

## Ethoxylation studies of two mole amine derivatives

*Master of Science Thesis in the Master Degree Programme,  
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Master of Science Thesis

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## Abstract

This thesis aims to optimize the two mole ethoxylation of a fatty amine. The influence of temperature, pressure, water and starter on the process was studied. The starter and water was added to the process as catalysts. Trials were made in three scales, lab, pilot and full scale.

To be able to draw conclusions from all the trials an experimental design was made in the program MODDE. The design was made for the lab scale trials and all the parameters were changed to be able to make a model where the interactions between the parameters were not ignored. The design was a full factorial design where the parameters are given a high and a low value and all the combinations are tried which led to 19 trials being performed in lab scale. The products from these trials were analysed for conversion, dioxane content, colour, chain elongation and ethylene oxide distribution. The methods used for the analysis were titration, GC headspace, colour measurements and NMR.

From the results of the lab scale trials the experiments in the pilot scale were designed. The parameters that were investigated in the pilot scale were temperature and pressure since it was concluded that starter and water did not have a very positive impact on the process.

The pilot trials indicated that the temperature, 170 degrees Celsius, used in the trials gave the best results. Dividing the feed of the ethylene oxide into two parts could also be beneficial to the process. To do that change in full scale more pilot scale trials are needed.

The full scale indicates that the existing settings are not optimal since the results for the lower temperature in the full scale trials, 170 degrees Celsius, give better results. The conclusion of the trials is that more experiments must be performed but a platform for further investigation is created by this thesis.

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# 1. Introduction

This Master thesis project has been executed at Akzo Nobel Surface Chemistry's research and development facility in Stenungsund, Sweden. A part of the work has also been performed in the production site at the same location. The work has been both a literature study and an experimental study. The work was performed over a period of twenty weeks starting in January 2012.

Akzo Nobel Surface Chemistry AB is a world leading supplier of specialty surfactants. They are producing anionic, non-ionic, cationic and zwitterionic surfactants that are used in products ranging from asphalt, cleaning, and petroleum to different food additives. This means that every day you use and consume a lot of different surfactants.

The aim of this thesis was to investigate and optimize the two mole ethoxylation of amine derivatives. The investigation will cover both the chemistry and the process of producing this product.

The raw materials for the investigated product are fatty amines and ethylene oxide. The fatty amines can come from natural sources or petrochemical sources. Fatty amines are named primary, secondary or tertiary depending on how many hydrogen atoms on the nitrogen atom that are replaced by a carbon chain. The fatty amine used in this project is a primary fatty amine which means that there are two hydrogen atoms on the nitrogen that are replaced with ethylene oxide (EO). EO is produced by the petrochemical industry and it is a very reactive compound.

The product is sold for different applications but also used as raw material for many polyethoxylated surfactants which means that the distribution of the EO is very important. A varied distribution of EO could lead to colouring, dioxane formation and other changed properties which all are affecting the quality of the product.

The experimental part of this thesis has been performed in a lab scale autoclave, a pilot plant and in the full scale process. The lab scale autoclave was a 2,5L stainless steel reactor with a stirrer and a heating and cooling system. The reaction conditions were altered to see how different parameters influenced the final product. The parameters that were altered were pressure, temperature, starter and water. The starter and water were added as initiators to the reaction. The experimental design was made in the program MODDE and the analysis results were used by the program to make a model that can be used to predict results for other trials within the range of the parameters.

The results from the lab scale trials were used to make a small pilot plant trial set up which in turns were used to decide which experiments that should be performed in full scale.

## 1.2. Purpose

The purpose of this project was to investigate the influence of temperature, pressure, starter and water on the ethoxylation of a fatty amine with the purpose of optimizing the process. The starter is the finished product that was added to the process to shorten the induction step in the process. To be able to do this investigation trials in lab, pilot and full scale were performed.

This should be performed without any changes to the process set up.

## 2. Background

To give a brief introduction to the project and the execution of the project some topics need an introduction. These topics will be introduced in the following section of the report.

### 2.1. Surfactants

Surfactants, or surface active agents, are compounds that absorb at surfaces or interfaces. The reason that these compounds are surface active is that they are amphiphilic which means that they have a hydrophobic part, the tail, and a hydrophilic part, the head see figure 1. This property causes the molecule to be present in two phases. This leads to a lowering of the surface tension, or interfacial tension, which in turns improves the possibility of creating stable emulsions. This is true since a lower interfacial tension means that the ability to expand the interface is increased and bubbles, drops or particles are then easier to suspend in a mixture. There are different types of surfactants and they are classified by their head group which can be non-ionic, anionic, cationic or zwitterionic. The tail of any surfactant normally consists of a carbon chain (1).

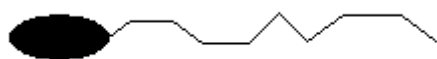


Figure 1. Surfactant with a hydrophilic head and a hydrophobic tail.

#### **2.1.1. Anionic surfactants**

The anionic surfactants have a negatively charged head group that most commonly consists of sulphate, sulphonate, carboxylate or phosphate. Anionic surfactants are the most common surfactants used today and one of the areas where the anionic surfactants are most used is detergents. The main reasons for using anionic surfactants are the ease of manufacturing and the low cost of production. One common anionic surfactant, alkyl sulphate, can be seen in figure 2 (1).



Figure 2. Typical anionic surfactant, alkyl sulphate

### 2.1.2. Cationic surfactants

The cationic surfactants have a positively charged head group where a nitrogen atom most commonly holds the charge. These amines have a big drawback and that is their ability to lose protons at high pH. The only ammonium compounds that are not sensitive to pH are the quaternary since they have no available protons for deprotonization. The quaternary surfactants are mainly synthesised by the nitrile route which is described in reaction 2. A typical quaternary amine surfactant can be seen in figure 3 below (1).

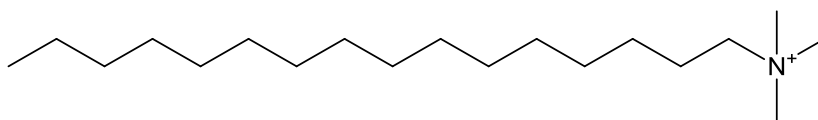


Figure 3. Cationic surfactant, quaternary amine.

### 2.1.3. Zwitterionic surfactants

The zwitterionic surfactants are molecules with two charges of different signs in the head group. The positive charge is mostly represented by ammonium and the negative charge often comes from a carboxylate. These surfactants are very kind to human tissue and are therefore used in applications like shampoo and creams. A typical zwitterionic surfactant can be seen in figure 4 below (1).

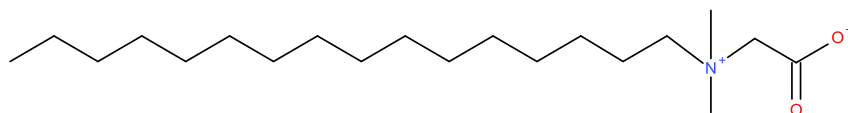


Figure 4. Zwitterionic surfactant, betaine.

### 2.1.4. Non-ionic surfactants

The non-ionic surfactants have no charge on the head group and this means that the size of the head group is not that static as it is for the other types of surfactants where the size of the head group is an almost fixed property. The head of a non-ionic surfactant most commonly consists of multiple ethylene oxide molecules reacted into one or more chains as can be seen in figure 5a and 5b (1) (2).

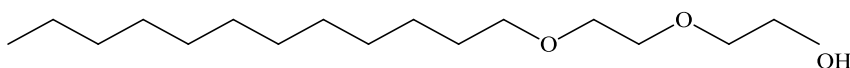


Figure 5a. Non-ionic surfactant with one ethylene oxide chain, fatty alcohol ethoxylate.



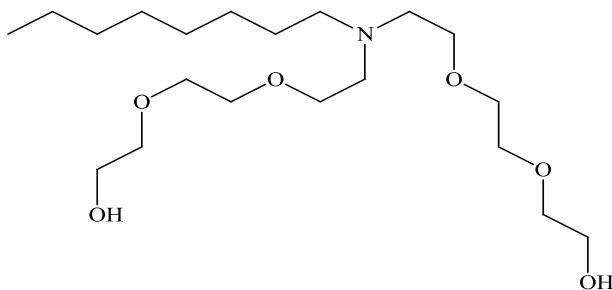


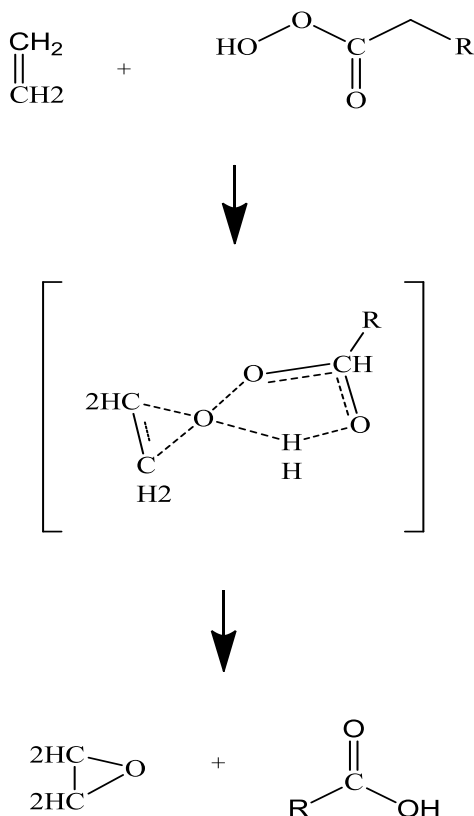
Figure 5b. Non-ionic surfactant with two ethylene oxide chains, fatty amine ethoxylate.

The number of added ethylene oxide monomers depends on the intended use of the surfactant and since a longer chain of ethylene oxide gives a larger hydrophilic part these kinds of surfactants are used as solubilizers and cleansing agents (3). The surfactant of interest in this thesis is used as an additive in polyester plastics to reduce static electricity. To be able to form longer chains of EO on the fatty amine, a catalyst is needed.

## 2.2. Ethylene oxide

Ethylene oxide is an epoxide which is a compound with a three membered ring, a cyclic ring, and is also called oxirane. Epoxides are manufactured from alkenes but they are also found in nature where they are used as an insecticide since the epoxides react with DNA or essential enzymes causing the insects to die since their normal functions are prevented (4).

There are different ways of making an epoxide, an alkene can be reacted with oxygen over a silver catalyst or the alkene can be reacted with a peroxyacid. The reaction with a peroxyacid is a reaction where multiple bonds are broken and created at the same time which is shown in reaction 1.



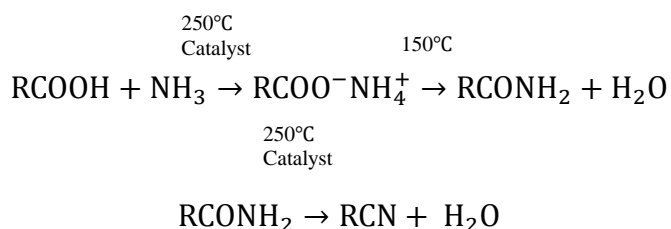
Reaction 1. Reacting peroxyacid and ethene to form ethylene oxide.

Ethylene oxide can also be formed by reacting ethene and oxygen over a silver catalyst. This is the way that the ethylene oxide used in this project is produced. Two ethene molecules react with one oxygen molecule where silver acts as a reaction inducer, i.e. a catalyst, and two ethylene oxide molecules are created.

## 2.3. Fatty amines

Fatty amines are nitrogen derivatives and they could be from both natural sources and petro-chemistry. The most common manufacturing route of fatty amines is hydrogenation of nitriles, but using fatty alcohols as a feedstock is also possible.

The nitriles that are most commonly used in fatty amine production are produced by reacting fatty acids and ammonia according to the steps below in reaction 2.



Reaction 2. The Nitrile route.

The nitriles are then hydrogenated and primary, secondary and tertiary amines are formed.

The carbon chains in a product can vary in length or be of a specific length but that puts higher demands on the feedstock. To achieve a product with a narrow range in carbon chains the fatty amine is distilled. It is very common to have carbon chains in some specific length interval, for example C<sub>16</sub>-C<sub>18</sub>. There could also be unsaturations in the carbon chain depending on the origin of the feedstock. When a fatty amine has coconut oil as feedstock the degree of saturation varies, meaning that the number of unsaturations can vary (5).

## 2.4. Experimental design

Experiments, or tests, are performed to gain knowledge about the impact on the result from different parameters. Experiments can be performed to improve processes, develop new products and overall improvement of a process, both product and non-product processes. To be able to use the results from experiments to draw conclusions the trials should be organized in a way that gives a valid model in the end.

In an experiment there are inputs and outputs but also factors that can be controlled and some that is not regulated or controlled. The factors that can be investigated in an experiment are the controlled factors and to make sure that the un-controlled factors are not interfering with the results an experimental design could be used.

There are different types of experimental designs, all with their benefits and disadvantages. The best-guess approach is when one factor is changed and the others are held constant without any system which means that the trials could go on for a long time and if the starting point is not that good it could be hard to arrive at a “best” point. This is an approach that could be successful if there is enough background knowledge but even with that knowledge this approach is very random and could be very time consuming.

Another approach is to look at one factor at a time. This means that a starting point is selected for the factors and then one of the factors is varied along its range while the others are held constant. This will result in a series of graphs that shows how the result varies with each of the factors. This is a very useful method but it fails to show any interactions between factors. To be able to account for any interactions between the factors a third approach can be used, the factorial approach.

This is an approach where all the factors are varied together. This means that if there are two factors to be varied and both of the factors have two levels, four experiments will be conducted to cover all interactions between the factors.

This approach can lead to a very large number of experiments and to minimize the number of experiments needed a fractional factorial design can be used.

The fractional factorial design is the most frequently used and it is very useful when there are many factors that should be tried and the aim is to find out which ones that have the biggest impact on the process. The approach is used when a full factorial

design is too time consuming or costly and the purpose is to reduce the number of experiments without impacting the conclusions and results of the design. The drawback with the fractional factorial design is that higher order interactions are not included in the model (6).

## 2.5. Analytical methods

Several analytical methods have been used to gain knowledge of the products and to be able to draw conclusions from the trials. In the following chapter these methods will be explained.

### 2.5.1 NMR

Nuclear magnetic resonance, NMR, is a property or phenomena that only some atoms possess. The atoms that have the ability to give a NMR signal have a property called nuclei spin which means that the nuclei acts like a magnet which is spinning around an axis. When a compound containing atoms with this property is placed in a strong static magnetic field during which the sample is also subjected to an electromagnetic energy at an appropriate frequency the nuclei of the atom absorb some of the energy which results in a unique spectrum for all compounds. The frequency of the electromagnetic energy depends on what type of nuclei that is examined. Hydrogen and carbon ( $C^{13}$ ) is the most common nucleus to observe since these spectrums can give information of the structure of most small organic compounds (7) (8).

### 2.5.2. GC

Gas chromatography is a separation method of a gas with multiple compounds. Often a liquid is inserted and evaporated inside the GC but a sample could also be taken from the headspace of gas (9). This is used when the most volatile compounds in a sample are to be quantified. The sample container is then heated up to a specific temperature depending on the substance to be quantified and then the sample is withdrawn from the gas phase of the container. This is the method used in this thesis for quantifying the dioxane in the samples. After the separation of the compounds in the gas, the compounds are detected by different detectors to quantify and determine what compound it is. To be able to quantify a substance a standard with a known concentration of the specific compound of interest must be added to the sample (10).

### 2.5.3. Titration

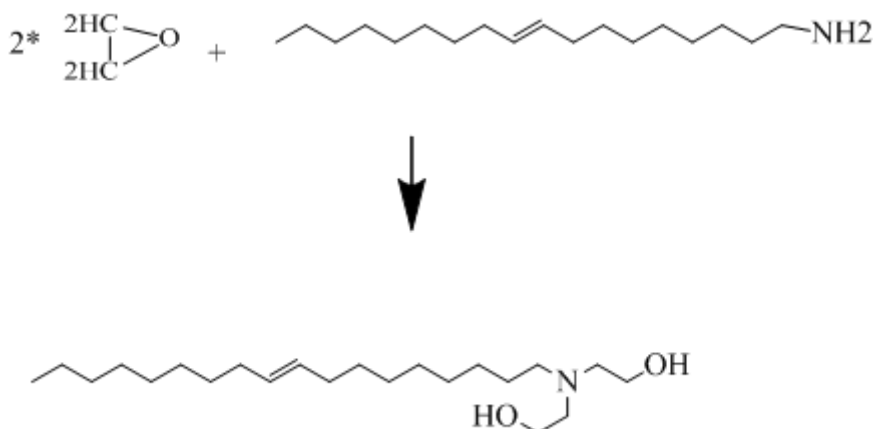
Titration is a method of quantifying a compound in a solution. This is done by addition of a titrant that interacts with the compound of interest in the solution. The interaction is a result from mixing acid and base. When the reaction is complete the needed volume of titrant is known and this also means that you know the concentration of the compound in the solution if the molar stoichiometry of the reaction is known and the amount of added sample is known. The titrant varies with the compound that is titrated and also the way of detecting complete reaction varies. In this project an electrode was used as detector to define the point of equilibrium and perchloric acid was used as a titrant (10).

#### 2.5.4. Colour measurement

Many products have a colour specification which means that the colour must be measured. The colour is measured by subjecting the sample to light of specific wavelength and detecting changes in the waves that go through the sample. Colour rarely impacts the chemistry and function of the compound but a coloured product is hard to use in a transparent end product.

### 2.6. Process description

The chemical reaction that takes place when ethylene oxide and fatty amine is mixed together is described in reaction 3 below. There are also some side reactions including the formation of dioxane from two ethylene oxide molecules. Dioxane is unwanted as a by-product since it is carcinogenic and irritating (11).



Reaction 3. Ethoxylation of fatty amines.

The process of ethoxylation is very temperature dependent. As described by Sanders et al. ethoxylation of fatty amines at high temperature without a catalyst, halts after reaction of two mole ethylene oxide due to thermodynamics (12). At lower temperatures it was possible to react up to ten mole of ethylene oxide onto the fatty amine. As a result the two mole ethoxylation of a fatty amine should not be performed at low temperatures since that could lead to a chain elongation that is unwanted.

The fatty amine is preheated in the reactor and to minimize the formation of by-products vacuum is drawn. The vacuum removes the air, water and carbonate, which all initiates side reactions.

A very important aspect in ethoxylation is the mixing since the reaction is very fast when it starts. To get a uniform product optimal stirring is required to distribute the ethylene oxide evenly in the reactor. The most effective way of mixing is a stirrer, but since EO is explosive that is not an option in this process. Different types of circulation are used instead because of this restriction. When using circulation as the mixing

method the distribution of ethylene oxide becomes a very important parameter in the system.

A system where the circulated liquid is returned over the top of the reactor without any distribution of significance the EO feed will end up in the free gas volume above the liquid surface and only the fatty amines at the top of the reactor will be able to react. If the feed of EO is sufficiently slow the concentration of EO in the reactor will be even but if the feed is too fast the distribution of EO will be very uneven throughout the reactor.

A way of improving the process system is to distribute the circulated liquid with spray nozzles resulting in better mixing of the EO and fatty amine (13).

The reaction pressure is often a fixed variable meaning that the EO feed is regulated by the pressure inside the reactor. This could lead to problems when the amount of raw material fed to every batch can differ leading to differences in free volume.

### 3. Experimental

The 2 mole ethoxylation of fatty amine is the process studied in this project and the project has included trials in three different scales, lab, pilot and full scale. In lab scale a rigorous experimental design was used to investigate the influence of temperature, pressure, water and starter (14) (15). Where starter was the finished product, used as a catalyst to shorten the induction step. The use of water has the same purpose as the use of a starter, to reduce reaction time by shortening the induction step.

#### 3.1. Experimental design

To gain as much knowledge as possible from the series of experiments conducted, a design of experiments was made using the program MODDE. The parameters of interest were put into the program with the upper and lower limits specified. Then a model is chosen and the program generates an experimental design where the trial order is given to minimize interferences from previous trials and surroundings on the model.

The model calculated by the program after inserting the specified results of the trials can then be used to predict the parameter settings to obtain the best possible result.

The parameters of interest in this trial were temperature, pressure, water and starter. The experimental design can be seen in table 1. The model to which the experimental design should be fit is a model where all interactions are taken in-to account, no replicates are run and to be able to get a better fit three centre point trials are run.

Table 1. Experimental design to fit the model.

<b>Experiment No</b>	<b>Run order</b>	<b>Pressure (bar)</b>	<b>Temperature (°C)</b>	<b>Water (wt %)</b>	<b>Starter (wt %)</b>
1	15	3	150	0	0
2	2	4,5	150	0	0
3	13	3	190	0	0
4	19	4,5	190	0	0
5	6	3	150	1	0
6	3	4,5	150	1	0
7	18	3	190	1	0
8	17	4,5	190	1	0
9	11	3	150	0	1
10	9	4,5	150	0	1
11	4	3	190	0	1
12	8	4,5	190	0	1
13	12	3	150	1	1
14	14	4,5	150	1	1
15	5	3	190	1	1
16	10	4,5	190	1	1
17	7	3,75	170	0	0
18	16	3,75	170	0	0
19	1	3,75	170	0	0

All the products from the trials were analysed for the important parameters that are shown with their units in table 2 below.

Table 2. Analysed parameters.

<b>Name</b>	<b>Unit</b>
Tot amine	meq/g
Tert amine	meq/g
Colour	Gardner
Reaction time	minutes
Dioxane content	ppm
EO distribution	EO/amine
Chain elongation	mole EO/mole amine
Conversion of fatty amine	%

Trials that were not included in the model were also run. These experiments tested a second way of adding the ethylene oxide to the process. The second way is to feed the EO in two steps. From the results of the experimental design performed in lab scale experiments were planned for pilot and full scale. The experiments performed in pilot scale and full scale are presented in table 3 and 4.

Table 3. Pilot experiments.

Experiment No	Temperature (°C)	Pressure (bar)
1	170	4,5
2	170	3
3 (divided EO feed)	170	4,5
4	150	3

Trial number 3 was performed by dividing the EO feed into two parts. The feed of EO was handled different, the addition of EO was not completely controlled by the pressure in the reactor.

Table 4. Full scale trials.

Experiment No	Temperature (°C)	Pressure (bar)
1	200	3
2	170	4,5
3	170	3

### 3.2. Material and method

To be able to draw the best conclusion possible from all trials the amount of fatty amine fed to the reactor is held constant in all scales. In the lab scale trials around 1100 grams of fatty amine was fed. When the experiments were up-scaled to the pilot around 80 kilograms were fed to every trial. In the full scale experiments around 6500 kilograms were fed to the reactor but for the third trial, raw material ran out and the feed was only around 60 percent of the two earlier trials.

The raw materials used in all trials are a fatty amine that Akzo Nobel's plant in Mons, Belgium produces and the ethylene oxide is made at the plant with ethene bought from Borealis. The fatty amine is solid at room temperature which means that melting of the raw material was the first step of the process. Since the melting point of the fatty amine was 30-40 °C the reactor must be preheated to prevent solidification of the raw material in the reactor since this could clog the circulation system. This is a problem that does not exist in the lab scale process since mixing is performed with a stirrer in that process. The vacuum systems of the different process scales are very different. In the lab scale water suction was used but in the bigger scales pumps are needed to be able to create vacuum in such big vessels. In the lab and pilot scale the temperature of the reactor was set to 60 °C and the mixing was started before the vacuum was drawn. After the first vacuum was drawn the reactor was pressurized with nitrogen purchased from AGA. The reactor was pressurized three times and between each time, vacuum was drawn. This procedure was followed to evacuate all unwanted gases in the reactor. To remove water that could be left from the rinsing of the reactor the temperature was set to 100 °C and vacuum was drawn for half an hour.



In the full scale process the temperature was set to 100 °C when the fatty amine was fed to the reactor. Vacuum was drawn to remove water and other unwanted compounds from the reactor. Nitrogen was used to pressurize the full scale reactor.

All the different scaled reactors are then closed when a full vacuum was achieved. The temperature was then raised to reaction temperature and when that was achieved the ethylene oxide was added. The systems for the ethylene oxide feed are different for the different scales. In the lab scale an ethylene oxide cylinder was attached to the autoclave reactor and then the EO was added to the reactor by pressure difference. The cylinder was put on scale that measures the amount of EO that was added to the reactor.

In the pilot plant the ethylene oxide came via pipes from the production unit of EO and the amount added to the reactor was measured by flow meters. The amount added to the full scale reactor was measured by flow meters as well. This method was not as accurate as the one used in the lab scale which can result in that the amount of EO fed to the reactor was not the optimal amount but it was of sufficient accuracy to be disregarded. The amount of EO added is calculated based on the molecular weight of the fatty amine. To avoid over ethoxylation the mole ratio in the lab and pilot scale has been 1:1,96 which means that only 98 percent of the two moles of EO were added to the reactor. In the full scale 100 percent of the two moles were added.

The speed of the ethylene oxide feed was controlled by the pressure in the reactor which was set constant so that the concentration of EO was held at such a level that side reactions were limited. When all the ethylene oxide was added to the reactor the pressure decreases due to reactions and when the pressure stabilizes the reaction was complete and the temperature was lowered and the product taken out.

In pilot and full scale trials only the temperature and the pressure were altered but in the lab scale also the addition of water and starter as reaction initiators were tried. The starter was added to the reactor together with the fatty amine and the procedure was after that the same as was described earlier. The water was added after the closure of the reactor and after the vacuum was drawn. After the addition of the water vacuum was only drawn to a half bar to ensure that the water was not drawn out of the reactor.

### 3.3. Characterization of products

The products were analyzed to be able to draw conclusions from the trials and the results from the analysis were put in-to the experimental design in MODDE.

#### **3.3.1. Titration**

To determine how much of the fatty amine that reacted during the reaction two titrations were made. The first titration determined how much nitrogen the product contained. For this titration around 0.35 grams of product was weighed in to a 150 ml beaker and the product was then dissolved in 75 ml glacial acetic acid. The titrant used in this titration was 0.1 M perchloric acid in acetic acid.

The result was given in meq/g (milliequivalents/gram of sample) and that result was calculated by the amount of titrant needed to reach the equilibrium point and the amount of sample added to the beaker.

The second titration was performed to see how much of the amine that became tertiary in the reaction. To do that the secondary and primary amines must be shielded so that only the tertiary amines were shown in the result. The same mass of sample was used for this titration but to shield the primary and secondary amines the sample was dissolved in 20 ml acetic acid anhydride and 2 ml glacial acetic acid. To let the solution react the beaker was covered and heated at a low temperature during stirring for half an hour. The titration was then performed in the same way as the first titration and the same titrant was used.

To calculate the conversion of the reaction the result from the titration of tertiary amines was divided with the total amine content.

### **3.3.2. NMR**

When ethoxylating a fatty amine the chains can grow which means that there are more than two ethylene oxide on every fatty amine. There is also the possibility that not both hydrogen atoms on the amine react which leads to an under ethoxylation. Both of these things can be seen in a NMR spectrum. The NMR that has been used in this project was from Varian. The analysis that has been performed is an H-NMR which means that the vibrations that are detected are the ones created by the hydrogen atoms in the molecule. The samples were prepared by adding one or two drops of the product to an NMR tube and then very pure chloroform from Fisher scientific was added to dissolve the product. The tube was inserted into the NMR and a spectrum was generated. The peaks of the spectrums were integrated and interpreted. The areas under the peaks were used to determine the chain elongation and the ethylene oxide distribution. All the areas were related to the CH<sub>3</sub> group that is in the end of the carbon chain and is represented by a peak at 1 ppm on the x-axis in the spectrum. The area of this peak was set to 30, due to the three hydrogen atoms in that molecule. A typical curve can be seen in figure 7.

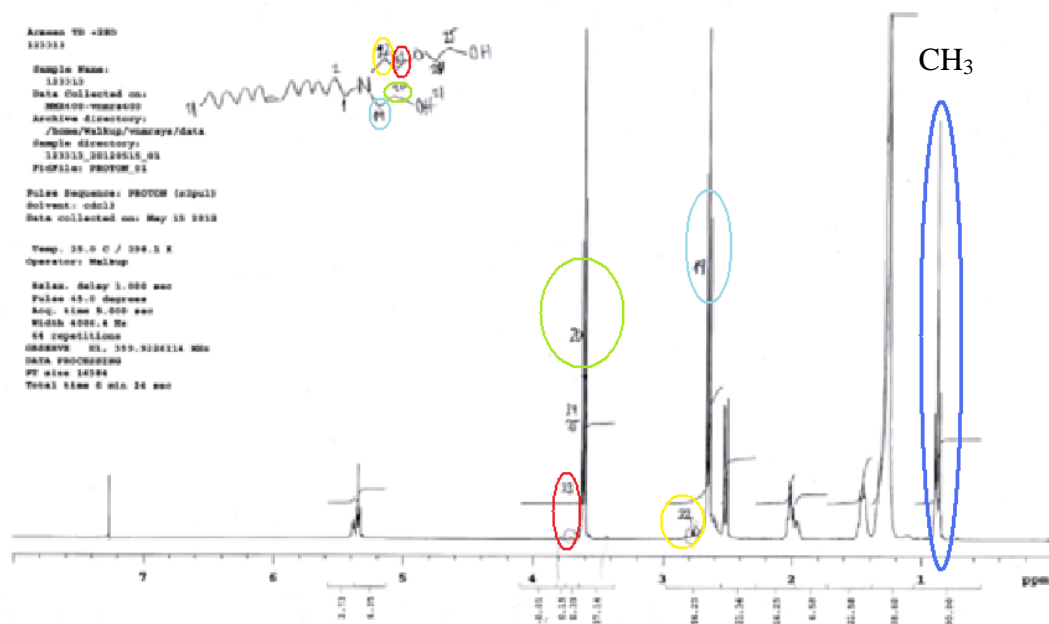


Figure 7. Typical NMR spectrum with interesting peaks marked..

### 3.3.3 GC

One of the side reactions in this process is the formation of dioxane from two ethylene oxide molecules. To measure the amount of this by-product created in the process GC can be used. Dioxane has a low boiling point which means that the head space method can be used when analyzing the product. This means that the product is heated to 80 °C which means that dioxane, unreacted EO and other volatile compounds are gasified. A sample is then withdrawn from the gas phase in the vial. To be able to quantify the amount of dioxane a standard is added to the sample. Each product is diluted with different amounts of standard accordingly to table 5 below.

Table 5. Vial specifications.

Sample vial	Added to product
A	1 ml buffer
B	0.5 ml buffer 0.5 ml standard
C	0.3 ml buffer 0.7 ml standard
D	1 ml standard

One gram of product is added to each vial. The standard was made by mixing pH 7 buffer and 0.2048 g pure dioxane from Merck. The original standard was then diluted 10 times before it was added to the vials. The specifications of the GC follow in table 6.

Table 6. GC specifications

Column	Length: 50m id: 0.53mm Phase: CP-sil 5CB, 5.0 $\mu\text{m}$
Injector	Split/splitless injector, 150 °C
Detector	FID, 275 °C
Column temperature	Initial temp: 4 min Initial temp: 80 °C Rate: 5 °C/min Final temp: 100 °C Final time: 8 min
Carrier gas	He 40kPa
Split slow	20 ml/min
Injector volume	1 ml
Headspace	Oven: 80 °C Transfer line: 85 °C Loop: 83 °C GC cycle time: 20 Inject time: 1.5 Loop eq. time: 0 Loop fill time: 0.2 Press time: 0.1 Vial eq. time: 15

The GC-FID analysis gives a spectrum that is integrated and the area under the curve that represents dioxane is then put into a mathematical model that calculates the amount of dioxane in the product based on the concentration of dioxane in the standard.

### **3.3.4. Colour**

The product was added to a cuvette and then put in-to the colour measurer that was a Lange, Lico® 400. The colour can be measured in different scales and the one used in this project was the Gardner scale.

## **4. Results and discussion**

In this chapter the results from the trials in all scales will be presented and discussed. The first part will cover the laboratory trials and then the pilot and full scale trials will be discussed.

### **4.1. Lab scale**

The primarily parameter when trying to optimize this process was the conversion. If the conversion is too low the reaction is not completed and an extra addition of EO after the first reaction is needed. That take a long time and the addition of a small amount of EO is very non ideal since only a small amount of the amine is affected by it. The

conversion was calculated from the result of the total amine titration and the tertiary amine titration and the results are presented below in table 7.

Table 7. Titration results.

Experiment No.	Tot amine (meq/g)	Tert amine (meq/g)	Conversion (%)
1	2,894	2,845	98,3
2	2,895	2,843	98,2
3	2,891	2,870	99,3
4	2,906	2,789	96,0
5	2,916	2,758	94,6
6	2,887	2,774	96,1
7	2,906	2,657	91,4
8	2,900	2,727	94,0
9	2,908	2,782	95,7
10	2,903	2,803	96,6
11	2,879	2,866	99,5
12	2,907	2,799	96,3
13	2,904	2,800	96,4
14	2,892	2,765	95,6
15	2,910	2,670	91,7
16	2,903	2,779	95,7
17	2,907	2,805	96,5
18	2,894	2,803	96,9
19	2,901	2,787	96,1

The amount of EO added to each trial was 98 percent of two moles which means that the theoretical value of the conversion can be 98 percent maximum. The reason that some trials have a higher value could be an error in the feed or it could be due to the fact that the amount of EO added to the process is based on a pure tertiary fatty amine. This is not completely true since some secondary fatty amines could also be in the rawmaterial along with impurities which are not accounted for.

The trials marked green have a very high conversion which indicates that a high temperature and a low pressure is good for the process. The trials marked yellow are the same trials as the ones marked green but with a lower pressure which indicates that the pressure was an important factor.

All the trials had a colour that was lighter than the limit which means that they were all passed in a colour perspective. What could be seen, which was also expected, was that a higher temperature gave a lower colour. The colour results can be seen in appendix 1.

A side reaction that can be influenced by all the investigated parameters are the formation of dioxane. To analyse the amount of dioxane in the products GC headspace is used. The results from this analysis are shown in table 8.

Table 8. GC results.

Experiment No.	Dioxane content (ppm)
1	3,72
2	9,65
3	20,83
4	5,11
5	24,84
6	10,97
7	23,66
8	14,85
9	10,62
10	32,34
11	4,65
12	42,40
13	2,78
14	9,57
15	1,87
16	3,07
17	49,47
18	58,45
19	4,17

It was difficult to see any consistency in the dioxane results but the yellow marked trials are the ones with only water added and these all had concentrations higher than 10 ppm. It is very interesting to see that when water and starter is added, the trials marked with blue, the dioxane content is lower which indicates that the combination of water and starter is working against the formation of dioxane. The explanation to this could be that both water and the hydroxyl group in the starter may hydrogen bond to the oxygen of ethylene oxide and thereby catalyse the ring opening. It should be mentioned that all the levels of dioxane are low and would be passed.

A side reaction that theoretically should occur more at lower temperatures is chain elongation. The amount of amines with a chain longer than one EO can be calculated from the NMR spectrum since the hydrogen on a carbon with an oxygen next to it appears to the left of the hydrogen on a carbon next to a hydrogen oxide in an NMR spectrum. This is shown in an NMR spectrum below in figure 8 where the green ring is showing the protons on a carbon in a longer EO chain, which is the chain elongation. The blue ring shows a peak that hide some peaks of interest. This peak most likely represent water. Since the peak is hidden the chain elongation and EO distribution is calculated on the peaks marked yellow in figure 8.

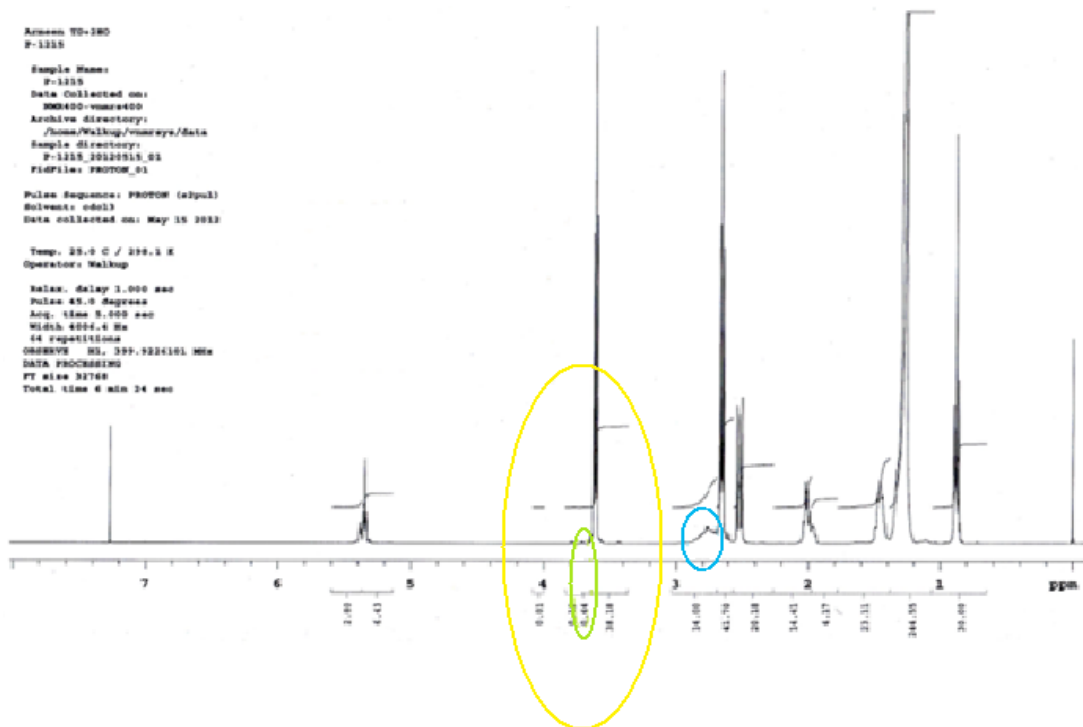


Figure 8. NMR spectrum showing the peaks of interest.

The results from the calculations of the chain elongation and the EO distribution can be seen in table 9.

Table 9. NMR results.

Experiment No.	Chain elongation (%)	EO distribution
1	1,05	1,96
2	1,2	2,02
3	0	1,98
4	1,93	2
5	3,05	1,94
6	0,78	1,95
7	8,03	2,03
8	4,55	1,95
9	2,65	1,96
10	0,75	1,99
11	1,1	2,02
12	1,93	1,96
13	3,43	2
14	2,68	2,01
15	6,38	1,97
16	3,28	2
17	2,23	1,96
18	0,8	1,92
19	0,43	1,95

It can be seen that when no starter or water is added to the process there is not much chain elongation. It can also be seen that the EO distribution is good since every amine has close to two EO molecules on them.

The reason that starter and water is tried as a reaction component is to reduce the initiation time and in table 10 the reaction times, which is the time it takes to add the EO, are presented.

Table 10. Reaction times.

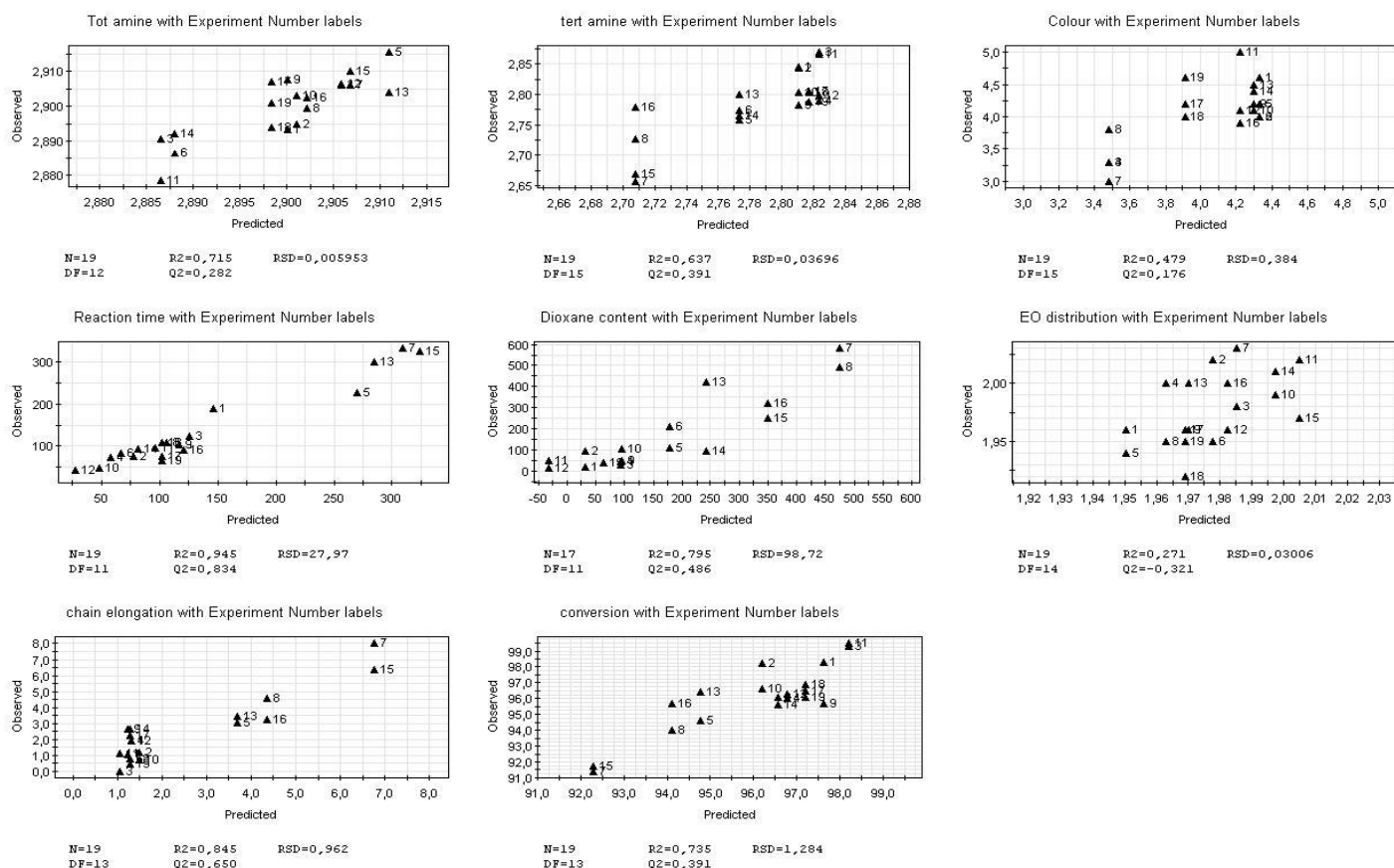
Experiment No.	Reaction time (minutes)
1	190
2	76
3	123
4	74
5	227
6	83
7	334
8	109
9	104
10	47
11	96
12	42
13	301
14	93
15	327
16	91
17	76
18	110
19	66

As can be seen by the trials marked green, addition of water slows the reaction down severely. This is due to the pressure build up by evaporated water. Since the water creates so much pressure very little EO can be added to the reactor which leads to a slow reaction.

To see how well the results agree with the results that would be predicted by the model generated by MODDE the predicted values are plotted against the true values in figure 9. The model was as mentioned earlier a model where all interactions are considered and no replicates were done.



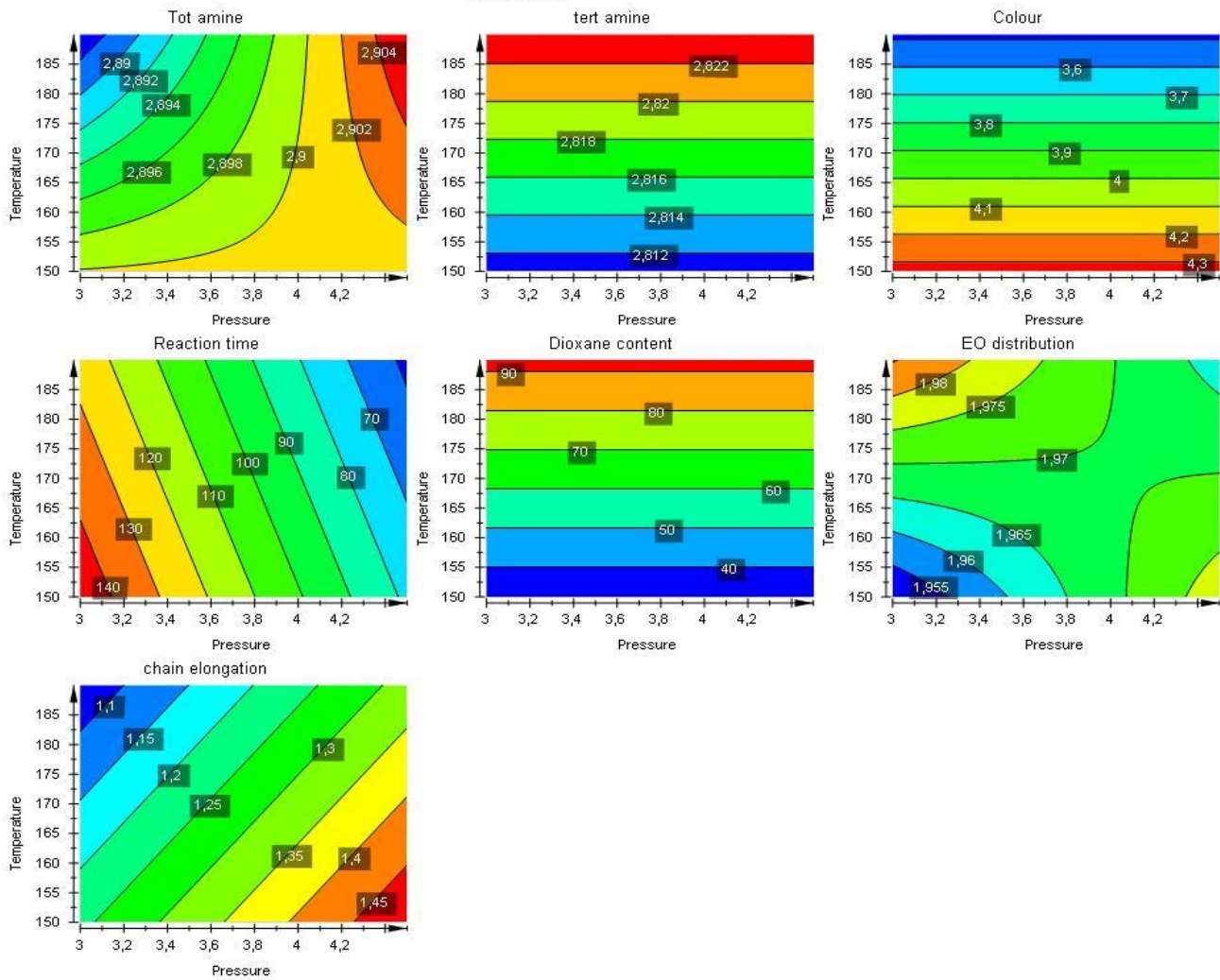
Investigation: Johanna Exjobb (MLR)



MODDE 9 - 2012-04-13 11:24:34 (UTC+1)

Figure 9. Comparison between predicted values and actual values.

These results indicate that the model is good at predicting some of the parameters where the results are linear and not that good at predicting the results where the results are more random. Especially reaction time can be predicted with good accuracy while the colour is very difficult to predict with the model generated by MODDE. It can also be seen in contour plots how each result is influenced by pressure, temperature, starter and water. When water and starter is included it is very hard to draw any conclusion since the model is very unreliable when these two parameters are included. The contour plots from the trials with water and starter are presented in appendix 1. The contour plots in figure 10 show how temperature and pressure influence the result.



MODEL 9 - 2012-04-12 11:17:45 (UTC+1)

Figure 10. Contour plots of the lab scale trials.

According to these plots a high temperature gives a high tertiary amine content and a low pressure and high temperature gives a low total amine, this combination gives a high conversion. This agrees with the results in the trials, that pressure should be low and temperature high. The results differ when other plots are observed, see appendix 1. To get a low dioxane content the temperature should be low and to get a short reaction time the pressure should be high. This leads to difficulties when the design for the experiments in pilot scale shall be decided. But it could be seen that water and starter should not be used in larger scales due to the fact that the benefits are non existing or very small. The use of water and starter could even be detrimental to the process Trials with different temperatures and pressures was decided do be run in pilot scale.

Trials where the EO feed was divided into two parts was also conducted and the results were compared to the trials with the same conditions but different feed of EO. The comparison can be seen in table 11.

Table 11. Comparison between the Swedish and American way of feeding EO.

Trial	Temperature (Celsius)	Pressure (bar)	Tot amin	Tert amine	Conversion (%)	Reaction time (min)
Divided feed	170	4,5	2,895	2,829	97,7	81
One feed	170	4,5	2,898	2,795	96,4	58

From these results it can be seen that the results for the trial with an American feed of EO gives much better results than the trial were the EO was feed according to the Swedish way. The drawback of the American way is the longer reaction time but if no extra addition of EO is needed for the product to pass that could be time well spent. The colours of the products are all low and the results are presented in appendix 2

## 4.2. Pilot scale

When deciding which trials to perform in pilot scale water and starter were excluded but different temperatures and pressures were tested. Unfortunately it was not possible to test any temperatures over 170 degree Celsius due to pressure restrains in the heatexchanger. The steam used for heating could not have a pressure above 12 bar which meant that the maximum temperature was 175 degrees.

When comparing the pilot scale set up with the lab scale set up the most evident difference between them is the mixing. In the lab scale almost ideal mixing is achieved by the stirrer but in the pilot scale the mixing is far from ideal which leads to differences between the process scales.

The same analyses were made for the products from the pilot trials and they are presented in the same way as the lab scale results. The conversion should be lower than the conversion in the lab scale trials due to non ideal mixing. Another parameter that could cause lower conversion is the larger free gas volume in the pilot reactor. This means that more EO can be added to the free volume before the set pressure is reached and this could lead to more side reactions which lowers the conversion. The titration results are presented in table 12 below.

Table 12. Titration results.

Experiment No.	Tot amine	Tert amine	Conversion
1	2,909	2,758	94,81
2	2,924	2,781	95,13
3	2,915	2,773	95,11
4	2,907	2,749	94,56

From these results it is very hard to see any pattern but as mentioned above the conversion is lower in general when compared to the lab scale trials. The indication was however that low pressure and the American trial gave better results.

The dioxane content should be low since no water or starter was added and this can be seen in table 13 and the GC spectrums are shown in appendix 3.

Table 13. GC results.

Experiment No.	Dioxane content (ppm)
1	5
2	10
3	0
4	15

The results indicate that a high pressure leads to a lower dioxane content which is contradictory since a higher pressure means more free EO in the free volume above the fatty amine leading to more opportunities for side reactions. Although it can be seen from table 11 that experiment number three where EO was fed in a different way leads to very low formation of dioxane.

Since the conversion is low also the EO distribution will be low since these two parameters are connected. The chain elongation should be low in all the experiments since there is no water or starter that can catalyse the elongation. The NMR results can be seen in table 14 and the spectrums are shown in appendix 4.

Table 14. NMR results.

Experiment No.	Chain elongation (%)	EO distribution
1	2,23	1,948
2	1,16	1,940
3	1,09	1,931
4	1,14	1,94

From these results it can once again be seen that experiment number three gives a good result, at least when it comes to chain elongation. The result for EO distribution is more uncertain since there is a peak in the NMR spectra that cover one of the peaks, see figure 8 earlier in the report. This leads to some uncertainties and the conversion should be trusted before the EO distribution.

The reaction time is influenced by temperature and pressure and the time decreases with temperature and pressure. The reaction times are presented in table 15 below.

Table 15. Reaction times in the pilot trials.

Experiment No.	Reaction time (minutes)
1	46
2	65
3	66
4	94

With these results it can be seen that there is a drawback with experiment three and that is the reaction time. Even though the reaction conditions are the same as experiment one the time needed for reaction is longer. This is due to the different feed of EO.

The colour of all four trials is almost identical and well within specification, see appendix 2.

### 4.3. Full scale

It was hard to draw any firm conclusions from the pilot trials other than that a low temperature was not optimal. This led to that different temperatures and pressures were tried in full scale.

The first full scale trial was run with the actual settings that was used in the factory, hence the high temperature. The third full scale trial could be neglected due to the fact that only around 60 percent of the fatty amine that was supposed to be fed to the reactor was available, although the results of trial three are presented along with the results of trial one and two.

The titration results and conversion is presented in table 16 below.

Table 16. Titration results for full scale trials.

Experiment No.	Tot amine	Tert amine	Conversion (%)
1	2,910	2,785	95,70
2	2,090	2,821	97,44
3	2,909	2,761	94,93

The first trial is run according to the normal settings and the second run is according to the best trial in the pilot scale. The American way of ethylene oxide feed was not tried since it was decided that more results were needed to justify full scale tests.

The conversion in trial two was best but the dioxane content is the highest. The amount of dioxane is within the limits for all three trials. GC results can be seen in table 17 and spectrums in appendix 3.

Table 17. GC results for full scale trials.

Experiment No.	Dioxane (ppm)
1	0
2	58
3	10

Since no chain elongation catalyst is present in any of the trials the percentage of chain elongation should be low since more than one EO was not wanted in each chain, see table 18 for results and appendix 4 for spectrums.

Table 18. NMR results for full scale trials.

Experiment No.	Chain elongation (%)	EO distribution
1	0,71	1,912
2	1,32	2,01
3	1,04	1,88

When looking at these results once again the second trial is most promising since the ethylene distribution is very close to two which as intended. As mentioned before the EO distribution is uncertain due to a covering peak but this could also create uncertainties when chain elongation is calculated. In figure 19 the reaction times of the full scale trials are presented. The trial with low pressure and temperature seems to have a longer reaction time but that is the trial with only 60 percent raw material fed to the reactor which could impact the result.

Table 19. Reaction time for the full scale trials.

Experiment No.	Reaction time (minutes)
1	68
2	70
3	81

## 5. Conclusion

The aim of this thesis was to try to optimize the ethoxylation of a fatty amine. The thesis only covered the initial step of ethoxylation when two moles of ethylene oxide is reacted to each mole of fatty amine. The laboratory trials showed that the use of starter and water was detrimental to the process. It was also seen in the lab scale that a high temperature and a low pressure gave good results.

In the pilot plant the temperature was limited to 170 degree Celsius and it would have been preferred if high temperature trials could have been performed since that would have helped draw accurate conclusions. Although the pilot trials indicate that the higher temperature gives a better result than the low temperature. It can also be seen that the American way of ethoxylating seems promising but further studies must be performed to confirm it. The differences between the pressures are not that distinctive and that is the reason that both high and low pressure is tried in the full scale. The reason that the difference is small between low and high pressure could be that it appears that less EO was added to the low pressure reaction which then leads to a lower conversion.

It is not possible to draw valid conclusion from three trials in full scale where one of the trials failed due to lack of raw material.

It can overall be concluded that starter and water as initiators are not beneficial for the process, however starter is not detrimental to the process like water, and that high temperature and low pressure appears to give a good reaction in a conversion aspect.

## 6. Recommendations and further work

To be able to draw more accurate conclusions a more rigorous experiment series in both pilot and full scale should be performed. More trials where the ethylene oxide feed was divided into two parts should be performed to investigate if it gives a more uniform result.

Since the process set ups differ very much between lab scale and pilot scale it could be a good idea to try using a starter in the pilot scale to investigate how it impacts the results in that scale. Experiments with water present should not be tried again since the pressure build up of the evaporated water makes the reaction very slow. Water also leads to higher dioxane content.

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Last I will thank my beloved family who have always been there for me and I know they always will be. To my love Simon, thanks for the support and patience when I have been wrapped up in work and all the hugs when I have been so tired.



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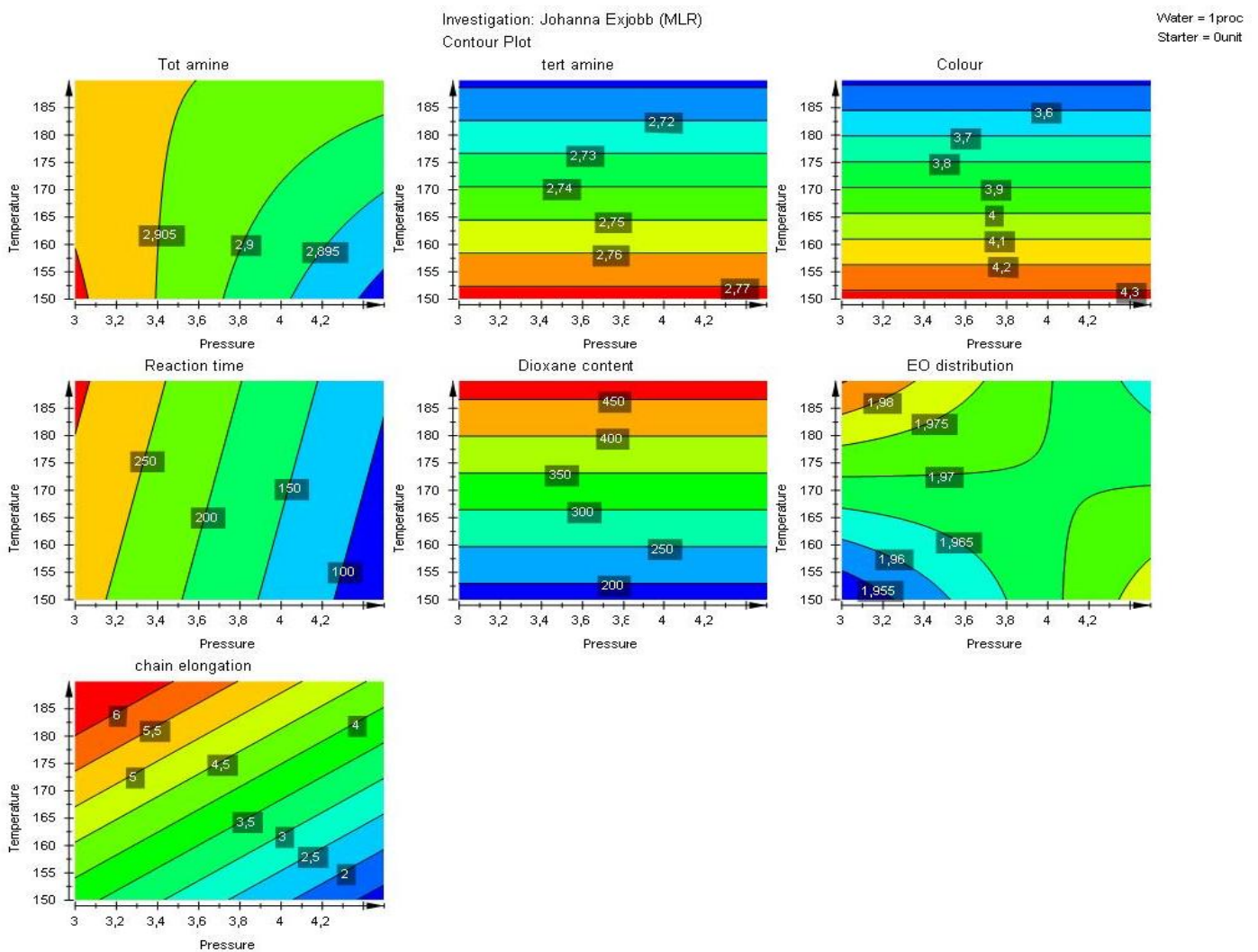
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# Appendix

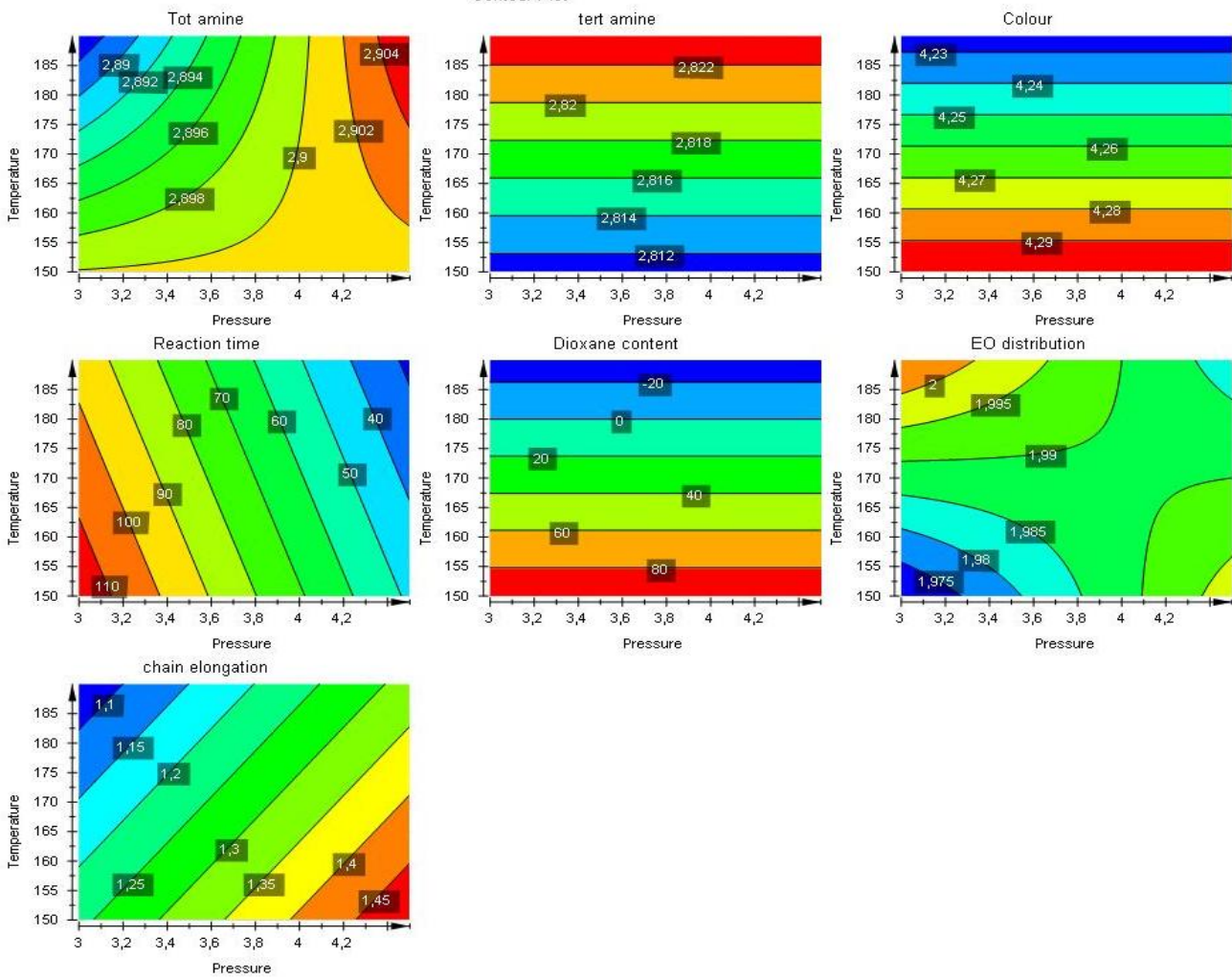
The data and results that are not presented in the report can be found here.

## Appendix 1.

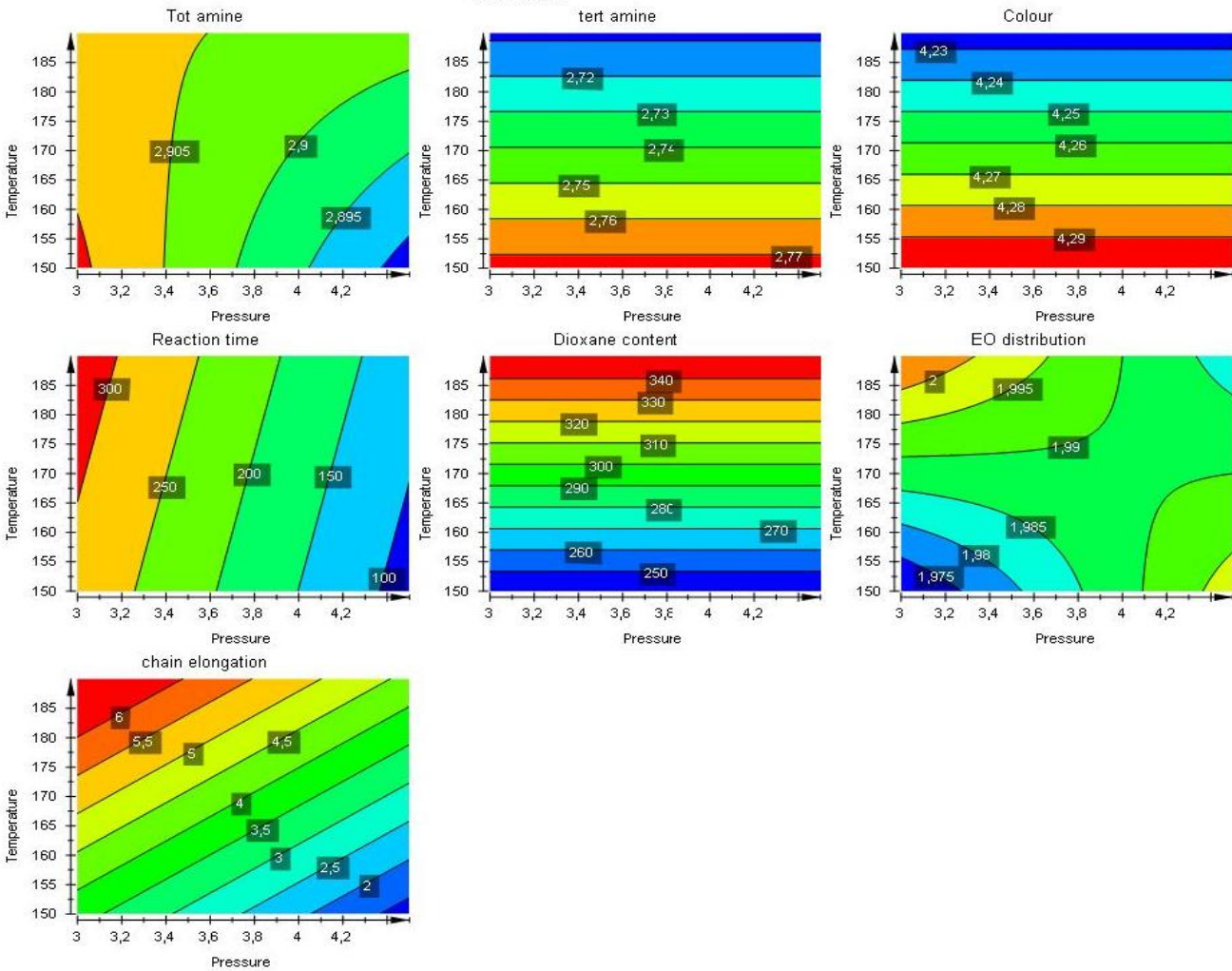
Contour plots of trials where water and starter is present.



Plot 1. Water present.



Plot 2. Starter present.



Plot 3. Both starter and water present.

From these plots it can be seen that the presence of water changes the plots dramatically. The chain elongation was higher and the dioxane content as well. The tertiary amine dropped if water was present which lead to a lower conversion and that were the reasons that water was not tried in bigger scale. Starter does not appear to impact the results at all which means that the addition of a starter does not benefit the process to an extent where the extra work needed is worth it.

## Appendix 2.

Table I. The colours of the laboratory trials.

Experiment No.	Colour (Gardner)
1	4,6
2	4
3	3,3
4	3,3
5	4,2
6	4
7	3
8	3,8
9	4,2
10	4,1
11	5
12	4,1
13	4,5
14	4,4
15	3,9
16	3,9
17	4,2
18	4
19	4,6

As can be seen from the results in table I the use of a starter makes the product darker and the use of water makes it lighter.

Table II. The colours of the pilot trials.

Experiment No.	Colour (Gardner)
1	3,3
2	3,5
3	3,4
4	3,4

Since the temperature in the trials are very alike and no starter or water has been added to any of the trials the result presented in table II is expected.

Table III. Colour of full scale trials.

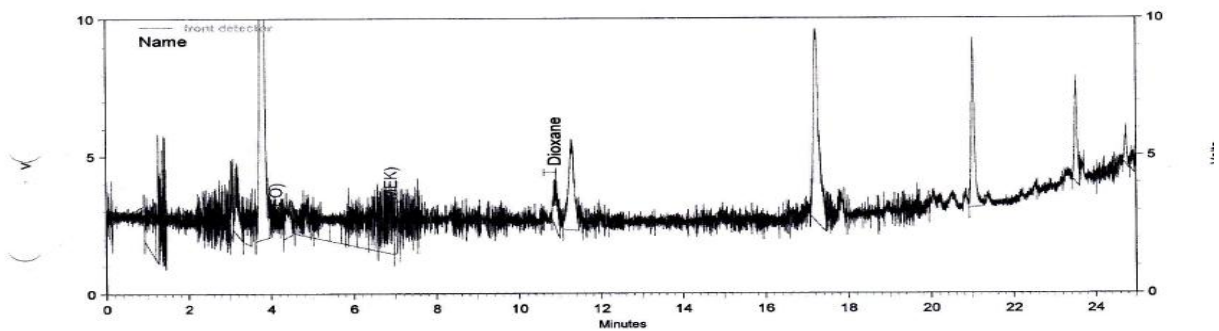
Experiment No.	Colour (Gardner)
1	3,5
2	3,1
3	3,3

The same results overall as in the pilot scale trials. The temperature is very high in trial one which should lead to less colouring but this cannot be seen in these results

### Appendix 3.

GC results for the pilot and full scale trials. For each of the products four GC spectrums are needed to quantify the amount of dioxane that they contain. The samples contain different amount of standard and the results are used to create a linear relation between the samples and in that way the amount of dioxane in the product can be calculated.

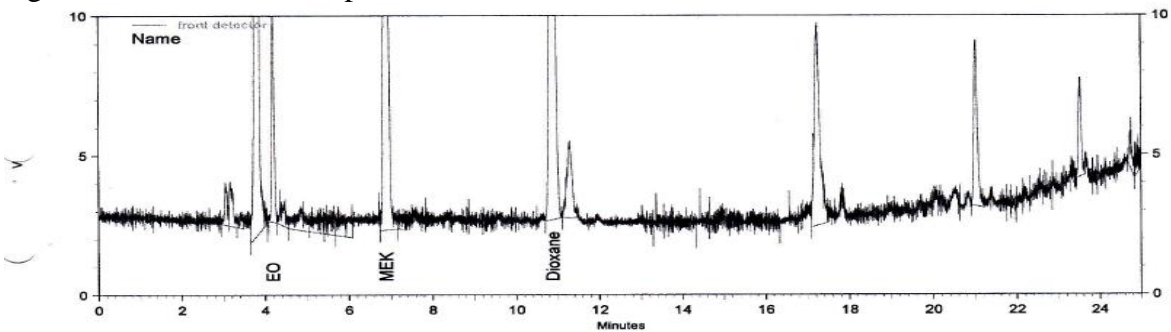
Pilot trial results are shown in figure I-V and the full scale results are shown in figure VI-IV. Sample vial A, B, C and D always have 0 ml, 0,3 ml, 0,7 ml and 1 ml standard respectively.



Channel A

front detector Results		
Name	Time	Area
EO		
MEK		
Dioxane	10.874	88925
Totals		88925

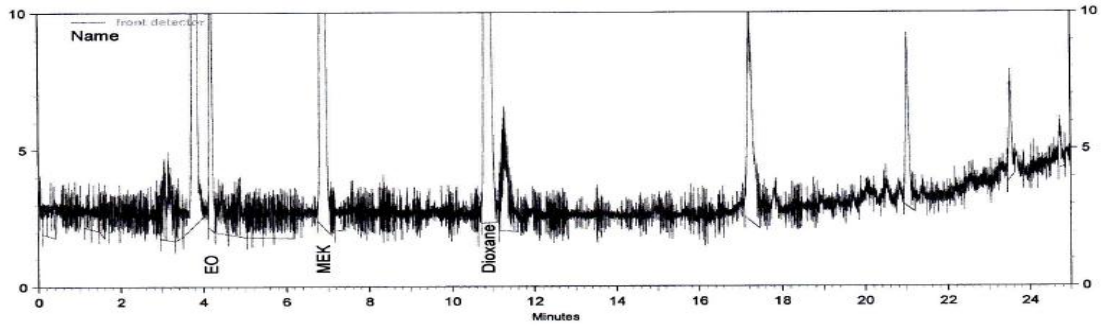
Figure Ia. Pilot trial 1, sample vial A.



Channel A

front detector Results		
Name	Time	Area
EO	4.186	241923
MEK	6.893	1886806
Dioxane	10.884	1592365
Totals		3721094

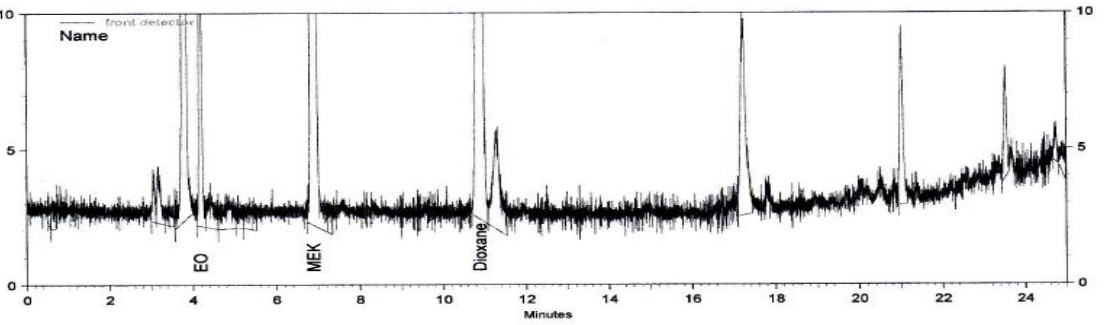
Figure Ib. Pilot trial 1, sample vial B.



Channel A

front detector Results		
Name	Time	Area
EO	4.186	393136
MEK	6.891	2602908
Dioxane	10.880	2271434
Totals		5267478

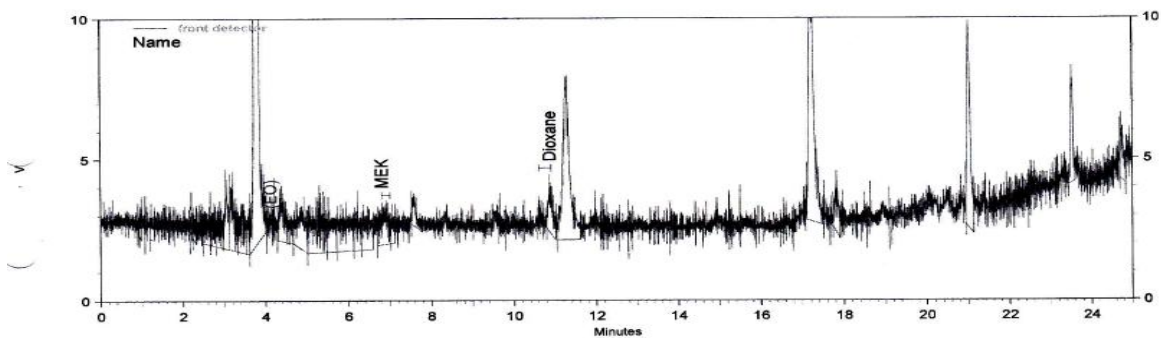
Figure Ic. Pilot trial 1, sample vial C.



Channel A

front detector Results		
Name	Time	Area
EO	4.182	451379
MEK	6.892	3742467
Dioxane	10.883	3189605
Totals		7383451

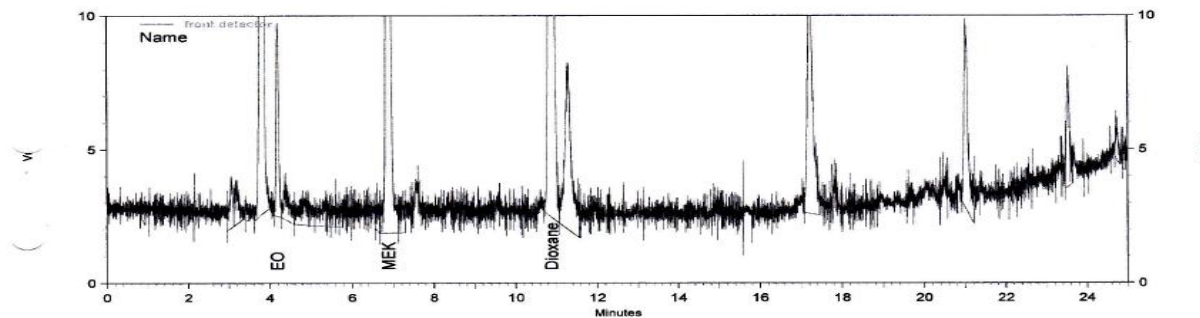
Figure Id. Pilot trial 1, sample vial D.



Channel A

front detector Results		
Name	Time	Area
EO		
MEK	6.811	127296
Dioxane	10.878	97740
Totals		225036

Figure Ia. Pilot trial 2, sample vial A.

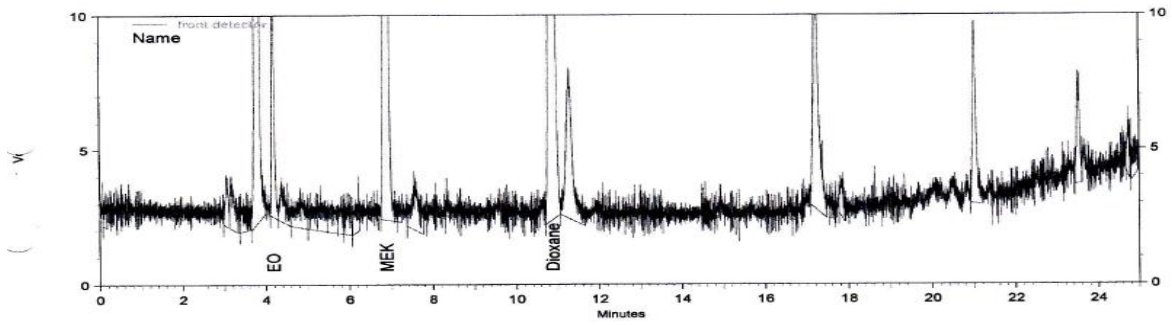


Channel A

front detector Results		
Name	Time	Area
EO	4.183	234379
MEK	6.888	1989255
Dioxane	10.883	1632509
Totals		3856143

Figure Ib. Pilot trial 2, sample vial B.

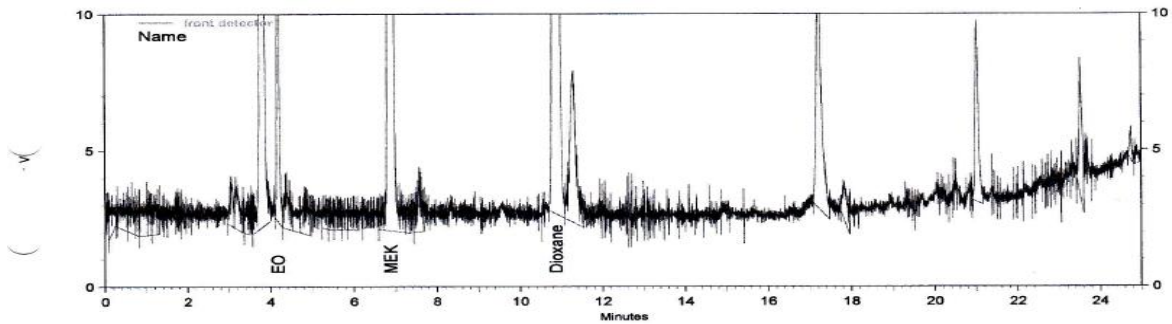




Channel A

front detector Results		
Name	Time	Area
EO	4.183	292478
MEK	6.891	2520858
Dioxane	10.882	2208443
Totals		5021779

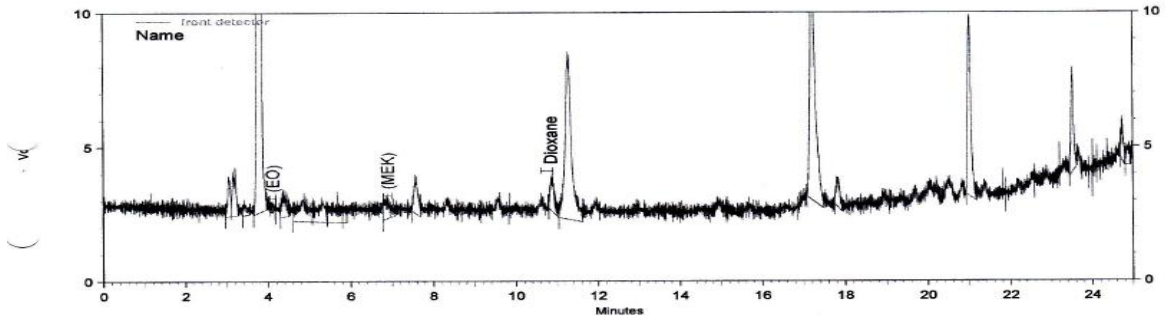
Figure Ic. Pilot trial 2, sample vial C.



Channel A

front detector Results		
Name	Time	Area
EO	4.182	334198
MEK	6.886	3607476
Dioxane	10.879	2960510
Totals		6902184

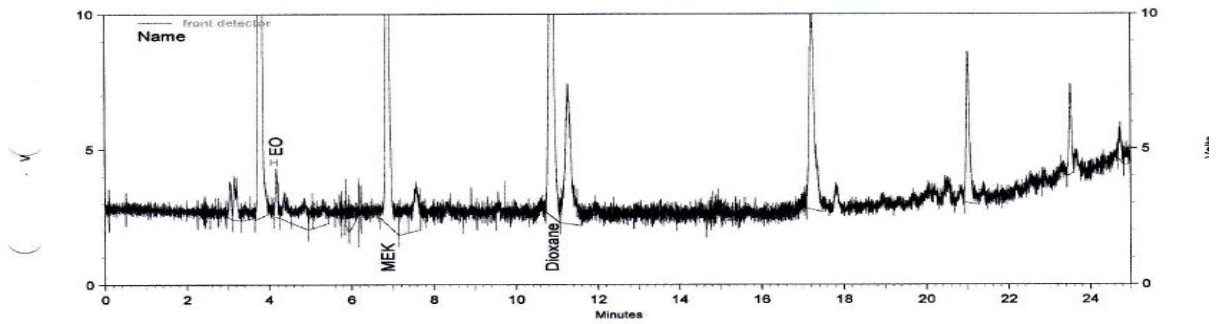
Figure Id. Pilot trial 2, sample vial D.



Channel A

front detector Results		
Name	Time	Area
EO		
MEK		
Dioxane	10.864	73951
Totals		73951

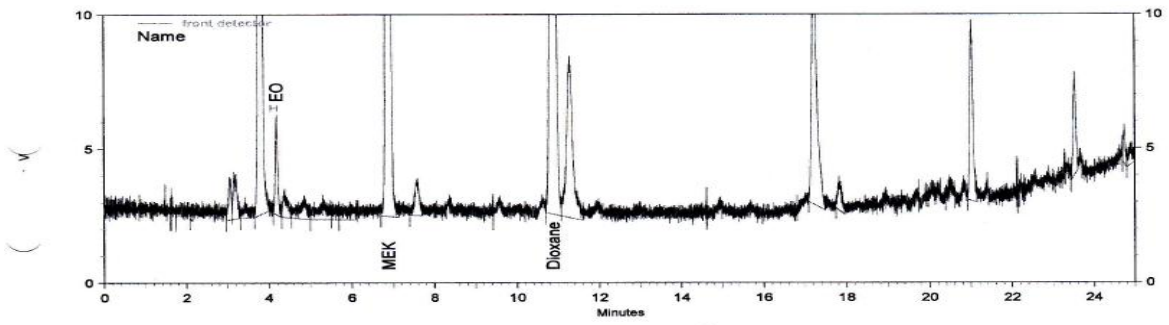
Figure IIIa. Pilot trial 3, sample vial A.



Channel A

front detector Results		
Name	Time	Area
EO	4.176	53624
MEK	6.885	729865
Dioxane	10.882	868451
Totals		1651940

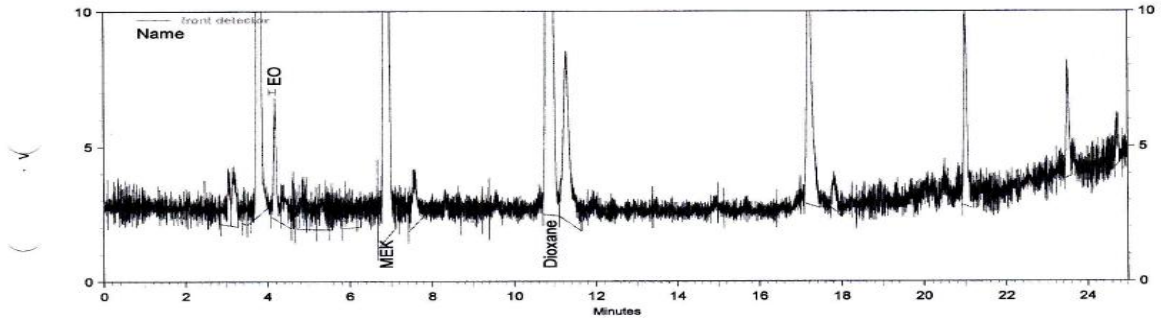
Figure IIIb. Pilot trial 3, sample vial B.



Channel A

front detector Results		
Name	Time	Area
EO	4.186	115171
MEK	6.889	2471550
Dioxane	10.882	2129166
Totals		4715887

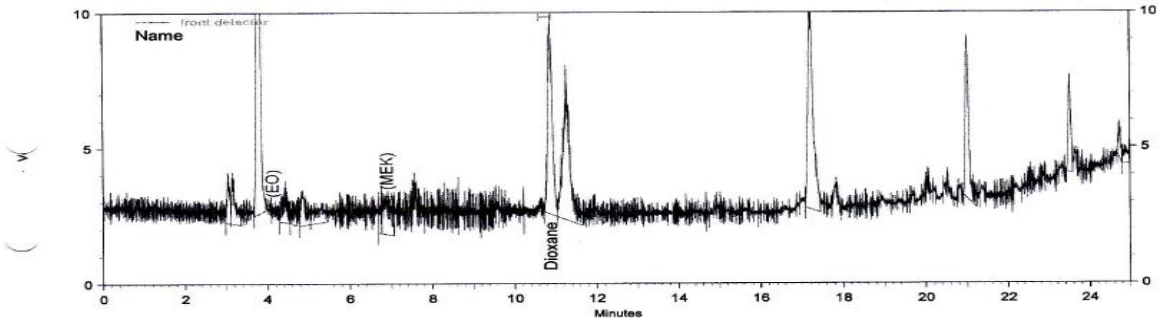
Figure IIIc. Pilot trial 3, sample vial C.



Channel A

front detector Results		
Name	Time	Area
EO	4.185	159458
MEK	6.887	3679946
Dioxane	10.880	3025498
Totals		6864902

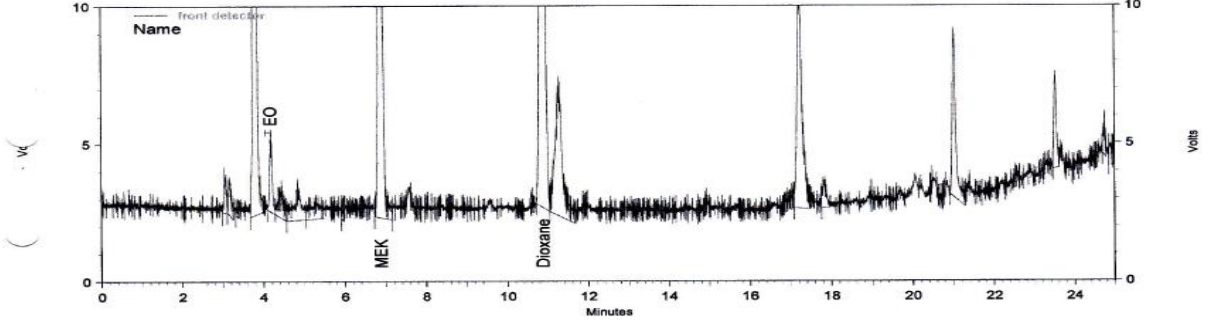
Figure III d. Pilot trial 3, sample vial D.



Channel A

front detector Results		
Name	Time	Area
EO		
MEK		
Dioxane	10.884	431116
Totals		431116

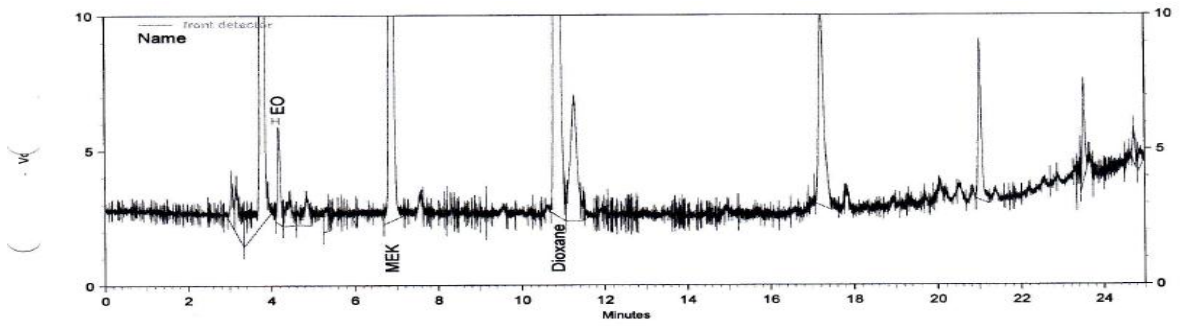
Figure IVa. Pilot trial 4, sample vial A.



Channel A

front detector Results		
Name	Time	Area
EO	4.175	87866
MEK	6.893	1131429
Dioxane	10.883	1527969
Totals		2747264

Figure IVb. Pilot trial 4, sample vial B.



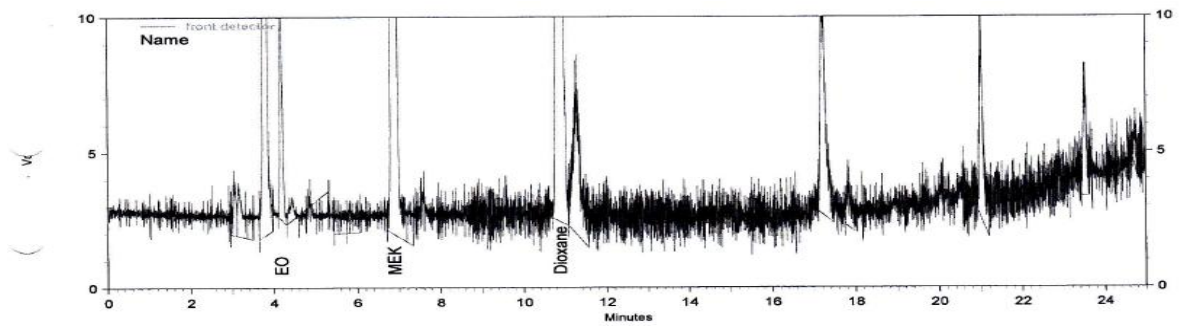
Channel A

front detector Results

Name	Time	Area
EO	4.176	129947
MEK	6.889	1572616
Dioxane	10.880	2043626

Totals		3746189
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Figure IVc. Pilot trial 4, sample vial C.



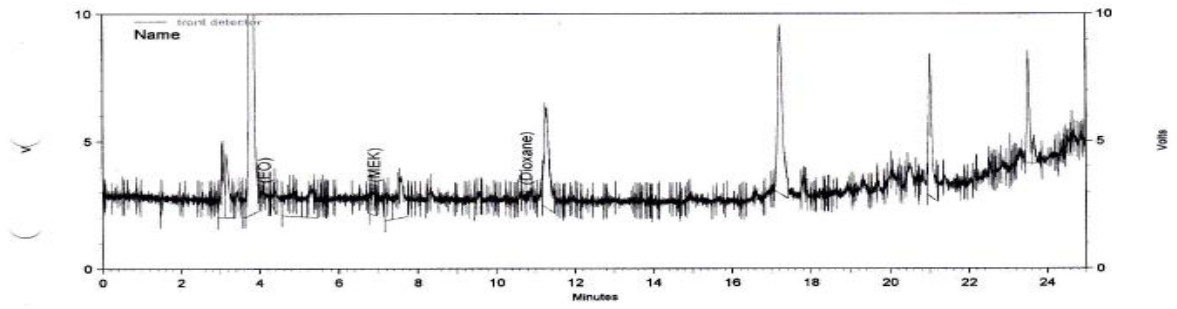
Channel A

front detector Results

Name	Time	Area
EO	4.184	258531
MEK	6.890	3772669
Dioxane	10.885	3610968

Totals		7642168
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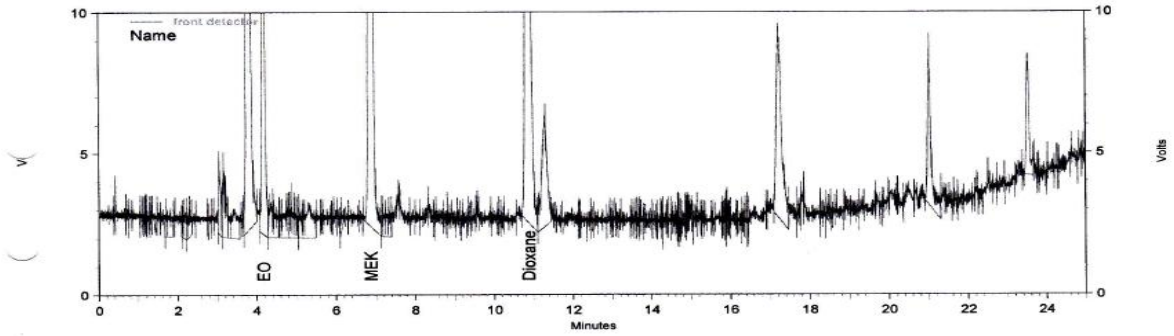
Figure IVd. Pilot trial 4, sample vial D.



Channel A

front detector Results		
Name	Time	Area
EO		
MEK		
Dioxane		
Totals		

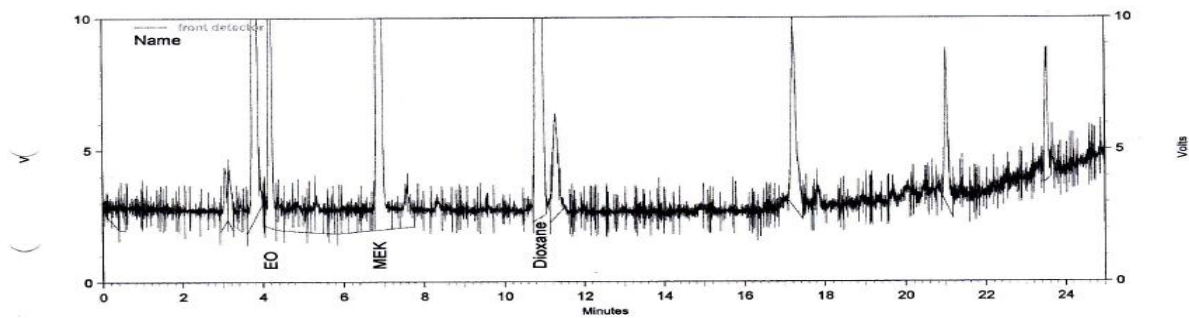
Figure Va. Full scale trial 1, sample vial A.



Channel A

front detector Results		
Name	Time	Area
EO	4.181	693934
MEK	6.885	1881798
Dioxane	10.884	1542425
Totals		4118157

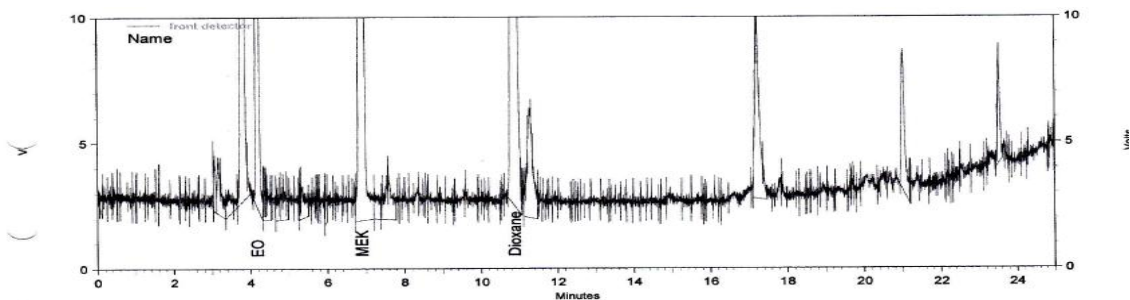
Figure Vb. Full scale trial 1, sample vial B.



Channel A

front detector Results		
Name	Time	Area
EO	4.185	877896
MEK	6.889	2795074
Dioxane	10.883	2225957
Totals		5898927

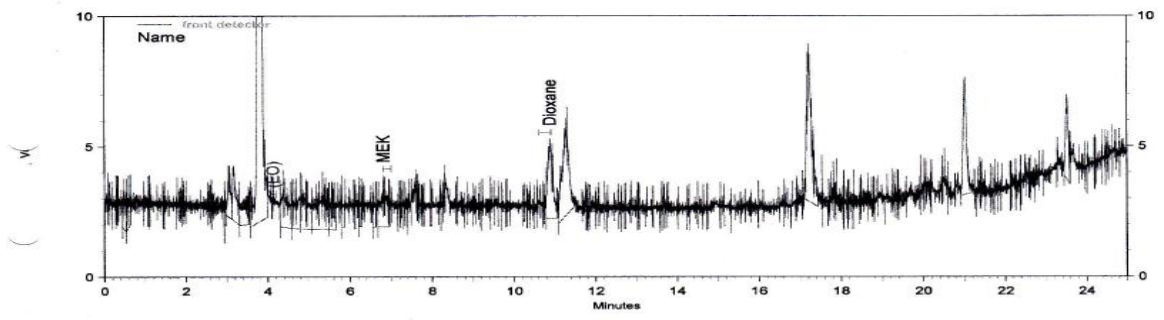
Figure Vc. Full scale trial 1, sample vial C.



Channel A

front detector Results		
Name	Time	Area
EO	4.183	1277580
MEK	6.888	3811305
Dioxane	10.883	3126536
Totals		8215421

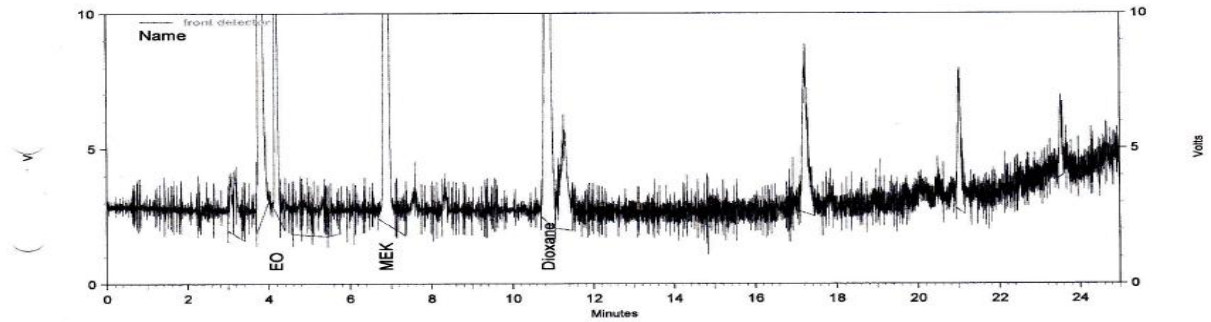
Figure Vd. Full scale trial 1, sample vial D.



Channel A

front detector Results		
Name	Time	Area
EO		
MEK	6.810	126770
Dioxane	10.880	197784
Totals		324554

Figure VIa. Full scale trial 2, sample vial A.

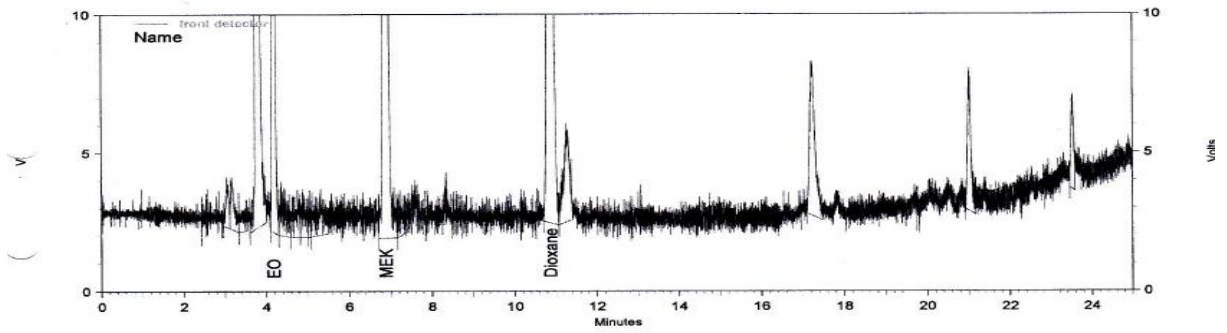


Channel A

front detector Results		
Name	Time	Area
EO	4.186	566344
MEK	6.884	1916029
Dioxane	10.882	1696202
Totals		4178575

Figure VIb. Full scale trial 2, sample vial B.

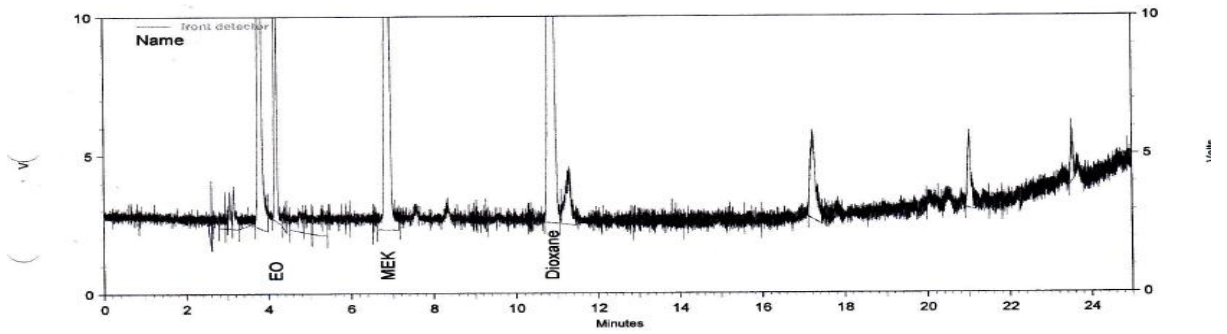




Channel A

front detector Results		
Name	Time	Area
EO	4.185	847338
MEK	6.887	2738451
Dioxane	10.882	2320728
Totals		5906517

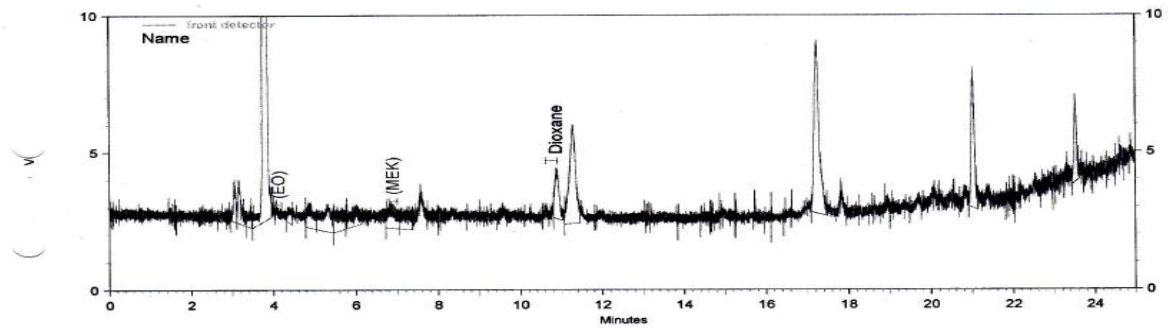
Figure VIc. Full scale trial 2, sample vial C.



Channel A

front detector Results		
Name	Time	Area
EO	4.182	441840
MEK	6.884	2076075
Dioxane	10.884	1780394
Totals		4298309

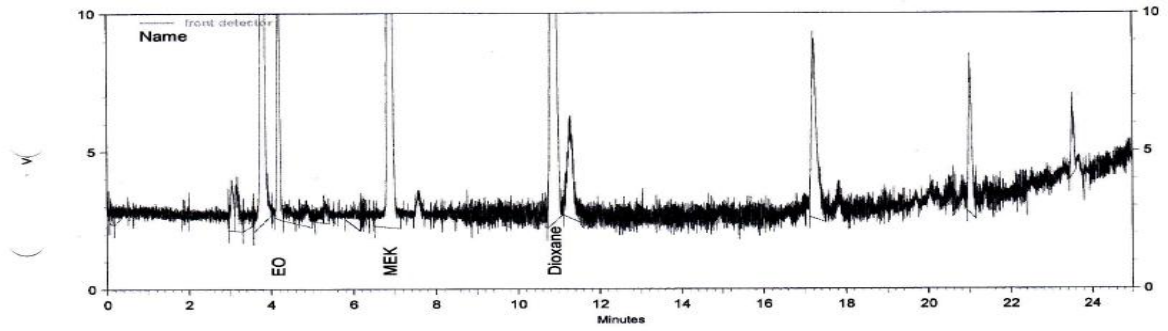
Figure VIId. Full scale trial 2, sample vial D.



Channel A

front detector Results		
Name	Time	Area
EO		
MEK		
Dioxane	10.877	101527
Totals		101527

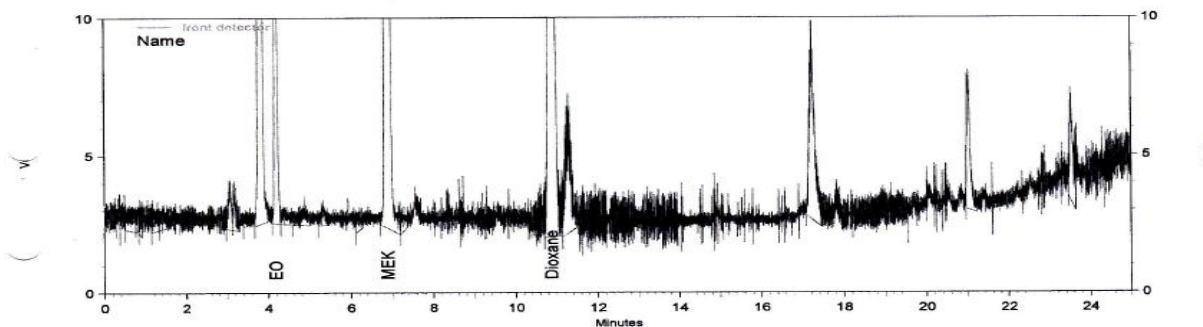
Figure VIIa. Full scale trial 3, sample vial A.



Channel A

front detector Results		
Name	Time	Area
EO	4.181	362316
MEK	6.893	1991305
Dioxane	10.893	1700067
Totals		4053688

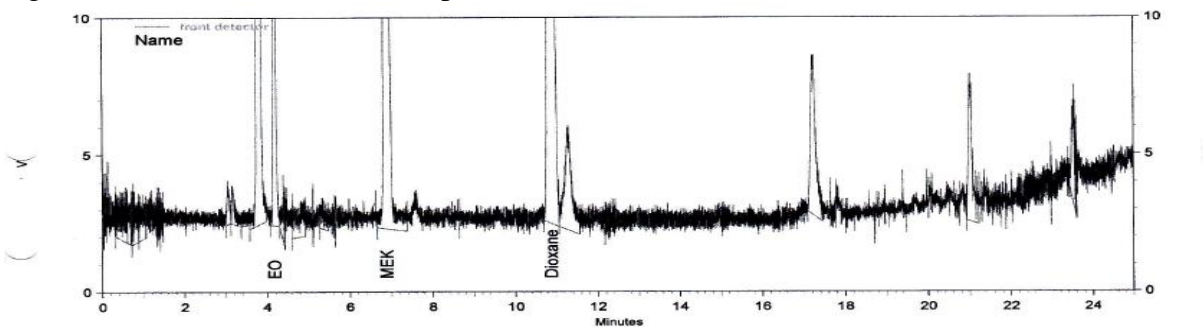
Figure VIIb. Full scale trial 3, sample vial B.



Channel A

front detector Results		
Name	Time	Area
EO	4.184	499822
MEK	6.894	2661927
Dioxane	10.879	2393700
Totals		5555449

Figure VIIc. Full scale trial 3, sample vial C.



Channel A

front detector Results		
Name	Time	Area
EO	4.178	416566
MEK	6.893	3710567
Dioxane	10.879	3104528
Totals		7231661

Figure VIId. Full scale trial 3, sample vial D.

## Appendix 4.

In this appendix the NMR spectrums for the pilot and full scale trials are presented. The spectrums are used for calculating chain elongation and EO distribution.

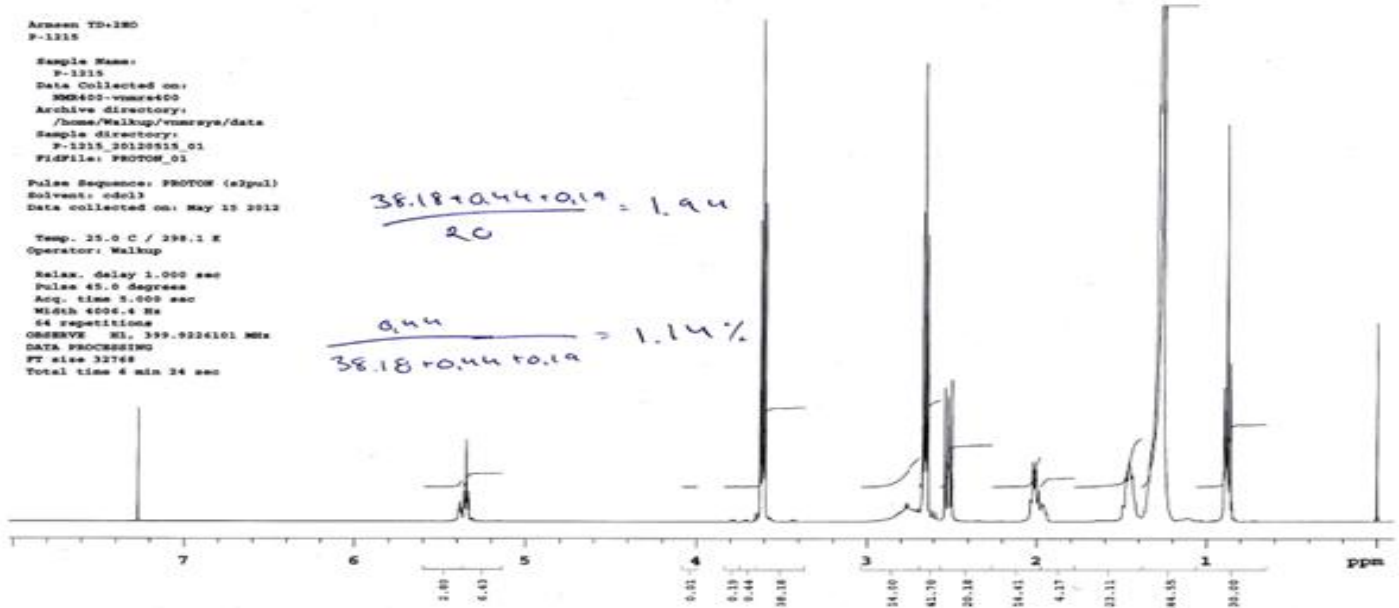


Figure IIX. NMR spectra for pilot trial one.

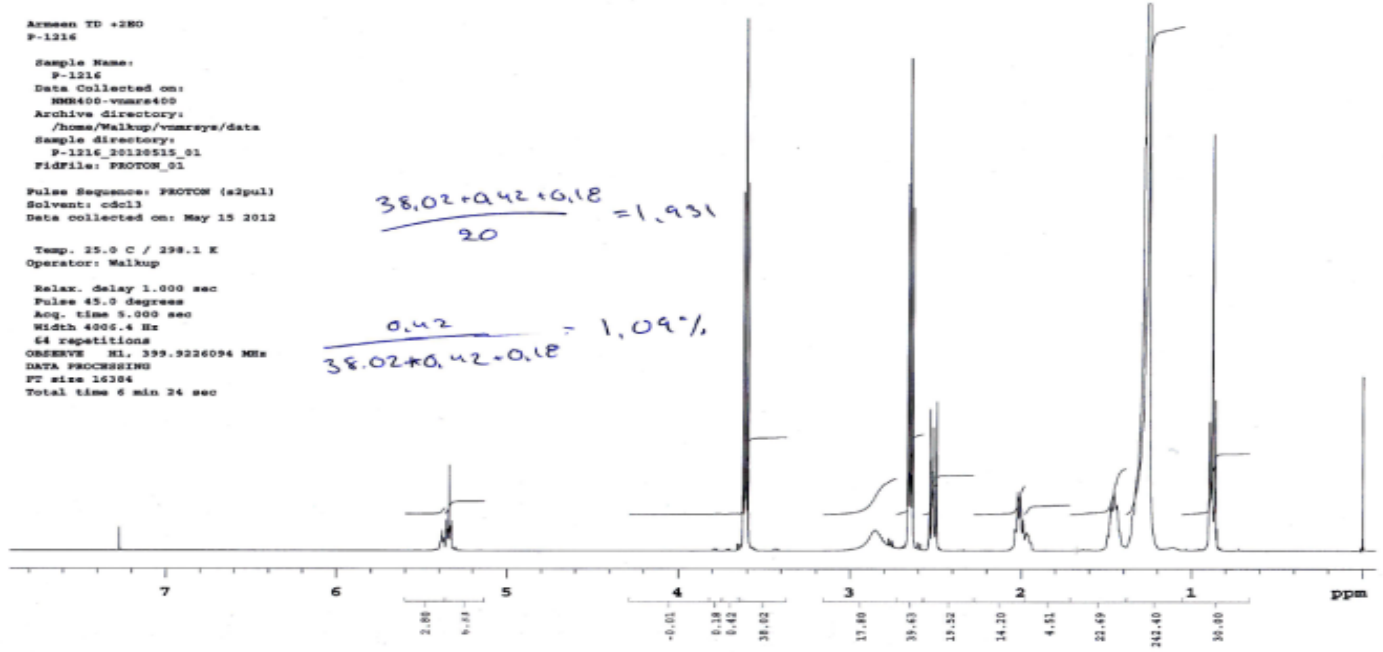


Figure IX. NMR spectra for pilot trial two.

Avance TD +280  
 P-1217  
 Sample Name:  
 P-1217  
 Date Collected on:  
 NMR400-vnmrs400  
 Archive directory:  
 /home/Walkup/vnmrsys/data  
 Sample directory:  
 P-1217\_20120515\_01  
 Fidfile: PROTON\_01  
 Pulse Sequence: PROTON (s2pal)  
 Solvent: cdcl3  
 Date collected on: May 15 2012  
 Temp. 25.0 C / 298.1 K  
 Operator: Walkup  
 Relax. delay 1.000 sec  
 Pulse 45.0 degrees  
 Acq. time 5.000 sec  
 Width 4006.4 Hz  
 64 repetitions  
 OBSERVE H1, 399.9226099 MHz  
 DATA PROCESSING  
 FT size 16384  
 Total time 6 min 24 sec

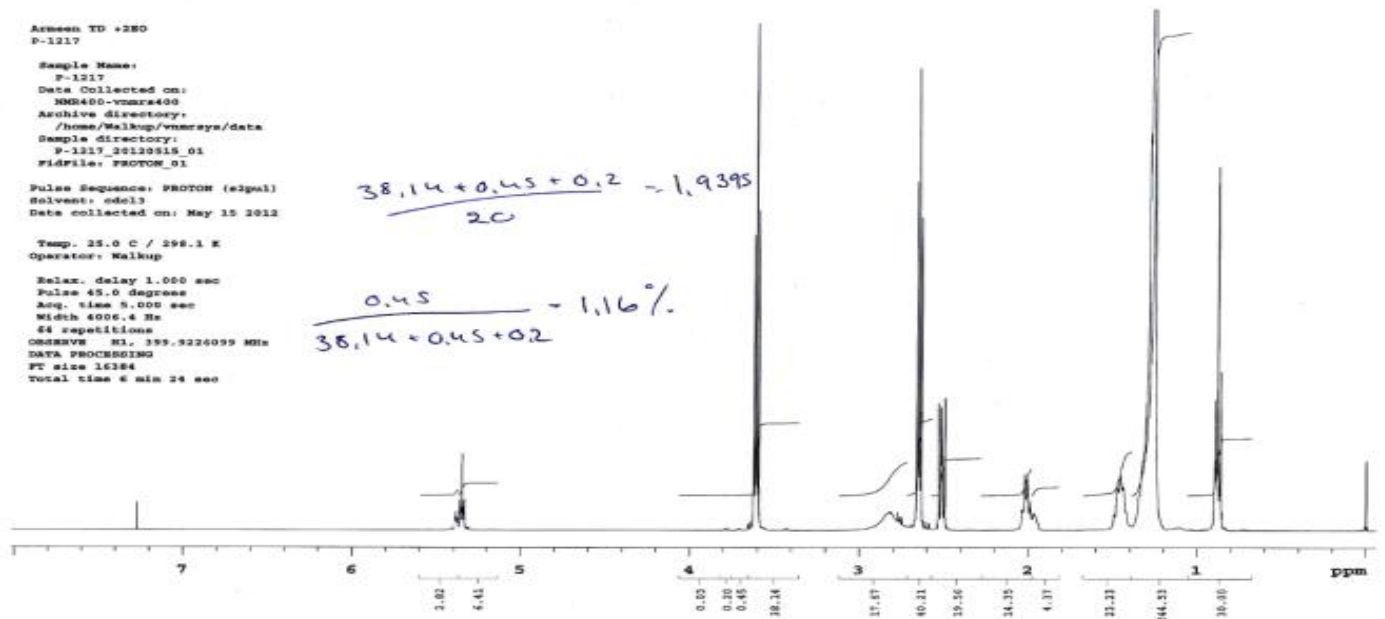


Figure X. NMR spectra for pilot trial three.

Avance TD +280  
 P-1218  
 Sample Name:  
 P-1218  
 Date Collected on:  
 NMR400-vnmrs400  
 Archive directory:  
 /home/Walkup/vnmrsys/data  
 Sample directory:  
 P-1218\_20120515\_01  
 Fidfile: PROTON\_01  
 Pulse Sequence: PROTON (s2pal)  
 Solvent: cdcl3  
 Date collected on: May 15 2012  
 Temp. 25.0 C / 298.1 K  
 Operator: Walkup  
 Relax. delay 1.000 sec  
 Pulse 45.0 degrees  
 Acq. time 5.000 sec  
 Width 4006.4 Hz  
 64 repetitions  
 OBSERVE H1, 399.9226094 MHz  
 DATA PROCESSING  
 FT size 16384  
 Total time 6 min 24 sec

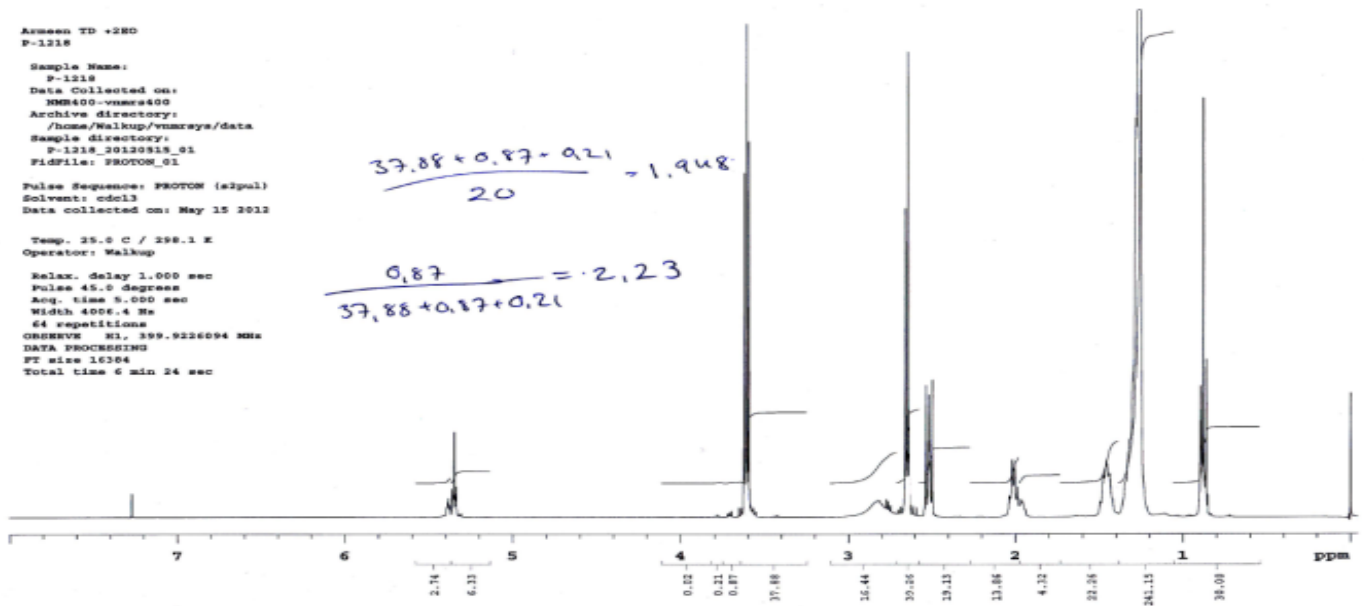


Figure XI. NMR spectra for pilot trial four.

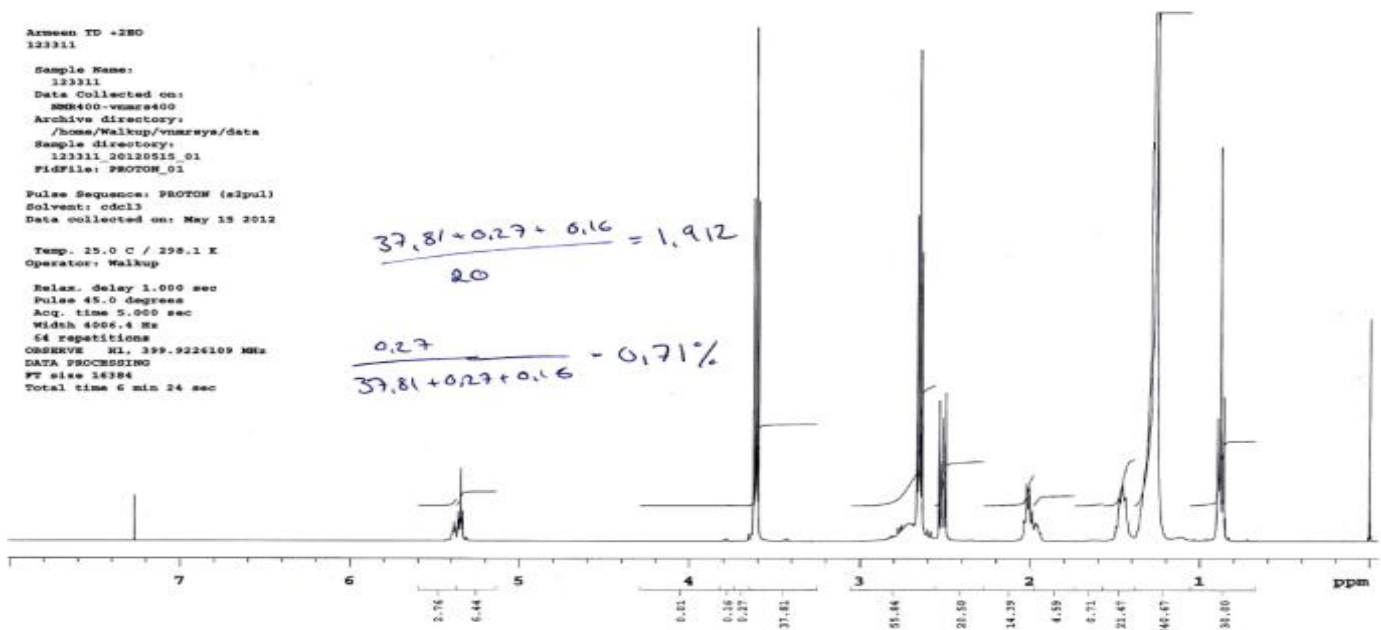


Figure XII. NMR spectra for full scale trial one.

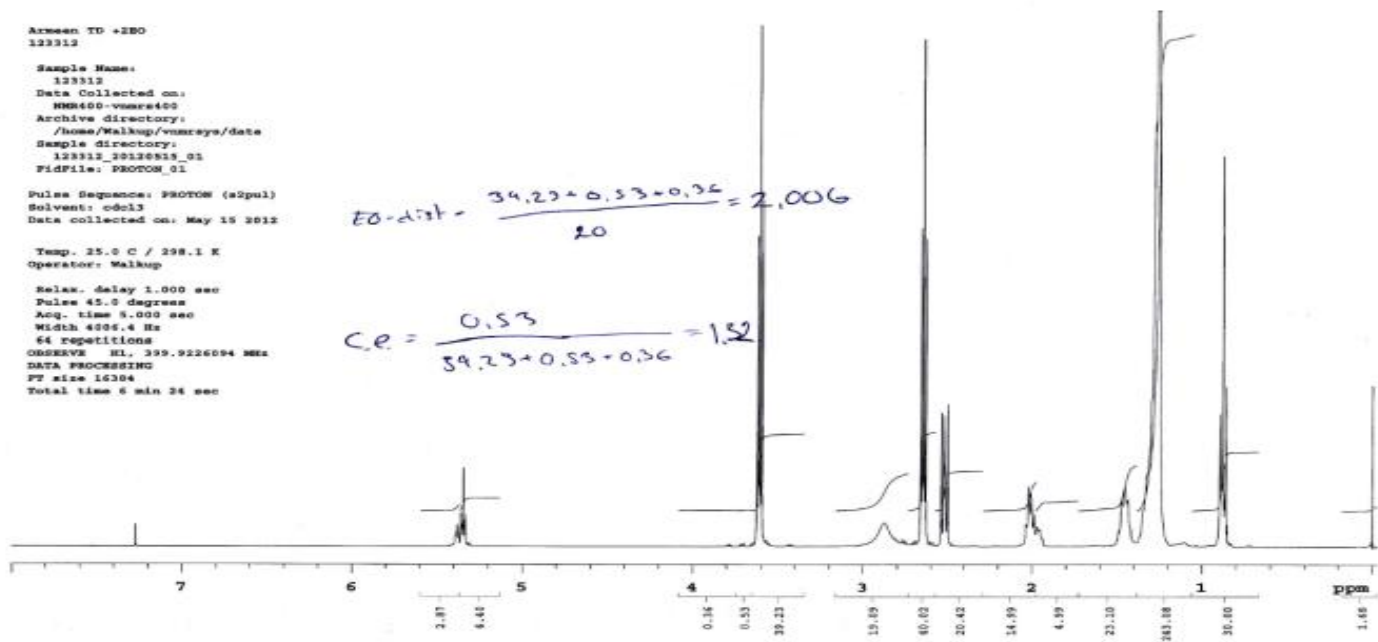


Figure XIII. NMR spectra for full scale trial two.

Armen TD +280  
123313  
Sample Name:  
123313  
Data Collected on:  
MMS400-vnmr400  
Archive directory:  
/home/Walkup/vnmr400/data  
Sample directory:  
123313\_20120515\_01  
FIDFile: PROTON\_01  
Pulse Sequence: PROTON (zgpg3)  
Solvent: cdcl3  
Data collected on: May 15 2012  
Temp: 25.0 C / 298.1 K  
Operator: Walkup  
Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 5.000 sec  
Width 4000.4 Hz  
64 repetitions  
ORIGIN: vl. 355.9226114 MHz  
DATA PROCESSING  
FT size 16384  
Total time 6 min 24 sec

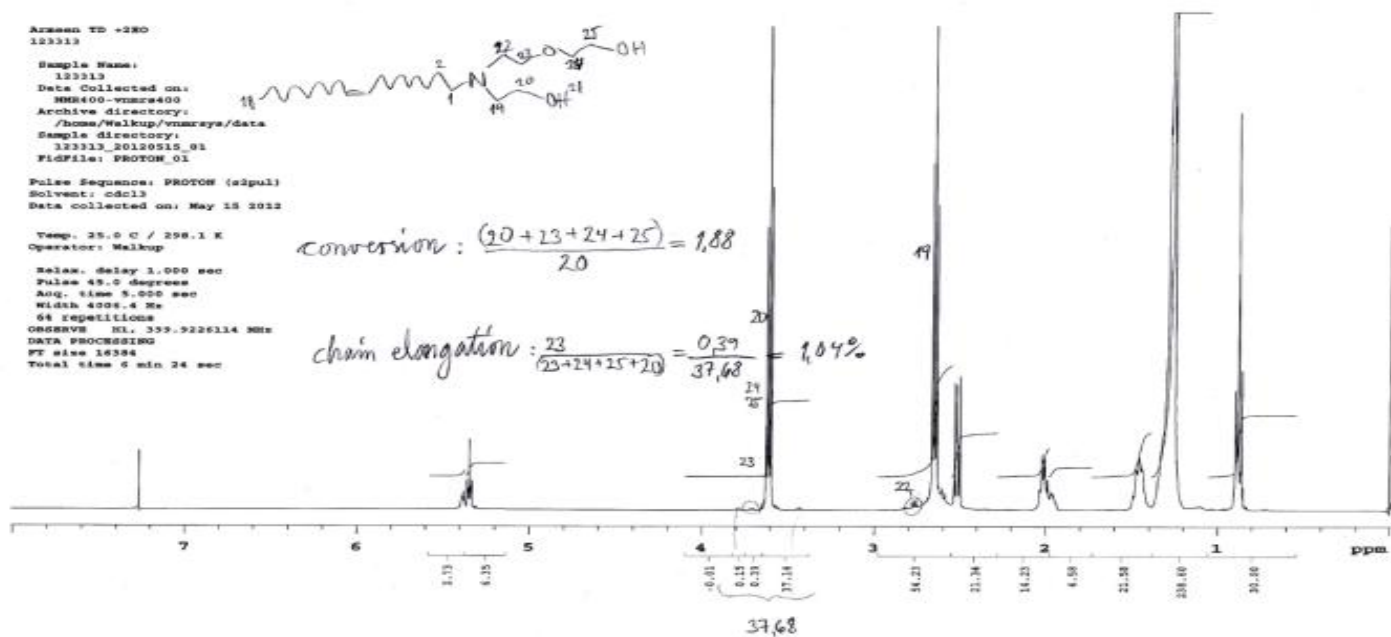
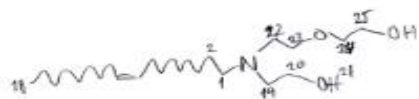


Figure XIV. NMR spectra for full scale trial three.