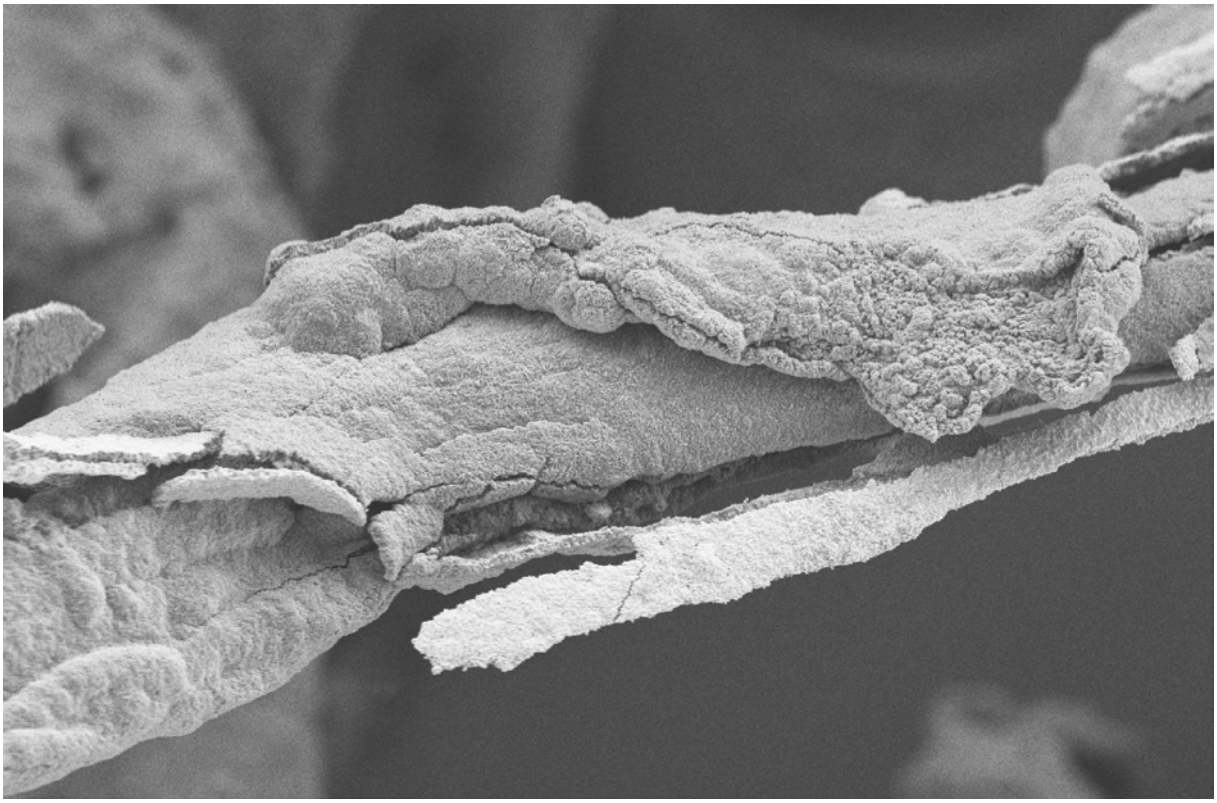

# The influence of reactivity additives upon swelling and accessibility of further reactions of cellulose

Bachelors Thesis in Chemical Engineering

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**Abstract**
The aim of this diploma work was to synthesise a non-ionic surfactant and investigate its properties and functions as a reactivity additive for the viscose process and study its influence upon the swelling and further reactivity of cellulose. Finding a more efficient reactivity additive is not only important for decreasing the necessitated chemicals in the process, but can also increase the economic competitiveness of the product. During the synthesis of the reactivity additive, potassium hydroxide and a Lewis acid were used as catalysts, in a combination with different degrees of ethoxylation for the reaction. As a result, six non-ionic surfactants with a broad and narrow range distribution of different chain lengths were obtained. Their structure and composition was analysed with NMR and HPLC, and the influence that these structural characteristics had upon the swelling of cellulose was then examined by utilizing thorough application tests, that included swelling studies, QCM-D, WRV, solubility identification and foaming tests.

The findings of the various experiments indicated that reactivity additive with a longer chain length of 25 ethylene oxides units per mole of starting alcohol in a combination with a narrow range distribution was beneficial for the swelling of cellulose. The narrow range distribution also was found to have a marginally greater influence upon the water retention value of swelled cellulose and a higher conversion of the starting alcohol. Thus, the conclusion can be drawn that a narrow range distribution with a longer chain length of ethylene oxide makes for a better additive in the viscose process, based upon the experiments conducted during this diploma work.

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# 1 Introduction

## 1.1 Background

Today we live in a world where the threat of the changing climate due to factors like emissions of greenhouse gases or other environmental problems is ever present. Phasing out products produced from non-renewable sources and replacing them with materials made from renewable resources becomes ever more important if we wish to succeed in sustainability. Finding good alternatives to chemicals and materials derived from sources that are renewable is of great importance. Utilizing the vast resources of biomass present on earth and then applying it as a raw material could be one way of finding a more sustainable way of living. One area of potential improvement is where we source the large quantities of fibre's we use every day.

Today we use both natural fibre and synthetic ones, and the difference in characteristics are not much but the energy consumption varies a lot. Natural fibre such as cotton grows on plants and they are a renewable source of fibres. However, these plants need a lot of water, fertilizers and pesticides, which cause a depletion of resources and possible sources of pollution. Also, they are grown on land that instead for fibre production could be used to grow food for the world's starving population.

The synthetic fibres on the other hand are produced in a factory and the chemical feedstock that is used in their production is often based upon petrochemicals. A further drawback linked to the usage of the petrochemicals is that their cost is depending on the oil price. In times that crude oil is cheap, they will be an economically viable way of producing fibres, however if oil prices rise so does their price due to increased raw material costs.

One major area of importance is the usage of cellulose and the selection of its derivatives, products and materials. The usage of this material keeps on growing and the applications are developing in the same speed. The solution of a problem is not always one straight answer, it is often required to have several solutions to be able to find a useful and a more sustainable way of working. By that said, neither a fully synthetic nor a natural fibre may be the answer, but somewhere in between the answer might be found. If we can use the advantage of chemicals which help us utilize the raw materials from trees, the extraction of cellulose would become more efficient. This creates a sustainable and better way of using cellulose from trees that we can plant and grow again, with the advantage of chemicals bringing more sustainable materials with specific characteristics. This is also where viscose fits into the picture, because it utilizes the availability of cellulose from bio-mass and the chemical modification to for a durable and applicable fibre.

## 1.2 Aim

The aim in this project has been to synthesize, analyse and investigate the performance of a reactivity additive in the form of a non-ionic surfactant for the viscose process. A good reactivity additive both helps with the swelling of the cellulose and further reactivity of it. As a result, the manufacturing process would become more efficient, since cellulose would be better utilized and fewer chemicals would be necessitated to obtain the desired product. A good reactivity additive could therefore make the viscose fibre a more viable solution for a

sustainable source of fibres and as well increase the economic competitiveness of the product.

# 2 Theory

## 2.1 The Structure and Composition of Wood

Cellulose is the most abundant biopolymer on earth and it is most readily available through the processing and purification of wood. Wood however has a complex structure and its composition is made up from several different types of compounds. The three most common ones in the composition of wood by weight are cellulose, hemicellulose and lignin. But other components are also present, these are pectins, proteins and extractives like acids, fats and phenolic substances to mention a few. The exact composition varies depending upon the different wood species.[1]

### 2.1.1 Cellulose

About 40-45 % of the dry weight of wood is made up from cellulose and it mainly exists in the cell-wall of the plant. The cellulose is made up from long chains of β-D-glucopyranose monomers (an isomer of glucose) that are linked together with by β (1→4)-glyosidic linkage to form the cellulose polymer, as illustrated in Figure 1. Since all the individual monomers are the same in cellulose it is classified as a homopolysaccharide. These chains can vary in the degree of polymerisation, but are usually about 10 000 units long.

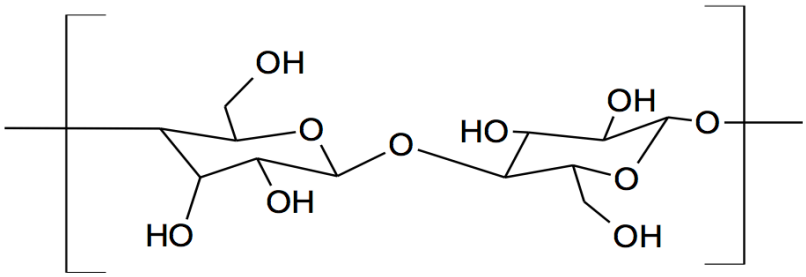


*Figure 1: A repeating unit of cellulose*

As the β-D-glucopyranose is linked together they are also able to form strong short range hydrogen bonds (2Å) in-between the OH – groups of the molecules and these result in a flat conformation, which makes it possible for weaker (long range 5nm) Van der Waals force attractions between the chains, which makes cellulose insoluble in water. As the chains of cellulose are packed together regions of a more crystalline structure can occur due to their high orientation, and naturally also amorphous regions are existing.[1,2]

### 2.1.2 Hemicellulose

After cellulose, hemicellulose is the next largest compositional fraction in wood of about 20-30 % by the dry weight. In contrary to cellulose the hemicellulose is a heteropolysaccharide and its chains are made up from a variety of different monosaccharides. The degree of polymerisation is also considerably shorter with about 200 units and the polymer is often branched unlike the ordinary cellulose. It is also found in the wall of the plant cell. [1,2]

### 2.1.3 Lignin

The lignin composition of wood, again depending on the type of species, is about 20-25 % of the dry weight. Just as the cellulose and hemicellulose the lignin is also found in the cell wall and there it consists of aromatic compounds that have become polymerised. The lignin is usually located in-between the cellulose and hemicellulose fibres. [1,2]

## 2.2 Viscose

The fibres that we have in our surroundings can have many different origins. There are synthetic fibres like Nylon or Polyester which are synthesised from smaller molecules which become polymerized during industrial processes. Often petrochemicals are used as the raw material. Then there are also natural fibres, for an example flax or cotton. These are usually grown in nature, and then processed into a useful product. They also offer a lower price in comparison to some synthetic fibres and since the material directly comes from the plant, renewability is an attribute that is associated to it. However, there are also fibres that are somewhat in between synthetic and natural, and these can be considered as semi-synthetic fibres. Viscose, the fibre of interest in this project is an example of a semi-synthetic fibre.

Viscose, or sometimes also known as viscose rayon or just rayon is a fibre produced from dissolved cellulose that is manufactured in the viscose process. This fibre was the first ever to be commercially produced and introduced to the market as an alternative to natural fibres like cotton. The reason for it to be classified as a semi-synthetic fibre is that the main raw material in its production, the cellulose, is a naturally derived polymer that through the viscose process is dissolved and regenerated (i.e. change in crystalline structure). Today we find the fibre in many places in our surroundings, and it is not only used as a material in the production of textiles. It can also be used in the manufacturing of hygiene products and for other industrial applications such as reinforcing products made from rubber, for an example conveyor belts or tires. [3,4]

### 2.2.1 The Viscose Process

The process of manufacturing viscose is relatively complex and involves many steps to retain the final fibre, these will be described in the following text. The raw material into the process is cellulose-pulp that has been extracted and purified from wood. Pulp is produced by the Kraft process or the sulphite process. If the pulp is produced using the Kraft process, a prehydrolysis is necessary to have a high cellulose content to be able to produce viscose. Producers of viscose often receive the pulp in the form of large sheets or boards. The pulp that goes into the viscose process is sometimes also referred to as dissolving mass or dissolving pulp. A process overview can be seen in Figure 2 below.

#### 2.2.1.1 Steeping

The initiating step in the viscose production is the steeping process. During this step, the dissolving mass is transferred into a continuously stirred vessel and there treated with a solution of Caustic soda (NaOH). The concentration of the caustic soda usually ranges from 17-19% and it allows for the sodium hydroxide to react with the cellulose and form alkali cellulose. For an effective production process in later steps it is important that the steeping process is effective in turning cellulose into alkali cellulose. Further aims also include removing some of the unwanted hemicellulose that still is present in this stage of the process and for the swelling of the cellulose to take place. It is also during this step where the reactivity additives that have been the focus in this project are added, to further increase the swelling.

#### 2.2.1.2 Pressing

When the steeping process is complete the newly formed slurry of swelled alkali cellulose is transferred into a pressing apparatus. Here the excess caustic soda and water can be separated and re-used in the steeping process again to increase the recycling of chemicals.

#### 2.2.1.3 Shredding

After the steeping, the pressed alkali cellulose needs to be turned into a porous and loosened mass. This is necessary to increase the penetration of chemicals into the mass that is exerted of in the later stages of pre-ageing and xanthogenation.

#### 2.2.1.4 Pre-Ageing

The alkali cellulose that has been produced in the steeping process typically has a relatively high degree of polymerisation. It is often is in the area around 750-850 units and in the following steps, the viscosity of the formed viscose dope needs to be lowered. This is accomplished by an oxidative reaction in which the long chains of the alkali cellulose are split to form shorter chains. The reaction is controlled by regulating the reaction time and temperature and if needed a catalyst could be added to further aid the depolymerisation of the alkali cellulose. The reaction vessel that often is used is a rotating drum in which the alkali cellulose is reacted with oxygen. After the pre-ageing stage the degree of polymerisation has decreased to about 270-350 units, but this figure may vary between different manufacturers.

#### 2.2.1.5 Xanthogenation

The next step in the viscose process is the xanthogenation. This step is performed with the aim of making the alkali cellulose water soluble. The alkali cellulose is reacted with $CS_2$ to form alkali cellulose xanthate. The reaction is performed under vacuum and the temperature is slightly raised since $CS_2$ is a liquid in room temperature and atmospheric pressure. Under these process parameters a gas-solid reaction is performed and the product becomes soluble in a water solution.

#### 2.2.1.6 Dissolving

Following the treatment with $CS_2$ the formed alkali cellulose xanthate in now dissolved in a solution of water and caustic soda for increased solubility. This is usually performed at low temperatures, around 0-10°C. The lower temperature and slight caustic soda content of the water tend to decrease the required amount of $CS_2$ used in prior stages. The now formed viscose dope has a syrupy-like consistency with an orange-brown colour.

#### 2.2.1.7 Ripening

Before the viscose dope retains all the right characteristics it needs to be ripened. During the ripening $CS_2$ is distributed more uniformly amongst the cellulose molecules and its position is altered somewhat. During the xanthogenation the $CS_2$ reacts with the most reactive carbon group, the C2-carbon atom of the cellulose molecule. However, this is not the thermodynamically most stable form of alkali cellulose xanthate. As the ripening continues the C6-carbon position will be favoured as it allows for a lower energy level, thus becoming a more stable compound. During the ripening step, more of the cellulose has time to become soluble, and thus resulting in less insoluble cellulose.

#### 2.2.1.8 Filtration

Prior to the actual spinning of the viscose fibres the viscose dope must be filtered thoroughly. To prevent the equipment used for the spinning to be clogged up by unreacted lumps and grains of cellulose, these need to be separated. The dope is usually passed through a series of filters where the finest ones have a mesh-size of 10-20 µm. The viscose dope is also deaerated with nitrogen gas to make sure that no air is present that could compromise the quality of the fibre.

#### 2.2.1.9 Spinning

The final major step of the viscose process is the spinning of the fibre. Viscose is pressed through a nozzle with many fine holes and into the spinning bath. The main function of the spinning bath is to coagulate the viscose and to regenerate the cellulose. The cellulose is regenerated through the chemicals present in the spinning bath. It is made up of a water solution containing sulphuric acid and sodium sulphate, amongst others. The viscose coagulates in the presence of sodium sulphate and sulphuric acid. The acid is responsible for regenerating the cellulose from alkali cellulose xanthate. As it does so, more sodium sulphate is formed, which as well is responsible for drawing water out of the fibre by salting it out.

As the fibres have been formed they can be further treated in the pursuit of desired properties, often their tensile strength is increased by elongating the fibre. Unlike some synthetic fibres, viscose behaves somewhat like thermosetting plastic, which means that once the fibre has been produced it cannot be reformed. As a result of these properties the stretching of the viscose fibre must happen soon after the regeneration of the cellulose. When the final stretching has taken place, the fibre is washed and run through a finishing bath where they for example can be treated with a lubricant or other chemicals that influence their finish.

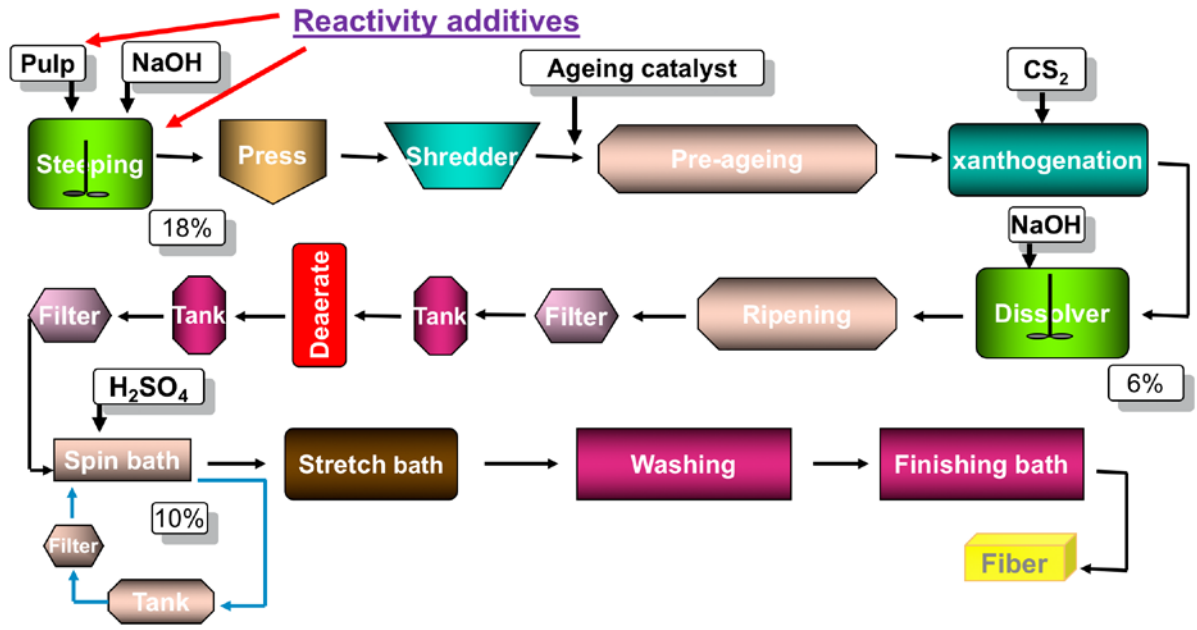


*Figure 2: The Viscose Process*

## 2.3 Surfactants

Surfactants are a large group of compounds, with a very versatile molecular structure their characteristics make them applicable for a wide range of applications. For an example, they can be used in detergents, paper coatings, paints, pharmaceuticals and food. What makes the surfactants so useful are their ability of being surface active. They can change the characteristics of solutions and affect for example the stability of compounds, rheology and other specific characteristics needed to produce and work for the specific application.

Surfactant molecules are amphiphilic which means that they contain a hydrophilic and a hydrophobic part. The hydrophobic part is often a hydrocarbon group which can either be formatted in a straight line or branched form. This part of the molecule is nonpolar and will not interact with the any polar environment such as with water. The hydrophilic part is the opposite, i.e. water loving, this part can be charged and will interact with polar environments. Depending on the surfactant the surface activity will vary, and the surfactants are divided into four different groups depending on the polar head group. [5]

### 2.3.1 Anionic Surfactants

The anionic surfactants are negatively charged and are most used for laundering, dishwashing liquids and shampoos. There are several advantages with this type of surfactant is the simplicity and low production cost and the good capacity of keeping the unwanted dirt away from the material. The polar groups consist of carboxylate, sulphate and phosphate and the most common counter-ions are sodium, potassium, ammonium, calcium and other protonated alkyl amines. Sodium and potassium affect the water solubility, whereas magnesium and calcium foster oil solubility. Products with amine/alkanol amine salts enables both water and oil solubility. The anionic surfactant is the most common type which constitutes approximately 60% of the worldwide surfactant production.[5,6]

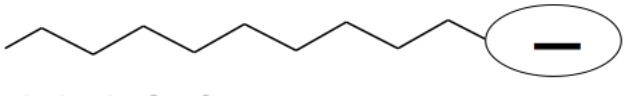

*Figure 3: Anionic Surfactant*

### 2.3.2 Cationic Surfactants

The cationic surfactants have the positive charge placed at the hydrophilic part. This positive charge makes it easy to be adsorbed to solid surfaces which normally have a negative charge. The characteristics makes it suitable for corrosion protection and fabric softeners. There are both amine and quaternary ammonium-based products, the amine works only as a surfactant in the protonated state, i.e. it will not work in high pH. Quaternary ammonium compounds are on the other hand, not pH sensitive. [5,6]

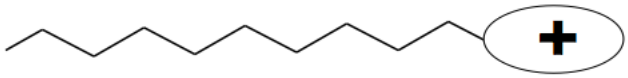

*Figure 4: Cationic Surfactant*

### 2.3.3 Amphoteric Surfactants

The head group of an amphoteric surfactant can be both positive and negative, i.e. either cationic, zwitterionic or anionic. The pH value on the surrounding affects the charge on the surfactant, if the pH is high the overall charge is anionic (negative) and if it is low the overall charge is cathodic (positive). Around neutral pH the surfactant can have both an anionic charge and a cationic charge, making the surfactant zwitter ionic. The change in pH and charge affects the properties concerning swelling, foaming, wetting and detergency, etc. and they depend strongly on the solution pH. The most common amphoteric surfactants are N-alkyl derivatives of simple amino acids, such as glycine($NH_2CH_2COOH$), betaine ($(CH_2)_2NCH_2COOH$) and amino propionic acid ($NH_2CH_2CH_2COOH$). These surfactants are usually not prepared from the amino acid, however, when reacting a long-chain of amine with sodium chloroacetate or a derivative of acrylic acid it will create a structure with one and two carbons, respectively, between the nitrogen and the carboxylate group. [5,6,7]

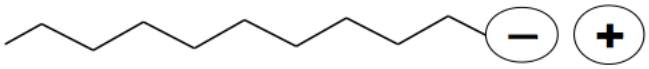

*Figure 5: Amphoteric Surfactant*

### 2.3.4 Non-ionic Surfactants

These surfactants do not have an electrical charge and may often be used together with anionic surfactant, where one advantage is that they do not interact with calcium and magnesium ions in hard water. The structure contains either a polyether unit, polyhydroxy unit or a polyoxyethylene chain as the hydrophilic part. Non-ionic surfactants are a thick liquid or syrups with a very sticky touch, which is the opposite to anionic surfactants [5,6]

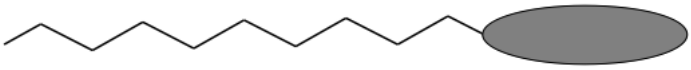

*Figure 6: Non-ionic Surfactant*

### 2.3.5 Cloud Point of Surfactants

One further important tool for analysing and observing a non-ionic surfactant is by observing its cloud point in an aqueous solution. It is usually determined by preparing a 1%- solution of the surfactant and then slowly heating it. As the temperature is raised to a critical point, the solution will form two phases and the surfactants will separate from the water. Light is scattered and by looking at the solution it will appear as it becomes cloudy. Generally, the cloud point of an ethoxylated non-ionic surfactant is increased as a larger number of EO is added to the surfactants chain. When it comes to the number of other compounds that are being dissolved by the surfactant, is usually the highest at the temperature range right under its cloud point. [6,8]

### 2.3.6 Surfactants in the Viscose process

Surfactants can be used for a wide range of applications in the viscose process, including modifier, finishing and spin bath additives. The basis of surfactants is that they lower the surface tension between two liquids, or a liquid and a solid. They have a major impact on both the process and the final product. The surfactants could be of many different types depending on the chemical structure and the environment in the production. To mention some benefits with surfactants, is that they can improve for example filterability and spin ability, make the production much easier to perform by reducing foaming and cloudiness and increase the quality and durability of the product together with a higher process efficiency.

The addition of good reactivity additives prior to the steeping process also allows for better swelling and improving its reactivity of the cellulose. By increasing the swelling both the alkalization of the dissolving pulp becomes more efficient, as well as later stages require less energy and chemicals for the dissolving of the pulp. For example, the energy consumption in the shredding stage is lowered and the amount of $CS_2$ during the xanthogenation stage can

be reduced, and less undissolved cellulose would be separated away during the filtration of the viscose dope.[9,10]

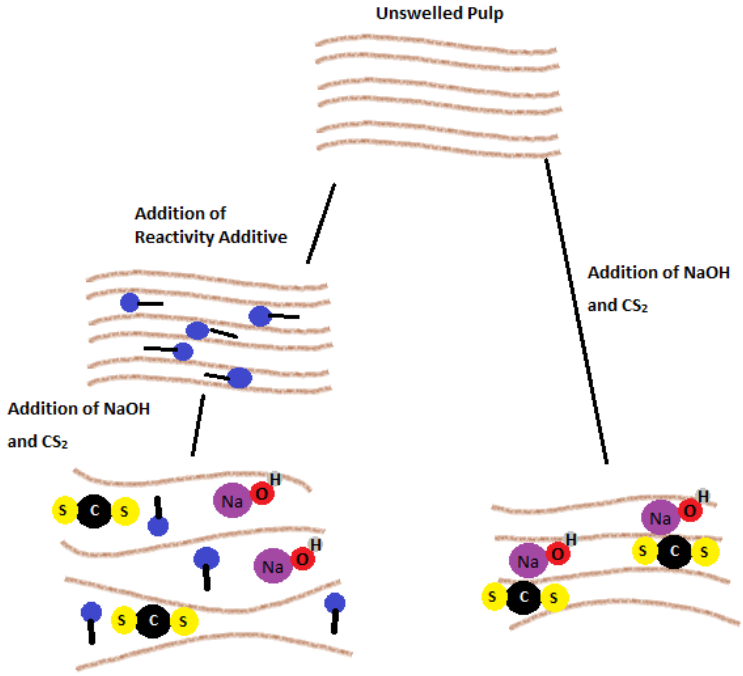


*Figure 7: Mechanism of reactivity additives upon the swelling of cellulose*

In the viscose process, surfactants can regulate for example the foaming which is of major importance for the production in a plant. The foaming can create problem if it is not regulated and under control because the volume of it can destroy both the product but also the equipment. The foaming usually arises as the viscose dope is treated with nitrogen to remove air from the dope. If bubbles of air would be present during spinning of the viscose dope, it could compromise the quality of the final fibre and creating weakness inside the molecule creating abruptions during spinning.

## 2.4 Synthesis of Broad Range and Narrow Range Surfactants

The different surfactants synthesised with the broad and narrow range catalysts will contain different by-products and amounts of each substance, the overall reaction can be seen in Figure 10 below. The biggest difference in the synthesis between these two is the type of catalyst. For the broad range product, a KOH catalyst was used while for the narrow range a Lewis Acid. The difference in catalyst will affect the reactivity and therefore also the formation of by-products in the resulting reactivity additive.

It is confirmed that the Broad range ethoxylates will have more unreacted alcohol then the narrow range product, as this is catalyst dependent. KOH, the base catalyst, is not as efficient as the Lewis-acid catalyst in terms of how well it catalyses the initial reaction of 2-ethylhexanol and ethylene oxide. This is also the reason for that the Lewis-acid catalyst is used during the beginning of the synthesis for the narrow range ethoxylate and thus gives a greater conversion of the starting alcohol. The higher amount of unreacted alcohol in the

broad range surfactant will result in a higher weight percentage value for the first point in the HPLC-UV analysis graph and a peak in the NMR spectrum.[11]

When synthesising a Narrow range surfactant, the amount of acetals in the product will be higher than for the Broad range. The higher acetal content in the narrow range surfactants is linked to the first step of synthesis. The Lewis-Acid catalyst is more likely to react with the oxygen atoms in the ethylene oxide chain, and therefore more such by products are formed during the synthesis. As a result of such characteristics a re-catalyzation is performed after an amount of 5 moles of ethylene oxide is added to each per mole of starting alcohol.[11]

The desired EO-length of the product is also more accurate for narrow range than for broad range ethoxylate, the HPLC-UV graph will therefore have higher peaks at the wanted EO length and the distribution will be more peaked for the narrow range in comparison with broad range surfactant.

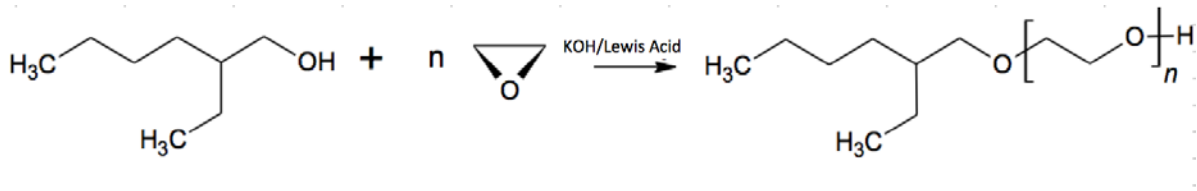


*Figure 8: Synthesis of products*

### 2.4.1 Toxicity of Broad and Narrow range surfactants

Another factor that may become important when selecting a suitable reactivity additive to use in the viscose process is its toxicity. There are studies that suggest that the EO chain length and distribution have a considerable effect upon the toxicity of non-ionic surfactants. Generally, the longer the EO chain length of the surfactant, the less toxic the surfactants became. This mainly was found to be the result of increasing hydrophilicity. The study also compared broad and narrow range distributions against one and other and it showed clearly that alcohol ethoxylates of a broad range were more toxic due to a larger amount of alcohol and shorter chained surfactants present.[12]

## 2.5 Analytical Methods

### 2.5.1 Nuclear Magnetic Resonance

Nuclear Magnetic Resonance (NMR) spectroscopy as seen in Figure 8, is an analytical chemistry technique used to obtain information about the structure and the chemical composition of a sample. The technique uses the information that is given when the nuclei of the atoms possess a magnetic current due to the presence of charged protons. This phenomenon creates a certain frequency which can be detected where the frequency is proportional to the strength of the external magnetic field. The stronger the magnetic field the higher the precession frequency.


*Figure 9: NMR - Set up*

The electrons surrounding the atoms have an opposite charge compared to the protons, if many electrons are present around the nucleus they will compose a shield around it. This makes the nucleus more detectable with a weaker external magnetic field and a lower precession frequency is therefore observed. Other factors that affects the precession frequency are ring currents (anisotropy) and the bond strain between the atoms.

From a NMR spectroscopy one can draw conclusions about which molecules that are in the sample and the quantity of them. The induction signal is recorded which is then obtained from the magnetic spin of the nuclei of hydrogens (protons) present in the sample. This data is then plotted with induction signal of hydrogen present in the sample against their corresponding magnetic spin frequencies. [13]

### 2.5.2 HPLC-UV

High performance liquid chromatography (HPLC) is an analytical technique that is used to separate a sample to be able to identify and quantify the different molecules inside the sample. The separation is relying on the interaction between molecules in the sample and the mobile and stationary phases. In a HPLC apparatus, the mobile phase is a liquid which is pressurized and its flow rate is regulated by a pump. The sample is transported by the mobile phase through the column where the stationary phase is located. Depending on the characteristics of the sample the mobile and stationary phase is varied to be able to separate the different molecules.[13]

There are also different types of HPLC depending on the sample, there are Normal Phase and Reverse Phase. The difference between Normal and Reverse phase is the charge of the mobile phase and stationary phase. In normal phase chromatography, the mobile phase is non-polar and the stationary phase is polar. This means that the less polar molecules in the sample will eluate faster than the more polar ones. In reverse phase it is the opposite, the mobile phase is the polar one and the stationary phase is non-polar, this lets more polar molecules in the sample to eluate faster. In this analysis, a Normal phase HPLC was used.[13]

After the separation, a detector is needed to be able to make use of the separation that took place in the HPLC-apparatus. The different molecules in the sample will have different retention times, meaning that it will take different times for each molecule to transport itself through the separation column (stationary phase) and to the detector located after the HPLC-apparatus. The detector is chosen after which molecules that is of interest in the sample, some are detected by using light, others need an electrochemical detection. In this analysis, a UV-VIS detector is used, the molecules in the sample must have a double bound to make it visible with the detector. For the ethylene oxide chains, such in this project are not detectable and thus must be marked prior to analysis.[14]

### 2.5.3 Quartz Crystal Microbalance

The fundamental principal that makes QCM-D, or also known as a “quartz crystal microbalance with dissipation monitoring” a very useful and sensitive sensor platform is its ability to oscillate under the addition of a current. This effect was first discovered by Jacques and Pierre Curie in 1880, when they exerted a quartz crystal for mechanical pressure. As

they did so, an electrical voltage could be measured and this became known as the piezoelectric effect. It also works in reverse and upon that principle QCM-D is based.[15]

As mass is added or removed from the surface, the quartz crystal will change its resonance. This effect can then be measured and used as a helpful tool to analyse for an example thin films that have been applied to the surface the QCM-D sensor. When adsorption or desorption occurs at the surface of the crystal the frequency in which it oscillates will change. The obtained frequency shift can then be inserted into the Sauerbrey equation and when combined with the Sauerbrey constant the mass change can be calculated. By measuring this very accurate conclusions can be drawn about the mass of substances that are bound to the surface.[16,17]

In this project, a QCM-D sensor coated with cellulose was used, where D stands for dissipation. The dissipation generally relates to the rigidity and viscoelastic properties of the thin film on the surface of the QCM-D sensor. As the cellulose on the sensor was exposed to different chemical compositions in the water solution, including the surfactant synthesised in this study, swelling and adsorption of the cellulose coat could be measured and examined. By applying different films to the surface of a QCM sensor, the method could be used in many different fields of research. For an example, other applications could be measurements of oxidation on a metallic film, enzymatic degradation of lipids that are coated on to a QCM sensor or even how different surfaces react to being exposed to moist air.[18]

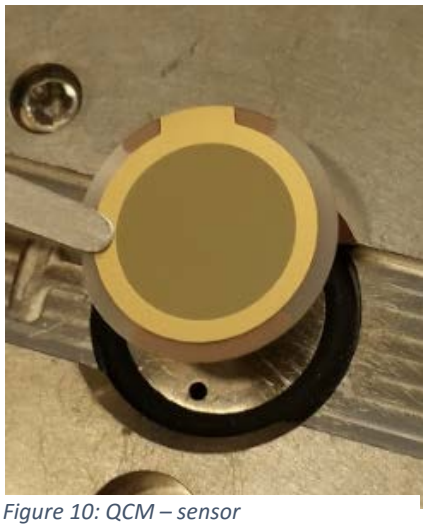

*Figure 10: QCM – sensor*

$$\Delta f = -\frac{C * \Delta m}{n}$$

$C = Sauerbrey\ Constant\ which\ is\ 17{,}7\ ng * Hz^{-1}$
$\Delta m = change\ in\ mass\ (ng)$
$\Delta f = frequency\ (Hz)$
$n = number\ of\ the\ overtone$

### 2.5.4 Scanning Electron Microscope

When studying and examining solid materials surface, a scanning electron microscope, also known as a SEM, can be a very useful tool to get information about the materials structure. The scanning electron microscope utilises that an electron gun can be used as a source of electrons. The electrons are accelerated and an electron beam is emitted on to the surface of the material. The electron beam is used to scan the surface of the sample and it will interact with the atoms that are present. As the emitted electron beam penetrates the samples surface, it will collide with its atoms and a scattering of electrons will occur.

The collision of the beam with the atoms of the sample can be both elastic and inelastic. Depending on which type of collision occurs different forms of scatterings will be created. When the beam collides with atoms present close to the surface an inelastic collision will take place and secondary electrons will be scattered from the sample. If the collision is elastic, it is usually a result of the electrons from the beam colliding with atoms further down in the sample. These will have a higher energy than the electrons that had an inelastic collision, and they are called backscattered electrons.

As the backscattered and the secondary electrons escape from the samples surface they can be detected as signals in an electron detector. These signals are then converted into an image with high resolution of the samples surface. Much information about the shape and structure of a solid material can be obtained with this method and it provides a useful tool for studying how the reactivity additives are attached to the cellulose fibres and their interaction with it.[19,20]

# 3 Materials and Methods

## 3.1 Ethoxylation Procedure

For this experiment a steel autoclave reactor was used to synthesize the products. The broad and narrow range surfactants were synthesized during two separate trials, and although the procedure to a large extent shared similarities they will both be explained in the following section.

Before the synthesis began the water content of the starting material, 2-ethylhexan-1-ol had to be checked. This was done by a Karl-Fischer titration. For the synthesis to be carried out successfully the water content needed to be low to ensure that the catalysts would work properly and initiate the reaction. To avoid opening the reactor in between the synthesis of every specific chain length, a larger amount of alcohol was added in the beginning. When the desired degree of ethoxylation had been reached only part of the product was drawn out of the reactor and saved for further analysis and applications testing. The remaining was used as a starting molecule for further ethoxylation.

### 3.1.1 Broad Range Surfactants

The first step in the experiment was to prepare the autoclave reactor. The reactor was filled with the starting material and KOH, the base catalyst that was in a 50% solution with methanol. The reactor was then closed and the procedure continued.
The next step in the experiment was to apply vacuum to the reactor and evacuate the air inside it. The reactor was then filled up with nitrogen to a pressure of around 2 bar, after which it was emptied under vacuum again to about 0.2 bar. This was then repeated in a total of 3 times to ensure that no air was left in the reactor. Also, a pressure test was conducted. The reactor was filled with nitrogen until the pressure was increased to 4.5 bar, and left there for about 10 minutes to ensure that no leaks existed.

As no leaks had been detected methanol from the catalyst needed to be separated away from the reactor. This was done by increasing the temperature in the reactor to 60°C and

then applying vacuum for 15 minutes. Under these conditions the methanol evaporated and exited the reactor.

With the methanol gone the reactor was now ready for the addition of further reactants. The temperature was increased to 130°C at which the 2-ethylhexanol began to boil. Pressure also needed to be raised in the reactor and it was increased by the addition of 10 grams of EO. This procedure increased the boiling point of the alcohol and the reaction temperature of 160 °C was reached.

As the reaction temperature had been reached, the addition of EO continued. In the aim of producing a surfactant with 10 EO-groups added per alcohol, a total amount of 527 grams of EO were added to the reactor. For every part alcohol 10 molar equivalents of EO were added. The dosing of EO happened during 30 minutes continuously in order to stay close to 160 °C and keep a constant pressure of 3 bar. As all the EO had been added the reactor was left to enable the down reaction to take place, until a constant pressure of about 0.5 bar had been reached. The temperature in the reactor was decreased to 70°C and pressure was induced by nitrogen, after which the product was taken out and neutralised with acetic acid. The water content was then measured with Karl-Fischer titration, the results were noted.

The remaining material in the reactor was then used as a building block for further ethoxylation. Again, pressure was dropped under vacuum and the temperature was increased to 160°C. As the reactor was at reaction temperature the dosage of EO could start again and the synthesis of a surfactant with an average chain length of 15 EO could start. To reach an average chain length of 15 EO a sufficient amount of EO based on the first reaction was added to the reactor. Again, it was added in 0.3 second pulses to keep the temperature and pressure even. When the entire amount of EO had been added, the down reaction took place. When the pressure evened out at 0.3 bar the temperature was decreased to 70°C, nitrogen was to build up pressure in the vessel and the product was taken out of the reactor. It was then neutralized with acetic acid and the water content was measured and noted.
To prepare the third and final surfactant of the broad range-variant the same procedure as described was followed. 10 molar equivalents of EO were added in order to obtain a surfactant with an average chain length of 25 using the 15 EO surfactant as a building block. After the down reaction had been completed product was once again taken out of the reactor and neutralized, its water content was then measured and noted.

### 3.1.2 Narrow Range Surfactants

The narrow range procedure is a bit different than the broad range in the first part of the experiment, the EO-length aim for the first part is 5. In the beginning the reactor was filled with the starting material and the catalyst Lewis Acid, the reactor was then closed and the reaction was initiated. As mentioned above, each time the reactor is opened and a reactant is added the air needs to be evacuated. The ester bounded to the Lewis Acid catalyst needs to be taken away, this is done by decreasing the pressure to around vacuum and the setting temperature at 50°C in order for the ester to evaporate. When the solution has reached 50°C the temperature was set to 100°C and the EO was added to get the desired length of 5,

when the reaction has stopped a sample was taken and analysed with NMR to get the specific length of the solution. If the length is correct the temperature was lowered to 50°C and the pressure was set to atmosphere, the reactor was then opened and KOH was added to neutralise the Lewis Acid. Then extra KOH was added to make the solution basic in order to make EO react and get the following EO-lengths 10,15 and 25, the procedure to get these lengths is the same as for broad range.

## 3.2 Procedure NMR

In order to determine the degree of ethoxylation and possible formation of by-products such as acetals and unreacted alcohol, NMR was a suitable analytical method for this structural analysis. The first step in the NMR-analysis of the ethoxylated products was the sample preparation. As some of the samples were partly solid they may be inhomogeneous and we had to place the containers with products in an oven in order to melt them. Once the samples were liquid, 3-4 drops of every product were added into NMR-test tube. The solvent used in this analysis was deuterated chloroform and it was added into the test tube. The test tubes were continuously turned upside down until all the product had been dissolved by the solvent. For an accurate NMR-spectrum it is also important that the test tubes are completely clean. To be able to prevent any residuals left on them from affecting the result, they were wiped clean before analysis with a cloth. Then the test tubes were placed in the NMR- apparatus and an H-NMR and $^{13}$C-NMR were performed on all the samples to obtain their corresponding spectrum.

*Figure 11. NMR - Test Tube*

When analysing the NMR-spectrum the different substances could be identified and quantified. This was done by identifying which peak corresponded to a specific hydrocarbon group in the molecule, the different peaks were integrated and a standard value of 60 was assigned to the six hydrogens of the two -$CH_3$ peak at the chemical shift δ 0.6 to 1.0 ppm. For illustrative purposes a typical NMR-spectrum of an ethoxylated alcohol has been added below and each peak has been assigned with its corresponding group.

## 3.3 Procedure HPLC-UV

During the ethoxylation reaction not only one product was formed, but many alcohol ethoxylates with different chain lengths. To analyse these and get an understanding about the distribution of chain lengths a normal phase liquid chromatograph was used in combination with a UV detector. To allow for an effective separation of the different chain lengths, gradient elution was applied and the flow through the column was 0.6 ml/minute. The apparatus used can be seen in Figure 12 below.

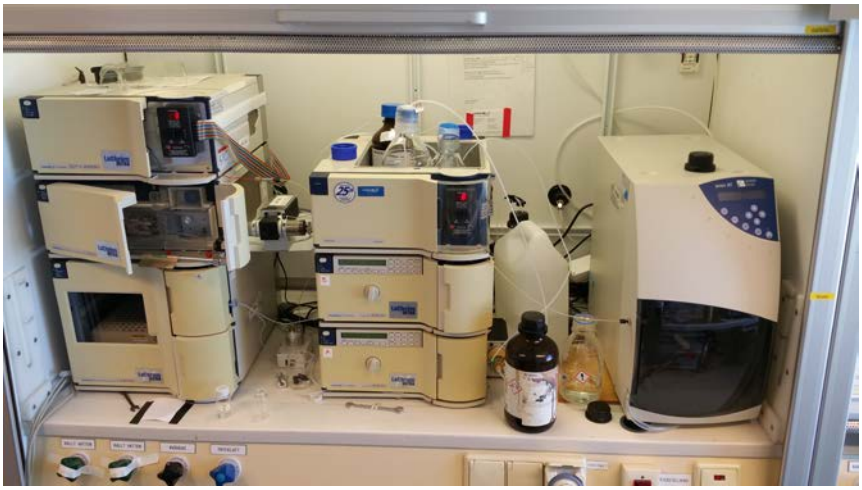

*Figure 12: HPLC-UV equipment*

### 3.3.1 Derivatization of sample

The first step in the HPLC-UV procedure was sample preparation. Since the ethoxylated alcohols did not contain any double bonds they needed to be derivatized and marked with a molecule that contained double bonds, to allow for detection. 0.25 mmol of the liquefied product and 0.50 mmol of 4-Nitrobenzoylchloride were added into 5 ml reaction vessel. The mixture was then placed in an oven at 90°C for 30 minutes and after that shaken. The reaction vessel and its contents were then allowed to cool down and 1 ml of a 0.5 M solution of sodium hydroxide was added in order to kill of the remaining reactants. The vessel was then placed in an oven at 50 °C for 15 minutes and shaken 3 to 4 times.

### 3.3.2 Extraction and separation

As the reaction had been completed an extraction of the products was necessary. 20 ml of a 30 % sodium chloride solution was poured into a separator funnel together with the products from the reaction vessel. The sodium chloride solution made the products less soluble in a water solution. As the solution was washed with 2*5 ml of ethyl acetate, the products were extracted into the organic solvent.

The separation of the products began with taking a syringe and pulling out its piston. Glass-wool was then placed in the bottom and it was packed with 10 grams of sodium sulphate. By passing the upper layer from the separator funnel (which consisted of ethyl acetate and product) through the syringe, the water that was still present was absorbed by the sodium sulphate.

First 5 ml of pure ethyl acetate was added to the column to be able to equilibrate it. Then the lower phase in the separator funnel was emptied into a beaker and the upper poured into the column. As the solution was dried by the sodium sulphate and passed through the column it was collected into a flask. The water solution from the beaker was washed one last time with a further 10 ml of ethyl acetate and poured through the column to dry. To ensure

that all products had been collected the column was washed with 2*5 ml of ethyl acetate. To obtain pure products the ethyl acetate solution was evaporated.

### 3.3.3 Analysis

During the analysis of the ethoxylated alcohols 2 different eluents were used to accomplish the right running conditions. They were prepared and eluent A was a solution of hexane and isopropanol with the volumetric ratios of 90:10. Eluent B had a volumetric composition of 90:10 with regards to isopropanol and water. The derivatized and evaporated sample that had been obtained in previous steps was then dissolved in a 50:50 solution of eluent A and B. 5 µl of the sample-solution was then applied to the column and the running conditions for the gradient elution were as followed:

*Table 1: Gradient elution conditions*

| Time (min) | Fraction A | Fraction B |
|---|---|---|
| 0 | 80 | 20 |
| 7.5 | 70 | 30 |
| 45 | 0 | 100 |
| 60 | 0 | 100 |
| 60.1 | 80 | 20 |
| 70 | 80 | 20 |

As the separation and the elution of the products continued they pass through the UV-detector. The detection of the products was displayed as a peak on the chromatogram. From the peak area and the molecular weight of the products the weight fraction could be calculated with the following formula.

$$W_n = \frac{A_n * (M_a + n * M_e)}{\sum_0^i A_n * (M_a + n * M_e)}$$

*Where*

$\mathrm{n} = \text{Mole of EO added to starting alcohol}$
$\mathrm{A_n} = \text{Area for corresponding peak to each surfactant}$
$\mathrm{W_n} = \text{Weight fraction of surfactant with n mol of EO added}$
$\mathrm{M_a} = \text{Average molecular weight of starting alcohol}$
$\mathrm{M_e} = \text{Molecular weight of EO}$
$\mathrm{i} = \text{Total number of detected peaks}$

## 3.4 Procedure for Swelling Test

First sheets of pulp were cut into 10 small circles with a diameter of 30 mm, it is of great importance that they are perfectly circular and that there is no contamination on the pulp. The 10 circles were then placed on a scale and the weight was recorded, they were then placed inside a 250-ml measuring cylinder and the initial height was recorded.

In order to prepare an additive solution with an accurate concentration, a 1% stock solution was prepared and used for the dilution. Into the cylinder 20 g of additive in water solution was added with a concentration of 2 kg per 1000 kg pulp, then 5 minutes were allowed to

pass and the height increase was recorded. Then 201,3 g of NaOH solution with a concentration 19,7 % was added for each experiment. The height was recorded over time during a time frame of 6, 7, 8, 9, 10, 12, 14, 20 and 30 min. To be able to measure the height as accurate as possible a hollow rod was used to carefully press down and straighten up any pulp that had been disoriented and turned itself in an other direction during the swelling. All the liquid was then drained using a sieve, the swollen pulps weight was then recorded. The change in height was plotted against time. An illustration of the procedure can be seen in Figure 13 below.

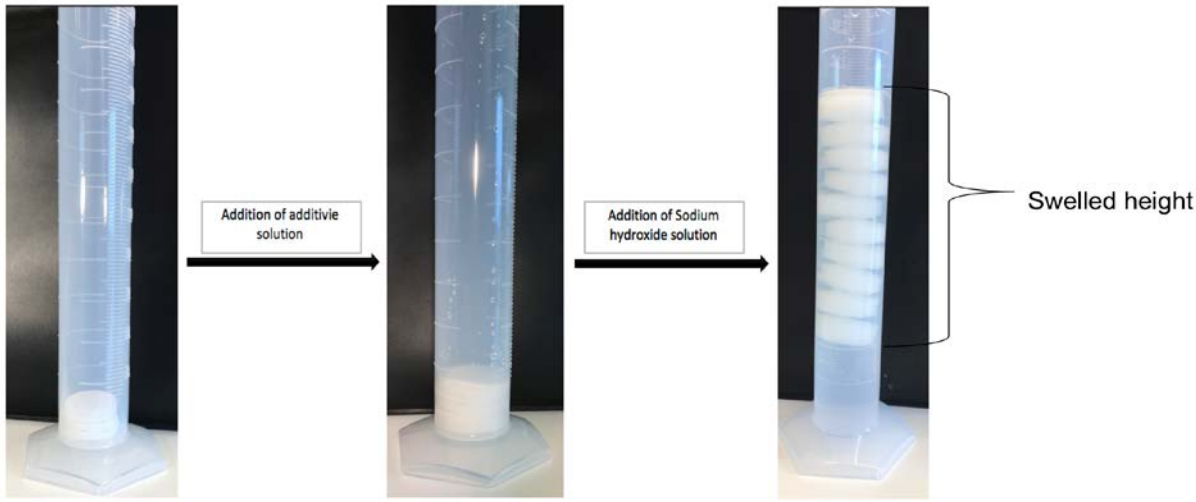


*Figure 13. Swelling procedure*

## 3.5 Procedure for Solubility Test in Sodium hydroxide and Sodium chloride

In this solubility test the Ethoxylated alcohols were dissolved into two different solutions, water solutions containing sodium hydroxide and sodium chloride regarding the molar equivalency of 0, 3, 5, 6, 9, 12, 15 and 18 w/w % sodium hydroxide. The exact molar percentages were calculated and solutions were prepared by diluting 30 w/w % sodium hydroxide with a 1 % stock solution containing reactivity additive that had been previously prepared.

Each solution was then prepared to a final volume of 15 ml with the above mentioned molar percentages. The solutions were filled in to vials and put into an oven with varying temperatures, to be able to find a change concerning solubility or phase-boundaries.

## 3.6 Procedure for Solubility Test in Acetone

Prior to the solubility test could begin the products were liquefied in an oven and turned into a homogenous solution. One gram of each product was added into a clean and dry Erlenmeyer flask. It was then dissolved in exactly 20 ml acetone and stirred until it had become a homogeneous solution. After that a burette was filled with Milli-Q water and the titration could start. The water was slowly titrated into the acetone product solution which was continuously stirred during the experiment. Water was added until the solution turned cloudy and the added volume from the burette was recorded. The volume of water added is

the Acetone-Water number and it gives information about the different products solubility characteristics.

## 3.7 Procedure for Ross – Miles Foaming Test

Further important property of the surfactants that needed to be analysed was their ability of foam formation. To determine this, the Ross-Miles foaming test was used. First the thermostat for the water surrounding the foaming tubes mantle was set to 50 °C. The foaming tube was then carefully rinsed out with ethanol and Milli-Q water to remove all left-over traces of previous experiments. As the desired temperature of 50 °C had been reached, the bottom valve was closed and 50 ml of a 0.05 % additive solution with a temperature as well of 50 °C was added.

A Ross-Miles pipette was then filled with an additional 200 ml of the same solution as mentioned above. The pipette was then placed on top of the tube and its contents emptied through a tap. As the additive solution was poured into the tube, the formation of foam could be recorded by measuring the height from the top of the foam down to the surface of the liquid. The time that it took for the foam to disappear was also recorded. After the experiment had been completed the foaming tube and Ross-Miles pipette were rinsed out with ethanol and water. The above steps were repeated for all the reactivity additives.

## 3.8 Procedure QCM-D measurements

To be able to understand furthermore how the reactivity additive works and interact with the cellulose pulp, QCM-D was used. First the cellulose coated QCM-D sensor were placed in a Milli-Q water bath for an hour, then the sensor was taken out with pincette and dried carefully with nitrogen-gas to ensure no water was present on the side where the electrode is placed. If water had been present on the side where the electrode was attached a shortcut would occur. The sensors were then placed inside the QCM-D apparatus and the swelling of the cellulose coated side on QCM-D sensor was studied. The process was closely studied on the computer, and as equilibrium occurred the next solution could be injected to the QCM-D sensor. The solutions used during this analysis were salt-water solution and salt-water with reactivity additive solution. The salt concentration was 9,98 molar-% and the reactivity additive was the same as in the swelling test.

## 3.9 Procedure Water Retention Value

By utilization this technique the water retention value (WRV) can be investigated and information about the swelling of cellulose can be gathered. The first step in the method was to prepare the same kind circle that was used in the swelling studies, with a weight of about 650 mg of pulp. Each circle was then placed inside a beaker containing and additive solution and was allowed soak for 30 minutes, after which sodium hydroxide was added and the swelling could carry on for another 2 hours and 30 minutes, the beaker was shaken every hour. The excess water was filtered away under suction with a Büchner funnel until no visible water appeared. The swelled pulp was placed inside a Vivaspin-tube, the centrifuged was then balanced with the samples and water, so that the centrifuge could function properly. The samples were then centrifuged for 10 minutes at 4000 rpm, after which the

wet cellulose samples were weighted and place in an oven at 105°C over one night. The next morning the dried samples were weighted. The water retention value was calculated with the following formula.

$$WRV = \frac{m_{wet\ cellulose} - m_{dry\ cellulose}}{m_{wet\ cellulose}} * 100\%$$

### 3.10 Procedure for scanning electron microscopy

The first step in the procedure for the electron microscopy was sample preparation. The same cellulose pulp that was used during the swelling studies was treated with different solutions of reactivity additive and sodium hydroxide. Swelling of the pulp took place in the same conditions regarding time and concentration as in the WRV-analysis.

Once the pulp had been swelled, excess solution was filtered away with a Büchner funnel. All the samples that contained moisture were then freeze dried until all traces water had evaporated from the samples. A small amount of the dried fibres was then put on top of small stubs, that had been lined with double-sided tape. To allow for conductivity and thereby detection in the scanning electron microscope, the fibres were the coated with gold using a sputtering coater for one minute and 20 seconds. Gloves were word during the entire procedure when handling the samples, this way any contaminations could be avoided. The prepared samples were then placed on a holder which was put inside the SEM, and the air in the chamber was evacuated. During the experiment a range of different magnifications were used, ranging from 200 to 8000 times in magnification. The current of the electron beam was also varied through the experiment, so that a retain a high-resolution image could be obtained depending of the magnification.

## 4 Results and Discussion

### 4.1 NMR-analysis

During the ethoxylation of 2-ethylhexanol using the two different procedures, six non-ionic surfactants were yielded that all had different degrees of ethoxylation, distribution of chain length and composition. The $^{1}$H-NMR and $^{13}$C-NMR analysis gave detailed information about the synthesised products, including which by-products had been formed and the quantity of them. An example of one of the gathered NMR-spectrums can be seen bellow, and each peak has been marked with its corresponding atomic position in the molecules that are seen bellow the spectrum (Figure 14 and 15).

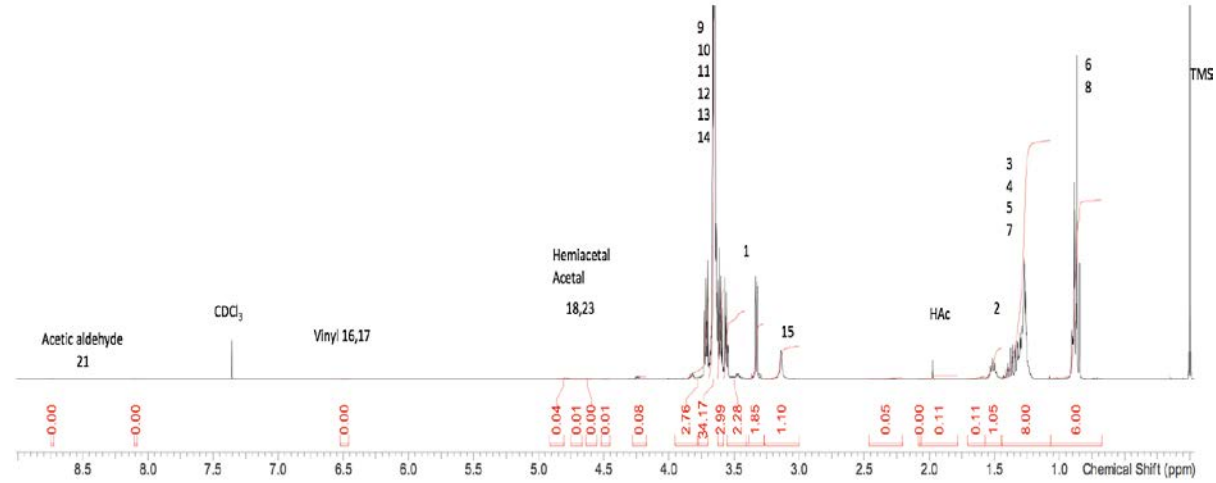


*Figure 14: Example of a $^{1}$H-NMR - spectrum*

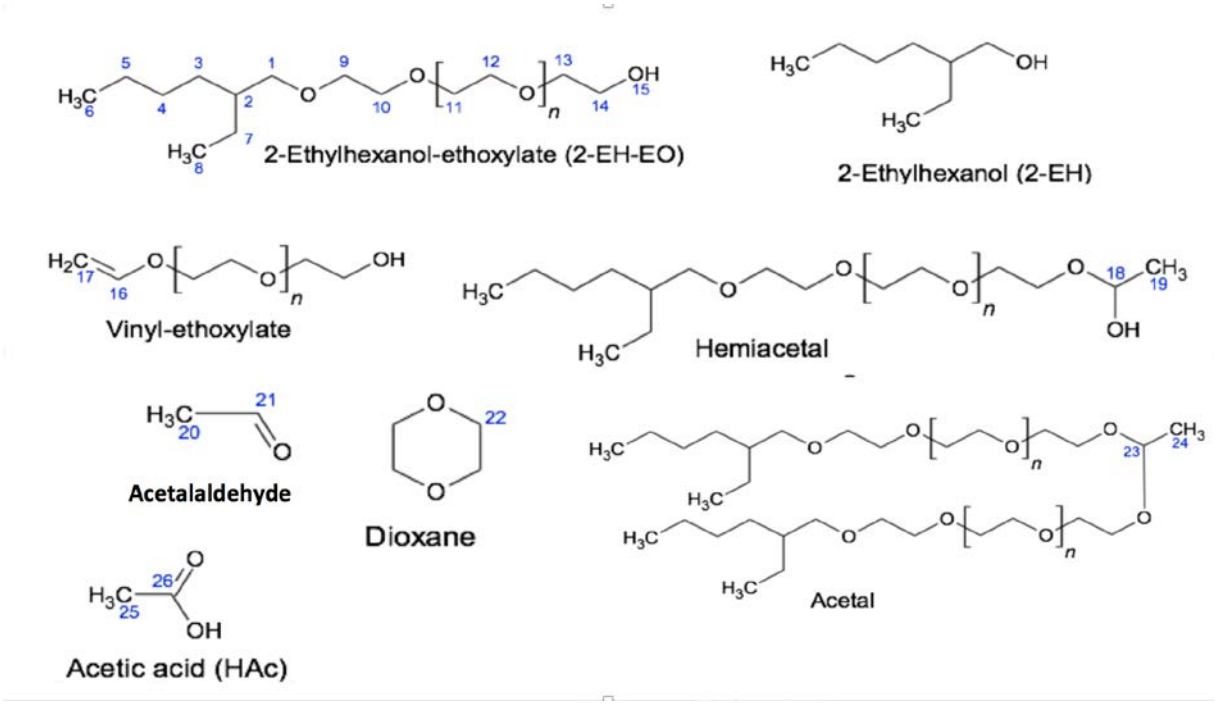


*Figure 15: Molecular structure of products and by-products*

The $^{1}$H-NMR and $^{13}$C-NMR spectra for all the products are located in the appendix, the example spectrum is used to identify the peaks and corresponding substance. The reason for performing two types of NMR in this experiment was to obtain as much information of the products as possible. For the determination of the amount of unreacted alcohol the $^{1}$H-NMR alone did not give us enough information. $^{13}$C-NMR has a greater spectral width and therefore enabled us to determine the amount of unreacted alcohol by being able to differentiate which peaks correspond to the alcohol. In the $^{1}$H-NMR they were not distinguishable due to signal overlap and couplings and to the smaller spectral width for $^{1}$H-NMR measurement.

*Table 1: Composition of products in molar-percentages*

| | Narrow Range 10-EO | Narrow Range 15-EO | Narrow Range 25-EO | Broad Range 10-EO | Broad Range 15-EO | Broad Range 25-EO |
|---|---|---|---|---|---|---|
| Ethoxylation degree | 10,55 | 15,43 | 25,05 | 10,37 | 15,47 | 25,02 |
| Acetic acid | 3,8 % | 3,3 % | 3,2 % | 3,8 % | 3,3 % | 3,4 % |
| Acetal | 5,9 % | 5,5 % | 7,8 % | - | - | - |
| Ester | 4,1 % | 4,6 % | 2,2 % | 3,5 % | 4,6 % | 5,8 % |
| Vinyl - ethoxylate | 0,1 % | 0,3 % | 0,3 % | - | 0,1 % | 0,4 % |
| Unreacted alcohol | 1,3 % | 1,7 % | 0,3 % | 9,8 % | 4,6 % | 1,2 % |

As seen in table 1 above and the NMR spectra for all the products in the appendix, the products formed were not only our targeted ethoxylated surfactants, but also quite some by-products. To begin with the first thing that can be noticed in the NMR-Spectra is the amount of unreacted alcohol. Although some amount is present in all the synthesised products, the largest amount is seen in the broad range with 10 and 15 EO added. With 9,8 mole % in the broad range ethoxylate with 10 EO it makes up a relatively substantial amount of the composition. Information about the degree of ethoxylation is also obtained by the NMR- analysis. It showed that all the synthesis had come quite close to the target chain length of 10, 15 and 25 molar equivalents of ethylene oxide added to the starting alcohol.

However as further ethoxylation was carried out and as products with longer chain lengths were synthesised the unreacted amount of alcohol was decreased for the broad range surfactant. It also needs to be noted that this composition was in molar percentages. The ethoxylated surfactants molecular mass is far greater than that of the unreacted fatty alcohol as the chain lengths are increased, meaning that the composition of unreacted alcohol in weight % is lower than in mole%. Controlling the amount of unreacted alcohol in the product is not only important for ensuring a high degree of conversion for the reaction, but also in some applications the more volatile unreacted alcohol gives of a rather unpleasant odour.

There is some acetic acid present in the products which can be seen by NMR analysis. The content is ranging from 3-4 mole % in all the products. The acetic acid is introduced to the surfactants after the synthesis in order to neutralise the KOH-catalyst. The content in weight % is much lower than the mole% as the molar mass of acetic acid is much lower than that of the fatty alcohol ethoxylate.

Other interesting by-products that had been formed during the synthesis were the different acetals. They only form in the narrow range ethoxylated products. A dramatic difference can therefore be seen in how much acetals the broad and narrow range surfactants contain (see structural differences of acetals in Figure 15 above). The higher acetal content in the narrow range surfactants could once again be linked to the catalyst that had been used during the first step of synthesis which was under acidic conditions. The Lewis-Acid catalyst is

coordinating to the oxygen atoms in the ethylene oxide chain, and in a rearrangement ethylene oxide is converted to acetic aldehyde which can react further and form acetals. Since the Lewis-Acid catalyst also gives rise to formation of dioxane the catalyst is only used for an addition of up to 5 moles of ethylene oxide per mole of starting alcohol, and then a change of catalyst to KOH was done to prevent further formation of by-products.

Traces of vinyl-ethoxylates and esters could also be found in the products. These form at high reaction temperatures during the ethoxylation. They were the most abundant in the broad range surfactant with a longer ethoxylate chains like the one with 25 moles of EO added per mole of starting alcohol.

## 4.2 HPLC-UV-analysis

When an alcohol is ethoxylated during a synthesis, not only one specific surfactant with a fixed chain length is formed, but instead many different varieties of this ethoxylated alcohol are obtained. Together the ethoxylated alcohols form a distribution of surfactants with different ethylene oxide chain lengths. How such a distribution curve looks is largely affected by the catalyst used. The following chain length distribution curves were constructed from the normal phase liquid chromatography analysis of the broad and narrow range surfactants produced in this project.

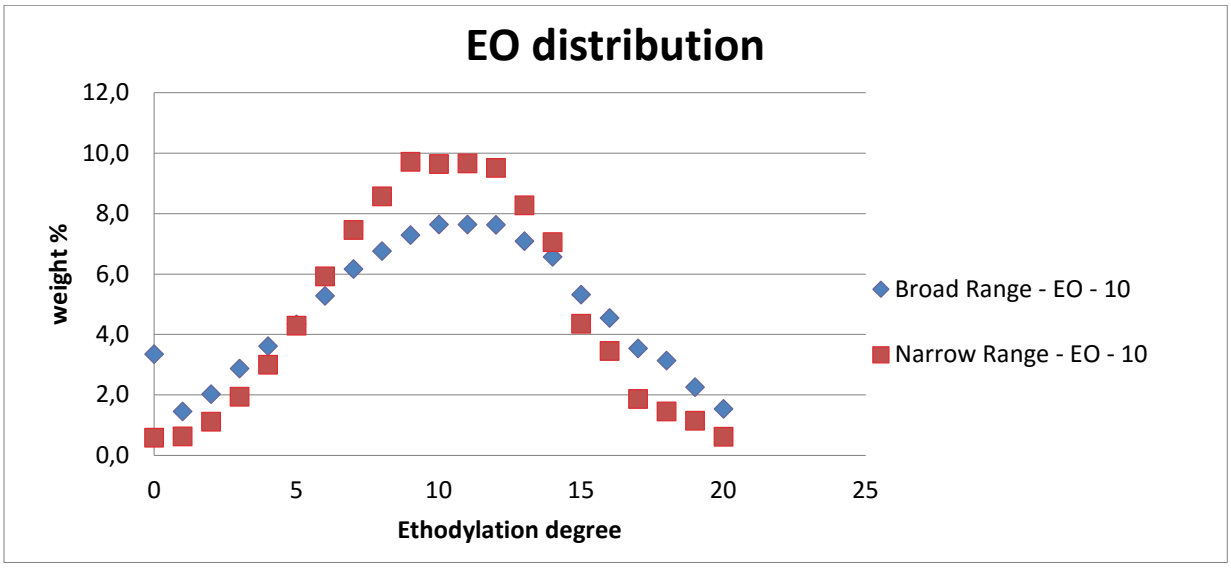


*Figure 16: LC-UV Distribution with EO-length 10*

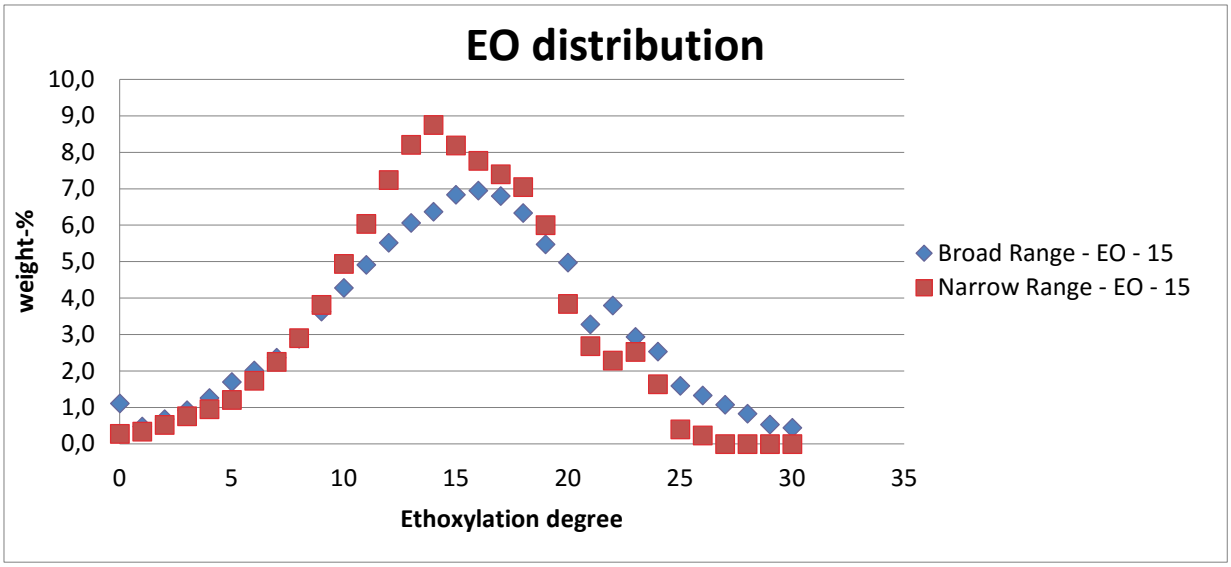


*Figure 17: LC-UV Distribution with EO-length 15*

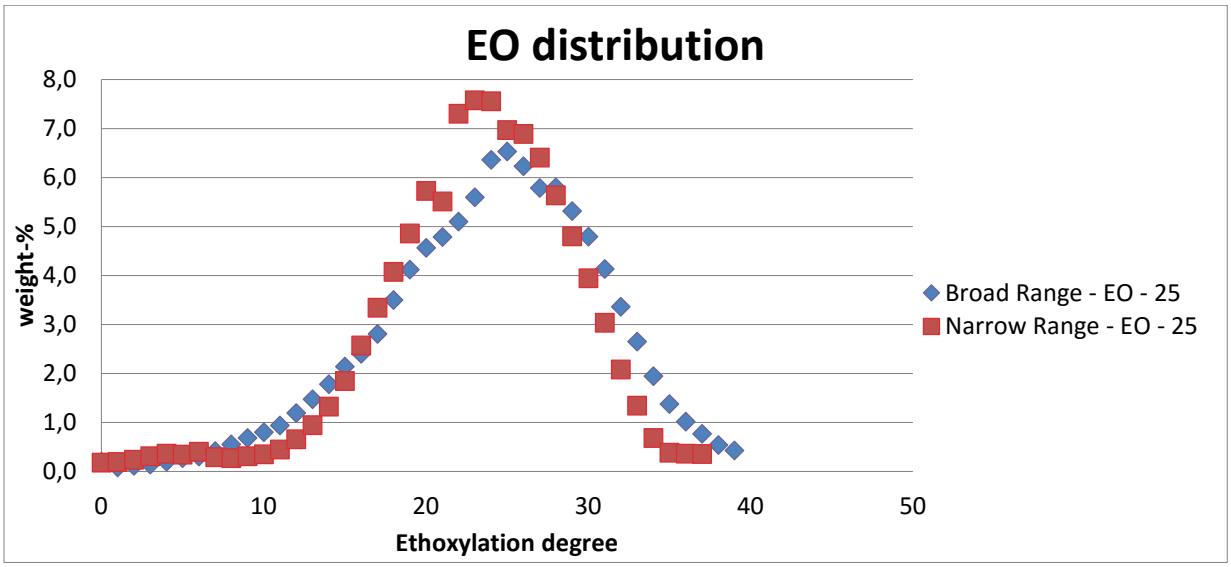


*Figure 18: LC-UV Distribution with EO-length 25*

As the area of each peaks in the chromatograms was multiplied with its corresponding molar mass, clear differences in the distribution of chain length could be seen amongst the alcohol ethoxylates with the same average chain length. It was clearly visible that the distribution for the narrow range surfactant had a shape that was more peaked around a specific chain length and thus containing a larger amount of the targeted surfactant. The predicted properties of each catalysts were confirmed and the results seemed to support what was found during the NMR analysis.

The larger amount of unreacted alcohol in the 10 and 15 EO surfactants was clearly visible in Figure 16 and 17 above, it could be seen in the start where the ethoxylation degree is zero in the diagrams. Due to the shape of the distribution curve there was also a larger amount of longer chained alcohol ethoxylates in the broad range surfactant. Also, noticeable by looking

at the curves is that the longer the EO chains get, the smaller the difference between the broad- and narrow range surfactants in terms of chain length. To a certain extent this might be explained by, the fact that ethoxylation continues in the pursuit of the longer chained ethoxylates, both more alcohol is reacted away and that the final chain length seems to centre around a single value when the broad- and narrow range surfactants are compared. The conclusion can be drawn by observing the chromatograms, that the catalyst chosen for the synthesis seems to have a larger influence on the chain length distribution when surfactants are produced with a lower degree of ethoxylation in the ranges of 0 to about 25 EO.

## 4.3 Swelling

The swelling results are divided into two different areas concerning weight and height, when analysing the data one can draw the conclusion that the reactivity additives and reference product increases the pulps ability to swell in height and absorb more fluid. The broad range and narrow range products performs better than the reference product in both cases, when studying the graph displaying the height, it is also clear that the swelling is increasing more rapidly than the reference product in the interval between five and six minutes. This behaviour can be seen below in Figure 19 and 20.

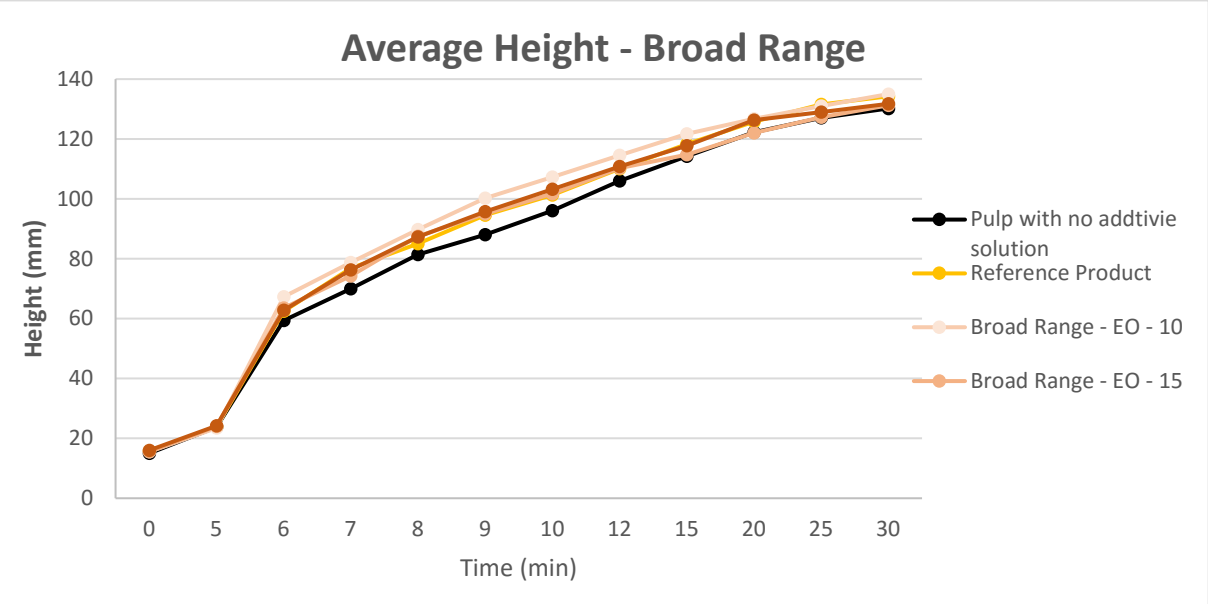


*Figure 19: Average Height - Broad Range*

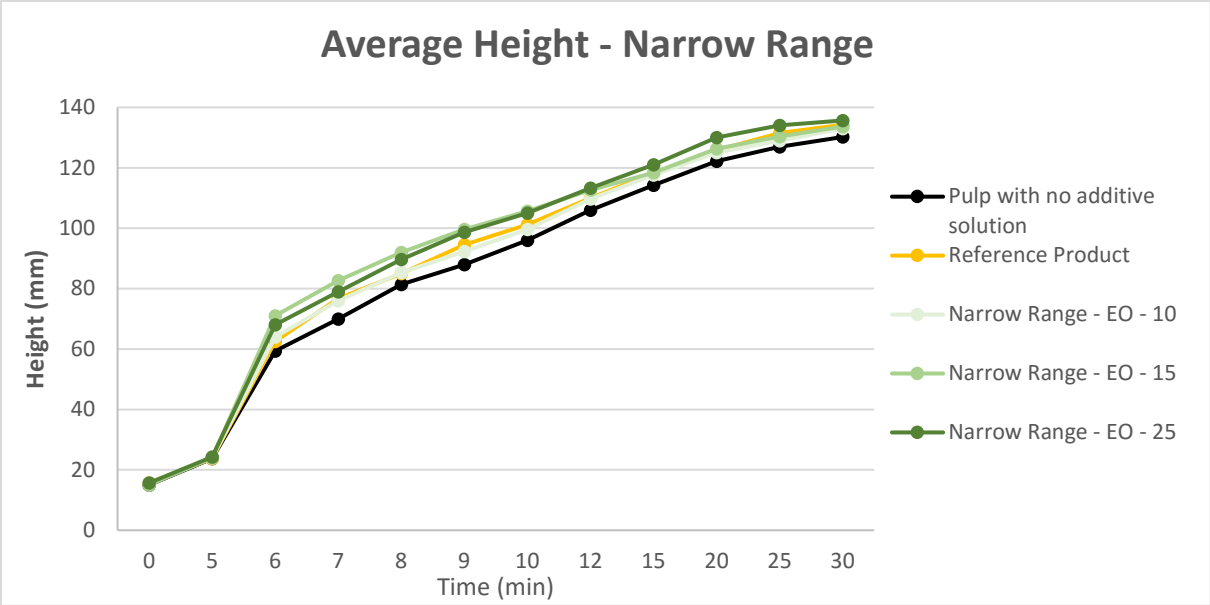


*Figure 20: Average Height - Narrow Range*

The data shows that the Broad Range with EO-length 10 got the highest height value and that the EO-length 25 performs best at weight. The narrow range on the other hand with EO-length 25 performs best on both weight and height, see Figure 21 and 22. When comparing the narrow range to the broad range it is clear from the graph with weight vs height that the Broad Range EO-25 absorbs most weight and that Narrow Range EO-25 got highest value on height, a comparative chart between the height and weight for the different reactivity additives can be seen in Figure 23.

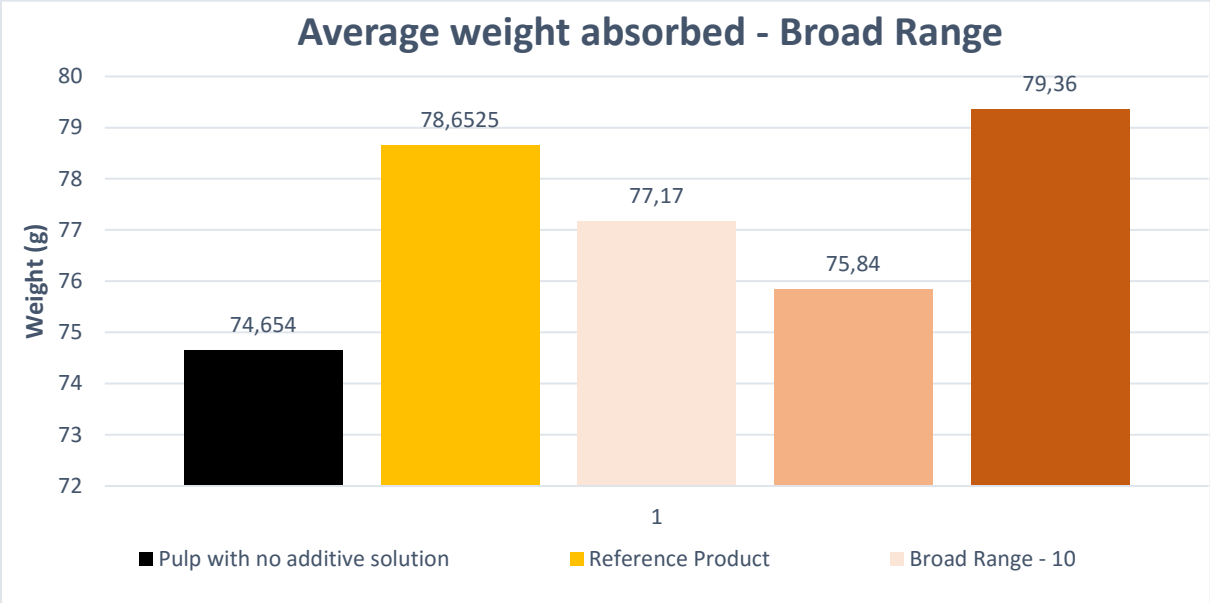


*Figure 21: Average Weight - Broad Range*

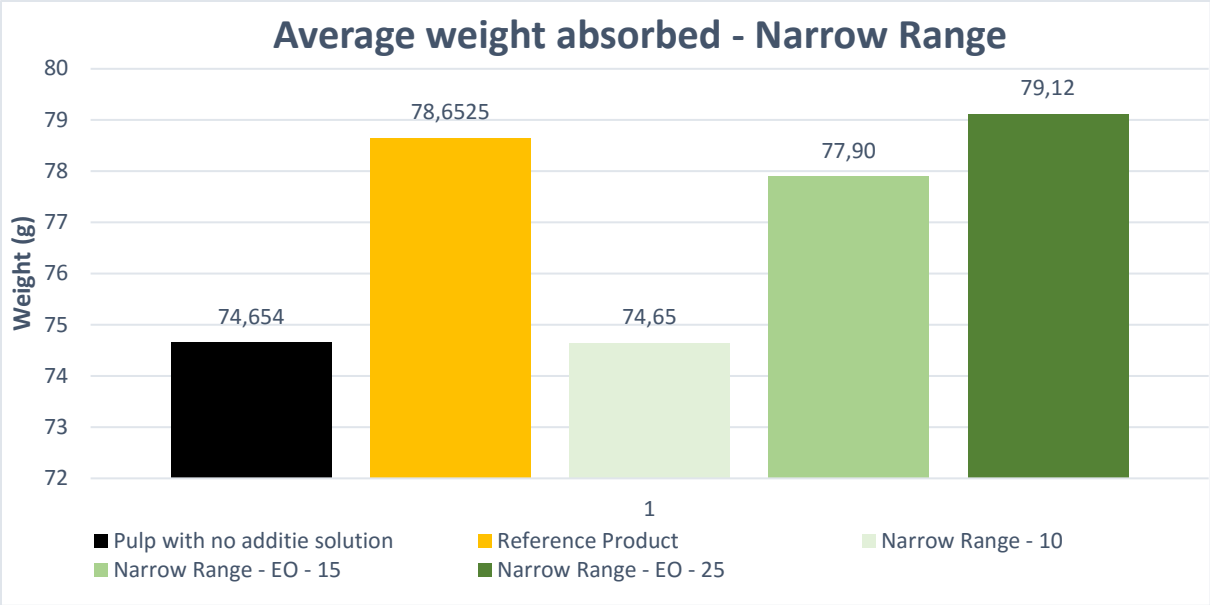


*Figure 22: Average Weight - Narrow Range*

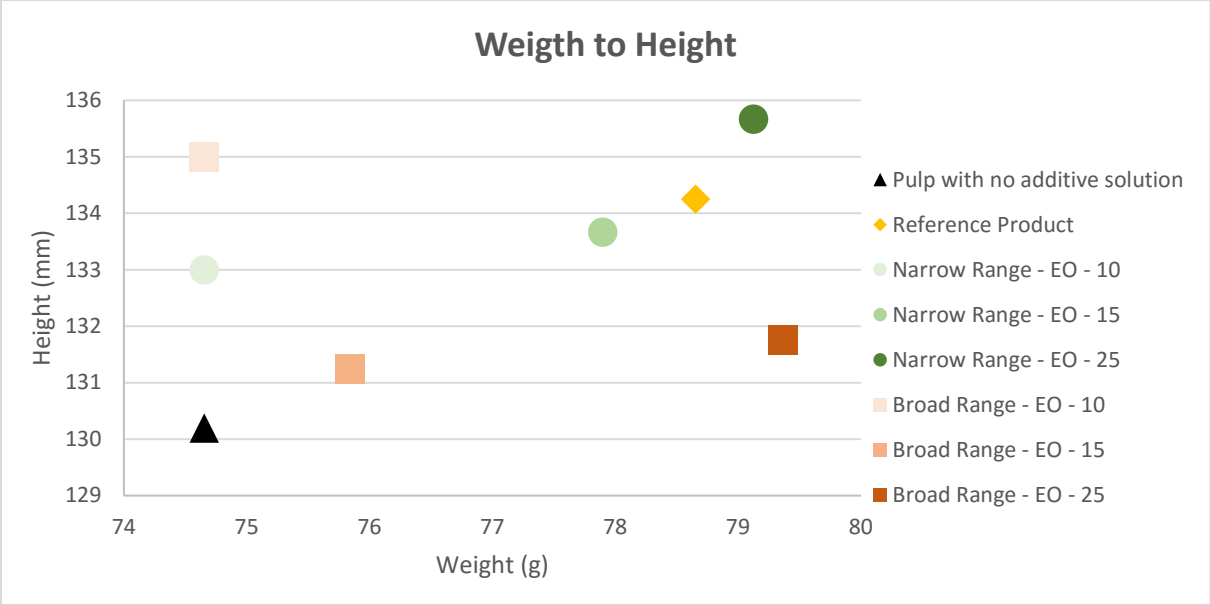


*Figure 23: Weight vs Height*

One can also speculate in the effect that the larger chain lengths have upon the swelling of cellulose. Cellulose by nature is a hydrophilic compound, but such as many other polymers it contains as previously mentioned both highly oriented (crystalline) regions and amorphous ones. These crystalline regions of cellulose do not swell easily in water, due to their compact structure. This may be where the chain length of the reactivity additive comes into play. The longer the chain length of the alcohol ethoxylate, the longer the hydrophilic EO-chain is. And this may allow for a greater attraction between the reactivity additive and the cellulose polymer and thus a greater capability to swell the cellulose.

## 4.4 WRV-Water Retention Value

To further strengthen the result regarding the weight absorption of cellulose, the water retention value for pulp that had been swelled in presence of the synthesised surfactants was evaluated. The water retention value offers a more accurate alternative with fewer possible sources of error. It is a better way of analysing the influence of reactivity additives concerning the weight of the swelled pulp and to determine the weight gained by the pulp directly. By swelling the pulp in a sodium hydroxide solution together with the reactivity additives, and then centrifuging away excess solution and drying it, offers an alternative estimation of the effect that the ethoxylated surfactants had upon the swelling of cellulose. The water retention value, as calculated in this project also takes the weight difference of the pulp prior to the swelling into consideration, it eliminates the factor where each circle of pulp has a different weight.

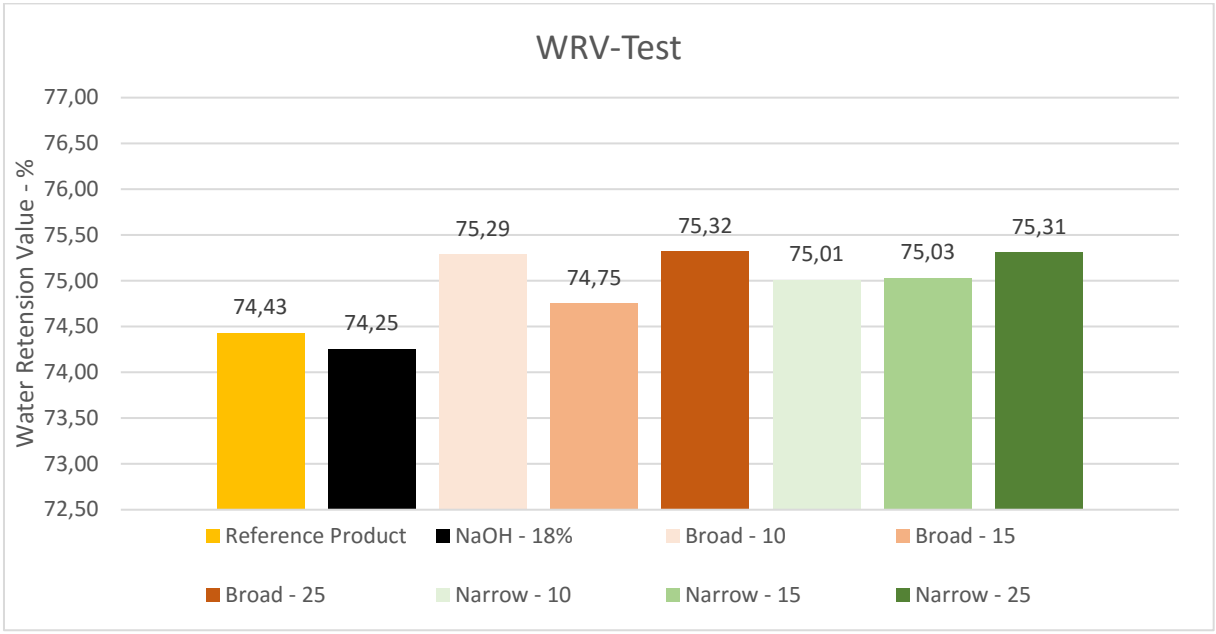


*Figure 24: Water Retention Values*

Many of the trends that could be seen during the swelling studies regarding the weight increase could be further confirmed during the water retention value analysis. In Figure 24 once again we see that only using sodium hydroxide for the swelling of cellulose results in the smallest weight increase. Also noticeable is that all the broad- and narrow range reactivity additives performed better than the reference product in this experiment.

When comparing the reactivity additives in between each other, the same products that stood out in the swelling studies regarding their potential of increasing the swelling of cellulose stood out in the water retention value experiment. Although not by a great margin both the broad- and narrow range surfactant with a chain length of 25 EO performed the best in this experiment.

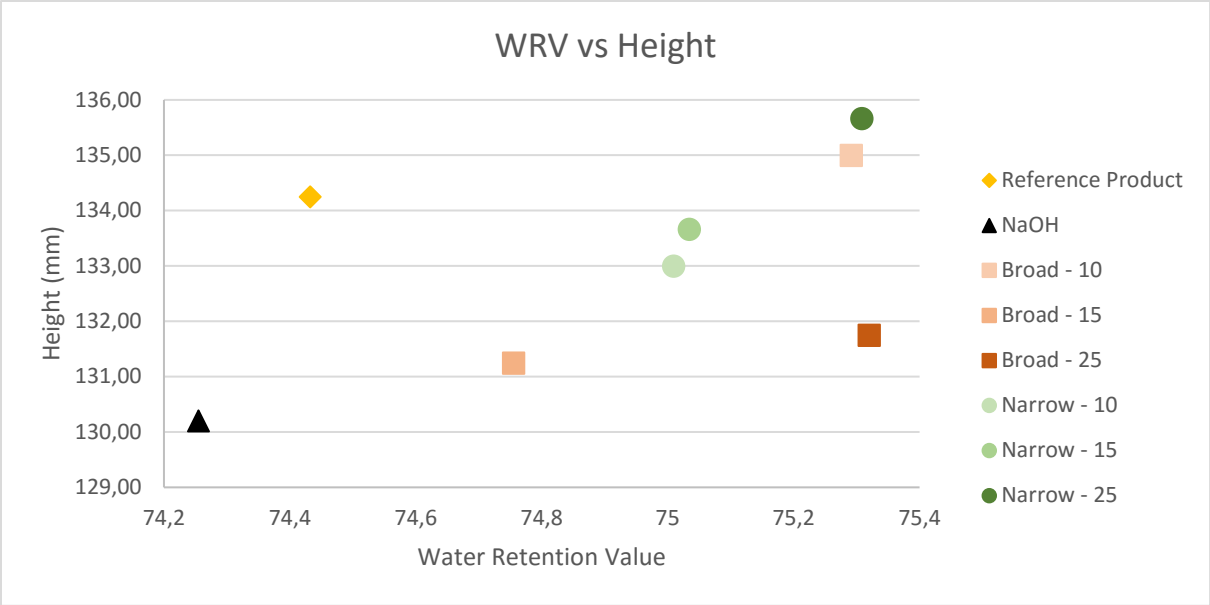


*Figure 25: WRV plotted against swelling height*

When the WRV values are plotted with the data collected from the swelling studies it gives us a better understanding concerning the differences in performance the different reactivity additives. The narrow range surfactant with an EO-length of 25 is once again performing better than the other alternatives when height and WRV are considered together. Interesting is also that the broad range surfactant with an EO-length of 10 seems to have a higher WRV-value than it had in comparison to the other reactivity additives during the swelling studies when considering weight gain. This analysis once again highlights the fact that all the reactivity additives including the reference product have a significant effect upon the swelling of cellulose.

## 4.5 Solubility test

### 4.5.1 Acetone-Water Test

To be able to understand the solubility properties of for the reactivity additives furthermore an acetone water test was conducted. As water was added into the acetone solution containing the products, a visible change in the cloudiness of the solution could be noted. At this point where the transition took place, the acetone was no longer capable of keeping the products and by-products dissolved in the solution, due to the added amount of water. The data from the test can be seen in Figure 26 below.

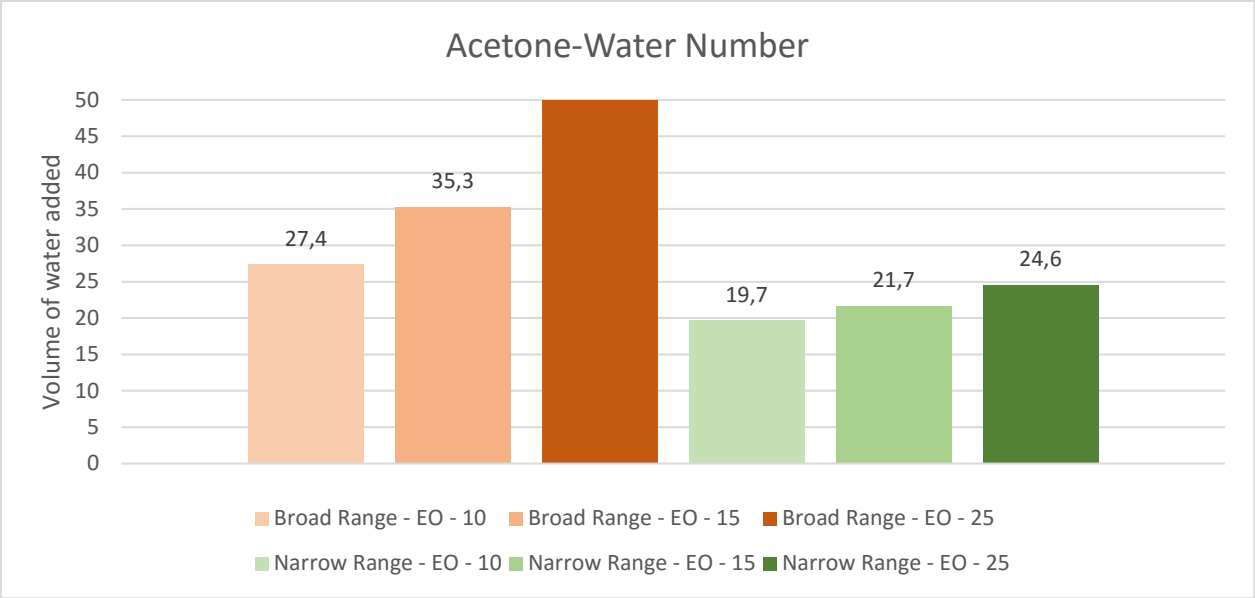


*Figure 26: Acetone Water-test*

Noticeable was that all the products are dissolvable in acetone, however the solubility when the water had been added varied between the products. It is clear from the data that the broad range surfactants are more soluble in water than narrow range. This can once again be traced back to the difference in composition concerning the number of by-products and chain lengths. The acetals is probably the reason for the lower acetone water number for the narrow range ethoxylates. This procedure did not however give us any information about broad range EO-25 because it was fully dissolvable in water.

### 4.5.2 Solubility in NaOH and NaCl-solution

The solubility was performed in two different solutions containing NaCl and NaOH. The data from the solubility test shows that reactivity additives are more capable to dissolve in NaCl than in NaOH. The observations that were made during the analysis were that the products either became clear, cloudy or phase separated. If the samples that were cloudy were allowed to rest for some time they all became phase separated, however for this change to happen to all the products more time would have been needed. It was still clear though that products that gave both cloudy and phase separated solutions were not soluble in the current conditions.

× = Cloudy, ● = Phase separation

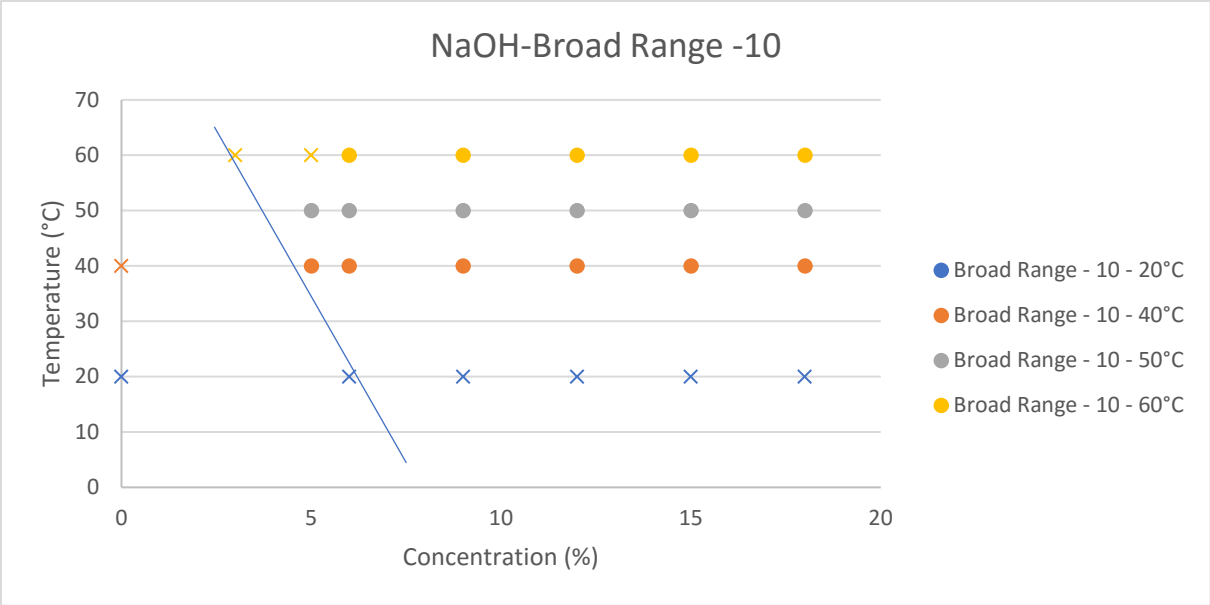


*Figure 27: Solubility Test – NaOH - Broad Range EO-10*

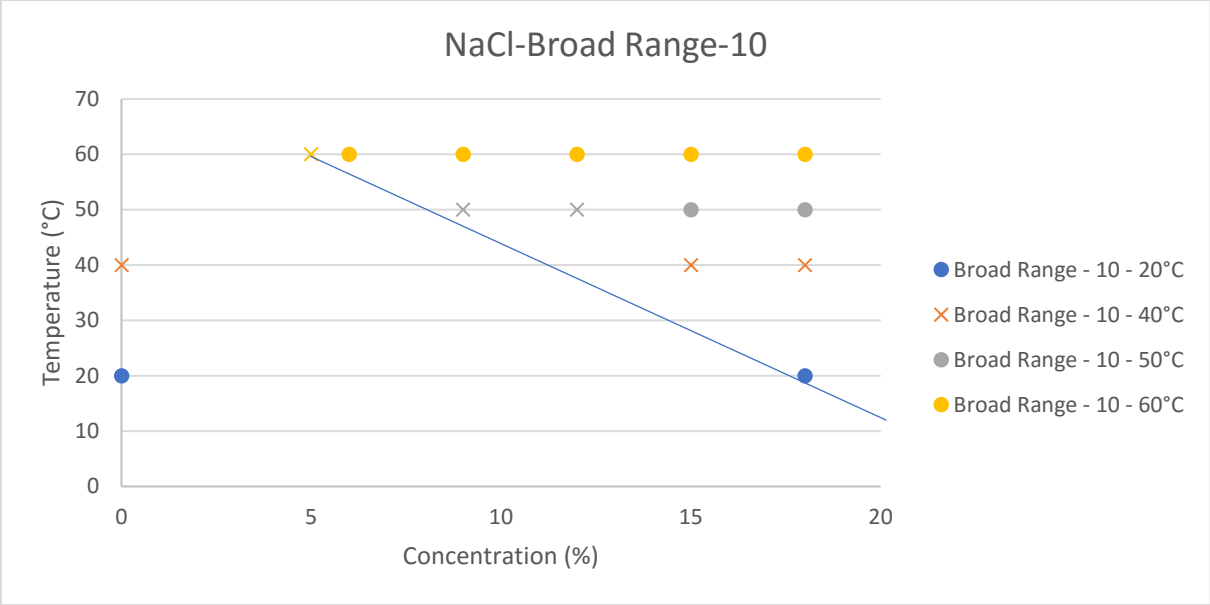


*Figure 28: Solubility Test - NaCl - Broad Range EO-10*

The effect of increasing the temperature of the solutions was also found to have a connection to the capability for the products of being dissolved in the various solutions. When looking at the broad range products, it was clear that an increase in temperature decreased solubility in the concentrations where it was capable of being dissolved. If one looks at the narrow range surfactants the solubility behaviours became far more complex. When the temperature was increased, it seemed that some of the by-products (acetals) only present in the narrow range products increased the solutions capability of being dissolved. The acetals in the surfactant create more ramifications in the structure making it harder to dissolve and interact with the solution.

For the solubility test in NaCl the results were much more consistent between the broad- and narrow range surfactants. As the temperature was increased all products behaved the same, meaning that the lower concentration of salt and temperature the higher the solubility. It was also observed that when for the longer chained surfactant, the solubility at higher temperature and concentrations of salt increased.

This ability to dissolve better in NaCl than NaOH is because of the Hofmeister series, which is based on how well ions can salt out or salt in proteins in an aqueous solution. The salt increases the solubility of nonpolar molecules, making the hydrophobic part weaker, when increasing the amount of salt the nonpolar molecules will salt out making it unsolvable. The reactivity additives are non-ionic surfactants making it more soluble for the salt solution than the NaOH one. The exact behaviour for all the reactivity additives can be seen in the appendix.

## 4.6 QCM

To be able to understand the swelling of cellulose and the reactivity additives affect upon it, QCM was a suitable method. The first step in the experiment was to established reference value when swelling cellulose with only a salt-water solution. It was found to result in an average mass increase of 70,8 ng/cm$^2$. To this value, the effect of the Narrow range product with a chain length of 25 EO could be compared. Experimental trials were also done with pure solutions of sodium hydroxide, to be able to determine the tolerance level of sodium hydroxide on the cellulose coated QCM-D sensor. The solutions contained concentrations of 0.001, 0.01, 0.1 and 1 Molar. The cellulose sensor functioned properly until the solution of 1 Molar sodium hydroxide was applied, the coating then started to disassemble from the sensor.

*Table 2: Mass change from QCM analysis*

| **QCM** | | |
|---|---|---|
| **Attempt:** | **Water → Water + Salt: (ng/cm$^2$)** | **Salt → Salt + Additive (ng/cm$^2$)** |
| **1** | 88,5 | 187,62 |
| **2** | 70,8 | 258,42 |
| **3** | 53,1 | 249,57 |
| **Average Value:** | 70,8 | 231,87 |

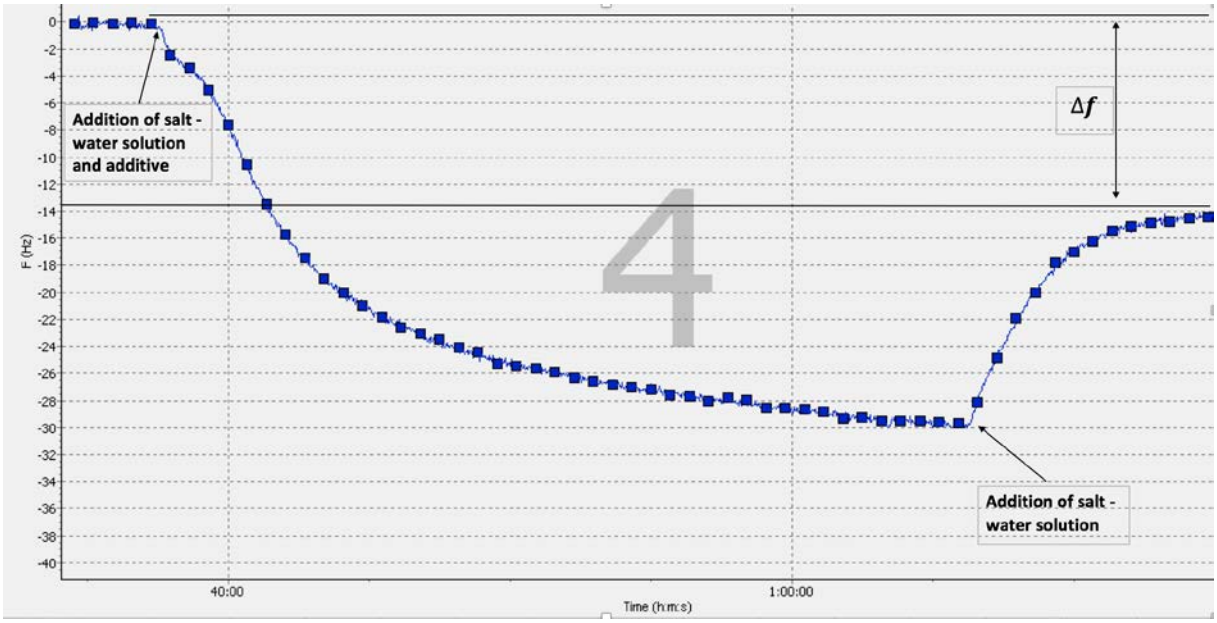

*Figure 29: QCM - Scheme for NaCl and Reactivity Additive solution*

Once the QCM sensor had been treated with a salt-water solution containing additive, an even greater change in mass could be detected during the QCM- analysis. From Figure 30 above it can be seen the frequency went down as the solution containing additive was applied. As the frequency had centred on a fixed value and the pure salt-water solution once again was applied a clear change in frequency could be noted. By the decrease in frequency, the conclusion could be drawn that there was both an adsorption of the reactivity additive on to the cellulose coated sensor, as well as that a certain amount of swelling had taken place. The resulting mass change was measured to an average of 231,81 ng/cm$^2$ for the three trails that were run. This experiment further confirmed the reactivity additives ability to cover the cellulose, bind to it and cause an elevated amount of swelling compared to only using a saltwater solution. It could also be noted that the dissipation was increased when the solution containing reactivity additive was applied.

## 4.7 Foaming

As mentioned above in the theory section one step in the viscose process comprises a deaerating procedure with nitrogen gas, the reactivity additives inside the reaction vessel will then start to create foam. The less foam the better for the equipment, because foam needs volume and that is a limiting factor.

From the foam test, it is easy to draw the conclusion that all products perform better in terms of foam height and durability of creating foam from the point where no further solution was added. The reference product got the highest foam height and took the longest time to disappear, whereas the broad and narrow range products could only create foam when the solution was added. However, they disappeared the second the solution in the Ross-Miles pipette had been emptied. The foam height was much shorter than the reference product and between the broad- and narrow range there was only a difference of 2 mm. This means that foaming is not an issue for the surfactants produced in this project.

*Table 3: Foaming data*

| Substance: | Foam height: | Time until disappearance of foam: |
|---|---|---|
| Broad Range 10-EO | 15 mm | 0 sec |
| Broad Range 15-EO | 15 mm | 0 sec |
| Broad Range 25-EO | 17 mm | 0 sec |
| Narrow Range 10-EO | 10 mm | 0 sec |
| Narrow Range 15-EO | 10 mm | 0 sec |
| Narrow Range 25-EO | 15 mm | 0 sec |
| Reference Product | 55 mm | 13 sec |

As the hydrophobic part of the surfactant increases, meaning that the chain length of the EO becomes longer, the tendency of creating foam was increased. From HPLC-UV analysis it could also be seen that the Broad range contained larger amount of longer chain length of EO.

From the NMR analysis, it was clear that the narrow range product contained more acetals than the broad range, the acetals have the characteristics of reducing foam. The combination of more acetals and slightly less amount of longer chains of EO in the narrow range products, creates a small but visible difference of foaming between the broad- and narrow range products.

## 4.8 SEM

By using a scanning electron microscope, the cellulose fibres that had been treated with the different solutions could be observed and examined in great detail. At a lower level of magnification, around 1000 times a good overview of the cellulose fibres could be seen in figure 30 below. The most pronounced difference at this magnification between the fibres was that the sample that had been swelled in a sodium hydroxide solution, had a clear coating of crystals on the surface. The fibres treated with the sodium hydroxide solution also appeared to be more ruptured than the untreated fibres, as well as a certain amount of exfoliation could be observed due to the collapse of the fibres after the swelling and freeze-drying.

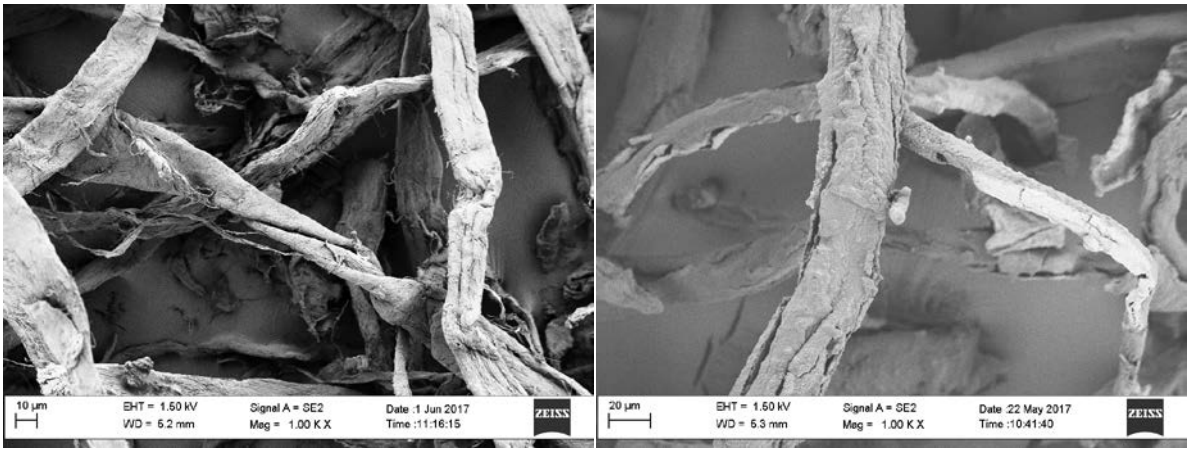


*Figure 30: Picture to the left is a sample with 1 % additive solution, to the right is a sample with additive and NaOH solution*

In further attempts to see any possible differences between the different samples, a higher magnification of 8000 times was applied. Again, no visible differences between the samples that had been treated with sodium hydroxide could be seen. At this magnification however, the surface of the fibres could be more closely studied and the previously mentioned crystals of sodium hydroxide were clearly visible in figure 31. More details also appeared on the samples that had been analysed without being treated with sodium hydroxide. Here the single fibrils on the surface of the cellulose fibres could be observed and a smoother surface was noted.

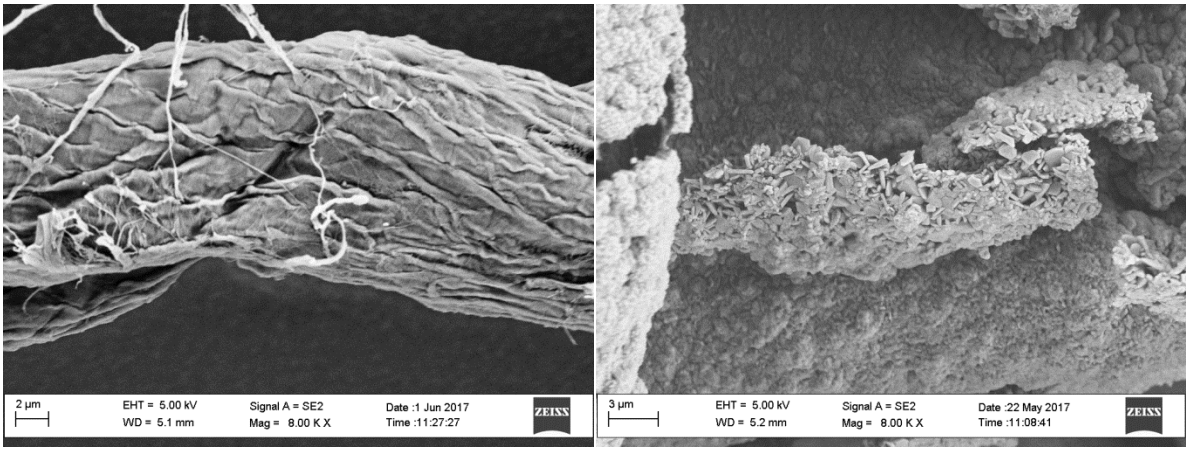


*Figure 31: The picture to the left is a sample with additive solution, to the right is a sample with additive and NaOH solution*

With this experimental procedure, no accurate conclusions could be drawn considering the effects that the different additives had on the cellulose fibres, as well as what influence the sonication had. The technique proved not to be applicable as used during this experiment for studying the influence of the reactivity additives upon the structure of cellulose. Perhaps to be able to see a clearer indication of how the reactivity additives affected the cellulose structure another method might be more suitable.

# 5 Conclusion

During this diploma work six non-ionic ethoxylated surfactants were synthesised and evaluated as reactivity additives for the viscose process. After the synthesis, structural analysis that included NMR and HPLC was carried out on the products, with the purpose of obtaining information about their composition and distribution of chain length. With the influence of these factors in mind, a series of applications tests were performed to evaluate the performance and characteristics of the synthesised reactivity additives. These included swelling studies, WRV, QCM, solubility tests and scanning electron microscopy. With the data and information gathered during these experiments conclusions about the reactivity additives influence upon the swelling of cellulose could be drawn.

It became very clear during the structural analysis that the usage of different types of catalyst had a large influence on the structure and chemical compositions of the synthesised reactivity additives. As the NMR analysis was completed, clear differences in the amount of unreacted alcohol could be seed in between the broad and narrow range products, with the broad range surfactants yielding a considerably lower conversion of the starting alcohol. The formation of by-products also was also quite different amongst the synthesised products, and in the narrow range surfactant a formation of acetals could be noted. The effect on the distribution of chain lengths for the two catalysts was also examined during the structural analysis with an HPLC analysis. As expected the Lewis acid catalyst narrowed the distribution down and peaked it to a greater extent than the base catalyst did.

When adding the results from all the different applications studies, one can draw the conclusion that the longer chain lengths with 25 EO generally performed better than the shorter ones with a chain length of 10 and 15 ethoxylates. During the swelling studies the effect of the longer chains lengths were more distinctive. The narrow range surfactant with a chain length of 25 was most effective concerning swelling of the cellulose pulp in terms of height. The broad range with a chain length of 25 was marginally better than narrow range surfactant with the same chain length in terms of weight absorbed. To further strengthen these conclusions the water retention value (WRV) for the different reactivity additives was analysed. The data from the WRV once again highlighted the fact that the alcohol ethoxylates with a chain length of 25 EO had a greater effect upon the swelling of cellulose pulp.

When drawing a final conclusion about which surfactant to use as a reactivity additive in the viscose process, it is clear that the narrow range surfactant with a chain length of 25 EO is the most appropriate one. It performs the best overall on all the applications analysis, it also reaches the highest conversion of starting alcohol which is beneficial for the production and in theory has a lower toxicity.

# 6 Recommendations and suggestions for further work

To obtain accurate and comparable results for the evaluation of reactivity additives and how they affect the swelling of cellulose, the method for conducting swelling studies needs some

improvement. The procedure used in this project was an industry standard and comparable trends were distinguished during the laboratory trails between the different additives. However, we believe that by improving a few key areas in the procedure even more notable trends could be seen and more accurate conclusions could be drawn.

The first difficulty that we noticed was to obtain a low spread on the swelled height between the different trails on the same product. If the raw data is analysed for the individual trials the swelling height during the experiment varies by quite a bit. During the first 15 minutes of swelling the height at each time point differs quite a lot in between the products. As the final measurement at 30 minutes was conducted the spread was smaller, however still noticeable. To draw accurate conclusions about the effect that different additives have on the swelling of cellulose a very large number of experiments would be necessary to compensate for the spread in the results obtained by this procedure. During this project about 3 swelling tests were made for each product. To ensure statistical accuracy for future work, it would be beneficial if the number of conducted tests would be increased. Using the current method however this would very time consuming, as it is hard for a single person alone to do more than one test at a time and each test takes about 30 minutes.

One way of solving this could be to identify which data points in the study are of greatest importance. During this thesis work it seemed that the final swelling height was of most interest for the evaluation of an additives performance, and thus rendering all the other data points redundant. If the measurement of all the intermediate heights could be cut out of the procedure, a lot of time could be saved. It would then be possible to conduct a larger number of tests to ensure statistical accuracy and also be time efficient.

A further difficulty in the pursuit of low spread and high accuracy results is linked to the measuring cylinder in which the experiments were conducted in. As done in this project the absorbed weight of the pulp sheets was measured by separating away the remaining sodium hydroxide and additive solution. The swelled pulp sheets were held in place with a stick and then the solution poured through a funnel. Perhaps a different type of measuring cylinder could be used, one with some kind of tap on the bottom. By minimizing all kinds of contact with the swelled pulp the results regarding absorbed weight would become could become more consistent.

Another alternative to the weighing procedure described above, would be to completely replace it with the method of analysing the water retention value of swelled pulp. As already mentioned in the results and discussion part of this thesis, it provides a more accurate way of interpreting the different reactivity additives performances. The results are far less influenced by the human error and the method also enables a far greater number of tests to be run on each product without consuming a lot of extra time.

A further method that would benefit from some additional development was the QCM analysis. During this thesis only one of the reactivity additives was examined due to limitations in time. For future studies however, it would be beneficial to analyse and

compare different additives against each other with this highly exact technique. Difficulties were also noticed when a low concentration of sodium hydroxide was mixed in with the salt and additive solution, even though the same concentration had been tested on a QCM sensor and there no complications were discovered. In one is to replicate the process parameters in the viscose process, a more careful procedure that includes sodium hydroxide would be necessitated for a better understanding of the effects the reactivity additives have upon the cellulose covered QCM sensor.

To further understand how the reactivity additives that were examined in this diploma work attach to the cellulose fibres a complementary type of microscopy would be useful. During this thesis only scanning electron microscopy was used and it did not give any information about how the reactivity additives covered the cellulose fibres, due to them not being visible in this method. Perhaps a technique involving fluorescence microscopy could be useful, if the reactivity additives were to be marked with a fluorescent molecule. Samples of cellulose could then be treated with the marked reactivity additives and analysed. Such a technique could give a greater understanding of how the additives distribute across a cellulose surface and attach to it.

# 7 Acknowledgements

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# Appendix 1

*Water Content measured with Karl-Fisher titration*

| **Product:** | Water Content: (%) |
|---|---|
| Broad Range 10-EO | 0,311 |
| Broad Range 15-EO | 0,23 |
| Broad Range 25-EO | 0,153 |
| Narrow Range 10-EO | 0,143 |
| Narrow Range 15-EO | 0,178 |
| Narrow Range 25-EO | 0,115 |

# Appendix 2

***Broad Range – EO – 10***

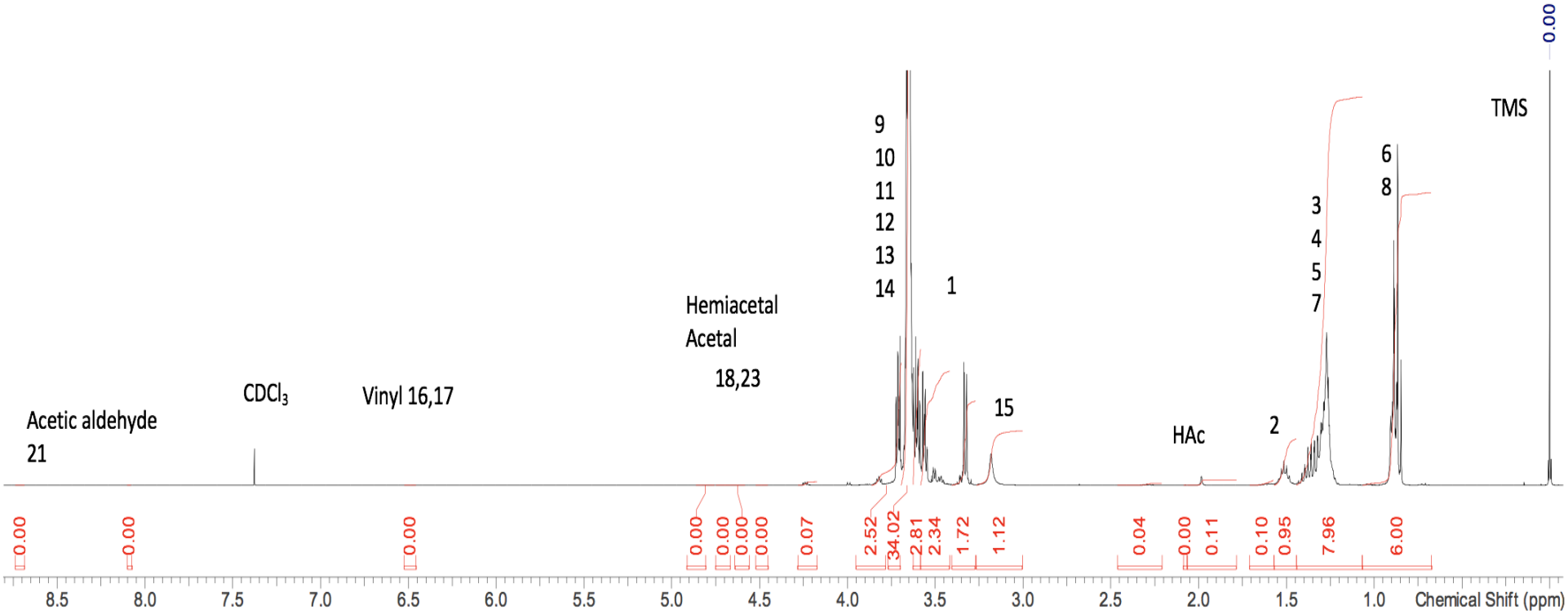



*Figure 1a. Proton NMR – spectra*

***Broad Range – EO – 10***

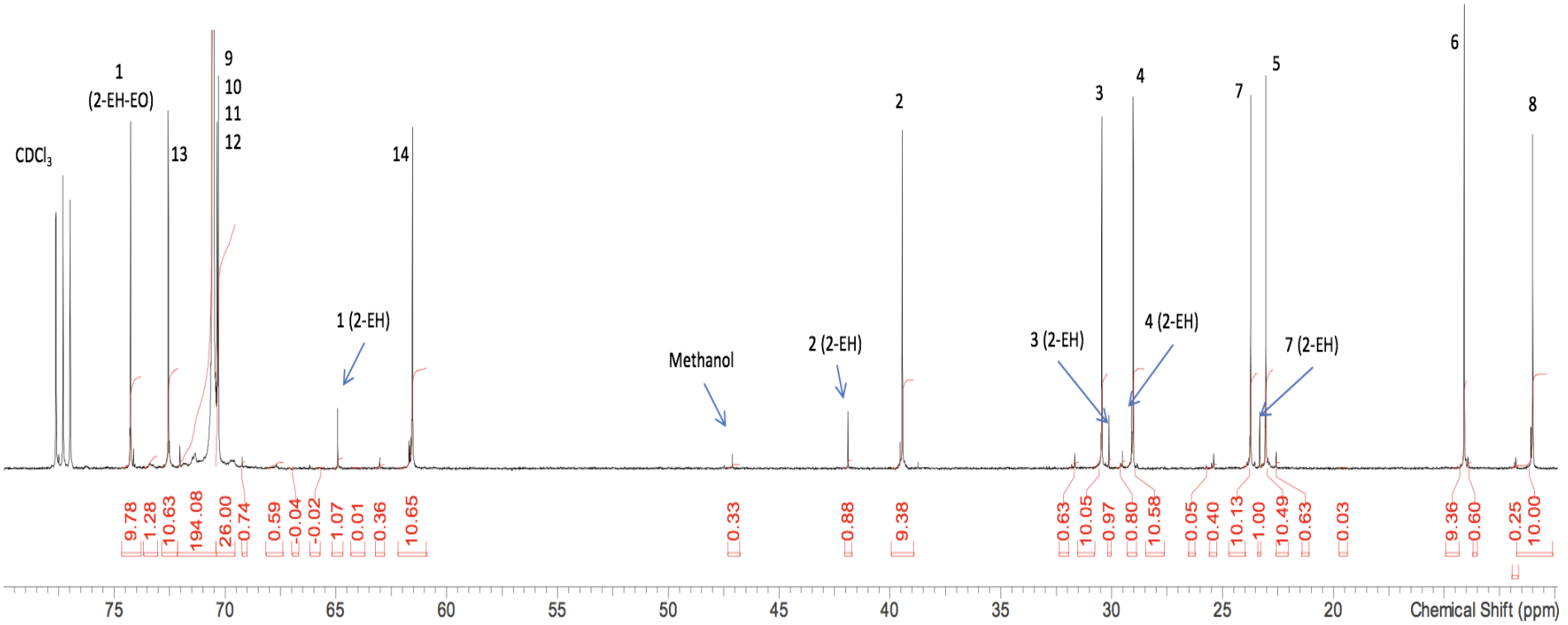



*Figure 1b. Carbon NMR – spectra*

***Broad Range – EO – 15***

II

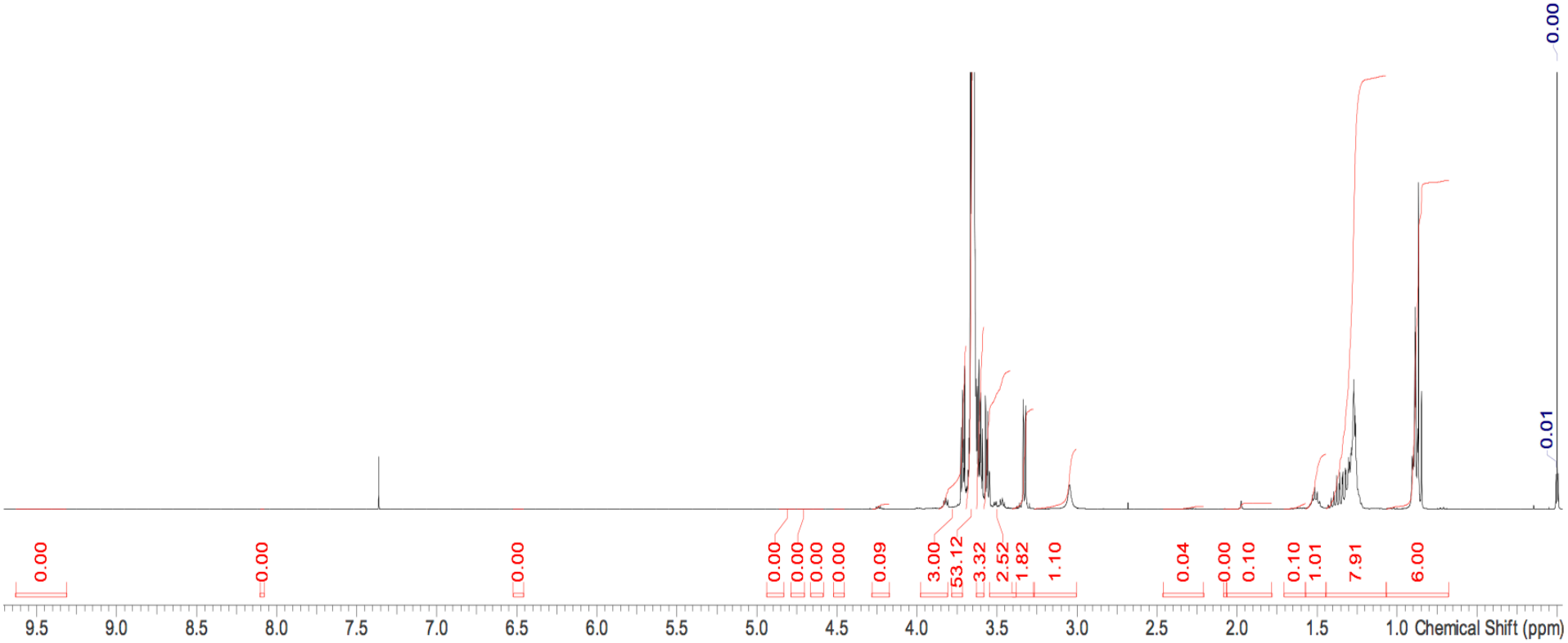



*Figure 2a. Proton NMR – spectra*

***Broad Range – EO – 15***

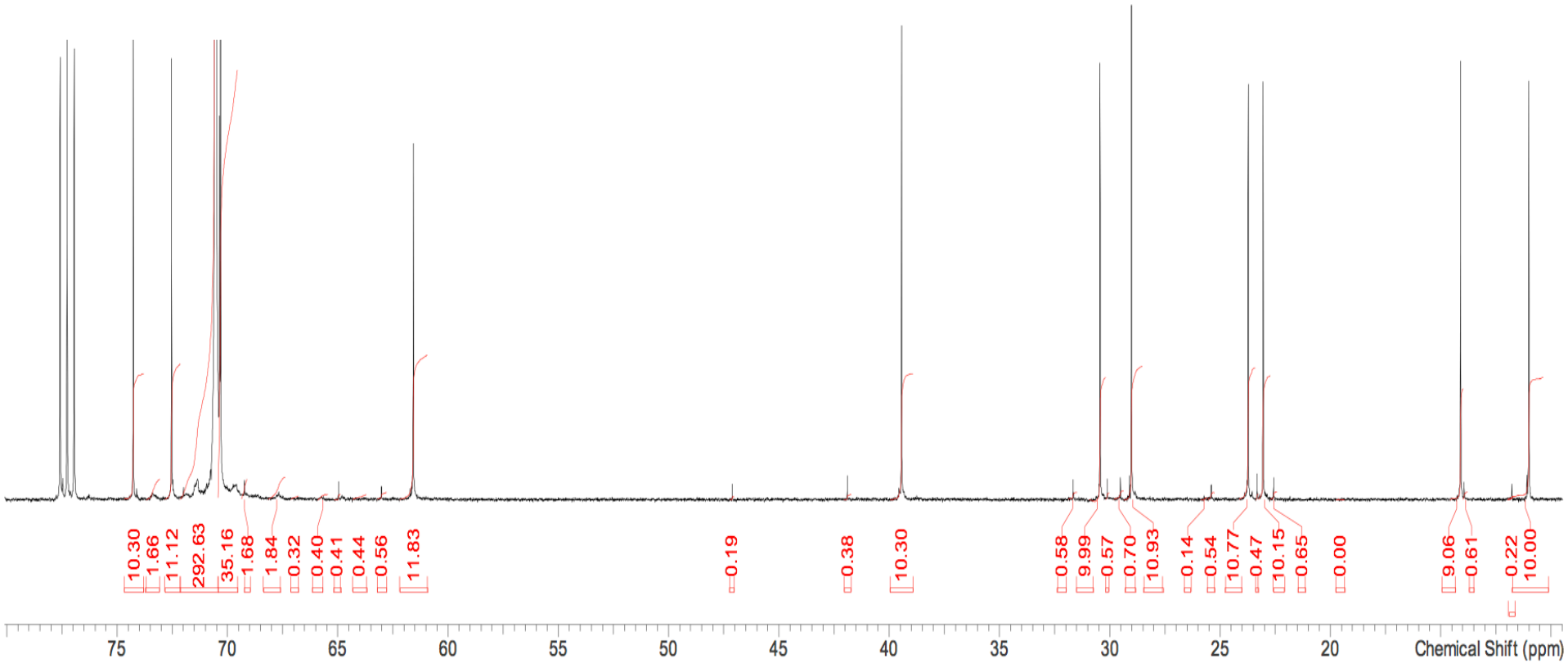



*Figure 2a. Carbon NMR – spectra*

***Broad Range – EO – 25***

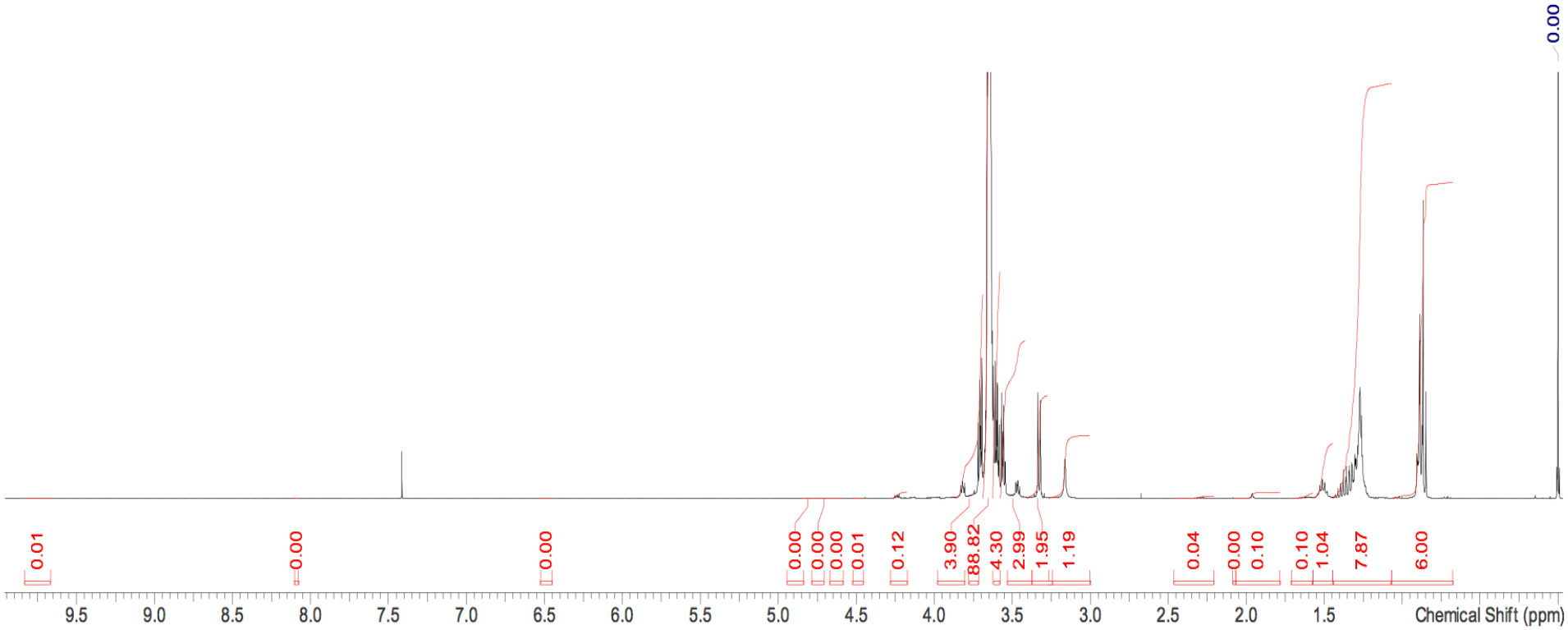



*Figure 3a. Proton NMR – spectra*

***Broad Range – EO – 25***

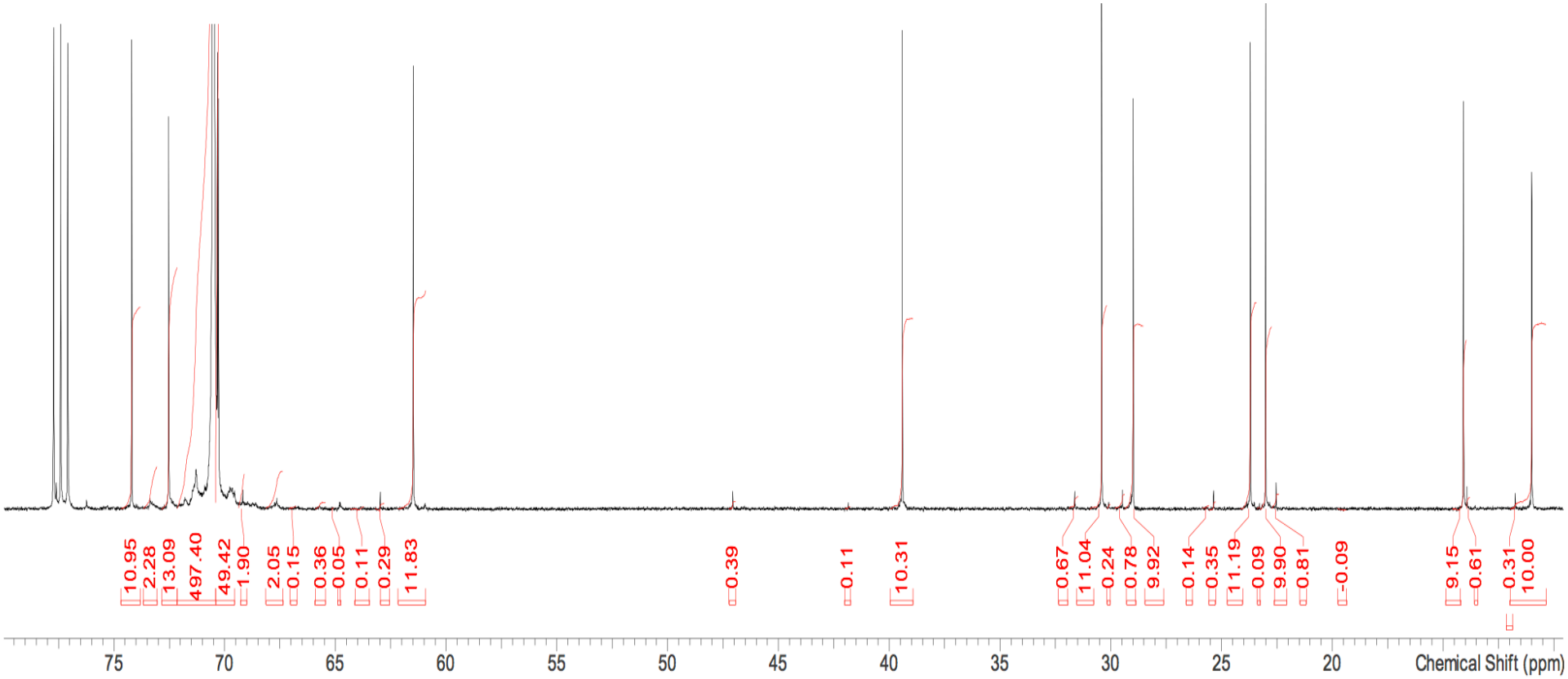



*Figure 3b. Carbon NMR – spectra*

***Narrow Range – EO – 10***

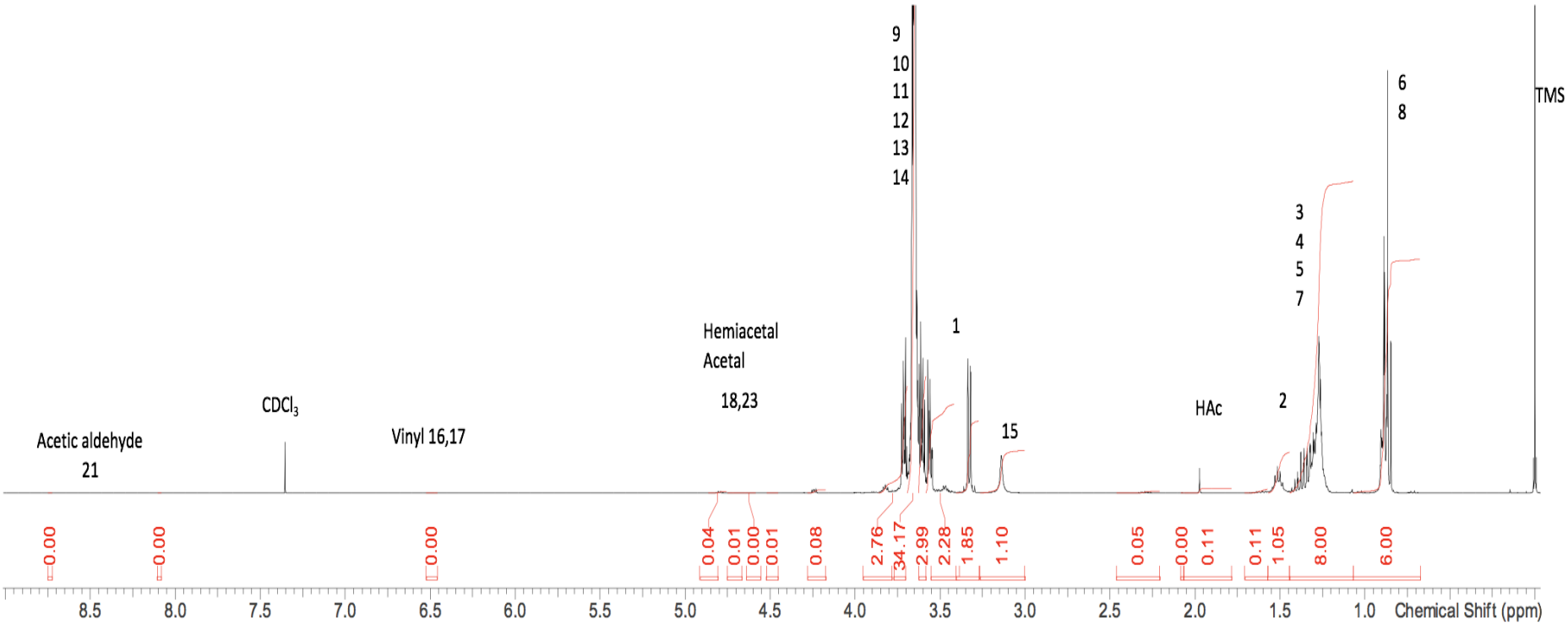



*Figure 4a. Proton NMR – spectra*

***Narrow Range – EO – 10***

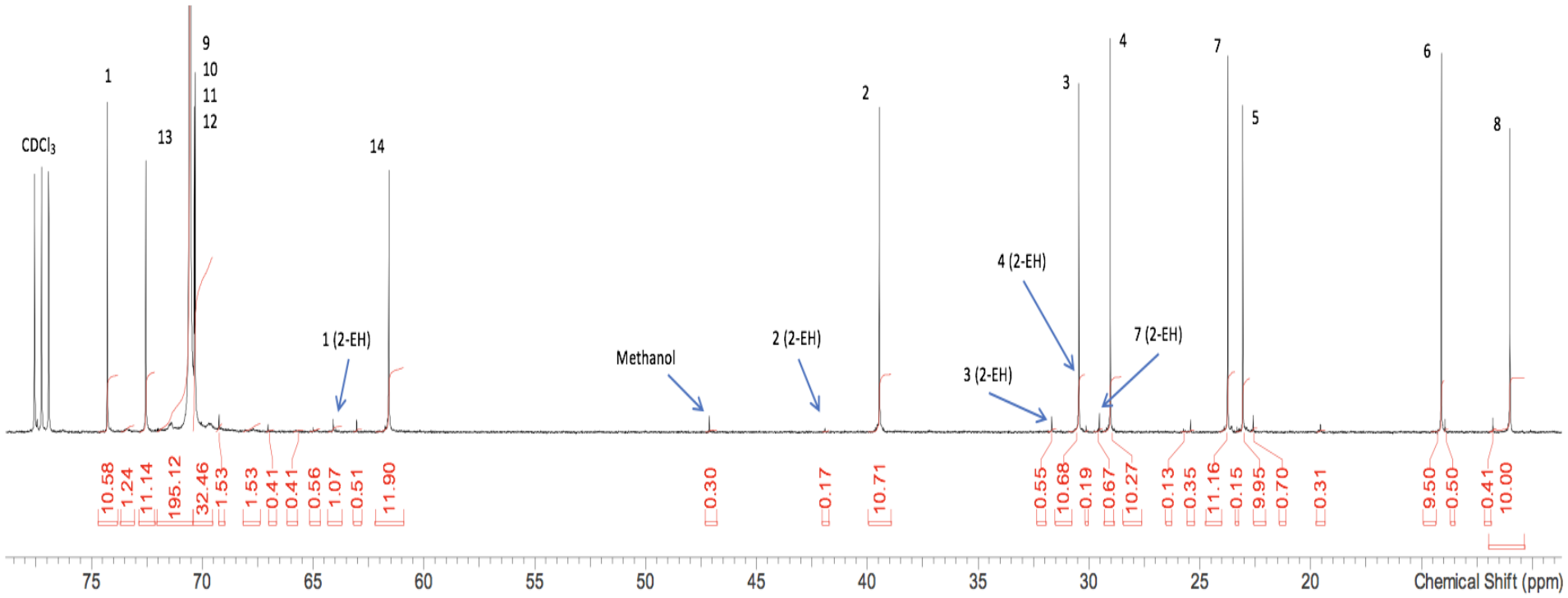



*Figure 4b. Carbon NMR – spectra*

***Narrow Range – EO – 15***

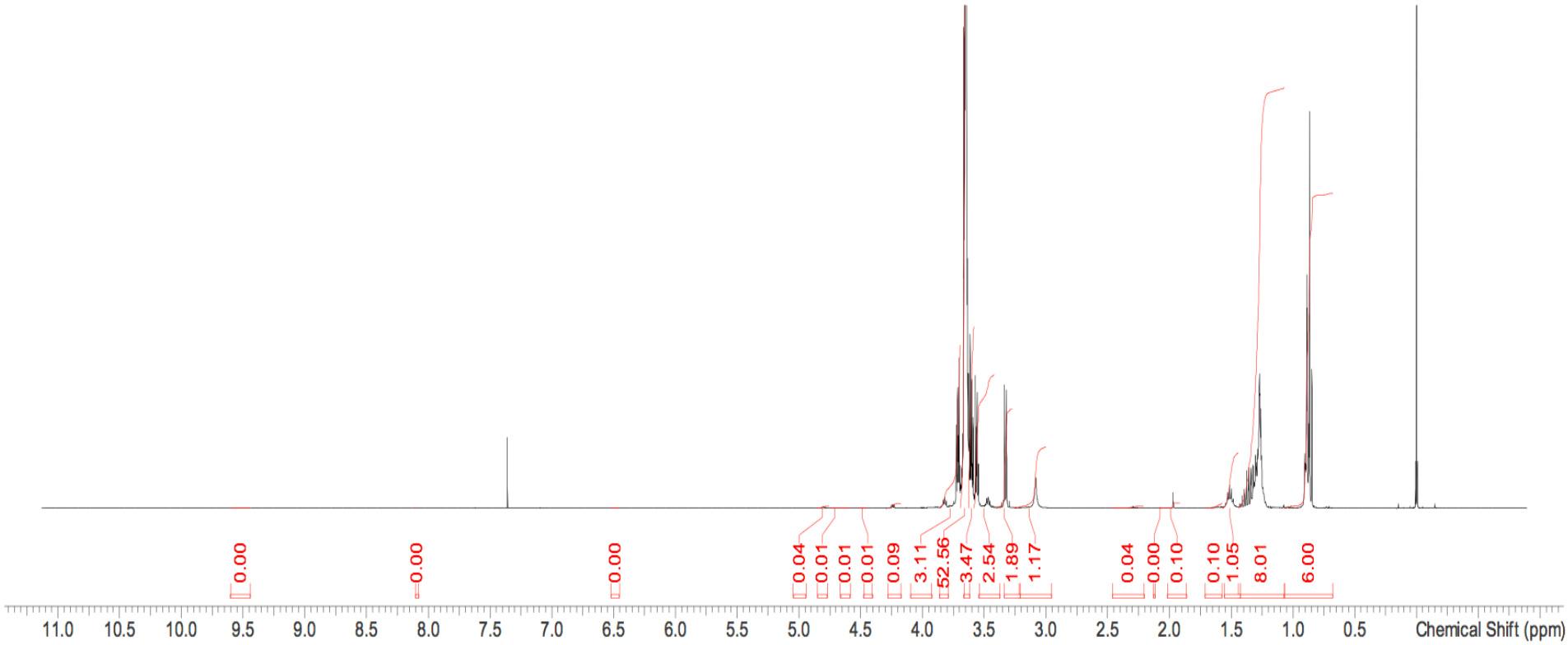



*Figure 5a. Proton NMR – spectra*

***Narrow Range – EO – 15***

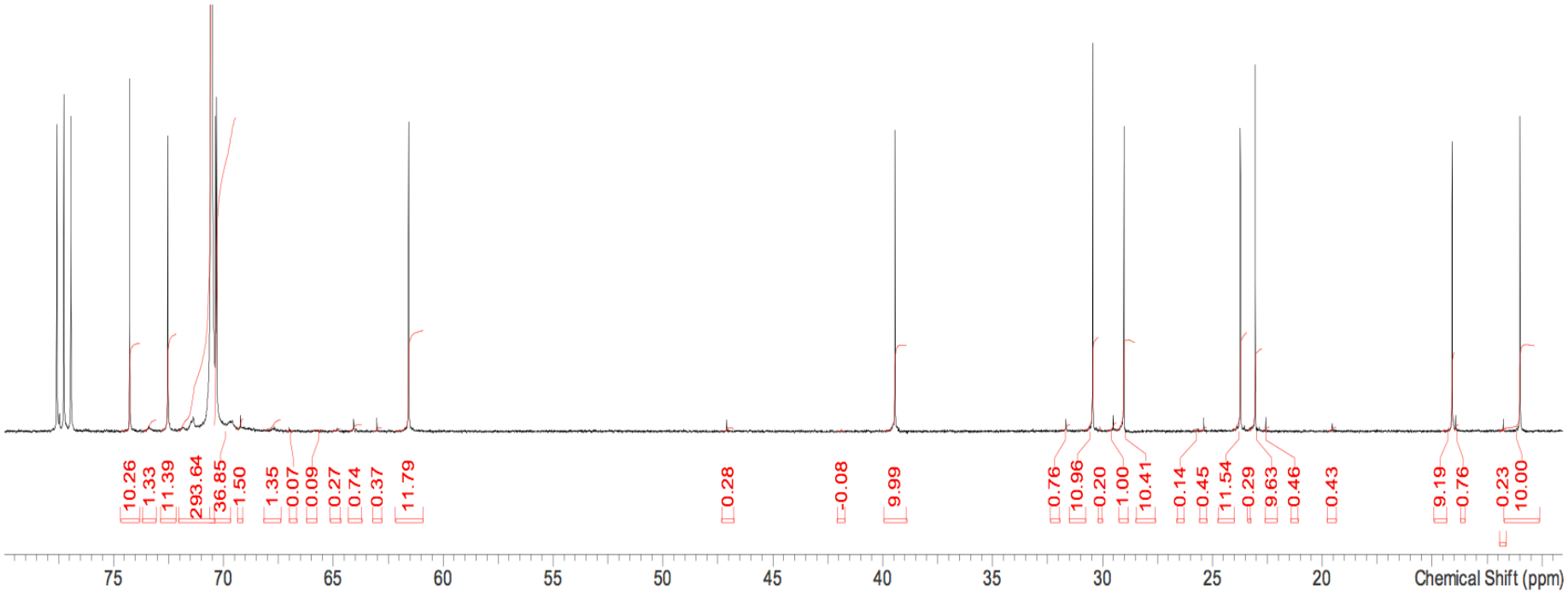
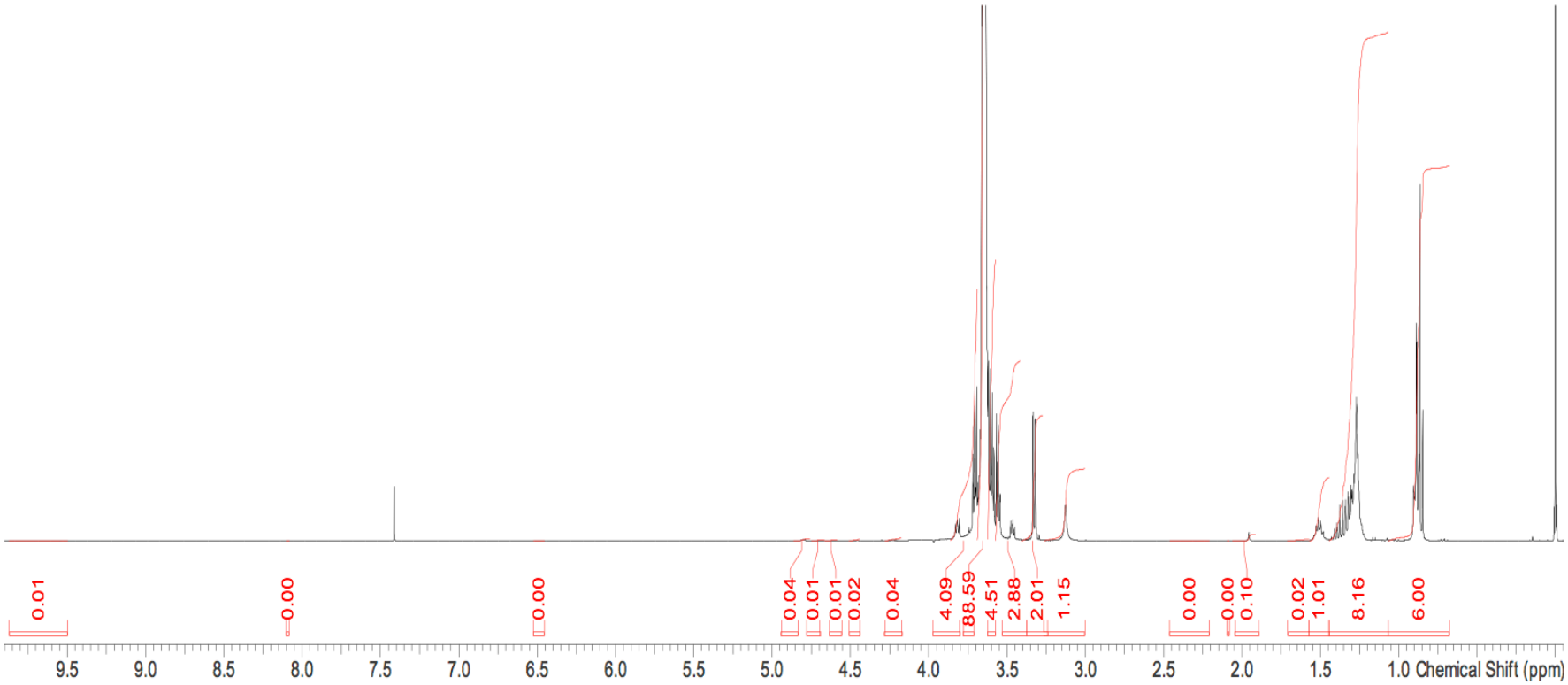



*Figure 5b. Carbon NMR – spectra*

***Narrow Range – EO – 25***

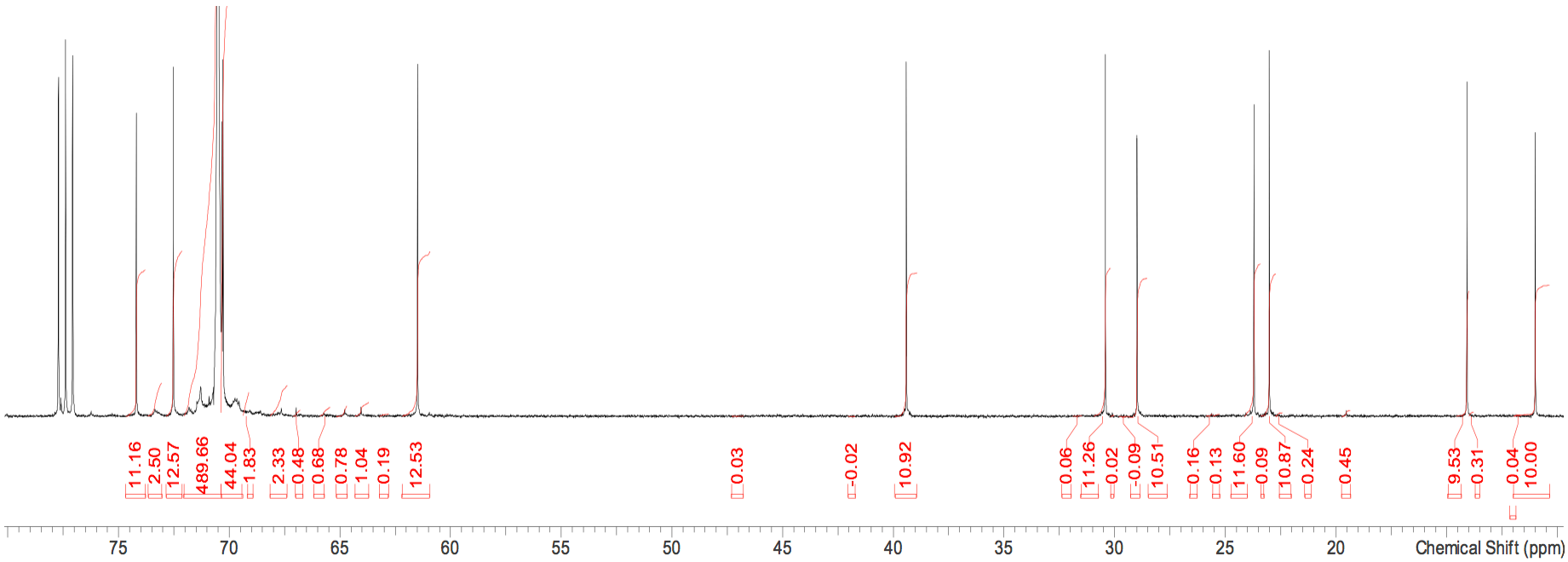
*Figure 6a. Proton NMR – spectra*

X




***Narrow Range – EO – 25***

*Figure 6b. Carbon NMR – spectra*

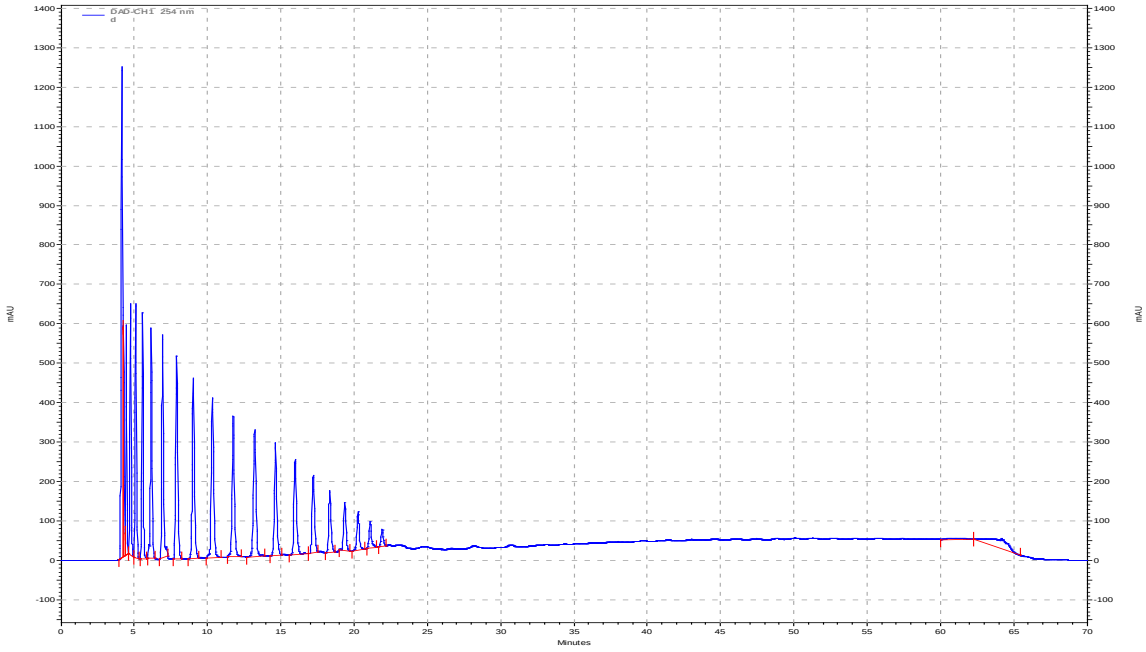

11.16
2.50
12.57
489.66
44.04
1.83
2.33
0.48
0.68
0.78
1.04
0.19
12.53
0.03
-0.02
10.92
0.06
11.26
-0.02
-0.09
10.51
0.16
0.13
11.60
0.09
10.87
0.24
0.45
9.53
0.31
0.04
10.00
75
70
65
60
55
50
45
40
35
30
25
20
Chemical Shift (ppm)

XII

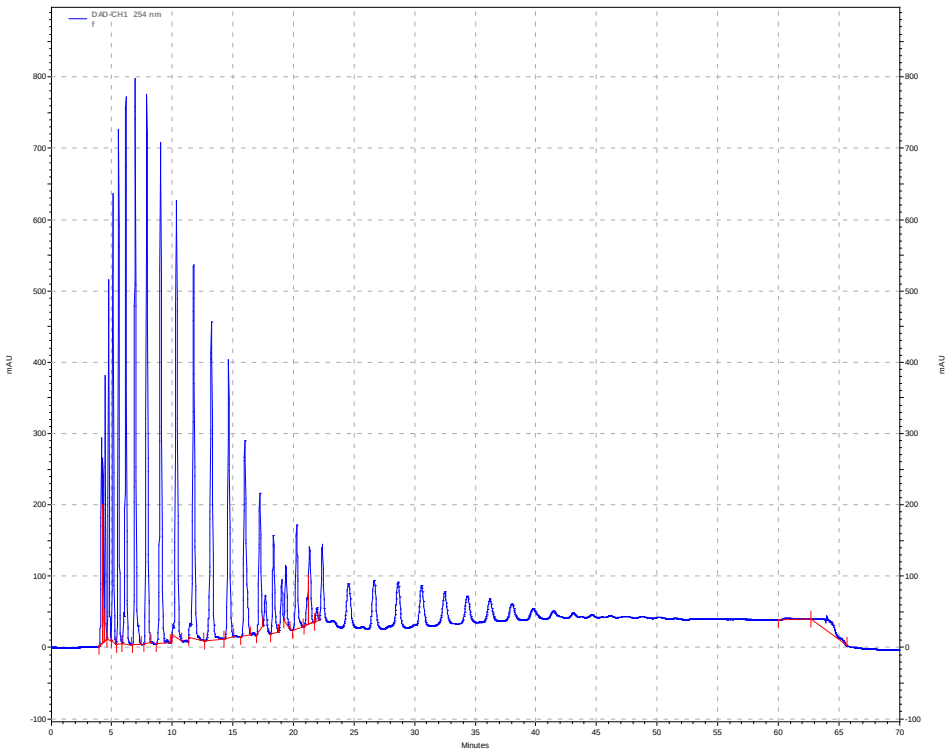
# Appendix 3

HPLC – UV (Chromatogram)

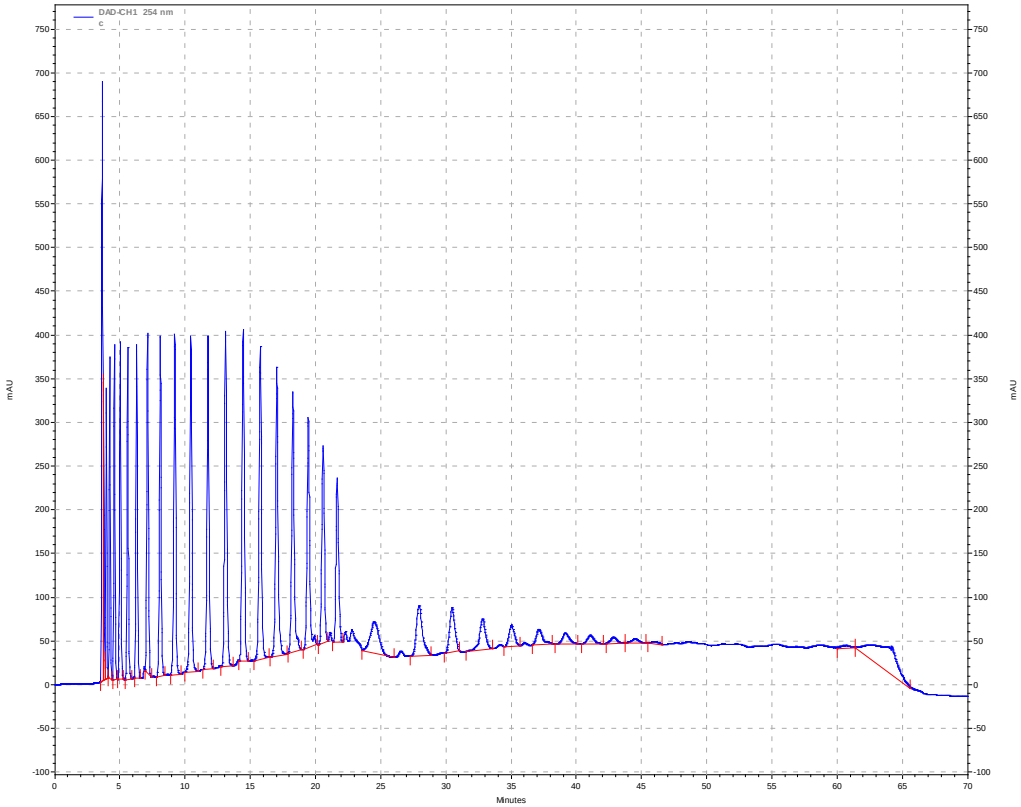
Broad Range – EO – 10



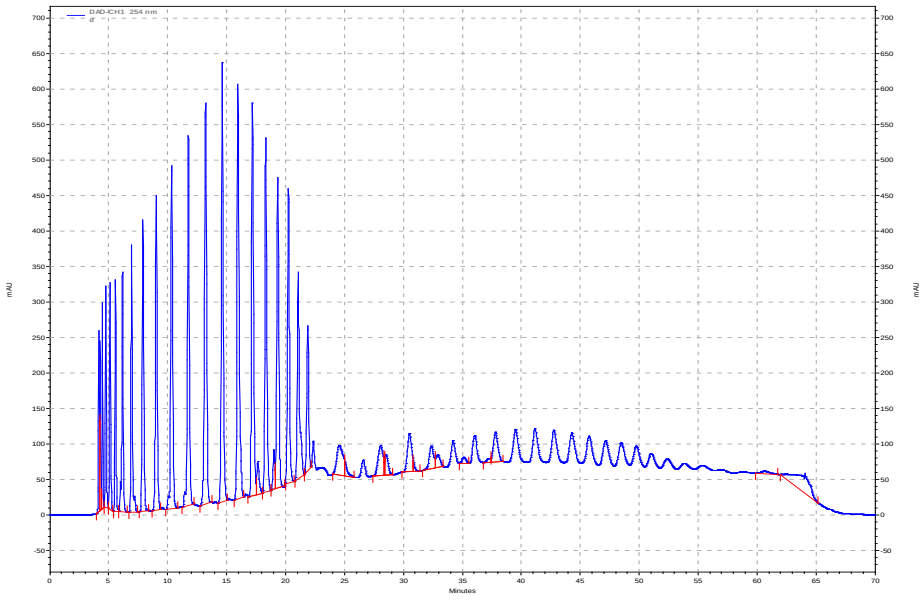

Narrow Range – EO – 10




Broad Range – EO – 15

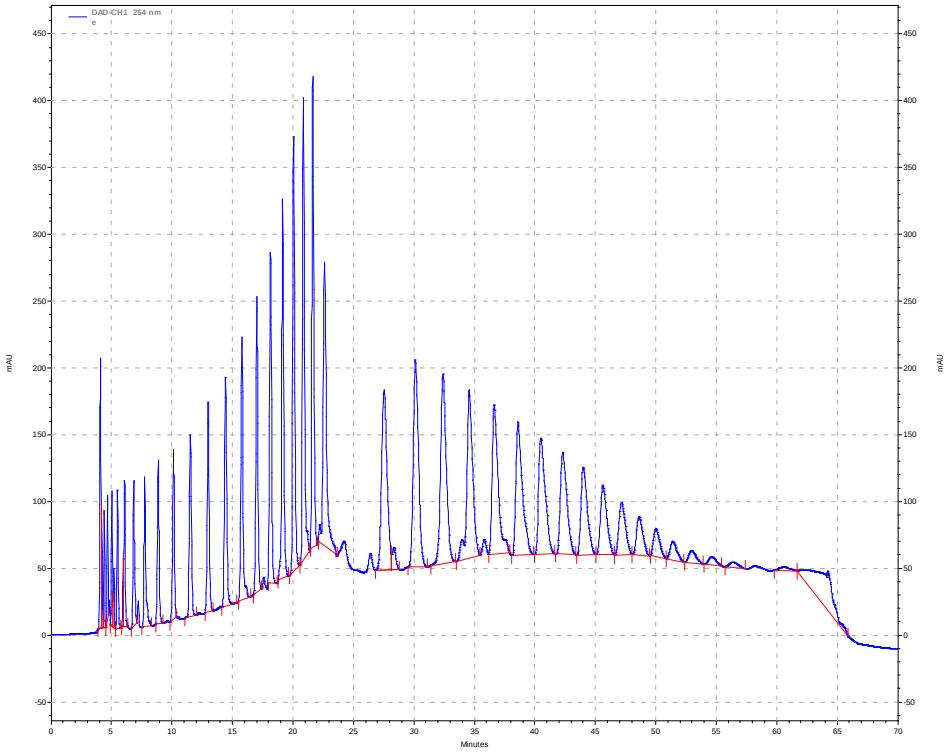



Narrow Range – EO – 15

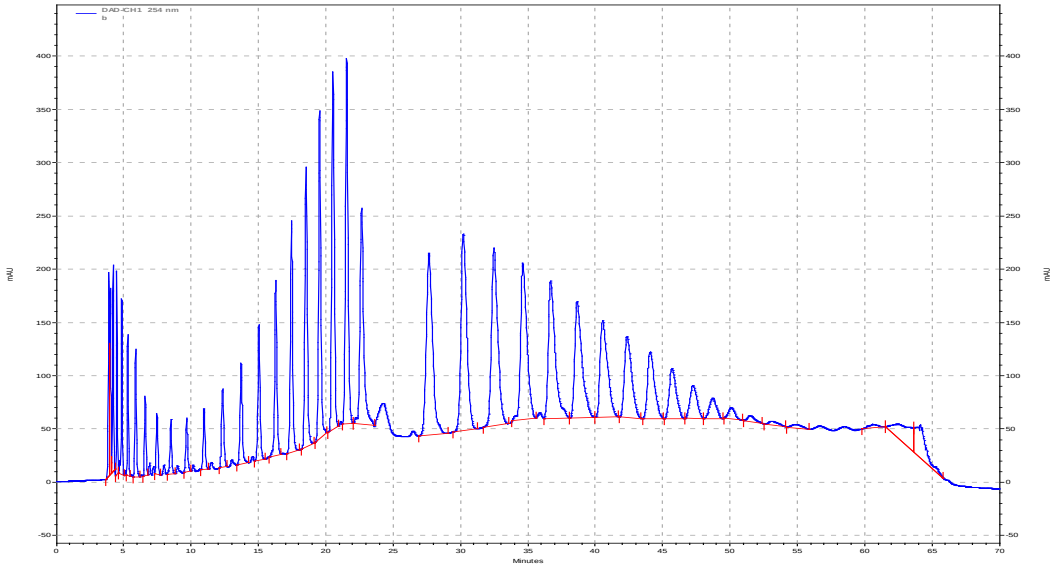



Broad Range – EO – 25

II




Narrow Range – EO – 25



# Appendix 4

Data from swelling studies

| Pulp with no additive | | |
|---|---|---|
| **Time (min):** | **Height (mm):** | |
| 0,00 | 15,00 | |
| 5,00 | 23,80 | |
| 6,00 | 59,40 | |
| 7,00 | 70,00 | |
| 8,00 | 81,40 | **Weight before (g):** |
| 9,00 | 88,00 | *Pulp* = 6,47 |
| 10,00 | 96,00 | *Pulp + flask* = 94,52 |
| 12,00 | 106,00 | **Weight after (g):** |
| 15,00 | 114,20 | *Pulp + flask* = 169,18 |
| 20,00 | 122,20 | *Weight increased* = 74,65 |
| 25,00 | 127,00 | |
| 30,00 | 130,20 | |
| **Increase %** | 868,00 | |

| Reference Product | | |
|---|---|---|
| **Time (min):** | **Height (mm):** | |
| 0,00 | 15,75 | |
| 5,00 | 23,75 | |
| 6,00 | 62,50 | |
| 7,00 | 76,75 | |
| 8,00 | 85,00 | **Weight before (g):** |
| 9,00 | 94,50 | *Pulp* = 6,52 |
| 10,00 | 101,25 | *Pulp + flask* = 94,52 |
| 12,00 | 110,00 | **Weight after (g):** |
| 15,00 | 118,25 | *Pulp + flask* = 173,17 |
| 20,00 | 125,75 | *Weight increased* = 78,65 |
| 25,00 | 131,50 | |
| 30,00 | 134,25 | |
| **Increase %** | 852,38 | |

| Broad Range - EO - 10 | | |
|---|---|---|
| **Time (min):** | **Height (mm):** | |
| 0,00 | 15,50 | |
| 5,00 | 23,50 | |
| 6,00 | 67,25 | |
| 7,00 | 78,75 | |
| 8,00 | 89,75 | **Weight before (g):** |
| 9,00 | 100,25 | *Pulp* = 6,52 |
| 10,00 | 107,25 | *Pulp + flask* = 94,56 |
| 12,00 | 114,50 | **Weight after (g):** |
| 15,00 | 121,75 | *Pulp + flask* = 171,72 |
| 20,00 | 126,75 | *Weight increased* = 77,17 |
| 25,00 | 131,00 | |
| 30,00 | 135,00 | |
| **Increase %** | 870,97 | |

| ***Narrow Range - EO - 10*** | | |
|---|---|---|
| ***Time (min):*** | ***Height (mm):*** | |
| *0,00* | 15,67 | |
| *5,00* | 24,00 | |
| *6,00* | 64,00 | |
| *7,00* | 76,00 | |
| *8,00* | 85,33 | **Weight before (g):** |
| *9,00* | 92,33 | *Pulp = 6,54* |
| *10,00* | 99,67 | *Pulp + flask = 94,62* |
| *12,00* | 109,67 | **Weight after (g):** |
| *15,00* | 117,67 | *Pulp + flask = 169,28* |
| *20,00* | 125,00 | *Weight increased = 74,65* |
| *25,00* | 129,00 | |
| *30,00* | 133,00 | |
| ***Increase %*** | *848,94* | |

| Broad Range - EO - 15 |
|---|

| Narrow Range - EO - 15 |
|---|

I

| Time (min): | Height (mm): | |
|---|---|---|
| 0,00 | 15,50 | |
| 5,00 | 24,00 | |
| 6,00 | 63,50 | |
| 7,00 | 74,25 | |
| 8,00 | 87,50 | **Weight before (g):** |
| 9,00 | 95,00 | *Pulp* = 6,48 |
| 10,00 | 101,75 | *Pulp + flask* = 94,54 |
| 12,00 | 110,25 | **Weight after (g):** |
| 15,00 | 114,75 | *Pulp + flask* = 170,37 |
| 20,00 | 122,00 | *Weight increased* = 75,84 |
| 25,00 | 127,25 | |
| 30,00 | 131,25 | |
| **Increase %** | 846,77 | |

| Time (min): | Height (mm): | |
|---|---|---|
| 0,00 | 15,00 | |
| 5,00 | 24,00 | |
| 6,00 | 71,00 | |
| 7,00 | 82,67 | |
| 8,00 | 92,00 | **Weight before (g):** |
| 9,00 | 99,67 | *Pulp* = 6,50 |
| 10,00 | 105,67 | *Pulp + flask* = 94,44 |
| 12,00 | 112,67 | **Weight after (g):** |
| 15,00 | 118,33 | *Pulp + flask* = 172,34 |
| 20,00 | 126,33 | *Weight increased* = 77,90 |
| 25,00 | 130,33 | |
| 30,00 | 133,67 | |
| **Increase %** | 891,11 | |

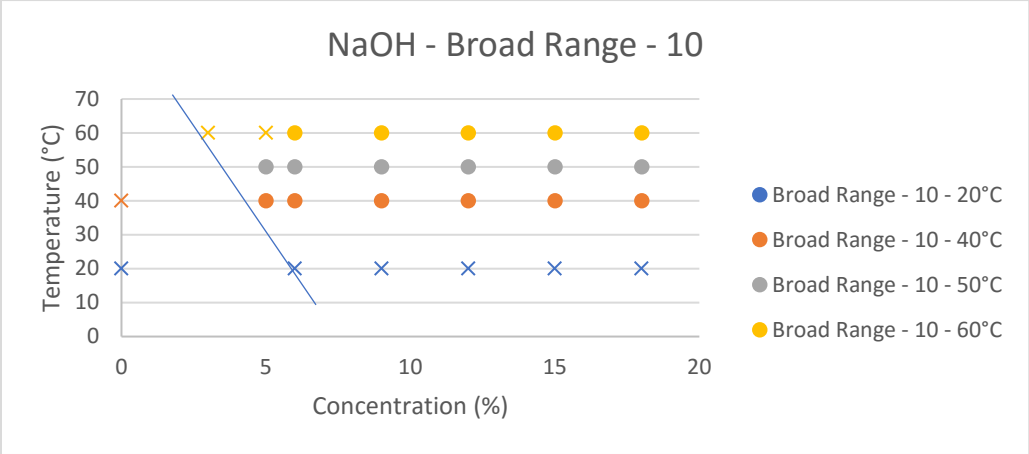
| **Broad Range - EO - 25** | | |
|---|---|---|
| **Time (min):** | **Height (mm):** | |
| 0,00 | 16,00 | |
| 5,00 | 24,25 | |
| 6,00 | 62,75 | |
| 7,00 | 76,25 | |
| 8,00 | 87,25 | **Weight before (g):** |
| 9,00 | 95,75 | *Pulp* = 6,43 |
| 10,00 | 103,25 | *Pulp + flask* = 94,46 |
| 12,00 | 110,75 | **Weight after (g):** |
| 15,00 | 117,75 | *Pulp + flask* = 173,82 |
| 20,00 | 126,25 | *Weight increased* = 79,36 |
| 25,00 | 129,00 | |
| 30,00 | 131,75 | |
| **Increase %** | 823,44 | |

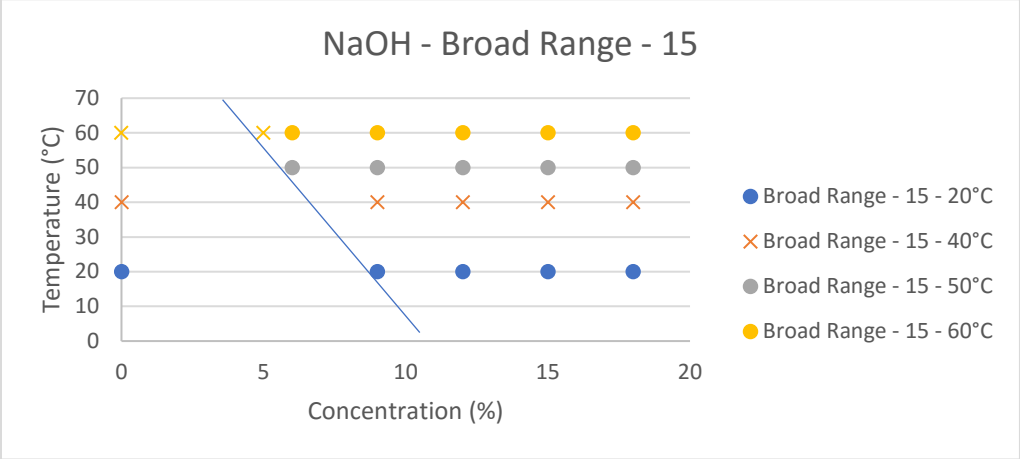
| **Narrow Range - EO - 25** | | |
|---|---|---|
| **Time (min):** | **Height (mm):** | |
| 0,00 | 15,67 | |
| 5,00 | 24,33 | |
| 6,00 | 68,00 | |
| 7,00 | 79,00 | |
| 8,00 | 89,67 | **Weight before (g):** |
| 9,00 | 98,67 | *Pulp* = 6,51 |
| 10,00 | 105,00 | *Pulp + flask* = 94,43 |
| 12,00 | 113,33 | **Weight after (g):** |
| 15,00 | 121,00 | *Pulp + flask* = 173,55 |
| 20,00 | 130,00 | *Weight increased* = 79,12 |
| 25,00 | 134,00 | |
| 30,00 | 135,67 | |
| **Increase %** | 865,96 | |

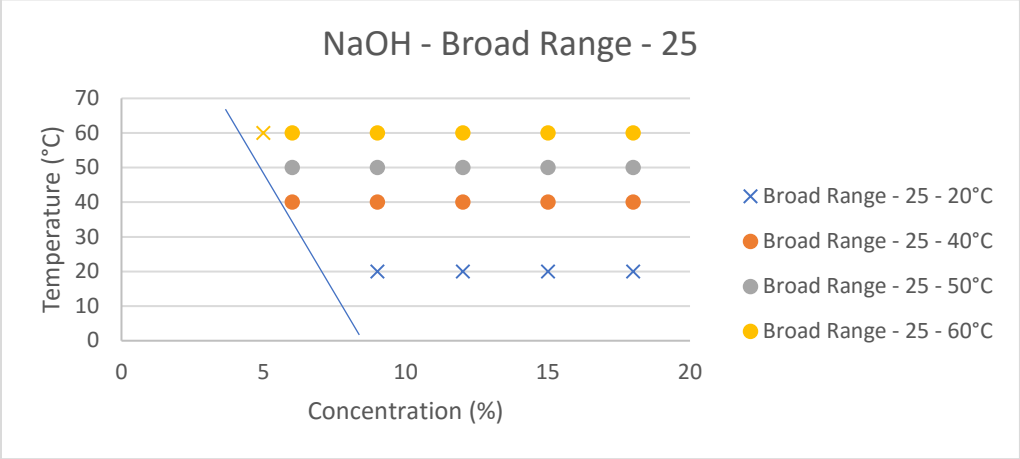
## Appendix 5

Solubility Test – NaOH and NaCl

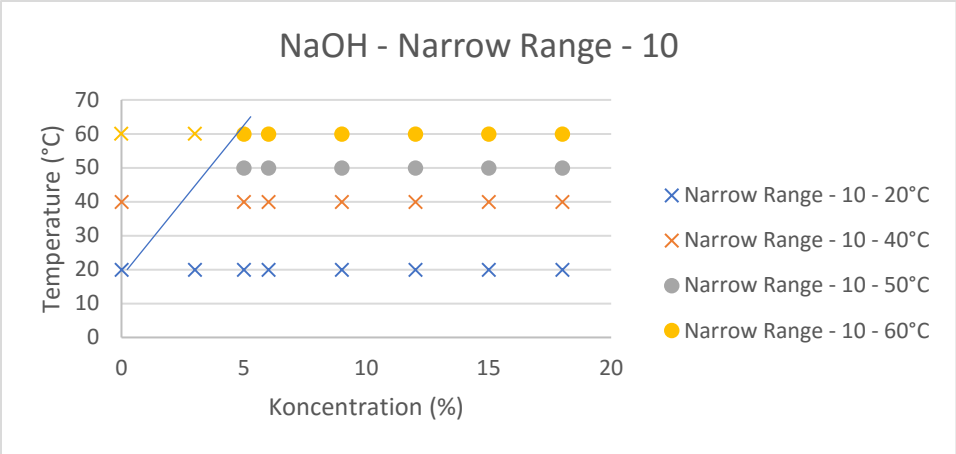
× = Cloudy, ● = Phase separation

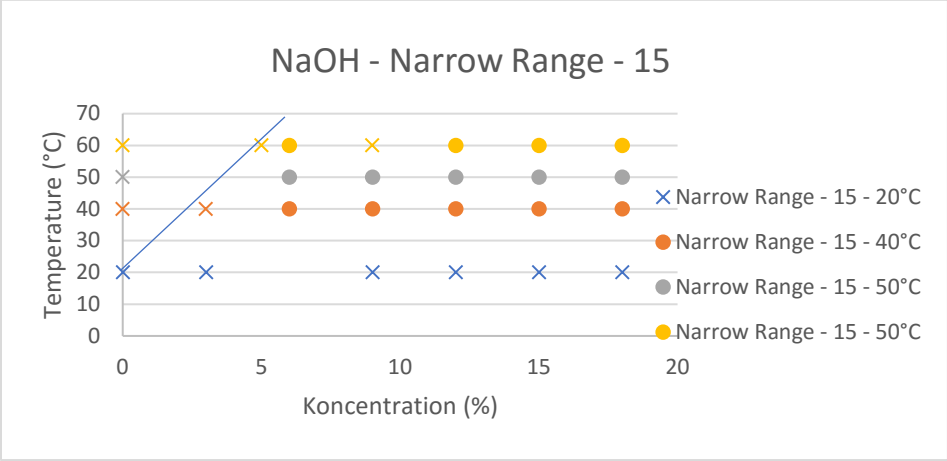


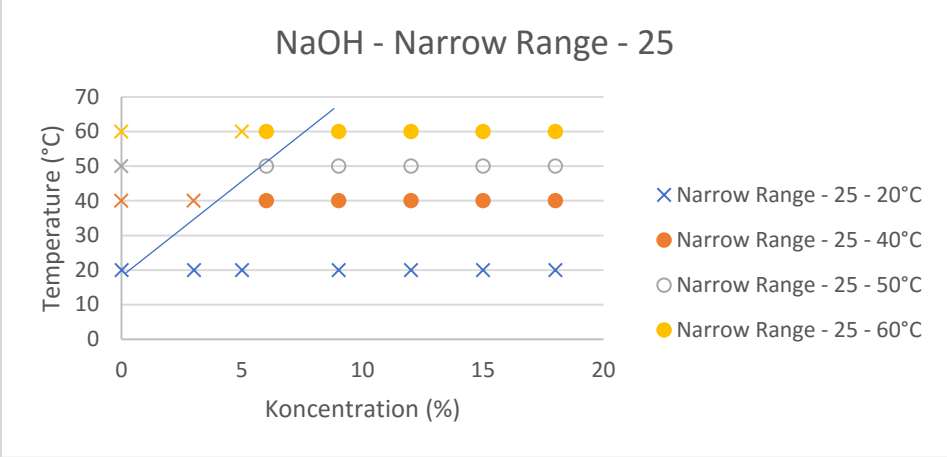



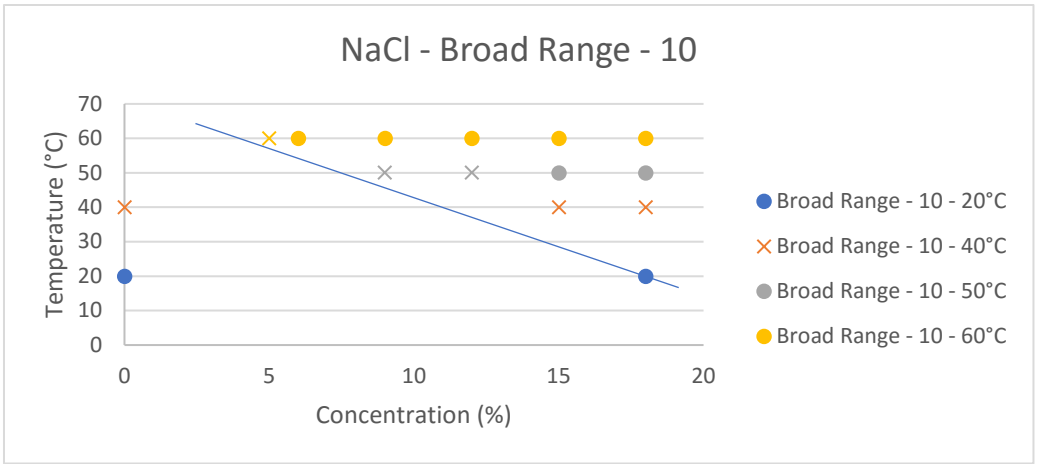

× = Cloudy, ● = Phase separation

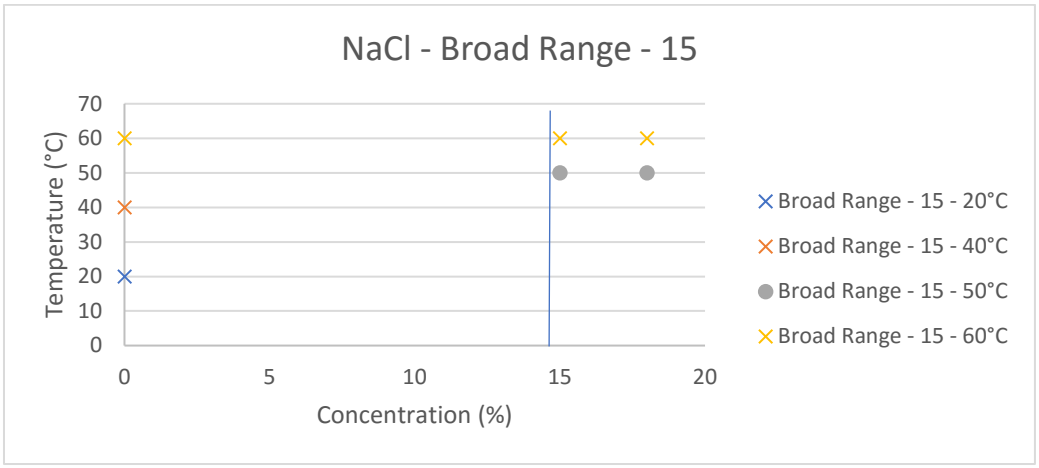


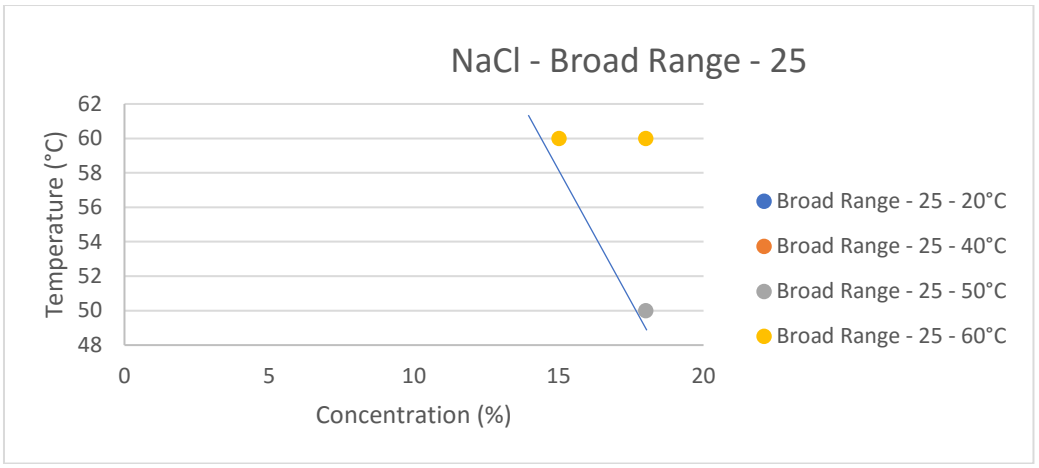




× = Cloudy, ● = Phase separation

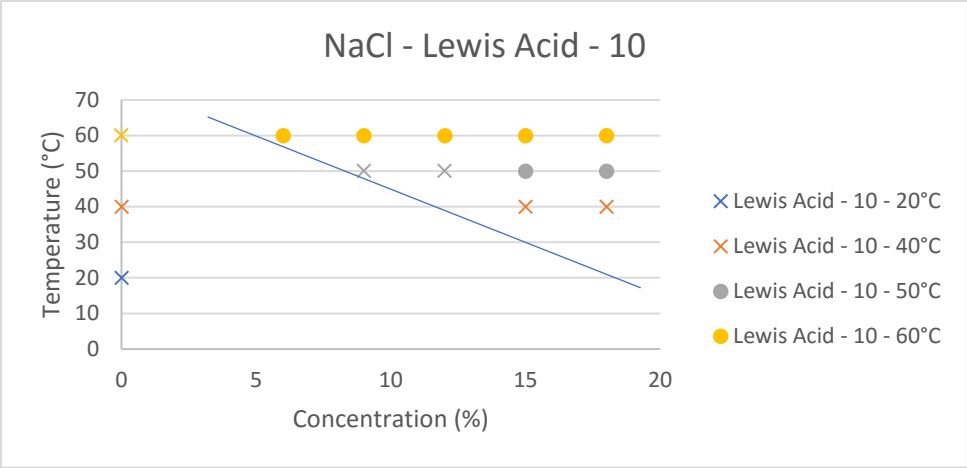


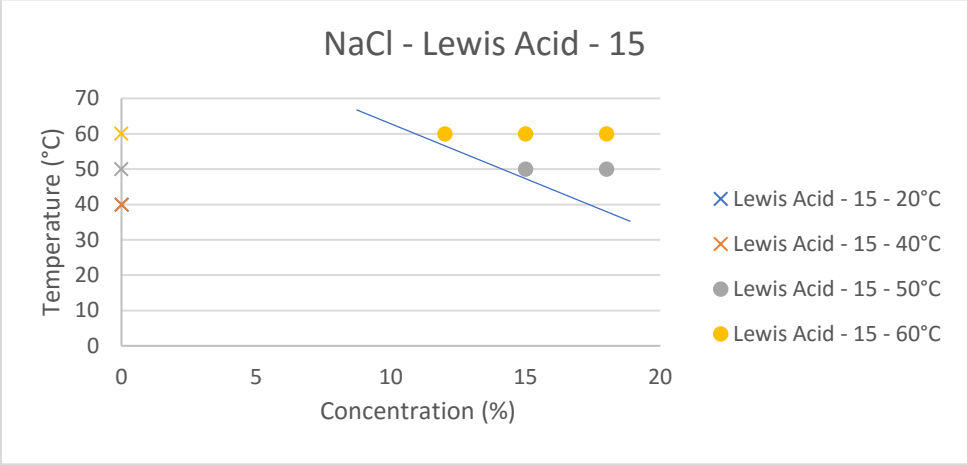



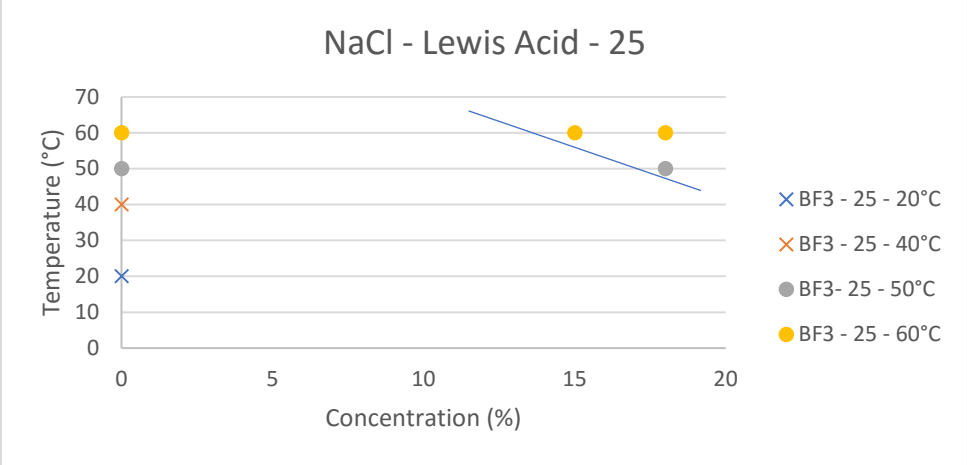




× = Cloudy, ● = Phase separation

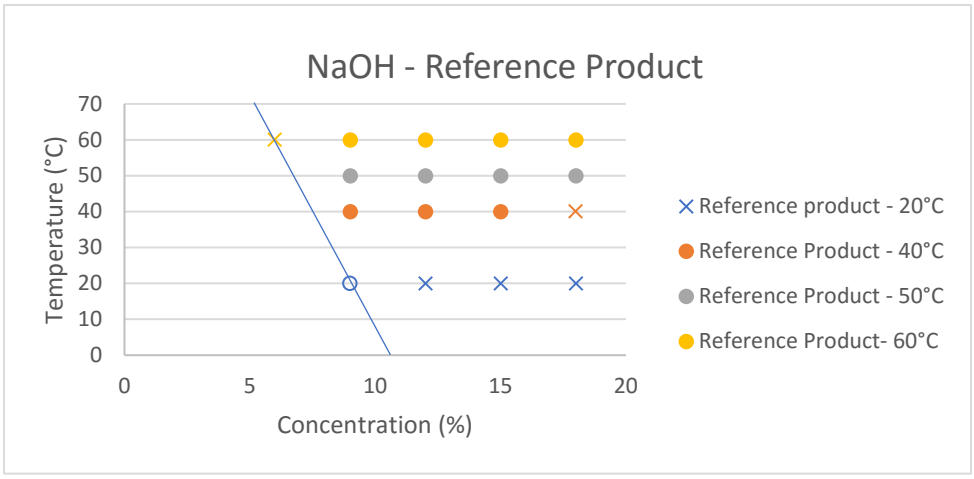
III

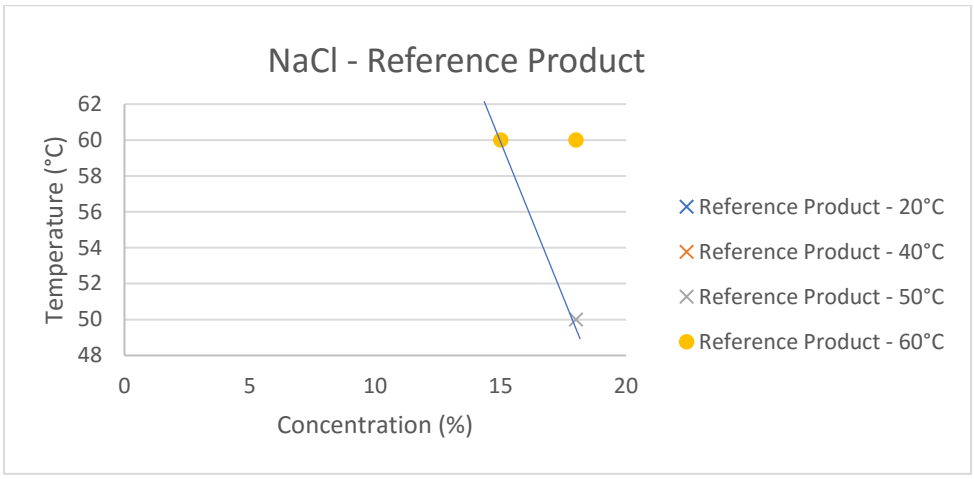



× = Cloudy, ● = Phase separation


NaOH - Reference Product
Temperature (°C)
70
60
50
40
30
20
10
0
0
5
10
15
20
Concentration (%)
Reference product - 20°C
Reference Product - 40°C
Reference Product - 50°C
Reference Product- 60°C


NaCl - Reference Product
Temperature (°C)
62
60
58
56
54
52
50
48
0
5
10
15
20
Concentration (%)
Reference Product - 20°C
Reference Product - 40°C
Reference Product - 50°C
Reference Product - 60°C

V

# Appendix 6

Solubility Test - Acetone Water

| Product: | Volume of water: |
|---|---|
| KOH - 10 | 27,4 |
| KOH - 15 | 35,3 |
| KOH-25 | ∞ |
| Lewis Acid - 10 | 19,7 |
| Lewis Acid - 15 | 21,7 |
| Lewis Acid - 25 | 24,6 |

# Appendix 7

*Water Retention Value*
***Analysis 1:***

| Substance: | Weight wet pulp: (g) | Weight dry pulp (g): | WRV - value: |
|---|---|---|---|
| Lewis Acid | 6,86 | 1,76 | 74,34 |
| NaOH | 6,5 | 1,67 | 74,31 |
| Broad - 10 | 8,14 | 2,01 | 75,31 |
| Broad - 15 | 7,53 | 1,88 | 75,03 |
| Broad - 25 | 7,95 | 1,94 | 75,60 |
| Narrow - 10 | 8,21 | 2,03 | 75,27 |
| Narrow - 15 | 7,76 | 1,95 | 74,87 |
| Narrow - 25 | 7,91 | 1,95 | 75,35 |

***Analysis 2:***

| Substance: | Weight wet pulp: (g) | Weight dry pulp (g): | WRV - value: |
|---|---|---|---|
| Lewis Acid | 6,59 | 1,68 | 74,52 |
| NaOH | 6,78 | 1,75 | 74,20 |
| Broad - 10 | 7,56 | 1,87 | 75,28 |
| Broad - 15 | 7,48 | 1,91 | 74,48 |
| Broad - 25 | 8,09 | 2,02 | 75,04 |
| Narrow - 10 | 7,48 | 1,89 | 74,74 |
| Narrow - 15 | 8,06 | 2,00 | 75,20 |
| Narrow - 25 | 7,76 | 1,92 | 75,27 |

***Average Values:***

| Substance: | Average WRV: |
|---|---|
| Lewis Acid | 74,43 |
| NaOH | 74,25 |
| Broad - 10 | 75,29 |
| Broad - 15 | 74,75 |
| Broad - 25 | 75,32 |
| Narrow - 10 | 75,01 |
| Narrow - 15 | 75,03 |
| Narrow - 25 | 75,31 |