alcohol on acid number is supported by Dehkhoda et al. [12].

Both models for the viscosity of rapeseed and jatropha oil show a maximum effect at 7.0 equivalents (figures: 13 p.29, 20 p.34). As with yield, a decrease is seen when more alcohol beyond this level is used. The reduction in effect and thereby increase in viscosity is larger for rapeseed than for jatropha. For jatropha the reduction mainly starts after 7.5 equivalents. The optimum based on the contour plot for acid number and the contour plots for viscosity therefore appears to be 7.0 equivalents for rapeseed. The optimum for jatropha is considered at 7.5 equivalents, the reason for a slightly higher level is because the reduction for viscosity is small compared to rapeseed while the requirement for acid number is higher.

In literature everything from 6.0 to 9.0 is advised. For most parts the recommendation is focused around 6.0 to 7.5 equivalents for the best yield. The results of the models here indicate that the optimum for yield is quite equal with little difference, considering that the yield is high already from 6.0 equivalents. However, for different oils there will be achieved different optimums and while yield is high, other responses like acid number and viscosity can give various optimums.

5.8. Effect of catalyst concentration

Increasing the catalyst concentration has an interesting increasing effect on acid number. The models indicate that 2 % v/v is the maximum concentration if a low acid number is to be achieved (figures: 12 p.28, 19 p.33). To reduce acid number further, even lower concentrations appears as the best general direction. A possible explanation for this effect might be that too much catalyst will cause hydrolysis, thereby giving more FFA.

The catalyst concentration has a maximum effect on viscosity at a concentration of 2.4 % for rapeseed and 2.6 % for jatropha (figures: 13 p.29, 20 p.34). A minimum 2 % v/v catalyst is needed for a low viscosity on rapeseed whereas a minimum of 2.2 % v/v is found for jatropha. Jatropha oil has a higher starting viscosity than rapeseed oil; this might account for some of the 0.2 % increase in catalyst. For both jatropha and rapeseed there is a minimum in viscosity along the 2.0 % v/v concentration of catalyst when time and temperature is increased from their center values. Therefore by considering this and taking into account the effect on acid number the optimum is considered at 2.0 % v/v for both jatropha and rapeseed oil.

From the literature it is difficult to state any precise recommended or most common concentration. However, the model here shows that for the sake of acid number the catalyst concentration should be as low as possible, whereas the viscosity can to some extent be controlled by other variables.

6. Conclusion

It can be concluded that time will be equal for the one-step process (acidic transesterification) and the two-step process (acid esterification + alkali transesterification). Both processes needs around 2 hours when the amount of FFA is above 1 %. Temperature is of absolute importance for the acidic transesterification and should be as high as possible. The temperature might even be higher than the boiling point of butanol with methods for sealing the reactor, cooling the vapor and back flow. Possibly alternative methods for heating should be investigated due the dependency on high temperatures. Alcohol equivalents have an optimum on 7.0 for rapeseed oil and 7.5 for jatropha oil, where further increase will have a negative effect on yield and viscosity. In general alcohol provides a decreasing effect on both viscosity and acid number, and an increasing effect on yield. Catalyst concentration does not affect yield when more than 1 % v/v is present. Catalyst conc. has an increasing effect on acid number and decreasing effect on viscosity. A maximum of 2 % v/v is recommended as a compromise between acid number and viscosity. For quality control H-NMR provides a general evaluation on impurities and effectiveness of the washing and evaporation processes. And finally, it is for most conditions easy to achieve a high yield. Responses such as viscosity and acid number are therefore more significant for optimization compared to yield.

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Appendix

A

A1: Observed, predicted and difference (residual) for jatropha oil

Exp. Nr.	Observed			Predicted						Residual		
	Yield	Visc	AN	Yield	+/-	Visc	+/-	AN	+/-	Yield	Visc	AN
1	94,6	12,9	2,82	94,1	1,0	13,2	1,4	2,44	0,9	-0,5	0,3	-0,4
2	97,5	7,6	1,86	97,9	1,0	7,3	1,4	1,89	0,9	0,4	-0,3	0,0
3	96,1	9,2	1,82	96,4	1,0	8,9	1,4	1,65	0,9	0,3	-0,3	-0,2
4	98,4	6,6	1,57	98,2	1,0	6,6	1,4	1,90	0,9	-0,2	0,0	0,3
5	97,1	13,1	1,18	97,2	1,0	12,1	1,4	1,61	0,9	0,1	-1,0	0,4
6	99,9	6,3	1,18	100,2	1,0	6,8	1,4	0,90	0,9	0,3	0,5	-0,3
7	99,4	7,7	1,15	99,5	1,0	8,1	1,4	1,09	0,9	0,1	0,4	-0,1
8	101,0	6,4	1,25	100,5	1,0	6,4	1,4	1,19	0,9	-0,5	0,0	-0,1
9	93,6	11,7	2,97	94,1	1,0	10,8	1,4	2,72	0,9	0,5	-0,9	-0,2
10	98,7	6,3	2,27	98,7	1,0	6,8	1,4	2,55	0,9	0,0	0,5	0,3
11	97,3	7,2	2,28	97,2	1,0	7,5	1,4	2,74	0,9	-0,1	0,3	0,5
12	100,0	6,9	4,04	99,7	1,0	7,2	1,4	3,37	0,9	-0,3	0,3	-0,7
13	95,4	8,2	1,83	95,5	1,0	9,1	1,4	1,69	0,9	0,1	0,9	-0,1
14	99,7	6,3	1,51	99,3	1,0	5,7	1,4	1,37	0,9	-0,4	-0,6	-0,1
15	99,1	6,6	2,28	98,5	1,0	6,1	1,4	1,98	0,9	-0,6	-0,5	-0,3
16	99,5	6,1	1,77	100,3	1,0	6,4	1,4	2,46	0,9	0,8	0,3	0,7
17	97,2	7,6	1,38	97,6	0,9	8,2	1,2	1,88	0,8	0,4	0,6	0,5
18	100,0	6,4	1,83	100,4	0,9	5,3	1,2	1,84	0,8	0,4	-1,1	0,0
19	99,4	7,0	1,43	98,6	0,9	7,5	1,2	1,83	0,8	-0,8	0,5	0,4
20	100,0	6,4	2,1	100,3	0,9	5,7	1,2	1,99	0,8	0,3	-0,7	-0,1
21	98,3	6,7	1,71	98,4	1,1	7,0	1,5	2,28	1,0	0,1	0,3	0,6
22	100,0	6,4	3,02	100,2	1,2	6,1	1,7	1,41	1,1	0,2	-0,3	-1,6
23	99,7	6,7	1,95	99,5	0,9	7,2	1,2	1,73	0,8	-0,2	0,5	-0,2
24	99,5	6,3	2,72	99,4	0,9	5,9	1,2	2,51	0,8	-0,1	-0,4	-0,2
25	99,7	6,1	2,08	99,7	0,4	6,1	0,6	1,92	0,4	0,0	0,0	-0,2
26	99,7	6,1	2,17	99,7	0,4	6,1	0,6	1,92	0,4	0,0	0,0	-0,2
27	100,0	6,1	1,93	99,7	0,4	6,1	0,6	1,92	0,4	-0,3	0,0	0,0
28	99,6	6,1	2,21	99,7	0,4	6,1	0,6	1,92	0,4	0,1	0,0	-0,3

A2: Observed, predicted and difference (residual) for Rapeseed oil

Exp. Nr.	Observed			Predicted						Residual		
	Yield	Visc	AN	Yield	+/-	Visc	+/-	AN	+/-	Yield	Visc	AN
1	94,5	12,9	2,67	94,5	1,3	12,7	1,3	2,16	0,7	0,0	-0,2	-0,5
2	98,9	6,7	1,44	99,0	1,3	6,8	1,3	1,55	0,7	0,1	0,1	0,1
3	98,0	7,4	1,32	97,6	1,3	7,7	1,3	1,44	0,7	-0,4	0,3	0,1
4	99,2	6,4	1,34	99,6	1,3	5,9	1,3	1,41	0,7	0,4	-0,5	0,1
5	97,2	11,4	0,60	97,2	1,3	10,9	1,3	1,05	0,7	0,0	-0,5	0,4
6	99,7	6,3	0,92	99,9	1,3	6,3	1,3	0,65	0,7	0,2	0,0	-0,3
7	99,1	7,5	0,83	99,7	1,3	7,4	1,3	0,71	0,7	0,6	-0,1	-0,1
8	100,6	6,3	0,94	99,8	1,3	6,9	1,3	0,90	0,7	-0,8	0,6	0,0
9	92,7	12,5	2,67	93,8	1,3	11,5	1,3	2,61	0,7	1,1	-1,0	-0,1
10	99,7	6,5	2,73	98,9	1,3	6,9	1,3	2,87	0,7	-0,8	0,4	0,1
11	98,0	6,9	1,78	97,6	1,3	7,2	1,3	2,08	0,7	-0,4	0,3	0,3
12	100,0	6,6	3,47	100,3	1,3	6,7	1,3	2,92	0,7	0,3	0,1	-0,6
13	96,3	8,0	1,28	95,7	1,2	8,8	1,3	1,24	0,7	-0,6	0,8	0,0
14	98,3	6,3	1,93	98,9	1,3	5,6	1,3	1,71	0,7	0,6	-0,7	-0,2
15	98,8	6,4	1,30	98,9	1,3	6,0	1,3	1,09	0,7	0,1	-0,4	-0,2
16	99,9	6,4	1,60	99,7	1,2	6,9	1,3	2,14	0,7	-0,2	0,5	0,5
17	98,3	7,3	1,10	97,7	1,1	7,9	1,1	1,20	0,6	-0,6	0,6	0,1
18	100,2	6,1	1,19	100,4	1,1	5,3	1,1	1,42	0,6	0,2	-0,8	0,2
19	98,9	6,4	1,02	98,2	1,1	7,4	1,1	1,40	0,6	-0,7	1,0	0,4
20	99,9	6,1	1,39	100,1	1,1	5,5	1,1	1,26	0,6	0,2	-0,6	-0,1
21	98,5	6,3	1,49	98,4	1,1	6,9	1,1	1,82	0,6	-0,1	0,6	0,3
22	99,1	6,2	1,03	99,4	1,1	6,1	1,1	0,88	0,6	0,3	-0,1	-0,2
23	99,9	6,2	0,65	99,4	1,1	6,7	1,1	0,88	0,6	-0,5	0,5	0,2
24	99,4	6,1	1,60	99,0	1,1	6,1	1,1	1,73	0,6	-0,4	0,0	0,1
25	99,4	6,3	1,37	99,4	0,5	6,0	0,5	1,21	0,3	0,0	-0,3	-0,2
26	99,1	6,3	1,41	99,4	0,5	6,0	0,5	1,21	0,3	0,3	-0,3	-0,2
27	98,4	6,2	1,50	99,4	0,5	6,0	0,5	1,21	0,3	1,0	-0,2	-0,3
28	99,3	6,2	1,41	99,4	0,5	6,0	0,5	1,21	0,3	0,1	-0,2	-0,2

B

B1: Example of a normal NMR spectrum with no triglyceride remains

B2: Example of a NMR spectrum with minor traces of triglycerides

B3: Example of a NMR spectrum with triglyceride remains

B4: NMR spectrum of jatropha oil

B5: NMR spectrum of rapeseed oil

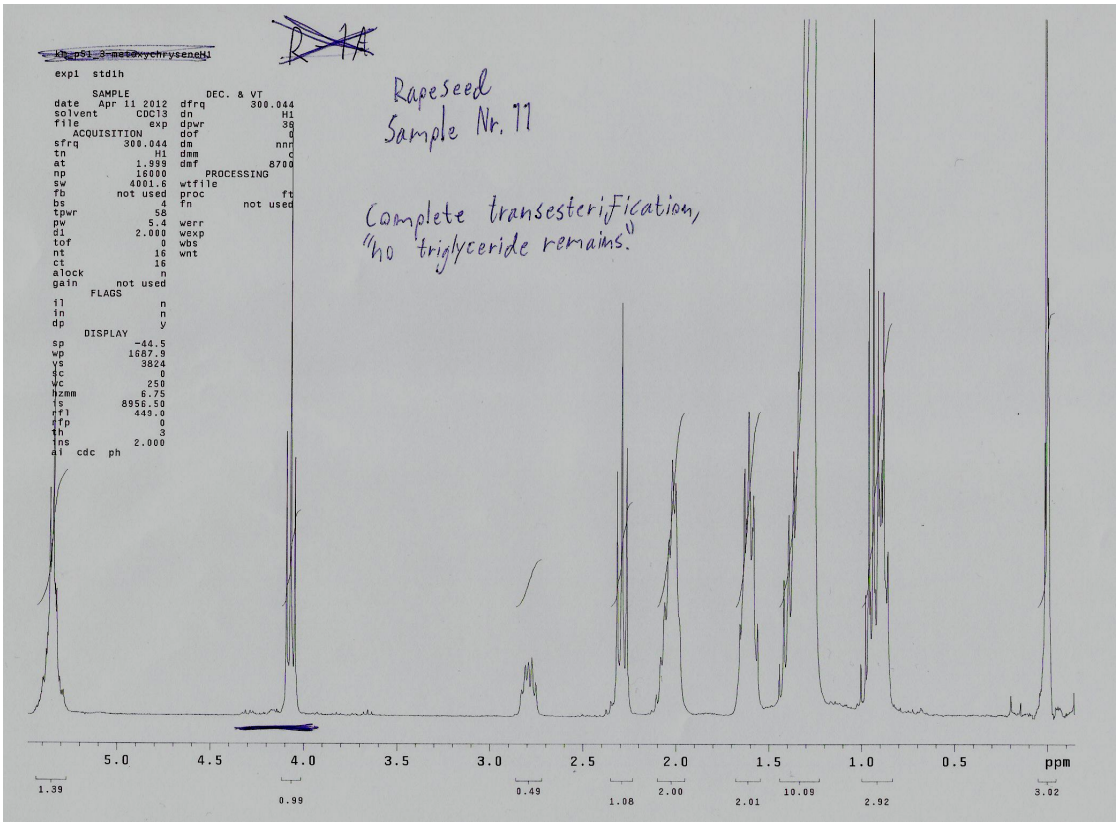
B6: NMR spectrum of oleic acid

B7: NMR spectrum of sample measured before rotary evaporator, showing emulsion

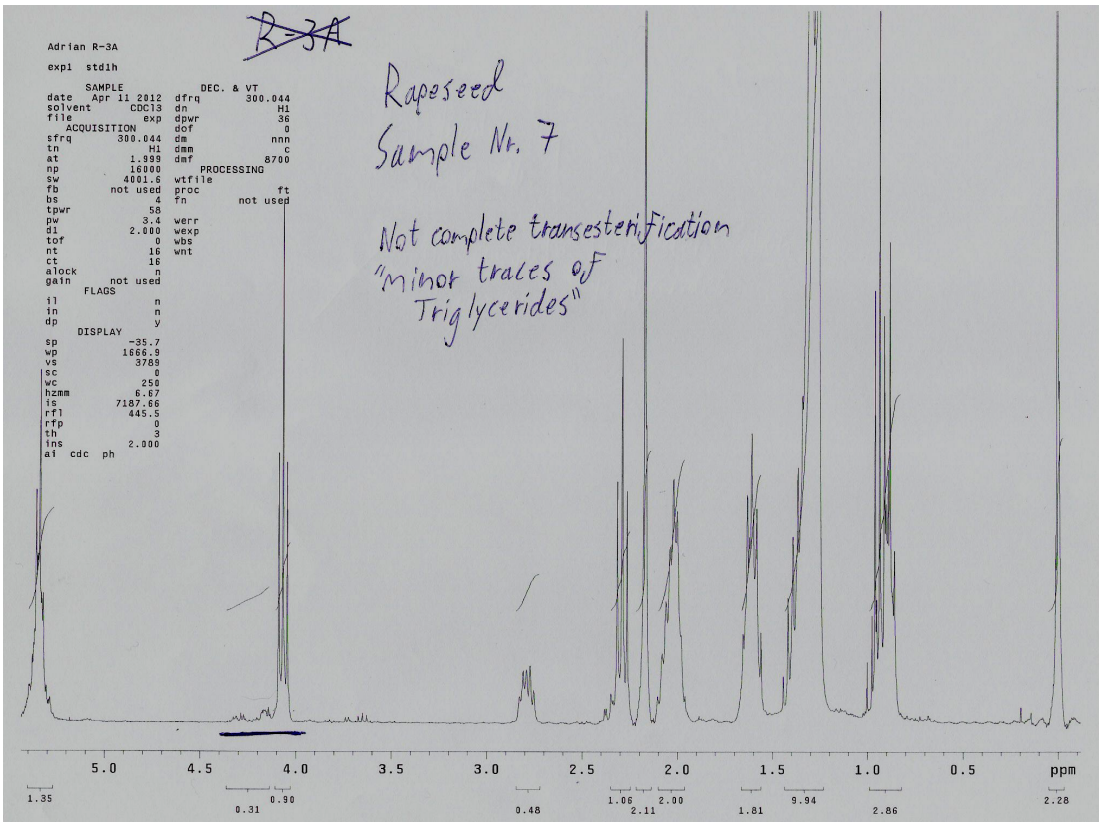
B8: NMR spectrum of sample with water added in it, showing emulsion

B9: NMR spectrum of sample with butanol added in it, showing butanol signal

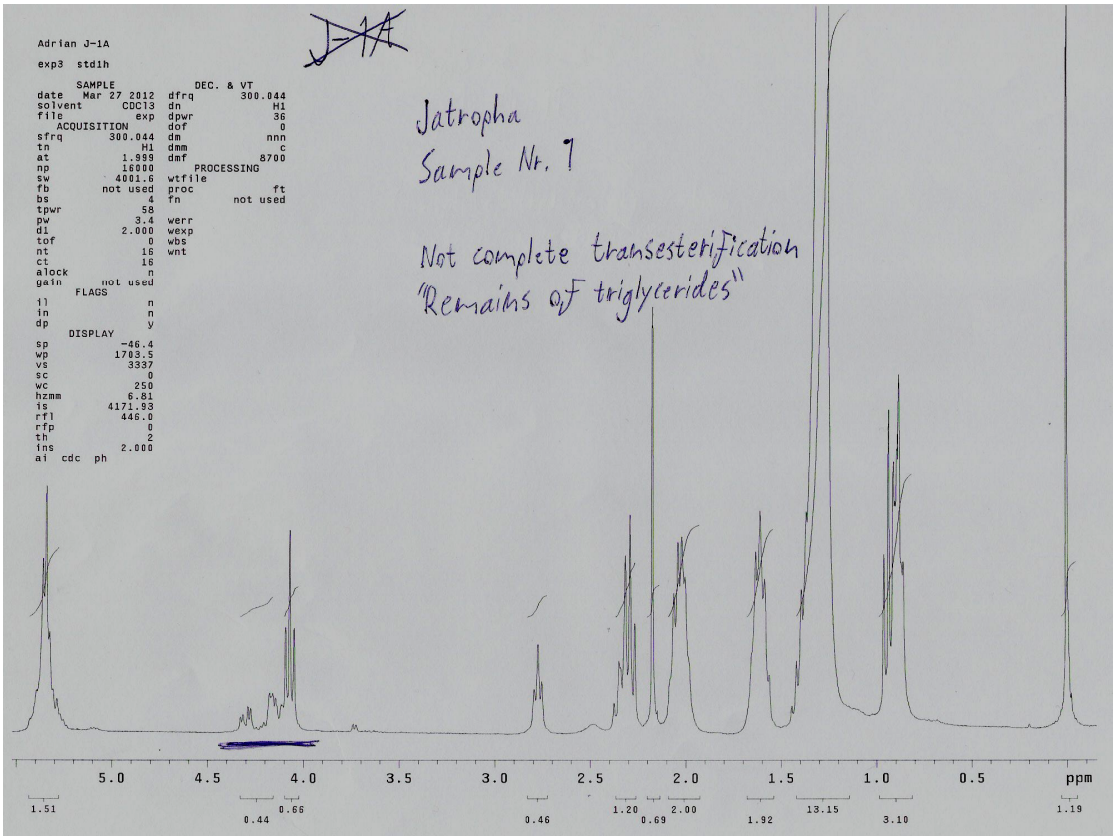
B1: Example of a normal NMR spectrum with no triglyceride remains



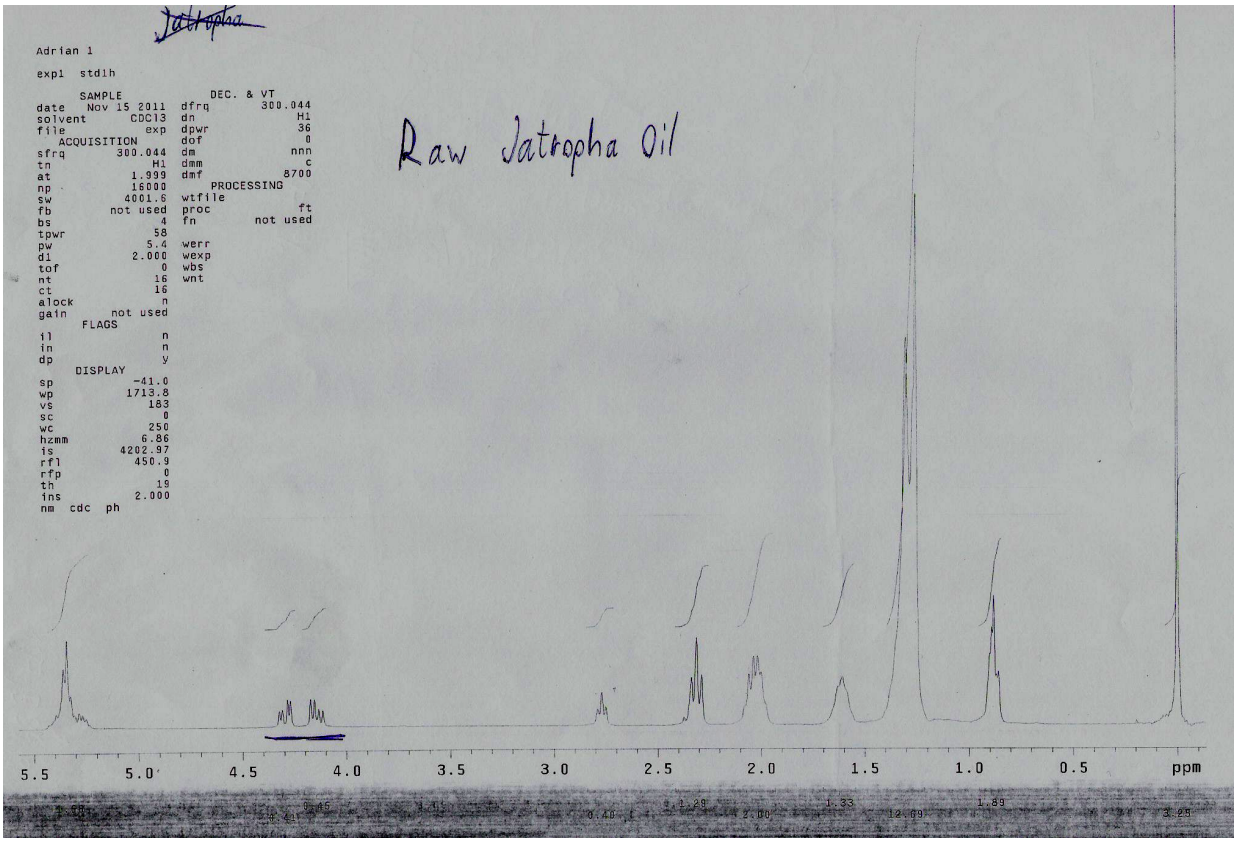
B2: Example of a NMR spectrum with minor traces of triglycerides



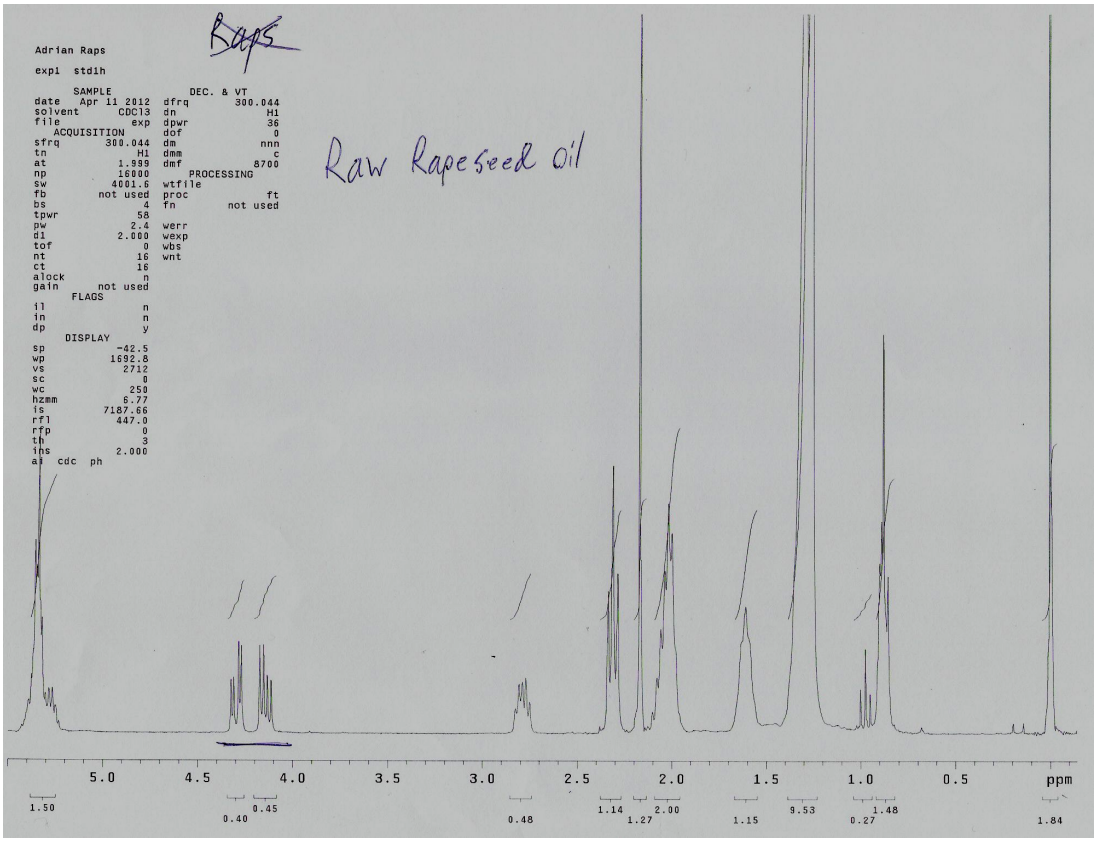
B3: Example of a NMR spectrum with triglyceride remains



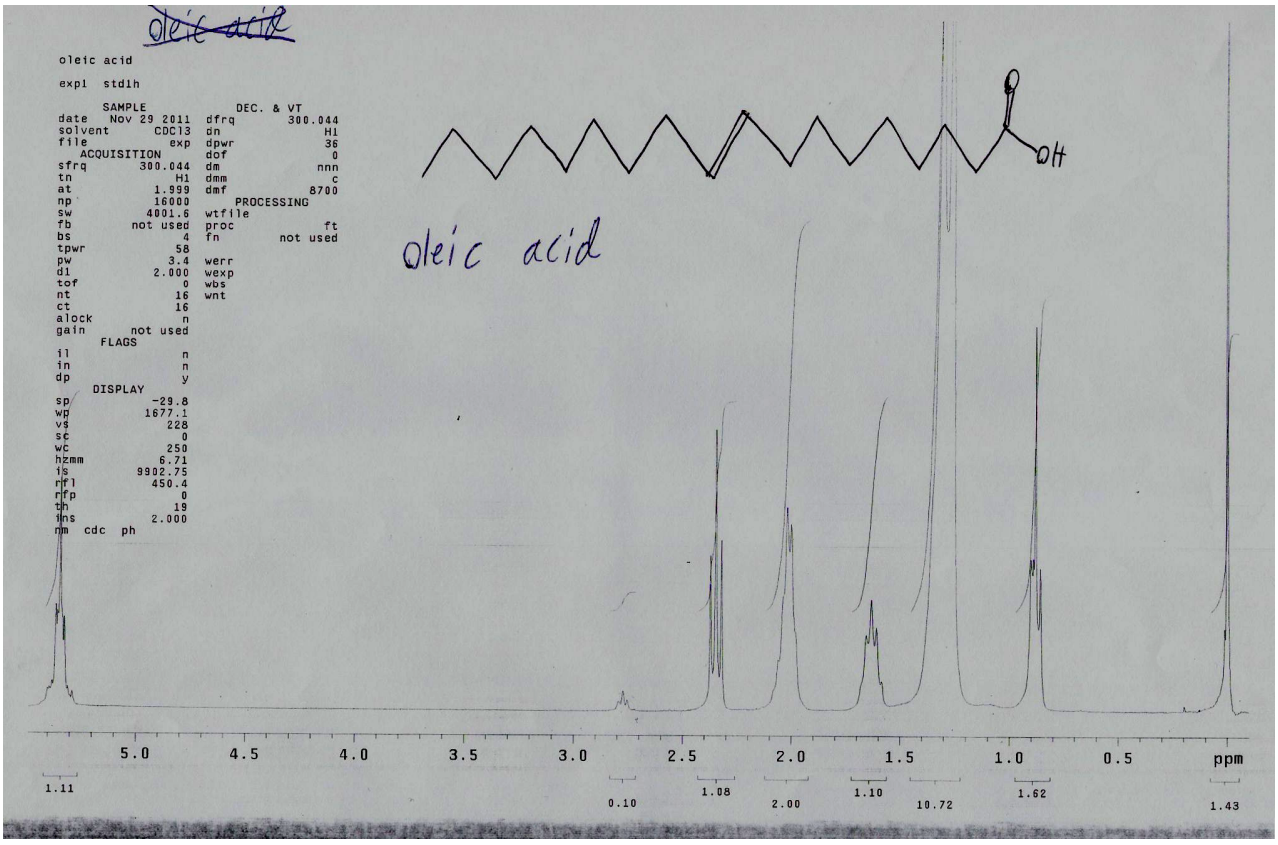
B4: NMR spectrum of jatropha oil



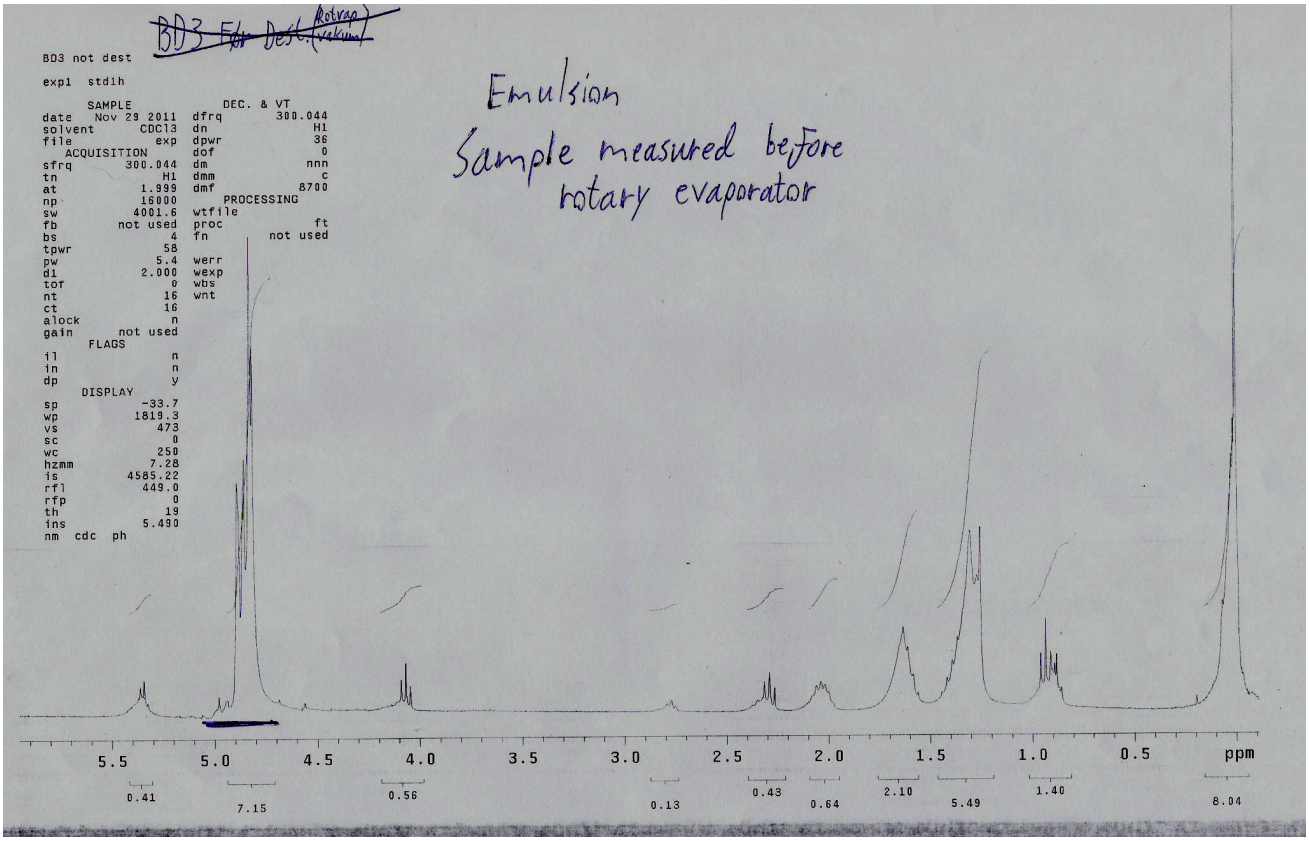
B5: NMR spectrum of rapeseed oil



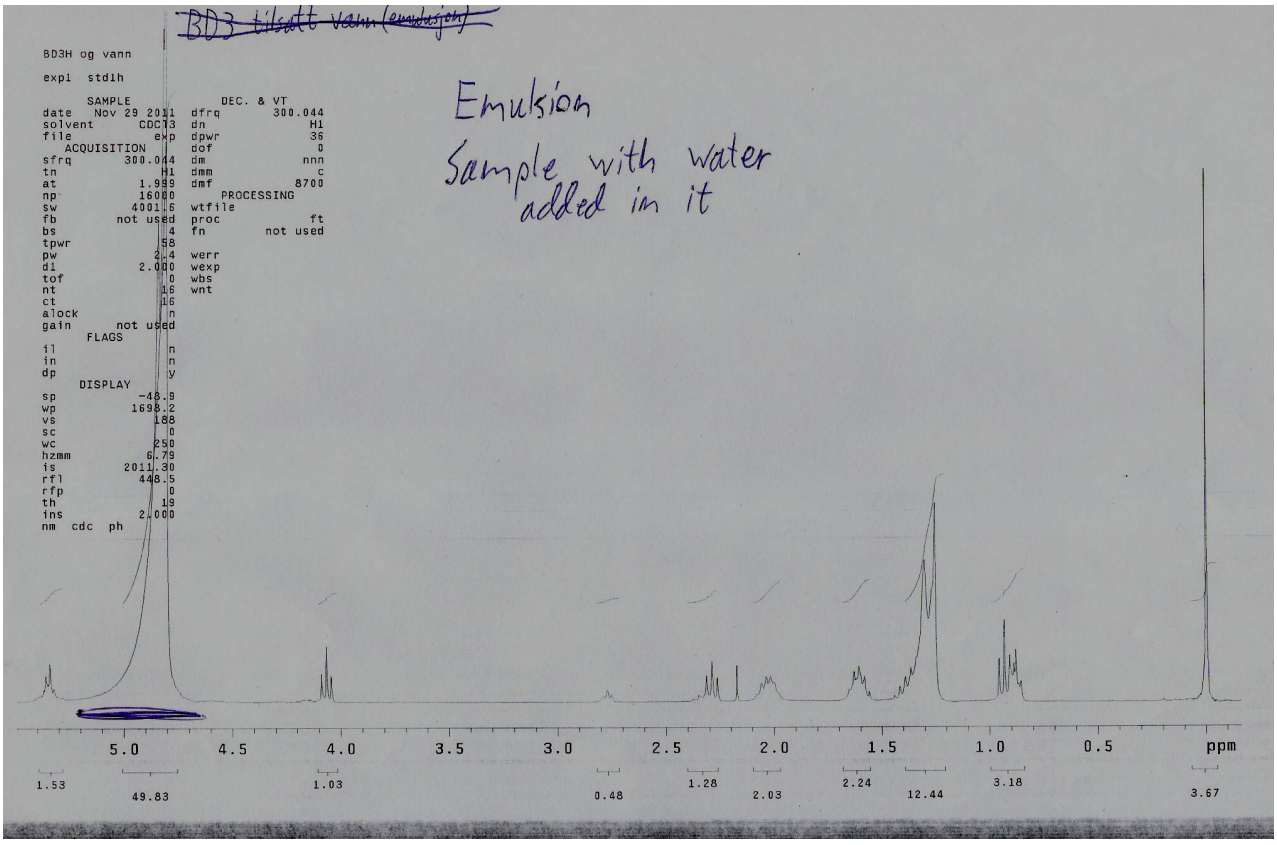
B6: NMR spectrum of oleic acid



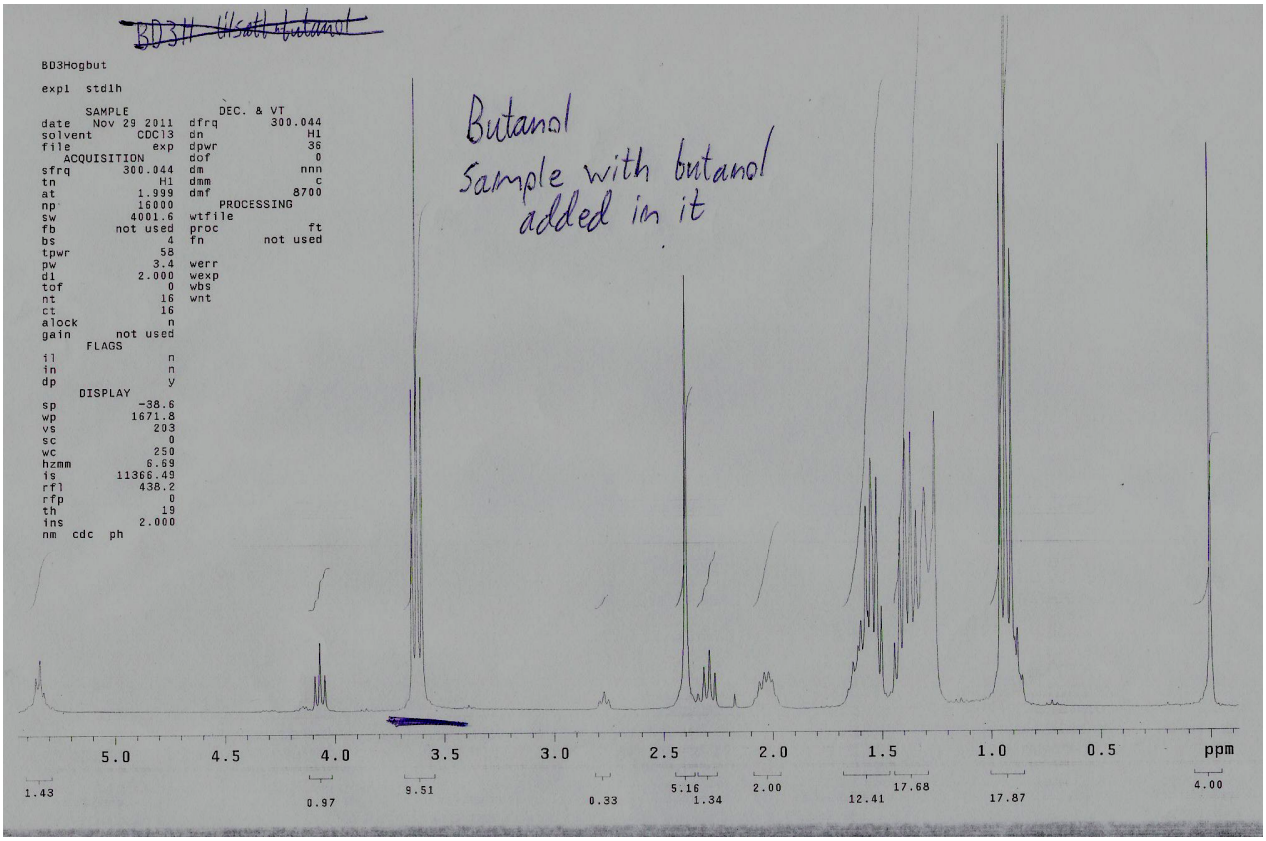
B7: NMR spectrum of sample measured before rotary evaporator, showing emulsion



B8: NMR spectrum of sample with water added in it



B9: NMR spectrum of sample with butanol added in it, showing butanol signal



C

C: Table showing density measurements, start refers to the value of the raw oil

Exp. Nr.	Jatropha g/cm^3	Rapeseed g/cm^3
Start	0,902	0,904
1	0,879	0,881
2	0,863	0,862
3	0,868	0,865
4	0,860	0,861
5	0,879	0,878
6	0,858	0,860
7	0,864	0,865
8	0,857	0,859
9	0,874	0,879
10	0,858	0,861
11	0,862	0,861
12	0,861	0,862
13	0,865	0,865
14	0,857	0,859
15	0,858	0,859
16	0,857	0,860
17	0,863	0,863
18	0,858	0,859
19	0,860	0,860
20	0,857	0,859
21	0,859	0,859
22	0,858	0,859
23	0,858	0,859
24	0,857	0,859
25	0,857	0,859
26	0,857	0,859
27	0,857	0,859
28	0,857	0,859