Phosphorous separation in the AKD plant in Trollhättan

A study showing if/how the amount of phosphorous changes due to different parameters

Bachelor of Science Thesis in Chemical Engineering

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Gothenburg, Sweden, 2011

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Chalmers University of Technology
Degree Program: *Chemical Engineering*
Program Division: *Department of Chemistry and Biotechnology*
Title: *Phosphorous separation in the AKD plant in Trollhättan*
Author: *Zeinab Abdallah*
Year: *2011*
Number of pages: *28*

Abstract

Paper is a very important communicating system and is immensely manufactured all over the world. It indicates that men have developed a lot since the Stone Age where communications were written on tablets or in caves. Paper is mainly used for drying, drawing, printing, writing and packaging.

Paper is manufactured by harvesting trees and processing it into pulp where later several materials or substances are added to alter the properties of the paper such as making it more water resistant. Sizing is when a substance such as AKD (alkyl ketene dimer), which is produced in the plant in Trollhättan, is added to the pulp to make the paper water resistant.

The purpose of this study was to study the phosphorous separation in the chlorination process in the AKD plant in Trollhättan.

The phosphorous amount were compared to several parameters such as the batch number performed in the process, the content of fatty acid in both the fatty acid chloride samples from both the 1st and 2nd chlorination reactors, the amount of phosphorous separated in the 1st, 2nd and 3rd separation processes in the chlorination process in 1st chlorination reactor.

A correlation between the batch number and the amount of phosphorous in the samples was performed and the result showed that the amount of phosphorous was not affected by the order of the batch numbers however it showed that the High Melting Point (HMP) fatty acid was lower and more stabilized than the Low Melting Point (LMP) fatty acid at a specific limit range. This correlation was shown in all the tests that were performed. However the correlation between the amount of phosphorous and the content of fatty acid, in the samples, showed a different result where the amount of phosphorous increased with an increase in the content of fatty acid.

Alteration of the stir time in 1st chlorination reactor was performed to see if any changes would occur in the system or if the amount of phosphorous would change in samples. The results of the small alterations performed in the reactor did not contribute to any changes in the amount of phosphorus in the sample.

A suggestion is to further investigate how much alterations could be done to the stir time in the 1st reactor.

1. Background

Eka Chemicals is a part of the multinational company AkzoNobel, which has closer to 65000 employees all over the world. AkzoNobel works with the production of pharmaceuticals, paint and various chemical. Eka Chemicals is specialized in producing paper chemicals.

Since 1996 Eka Chemicals in Trollhättan has been working on the production of AKD-wax (alkyl ketene dimer), which is one of several other paper chemicals that is produced and added into the paper manufacturing to influence the paper's properties. The wax is produced in two different qualities where the difference lies in the number of carbon atoms. The wax is later transported into Eka's dispersion facilities to be further processed to AKD-emulsion, which is used as a sizing agent in paper manufacturing.

Paper is a material that is used for writing, printing, drawing, packaging and also for drying. To enhance the printability with water based ink, i.e. less blurring; the sizing agent such as the AKD-emulsion is added. The function of the sizing agent is that it alters the properties of the paper to make it more hydrophobic (more water resistant) giving better printability and better wet strength, i.e. cannot be easily ruined in contact with water.

In the plant, Eka Chemicals in Trollhättan, the substance AKD is produced by a two step reaction, the chlorination and the dimerization reaction.

The chlorination, which is performed in two steps, has the main purpose is to produce the substance called acid chloride. Acid chloride is an extremely reactive chemical that easily could be further reacted to the AKD. The properties of the acid chloride are that it releases the chlorine atom and reacts to other substances.

During the first chlorination step a separation step is performed. If this separation isn't separated correctly, problems can occur in the second chlorination step in the formation of phosphorous acid and in the washing step of the AKD.

The dimerization is the second reaction step, where two acid chloride molecules react with each other in the presence of the help chemical Triethylamine, TEA.

Except for producing AKD one also produces the byproduct Triethylamine-hydrochloride, TEA-HCl, which is formed by bonding the chlorine molecules with TEA. [1, 7]

1.1 Paper and Paper Manufacturing

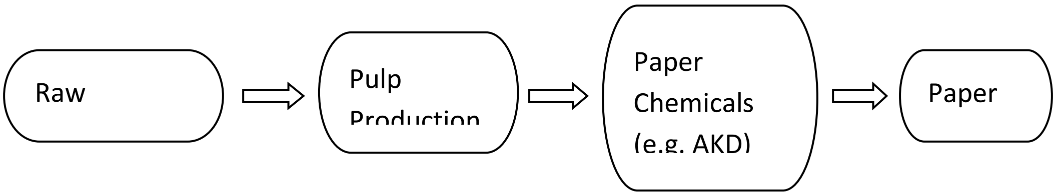
Paper has not only been an important system of communication but it is also commonly used as blue prints for many great inventions, studies and reading. If men hadn't invented and developed paper, the world would probably still be living in the Stone Age where communications with each other would be through inscriptions on cave walls and tablets. Worldwide consumption of the harvested trees used for pulp production is 42 percent i.e. 175 million tons (2006).

The wood that is harvested to achieve pulp making contains important substances such as cellulose fibers (the main material in paper making) and lignin (a polymer that binds the fibers together) and hemicelluloses (a carbohydrate polymer). The aiming of pulping is to break down the bulk structure of the fiber source into constituent fibers. The most preferable type of tree is coniferous tree because the cellulose fiber in this pulp is longer therefore making a much stronger paper.

As can be seen in figure 1, there are two types of processes, commonly used to convert wood logs into wood pulp, mechanical pulp and chemical pulp.

Mechanical pulp is where the logs are first processed to remove the barks before sending them to the grinders where they are broken down into pulp by pressing it between two big revolving boards.

Chemical pulp is where the wood chips from the de-barked logs are cooked and boiled at a high pressure in a chemical solution.



Scheme 1. *This scheme shows the processes that the raw material goes through to produce paper.*

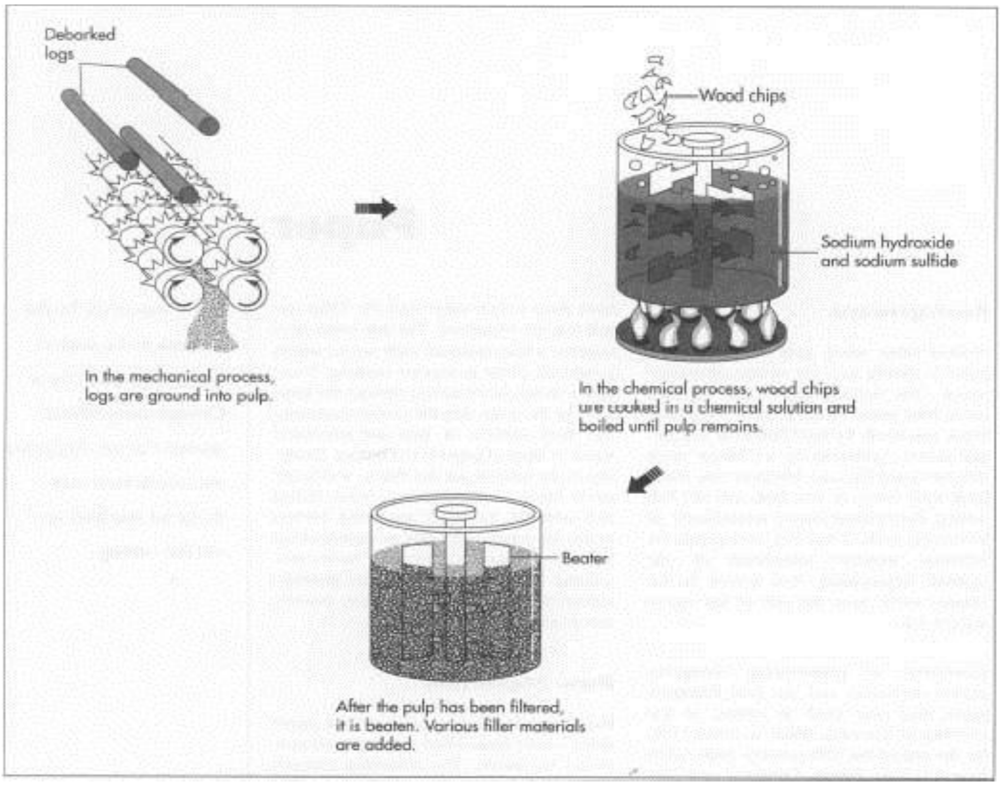


Figure 1. *A schematic figure of the mechanical pulp and the chemical pulp.*

The beaten pulp is thereafter sent to the head-box where (or just before) different chemicals are added. Typical chemicals that are added are different filler materials, such as clays – and chalks, and chemicals for retention – and sizing. The materials and chemicals influence the qualities and properties of the paper.

Typical sizing chemicals could be Rosin, ASA (alkyl succinic anhydride) and AKD. Depending of the usage of the paper, the choice of sizing chemical is different, e.g. printing paper could use either ASA or AKD but liquid packaging board uses only AKD. Sizing chemicals are used to make the paper hydrophobic (water resistant).

At the final stage the pulp is fed from the head-box into a moving belt with rollers through a paper machine where the formation of paper occurs. The paper is dried by pressing rollers and steam-heated cylinders to remove the remaining water. [9, 10]

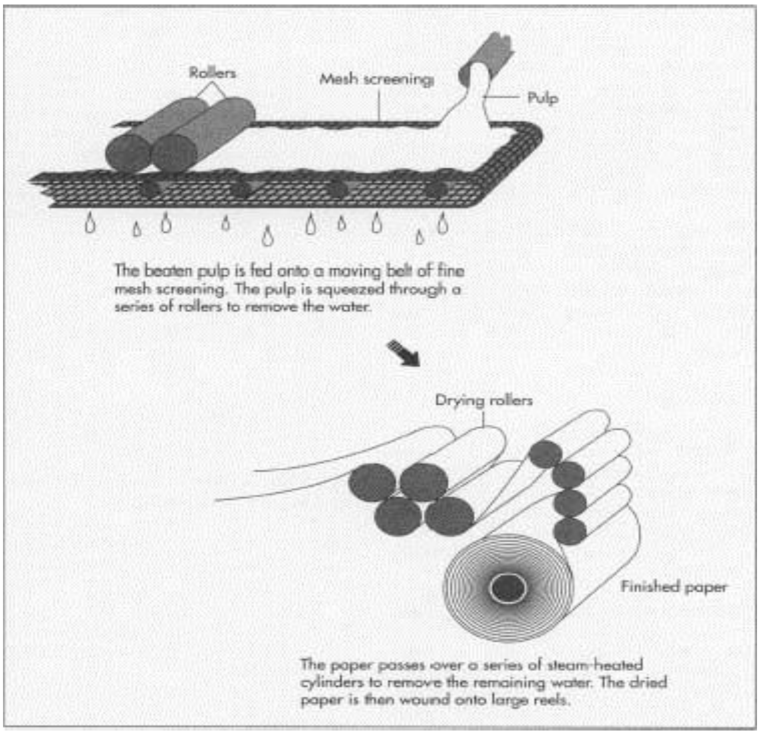


Figure 2. *The pulp is sized and formed into paper.*[10]

1.2 AKD in Paper Manufacturing

Paper is mainly produced by uncovering cellulose from various wood raw materials, where the main types of wood used in Sweden are birch and conifer. This is performed by boiling the substances that binds the fibers in the raw material.

Cellulose is a hydrophilic material, i.e. consisting of a carbon backbone with many hydroxyl groups attached, and it is one of the most costly parts in a paper. Depending on the final usage of the paper, different chemicals are added to alter the properties of the paper when making it. One such chemical is sizing agents, e.g. AKD, that makes the paper more hydrophobic (water resistant) and gives the paper qualities such as wet strength and good printability. Other chemicals that are added are typical kaolin to lower the production cost.

Before AKD is transported to the paper industries, it is homogenized in Eka's dispersion facilities to make it lasting and stable. This is done by mixing the AKD wax with water and other chemicals. In the paper factory the AKD-emulsion is mixed with the pulp and is divided equally into the mass. In the dry section of the paper machine, the particles are melted, flows through the mass and react there with the hydroxyl groups of to the cellulose, which at the same time makes the paper hydrophobic.[1]

Normally when water touches the paper, it is absorbed very quickly through the fibers due to the capillaries in the paper structure and it is this process that is affected by adding a sizing agent.

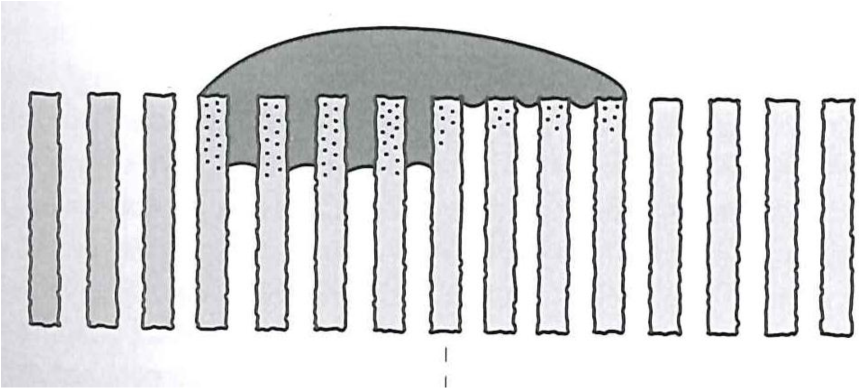
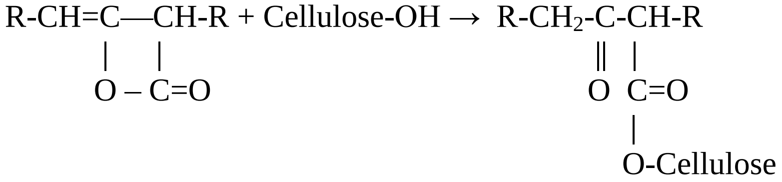


Figure 3. *A schematic picture of a water droplet on the paper fibers; to the left without sizing agent and to the right with a sizing agent.*

As can be seen in figure 3, the sizing agent stops the water from diffusing into the fibers. In fact the sizing agent AKD slows the process and lowers the surface energy.

When the dispersed AKD is deposited on the fiber, it is surrounded by water and will not spread along the fiber because it would cause an undesirable contact between the water and the hydrocarbon material. When the water has evaporated the dispersion spreads along the fiber surface and a reaction between the cellulose and the dispersion takes place as shown in reaction (1).

(1)



$$\text{R-}\underset{\underset{\text{O}}{|}}{\text{CH=C}}\text{—}\underset{\underset{\text{– C=O}}{|}}{\text{CH}}\text{-R} + \text{Cellulose-OH} \rightarrow \text{R-CH}_2\text{-}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{-}\underset{\underset{\underset{\underset{\text{O-Cellulose}}{|}}{\text{C=O}}}{|}}{\text{CH}}\text{-R}$$

Sizing (hydrophobizing) reaction: *This is the reaction that occurs on the fiber surface between the AKD dispersion and the fiber Cellulose.*[2]

1.3 The Aim of the Study

The purpose of this study was to study the phosphorous separation in the chlorination process in the AKD plant in Trollhättan. By doing this, one wants to see how the chlorination process works on regular basis and how it is affected by normal standard operations.

2. The AKD process

The purpose of the chlorination process is to make the fatty acid more reactive by converting it to an acid chloride. The chloride is a very good leaving group for further reactions, e.g. the AKD reaction but it also reacts strongly with water producing the fatty acid and hydrochloric acid. The chlorination process is entailed that the hydroxyl group in the end of the fatty acid molecule is exchanged to a chlorine molecule.

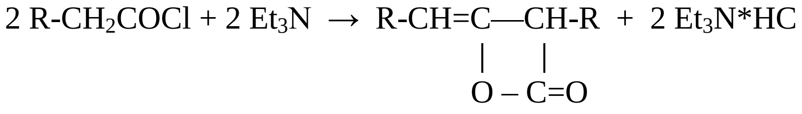
As mentioned earlier the chlorination is performed in two steps with different chlorinating agents, the first one by using phosphorous trichloride, PCl_3 and the second one by using thionyl chloride, $SOCl_2$.

It is performed like this in order to optimize both the costs and the quality of the acid chloride. The phosphorous trichloride is more cost efficient but if one only use it in the process the amount of phosphorous in the product gets higher than the desirable amount and will thereby cause disturbance in the dimerization where the final product is produced. If only the thionyl chloride would be used as a chlorinating agent it would create large amounts of SO_2 which will be required to be taken care of which the plant is not designed for.

Two fatty acid chlorides are then further reacted to AKD by using Triethylamine as a helping chemical.

$$(2)\quad 2\ PCl_3 + 6\ RCOOH \rightarrow 5\ RCOCl + RCOOH + H_4P_2O_5 + HCl$$

$$(3)\quad SOCl_2 + RCOCl + RCOOH \xrightarrow{\text{Filter aid}} 2\ RCOCl + SO_2 + HCl$$

(4) 

$$2\ R\text{-}CH_2COCl + 2\ Et_3N \rightarrow \begin{array}{c} R\text{-}CH{=}C{—}CH\text{-}R \\ \quad |\quad\ \ | \\ \quad O-C{=}O \end{array} + 2\ Et_3N{*}HC$$

In the first chlorination step (reaction (2), which is performed in a reactor called 1st chlorination reactor, the phosphorous trichloride is reacted with fatty acid and forms fatty acid chloride along with other substances such as phosphorous anhydride and hydrochloride acid.

The reaction (3), which is called the final step of the chlorination process, occurs in a reactor called 2nd chlorination reactor. The fatty acid chloride is mixed with thionyl chloride but also with the remaining fatty acid because all fatty acid does not react completely in the first step.

The reaction (4), which is called the dimerization, is where two acid chloride molecules react with each other in the presence of the help chemical Triethylamine, TEA, and produces the final product/sizing chemical AKD and the byproduct Triethylamine-hydrochloride, TEA-HCl.

2.1 The first chlorination step

The first chlorination step is performed in 1st chlorination reactor where fatty acid is added and there after the dosage of the phosphorous trichloride is done during mixing. When the dosage of the phosphorous trichloride is finished the mixer runs for an additional 30 seconds. This last mixing step was altered for two batches to investigate the mixing effect on the phosphorous separation.

The following reaction steps (5-9) describe the sub reactions that occur in the first chlorination step however the fatty acid that remains in the solution are not shown in this reaction scheme.

(5) $2\ \mathrm{R\text{-}COOH} + 2\ \mathrm{PCl_3} \rightarrow 2\ \mathrm{R\text{-}COCl} + 2\ \mathrm{HOPCl_2}$

(6) $2\ \mathrm{R\text{-}COOH} + 2\ \mathrm{HOPCl_2} \rightarrow 2\ \mathrm{R\text{-}COCl} + 2\ \mathrm{(OH)_2PCl}$

(7) $\mathrm{R\text{-}COOH} + \mathrm{(OH)_2PCl} \rightarrow \mathrm{R\text{-}COCl} + \mathrm{H_3PO_3}$

(8) $\mathrm{H_3PO_3} + \mathrm{(OH)_2PCl} \rightarrow \mathrm{(OH)_2P\text{-}O\text{-}P\text{-}(OH)_2} + \mathrm{HCl}$

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(9) $5\ \mathrm{R\text{-}COOH} + 2\ \mathrm{PCl_3} \rightarrow 5\ \mathrm{R\text{-}COCl} + \mathrm{(OH)_2P\text{-}O\text{-}P\text{-}(OH)_2} + \mathrm{HCl}$

Chlorination reaction step 1: *Sub reactions (5-8), Total reaction (9)*

The hydrochloric acid, which is formed as a gas, is evaporated from the reactor and absorbed by a scrubber. The hydrochloric acid can later be reused in the plant.

The reaction is slightly endothermic and requires heat to be able to achieve the desirable amount of product.

During the reaction the mixture becomes a two phase system which is separated. The solution separates into two phases where the upper phase consists of the acid chloride and fatty acid while the lower phase consists of the different phosphorous substances. The lower phase is later drained and transported for further reprocessing to phosphorous acid, H_3PO_3, while the upper phase is transported to the next chlorination step in the 2nd chlorination reactor.

If the separation in the first chlorination step is not complete there will be problems in the process down streams, both in the final chlorination step, in the production of the phosphorous acid and in the dimerization. If the phosphorous phase contains too much fatty acid and acid chloride, it would lead to a contaminated phosphorous acid. An increased amount of phosphorous material in the fatty acid chloride leads to an increasing dosage of the chlorinating agent $SOCl_2$ in the final step and the appearance of the filter cake becomes tenacious and sticky.

Problems in the dimerization process may be due to that the phosphorous substances will bind to the acid chloride giving surface active components e.g. phosphonates and will thereby cause problems in the washing process of the final AKD. If the acid chloride contains a high amount of surface active substance, the AKD washing will become an emulsion, which makes it impossible to wash.

2.2 The second chlorination step

As mentioned previously there is fatty acid left after the first step of the chlorination process, therefore in the second chlorination step the other chlorinating agent $SOCl_2$, thionyl chloride, is reacted as shown in reaction (10). The $SOCl_2$ reacts with the fatty acid creating the fatty acid chloride together with hydrochloride and sulfur dioxide which are evaporated and collected in a scrubber.

The thionyl chloride is a very aggressive substance and may also react with the undesirable phosphorous substance making a sticky hydrophilic material which has to be separated. To achieve this separation, dicalite and active carbon are added. The filter aid gives a large surface area where the phosphorous substances and other contaminated substances that are left in the solution could be collected and filtered of.

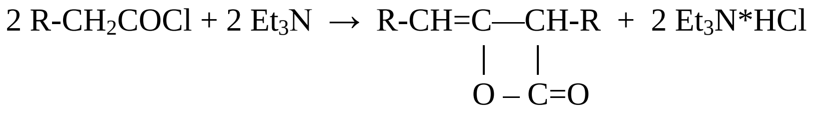
(10) $R\text{-}COOH + SOCl_2 \rightarrow R\text{-}COCl + HCl + SO_2$

Chlorination reaction step 2: *Shows how the fatty acid reacts with thionyl chloride and forms acid chloride.*

2.3 The dimerization step

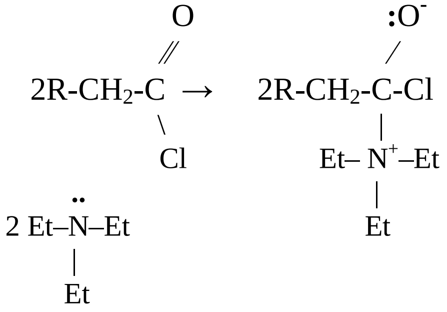
As seen in reaction 11, the fatty acid chloride is transported into the dimerization process for the final synthesis with the help chemical TEA to produce the final product AKD.

(11)



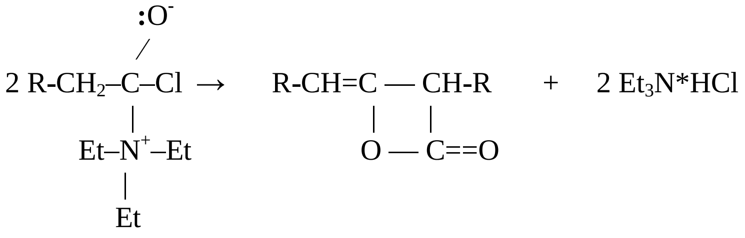
$$2\ R\text{-}CH_2COCl + 2\ Et_3N \rightarrow \begin{array}{l} R\text{-}CH{=}C\text{—}CH\text{-}R \\ \qquad\quad\ |\quad\ | \\ \qquad\quad O - C{=}O \end{array} + 2\ Et_3N{*}HCl$$

(12)



$$\begin{array}{l} 2R\text{-}CH_2\text{-}\overset{\overset{O}{/\!/}}{\underset{\underset{Cl}{\backslash}}{C}} \rightarrow 2R\text{-}CH_2\text{-}\overset{\overset{:O^-}{/}}{\underset{\underset{\underset{\underset{Et}{|}}{Et-N^+-Et}}{|}}{C}}\text{-}Cl \\ 2\ \underset{\underset{Et}{|}}{Et\text{–}\overset{\cdot\cdot}{N}\text{–}Et} \end{array}$$

(13)



$$2\ R\text{-}CH_2\text{–}\overset{\overset{:O^-}{/}}{\underset{\underset{\underset{\underset{Et}{|}}{Et-N^+-Et}}{|}}{C}}\text{–}Cl \rightarrow \begin{array}{l} R\text{-}CH{=}C\text{ — }CH\text{-}R \\ \qquad\quad\ |\qquad\ | \\ \qquad\quad O\text{ — }C{=}{=}O \end{array} + 2\ Et_3N{*}HCl$$

Reaction 12 and 13 show the mechanism occurring when triethylamine and fatty acid chloride reacts. The ion pair on the nitrogen atom in the triethylamine makes a nucleophilic attack on the positive carbon atom. Then it eliminates the chloride ion and at the same time a hydrogen atom is removed from the nitrogen and reacts with the chlorine atom and forms hydrochloric acid.

Afterwards the triethylamine is removed from the acid chloride and reacts with the hydrochloric acid and forms triethylamine-hydrochloride. At the same time the two acid chloride molecules forms AKD.

In the dimerization process two fatty acid chloride molecules reacts with each other in the presence of the help chemical Triethylamine, TEA and forms the sizing product AKD. At the same time the two chlorine atoms attached to the acid chloride binds to the help chemical and forms Triethylamine-hydrochloride, TEA-HCl. There are several of steps in this process before the AKD becomes a completed product in the form of small pastilles.

In the first step of the dimerization, the chemicals are dosed slowly into the dimerization reactor to control the size of the wax crystals. If they are dosed quickly in the beginning the size of the crystals becomes wrong which gives a product with a higher viscosity. Later on when the dosage of chemicals is finished, the chemicals are mixed strongly so the byproduct TEA-HCl can form crystals with the right size.

The next step in the dimerization is called the washing step, which is divided into two steps because the AKD product if washed with two different chemicals, hydrochloric acid and water.

In the first step, the acid wash the AKD is washed with hydrochloric acid in order to clean AKD from TEA. A separation occurs to separate the TEA-HCl from the AKD and then the TEA-HCl is drained to a TEA-recycling system to gain TEA again.

In the mean time, when the acid wash is ongoing, a preparation for the water wash is occurring. Another separation of the AKD phase and the water phase is performed, where the water phase is later drained to another reactor. The stir time in the washing reactor is very important due to if the chemicals are not stirred slowly the stirring can affect the AKD wax by breaking it to small particles and an emulsion is formed.

The final step of the dimerization is the drying process, where the AKD is dried because it contains a lot of water. The water and remaining parts of TEA and TEA-HCl are transported through to the scrubber systems. When the drying is finished the AKD is transported in the storage tank where it is later cooled down, filtered and is formed into pastilles so it can be packed into big bags.

The dimerization is performed both in the batch line and the continuous line. [1, 8, 11, 12]

3. Raw material used in the Chlorination process

As mentioned in the previous chapter, the chlorination process is done in two reactions. In this chapter the characteristics of the fatty acid, the phosphorous trichloride and thionyl chloride and the other raw materials will be discussed.

3.1 Fatty acid, RCOOH

A fatty acid is a carboxylic acid with a long aliphatic chain that is either unsaturated or saturated. The used fatty acids are typically saturated with a difference in chain length and melting point. Therefore they are separated into two types of fatty acid, low melting point (LMP) fatty acid and high melting point (HMP) fatty acid. The LMP fatty acid comes normally from tallow or palm and the HMP fatty acid comes typically from rapeseed.

The fatty acid must always be delivered in liquid state so it could be transferred into the system. Both fatty acids are required to be heated to a certain temperature, 60° C, when being transferred into the system because of the possibility of the acid freezing.

The fatty acid that is delivered has to be saturated, has to have a low peroxide value and a good color to give a good product quality. The saturation is measured by the iodine value which tells the amount of the double bonds existing in the fatty acid. [1, 3, 4, 13]

3.2 Phosphorous trichloride, PCl_3

Though phosphorous trichloride has become a much more expensive raw material to buy it is still the main chlorination reactant that is used in the chlorination process.

As can be seen in reaction (14), phosphorous trichloride is produced by the combustion of liquid phosphorous in dry stream of chlorine gas. It is mainly used to manufacture the phosphorous acid (phosphonic acid), which is formed as byproduct in the chlorination process, step 1.

$$(14) \quad P_4 + 6Cl_2 \rightarrow 4\ PCl_3$$

The phosphorous trichloride has no color as a liquid in room temperature and it reacts strongly with many other substances and is therefore poisonous. For instance reactions with water produce phosphorous acid and hydrochloric acid. In extreme cases the formation of phosphine may occur, which is a very flammable and highly toxic chemical substance. [1, 5, 13]

3.3 Thionyl chloride, $SOCl_2$

Thionyl chloride is a very desirable chlorinating agent in the chemical industry. Thionyl chloride is used for production of acid chlorides from carboxylic acids such as fatty acids.

Thionyl chloride is a nonflammable chemical substance and it has a very pungent odor that irritates. It can be produced in two different ways; i) reaction between sulfur, chlorine and oxygen or ii) reaction between sulfur trioxide and chlorine. Thionyl chloride has almost the same characteristics as phosphorous trichloride but the difference is that when thionyl chloride is mixed with water, besides the formation of hydrochloric acid gas, sulfur dioxide is formed and is a very smelly poisonous gas. [1, 6, 13]

3.4 Dicalite, filter aid

The second and final step in the chlorination process starts by adding a filter aid, Dicalite, into the reactor 2nd chlorination reactor. The function of this substance is that it adsorbs a large part of the hydrophilic phosphorous substance that the thionyl chloride creates. Dicalite is a white powder based on silica, SiO_2.The silica dust must be treated very carefully because there is a risk of getting silicosis, a disease causing lung damages. [1, 13]

3.5 Activated Carbon

Activated carbon is added in the final stages of the second chlorination step along with thionyl chloride. The purpose is to adsorb different hydrophobic (organic) phosphorous and/or sulfuric substances, which could discolor the final product AKD. [1, 13]

4. Materials and Method

This chapter covers the materials and the different methods used during the analysis that was performed to determine the amount of phosphorous substance in the fatty acid chloride, in the 1st chlorination reactor and in the 2nd chlorination reactor.

4.1 Observations

To be able to distinguish how the amount of phosphorous changes from each one of those processes, samples were collected from each chlorination steps. The first sample is taken after the first chlorination step and the second sample is taken when the second chlorination step is done and the fatty acid chloride is transferred into a storage tank.

To be able to determine the amount of the phosphorous substance in the two processes, an analysis method that can calculate the amount of phosphorous substance from 50 ppm to 4000 ppm, was performed.

Another observation was that some changes were done in purpose of observing if and how those changes would affect the amount of phosphorous in the fatty acid chloride and the other systems in the plant.

The change/test that was performed included that the stir time in the 1st chlorination reactor was altered to a desirable time. This was performed accordingly to old theories in purpose of showing if the phosphorous substance where more bonded to the fatty acid when being stirred for a longer period of time.

4.2 Method

The purpose of the analysis of phosphorous was to determine the level of phosphorous in organic materials such as fatty acid chloride and AKD down to 50 ppm. The method consists of a combustion part, where the sample is digested by strong acids and microwave, and an analysis part of the complex color which is run by an UV-spectrophotometer. The samples from the batches were removed in order in the process and the qualities of the acid chloride, as mentioned earlier, could vary from LMP to HMP.

Two microwave ovens, as shown in figure 4, were used in the analysis, which made it possible to analyze more samples in each round. The ovens consist of two cells each for the samples and the function of the microwaves is to combust all carbon in the sample so that only the phosphorous remained in the sample.

Figure 4. *The two microwave ovens connected to the two chemical bottles, nitric acid and hydrogen peroxide (lying in between the two ovens).*

The UV-spectrophotometer measures the color complex of the sample in absorbance. A given calibration curve works as a standard for the calculation of the amount phosphorous. The calibration curve has a maximum limit for the absorbance for the different samples, 1st chlorination reactor and 2nd chlorination reactor samples.

Each analytical run required < 1 gram sample and each analytical run could take up to 2-3 hours. [12, 13]

4.3 Materials

- ✓ UV-spectrophotometer, a double beam instrument that can measure 10 cm cuvettes.
- ✓ 10 cm glass or quartz cuvettes
- ✓ 1 cm quartz or plastic cuvettes
- ✓ Microwave ovens with associated tubes
- ✓ 50 ml and 100 ml flasks
- ✓ 2.5, 5, 10, 20 and 50 ml pipettes
- ✓ Pasteur pipettes, plastic or glass
- ✓ 250 ml beakers, the high model
- ✓ Litmus paper

4.4 Chemicals

- ✓ Sulfuric acid (concentrated)
- ✓ Nitric acid (concentrated)
- ✓ Hydrogen peroxide, 30 % p.a.
- ✓ Sodium hydroxide, 32 %
- ✓ Ammonia (concentrated)
- ✓ Ascorbic acid
- ✓ Molybdate solution (color complex), containing ammoniumhepta molybdate and potassium antimony oxide tartrate

4.5 The Laboratory Performance

The samples that were analyzed were removed from the chlorination steps, 1st chlorination reactor and 2nd chlorination reactor. The two types of samples are performed separately because both samples have different measurement for the analysis. After estimating the time and the work needed for each analysis run, a very profitable work schedule was performed, meaning the amount of samples analyzed were between 8-16 samples a day. Though there were occasionally some problems with the instruments the analysis work was not affected.

The sample from 1st chlorination reactor is a sample with high levels of phosphorous, because it is measured between levels of 400 – 4000 ppm phosphorous. Unlike the sample from 1st chlorination reactor, the sample from 2nd chlorination reactor is called a sample with low levels of phosphorous, because the measurement level of the phosphorous is between 50-400 ppm.

The samples from the 1st chlorination reactor are weighed to a maximum amount of 0.5 grams (0.8 grams of 2nd chlorination reactor samples) into the tubes, but suggested amount is 0.3 grams (0.7 grams of 2nd chlorination reactor samples).

Then 10 ml sulfuric acid was added to the samples. The sulfuric acid is a chemical that helps in increasing the temperature during the combustion in the microwave. After adding the acid, the tubes are put into the microwaves and the combustion was started.

During the combustion, the nitric acid was added primarily in several steps at definite temperatures and nitrous gases are formed. Those gases are ventilated through the pipe to the scrubbers. In the final stage of the combustion, hydrogen peroxide were added making some of the nitrous gases to disappear.

After the dosage of the hydrogen peroxide was completed, the burning ended and the tubes that contained the samples had a temperature of 200 °C, which meant that they had to be cooled before being neutralized. When the samples were cooled, they were poured into 250 ml beakers and then neutralized by adding 20 – 25 ml ammonia.

To be able to determine if the samples were neutralized, a litmus paper was used. The paper was put in the sample in the beaker and when it had a purple color, the sample was still acidic and more ammonia was added. But when the paper got a yellow - orange color it indicated that the sample was neutralized.

The neutralization required more than one small paper of the litmus because the ammonia reacted strongly with the sample, which made it a lot hotter and much faster than usual making that made the paper's quality less trusted. There are two different ways to neutralize the samples and not destroy the litmus paper. It was to either use a beaker filled with cold water or by adding the ammonia thoroughly and quickly to the samples. Both methods were used but the latter was the easiest one to perform.

Afterwards, the samples were diluted with water to a certain level into the 100 ml flasks and later they were cooled down once again before they were further processed.

The final step of the analysis was transferring a given quantity of the samples to 50 ml flasks (100 ml if 2nd chlorination reactor samples were processed), where they are mixed with two solutions, forming a color complex, that gives a blue color. The intensity of the blue color indicated how much phosphorous the samples contained.

A zero sample, a blank, is a sample containing a given quantity of water and a given quantity of the color complex, was diluted and measured in order to be sure that the color complex was not contaminated. The blank had a maximum value in absorbance depending on the type of analyzed sample. 1st chlorination reactor had a maximum value of 0.005, while 2nd chlorination reactor had a maximum value of 0.05 in absorbance.

Figure 5. *These are an image of when samples from 1st chlorination reactor (left) and 2nd chlorination reactor (right) were processed. The colorless flask (left image) is the blank that was done.*

As can be seen in figure 5, the images show how the color, in the samples, was developed when the color complex was mixed with the sample. The blue color in the 2nd chlorination reactor sample is very pale and that is because the second chlorination step takes care of the phosphorous substances extremely well, which means that the amount of phosphorous in the filtered sample was reduced. When the sample was analyzed in the UV-spectrophotometer, an absorbance for the sample was calculated and through a theoretical calculation the amount of phosphorous was estimated.

5. Results and Discussion

In this chapter, the results from the phosphorous analysis will be presented and discussed. A correlation between different parameters, which are parameters that are updated daily by the shift personnel, was performed.

5.1 The Variance of the analysis (1st and 2nd chlorination reactor)

Before the phosphorous analysis was used for evaluating the process a variance analysis were performed. This was performed in order to see if the final result of one sample could be trusted. The same sample was divided and put into four cells in the microwave oven and this was done with both a 1st chlorination reactor sample and 2nd chlorination reactor sample, see result in table 1 and 2. The samples were analyzed individually.

Cell	Quality	Batch nr.	Amount (g)	Absorbance	P (ppm)
1	LMP	12200	0.3085	0.4661	1956
2	LMP	12200	0.3139	0.4865	2007
3	LMP	12200	0.3187	0.4870	1979
4	LMP	12200	0.3121	0.5053	2097

Table 1. *The variance in the analysis from 1st chlorination reactor*

Cell	Quality	Batch nr.	Amount (g)	Absorbance	P (ppm)
1	LMP	12199	0.7016	0.5119	94
2	LMP	12199	0.7252	0.5329	95
3	LMP	12199	0.7080	0.5516	101
4	LMP	12199	0.7006	0.5017	92

Table 2. *The variance in the analysis from 2nd chlorination reactor*

As can be seen in table 1 and table 2, the variance in the analysis are small with a standard deviation of only 62 and 4 respectively. This indicates that the analyses of different samples could be performed at the same time, and the final result would still be credible.

5.2 The Amount of Phosphorous compared to Batch number in order

A correlation between the analyzed samples, samples from 1st chlorination reactor and 2nd chlorination reactor, and the batch numbers in the process was performed. The samples were also separated by the type of quality, LMP and HMP.

This analysis shows primary that there are no structural errors in the sampling of the study, e.g. that a series of batches have increasing phosphorous amount or decreasing phosphorous amount.

This analysis does also show that there are a difference between the different raw materials, LMP and HMP. As can be seen in figure 6, the amount of phosphorous of the LMP samples are more spread than the HMP and that the HMP shows a better stability in the dispersal of a specific limit range. Another fact that can be stated is that the HMP samples have generally a lower amount of phosphorous than the LMP samples.

As can be seen in figure 7, unlike the LMP samples from 1st chlorination reactor, the LMP samples from the 2nd chlorination reactor do not spread much from the HMP samples.

The reason that HMP samples show a better stability might be because this type of fatty acid is purchased with a slightly higher specification. Due to this, the limit of the properties in a HMP fatty acid, such as the iodine value, the peroxide value etc., has been set at a lower limit value than the LMP fatty acid.

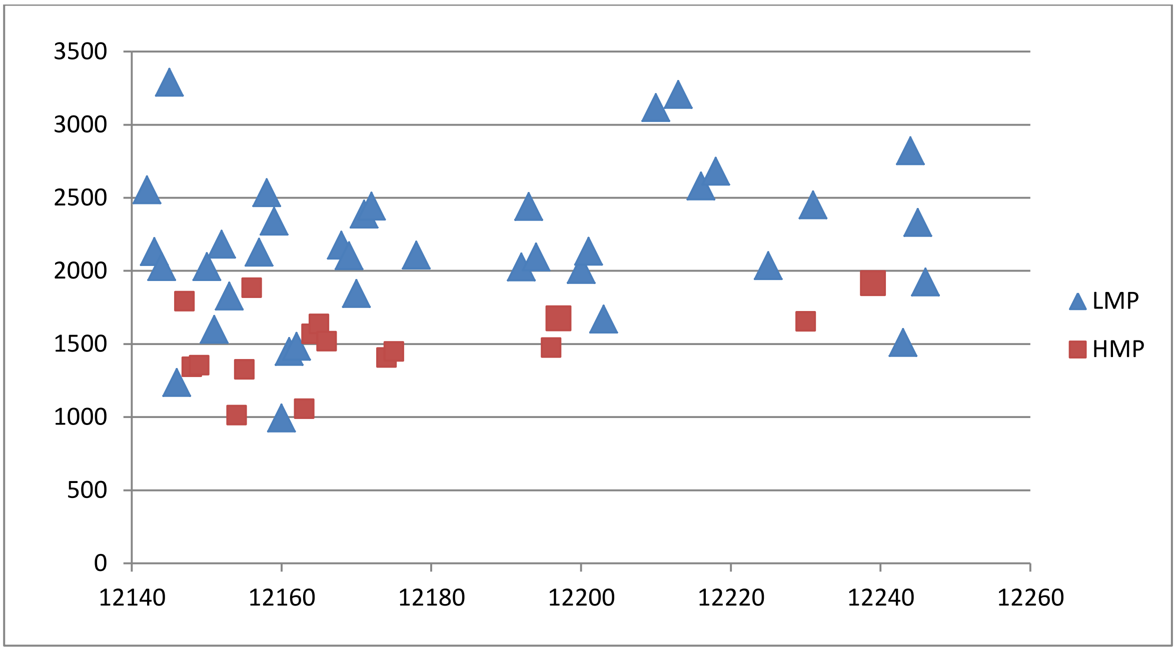


Figure 6. *1st chlorination reactor: A correlation between the amount of phosphorous in the samples (in ppm) (LMP and HMP), and the batch numbers.*

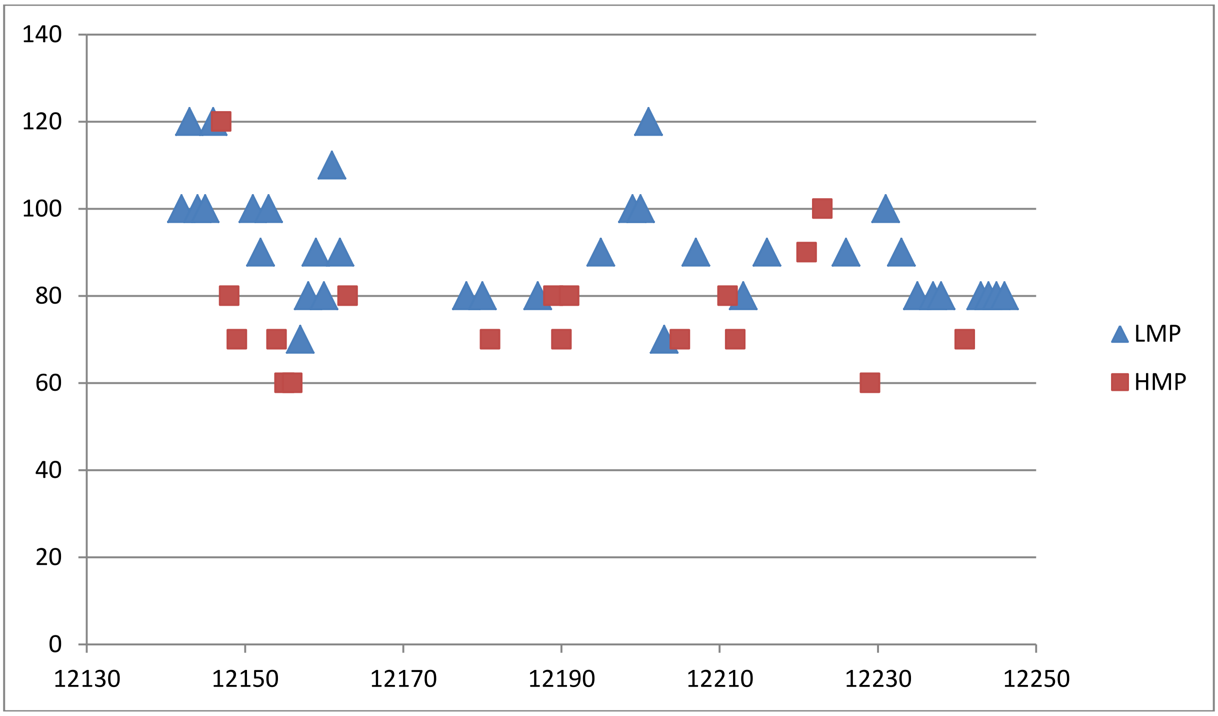


Figure 7. *2nd chlorination reactor: A correlation between the amount of phosphorous (in ppm) in the samples (LMP and HMP), and the batch numbers.*

5.3 The Amount of Phosphorous compared to the content of Fatty acid in the samples

On daily basis, the shift personnel remove the samples from 1st chlorination reactor and 2nd chlorination reactor for analysis to control the content of fatty acid and thionyl chloride (this is only controlled in the sample from the 2nd chlorination reactor) in the fatty acid chloride.

A correlation between the amount of phosphorous and the content of fatty acid in the sample from both 1st chlorination reactor and 2nd chlorination was performed. Once again the samples were separated into the two types, LMP and HMP.

As can be seen in figure 8, the increasing content of fatty acid gives a weak increase in the amount of phosphorous in the samples. We do not have a good explanation for this correlation. Once again the HMP samples are lower and more stabilized and spread in only a specific limit range, 1000 – 2000 ppm, while the LMP samples has a spread in a bigger and higher limit range, 1000 – 3500 ppm.

Figure 9, the amount of phosphorous versus the fatty acid content after the 2nd chlorination, does not show the same connection. This is probably understandable since the fatty acid content here is due to the amount of thionyl chloride which is added during the second reaction. Also here can we see that the HMP samples still show more stability in a lower limit range.

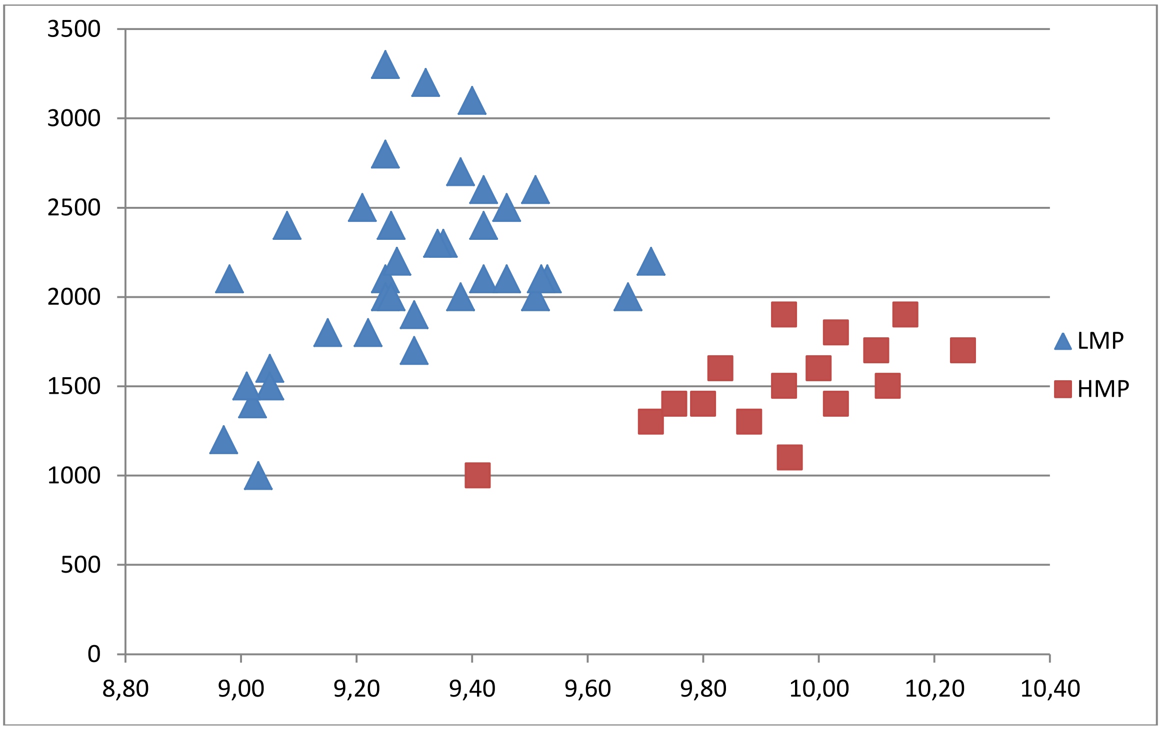


Figure 8. *1st chlorination reactor: A correlation between the amount of phosphorous (in ppm) in the samples (LMP and HMP), and the content of fatty acid in the samples*

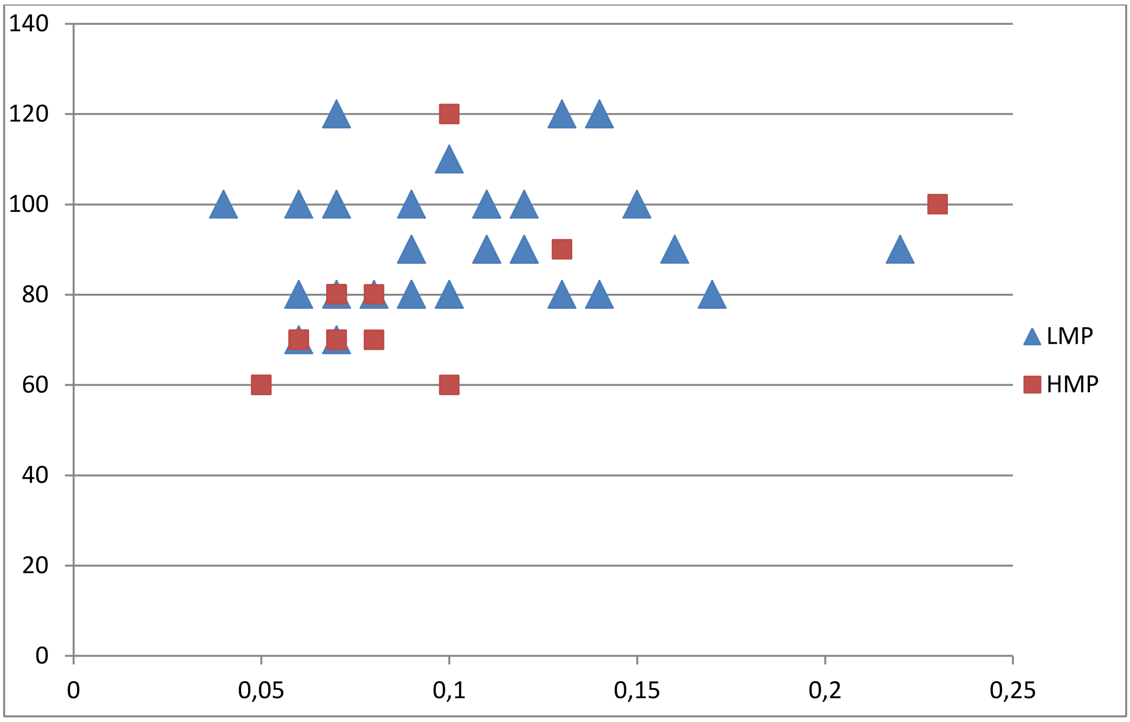


Figure 9. *2nd chlorination reactor: A correlation between the amount of phosphorous (in ppm) in the samples (LMP and HMP), and the content of fatty acid in the samples (%).*

5.4 Correlation of the amount of phosphorous in the 2nd chlorination reactor to the amount of phosphorous in the 1st chlorination reactor.

As can be seen in figure 10, the phosphorous content reduces immensely in the fatty acid chloride after the second and final chlorination step. We can also see that there is no correlation between the amount of phosphorous after the 1st chlorination and 2nd chlorination.

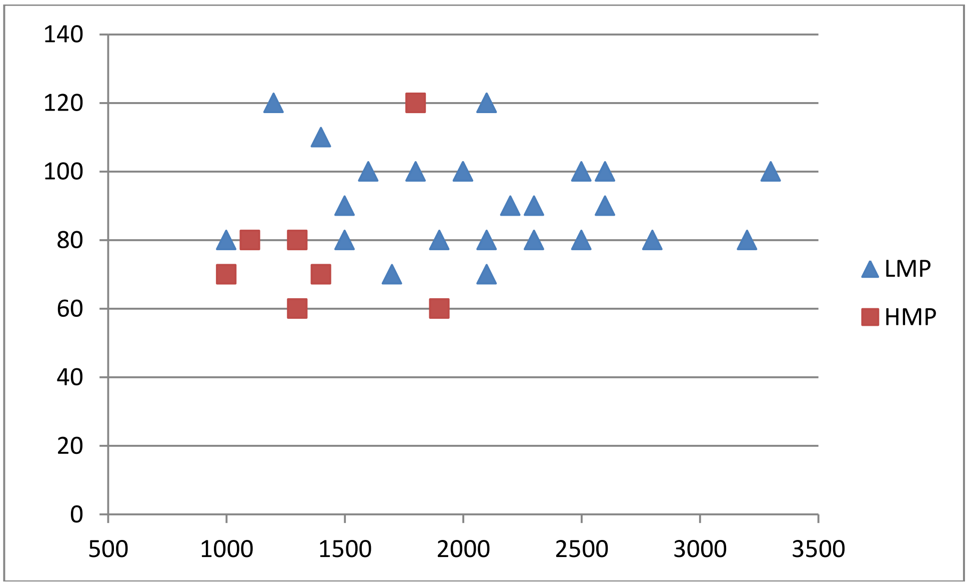


Figure 10. *A correlation between the amount of phosphorous (in ppm) in the samples, in 2nd chlorination reactor to the amount of phosphorous (in ppm) in the samples, in 1st chlorination reactor*

5.5 Alteration of the stir time in the 1st chlorination reactor

As mentioned previously, two small alterations were performed with the mixer in the 1st chlorination reactor. The alterations done were to increase the second part of the stir time in the reactor to 1 minute and 2 minutes, which is more than the original stir time at 30 seconds. The alterations did not contribute to any changes of the value of the phosphorous in the samples or the whole system. Unfortunately the project time did not admit to perform any more changes.

6. Conclusions

- The batch order does not affect the amount of phosphorous in the fatty acid chloride during the 1st and 2nd chlorination.

- Fatty acid chloride of the quality HMP has a lower spreading of the amount of phosphorous than LMP.

- The analysis showed that there are no systematic errors since there was no correlation to the batch order.

- The amount of phosphorous has a weak increase with increasing content of the fatty acid in the samples, both HMP and LMP in the 1st chlorination.

- No correlation between the amount of phosphorous and the content of the fatty acid in the samples was found in the 2nd chlorination.

- Stir time in 1st chlorination reactor: No changes were noticed by the alterations that were performed.

7. Future Recommendations

At the beginning of this study, as mentioned in the first chapter, there were some parameters that were meant to be tested but due to different circumstances in theplant they could not be performed. However, there are some recommendations on further work in this matter.

- The dosage of the phosphorous trichloride could be slightly changed such as decreasing or increasing the amount of dosage that will not affect the surrounding systems in the plant.

- Another interesting aspect is the properties of the fatty acids that are delivered from the two suppliers could be investigated. This could be done by observing the delivery time of the fatty acids and link it to the batches numbers in the process. Then maybe a connection between those two would be noticed.

- Looking back on the tests that was performed with the mixer in the reactor 1st chlorination reactor, though they were performed shortly, the results showed that there was no difference in the amount of phosphorous by altering the second stir time just a few minutes. The suggestion is to try and run the mixer a longer period of time, 15 min or 30 min.

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Personal Contact

11. Shift Personnel at Eka Chemicals (2011-04 to 2011-05)

12. Own Experience from working in Eka Chemicals

13. Karin Ohlsson, Process Engineer, Eka Chemicals AB. Numerous meetings and discussions throughout the assignment (2011-04 to 2011-06)

14. Caroline Chouha, Senior Laboratory Scientist, Eka Chemicals AB. Numerous discussions throughout the assignment. (2011-04 to 2011-06)

15. Ingela Svensson, Senior Laboratory Scientist, Eka Chemicals AB. Numerous discussions throughout the assignment. (2011-04 to 2011-06)

Appendix A – Analysis Results 1st chlorination reactor and 2nd chlorination reactor, LMP samples

Quality	Batchnr.	Date of analysis	Amount of sample (g)	Absorbance	P % in FA (1st Chl.reac) (ppm)	Shown result
LMP	**12142**	2011-04-28	0,3234	0,6377	2554	2600
LMP	**12143**	2011-04-28	0,3284	0,5407	2132	2100
LMP	**12144**	2011-04-28	0,299	0,4683	2028	2000
LMP	**12145**	2011-04-28	0,3204	0,8137	3291	3300
LMP	**12146**	2011-05-02	0,3076	0,2939	1236	1200
LMP	**12150**	2011-05-05	0,3238	0,5072	2028	2000
LMP	**12151**	2011-05-05	0,3081	0,3805	1598	1600
LMP	**12152**	2011-05-05	0,3012	0,5072	2181	2200
LMP	**12153**	2011-05-05	0,3067	0,433	1828	1800
LMP	**12157**	2011-05-09	0,3339	0,5485	2128	2100
LMP	**12158**	2011-05-09	0,3131	0,6126	2534	2500
LMP	**12159**	2011-05-09	0,3142	0,5675	2339	2300
LMP	**12160**	2011-05-09	0,3252	0,2495	992	1000
LMP	**12161**	2011-05-09	0,3205	0,3586	1448	1400
LMP	**12162**	2011-05-09	0,3085	0,3536	1483	1500
LMP	**12168**	2011-05-12	0,3671	0,6166	2176	2200
LMP	**12169**	2011-05-17	0,3212	0,5214	2102	2100
LMP	**12170**	2011-05-17	0,313	0,4459	1844	1800
LMP	**12171**	2011-05-17	0,2971	0,5479	2388	2400
LMP	**12172**	2011-05-17	0,3218	0,6069	2443	2400
LMP	**12178**	2011-05-25	0,3103	0,5048	2107	2100
LMP	**12192**	2011-05-19	0,3024	0,4734	2027	2000
LMP	**12193**	2011-05-25	0,3204	0,6036	2440	2400
LMP	**12194**	2011-05-19	0,3071	0,4966	2094	2100
LMP	**12200**	2011-05-18	0,3133	0,4862	2009	2000
LMP	**12201**	2011-05-17	0,2941	0,4848	2134	2100
LMP	**12203**	2011-05-19	0,3004	0,3875	1670	1700
LMP	**12210**	2011-05-26	0,303	0,729	3117	3100
LMP	**12213**	2011-05-26	0,3209	0,7941	3206	3200
LMP	**12216**	2011-05-26	0,312	0,6217	2581	2600
LMP	**12218**	2011-05-26	0,3153	0,6527	2682	2700
LMP	**12225**	2011-05-26	0,3224	0,5065	2034	2000
LMP	**12231**	2011-05-26	0,3182	0,6019	2450	2500
LMP	**12243**	2011-05-20	0,3091	0,3604	1509	1500
LMP	**12244**	2011-05-20	0,3273	0,3567	2821	2800
LMP	**12245**	2011-05-20	0,3192	0,5744	2331	2300
LMP	**12246**	2011-05-20	0,3094	0,4597	1924	1900

Quality	Batchnr.	Date of analysis	Amount of sample (g)	Absorbance	P % in FAC (2nd Chl.reac) (ppm)	Shown result
LMP	**12142**	2011-05-02	0,311	0,4669	96	100
LMP	**12143**	2011-05-02	0,317	0,5712	117	120
LMP	**12144**	2011-05-02	0,3065	0,5005	105	100
LMP	**12145**	2011-05-02	0,3271	0,5246	103	100
LMP	**12146**	2011-05-03	0,7231	0,6529	118	120
LMP	**12151**	2011-05-05	0,7689	0,5668	95	100
LMP	**12152**	2011-05-06	0,7106	0,486	88	90
LMP	**12153**	2011-05-06	0,7003	0,5347	99	100
LMP	**12157**	2011-05-11	0,7065	0,4027	72	70
LMP	**12158**	2011-05-11	0,766	0,4682	78	80
LMP	**12159**	2011-05-11	0,7209	0,4847	86	90
LMP	**12160**	2011-05-11	0,7137	0,4565	82	80
LMP	**12161**	2011-05-11	0,7084	0,6183	113	110
LMP	**12162**	2011-05-11	0,7158	0,498	90	90
LMP	**12178**	2011-05-25	0,7022	0,424	77	80
LMP	**12180**	2011-05-25	0,7066	0,4391	79	80
LMP	**12187**	2011-05-25	0,7058	0,4309	78	80
LMP	**12195**	2011-05-19	0,7142	0,5086	92	90
LMP	**12199**	2011-05-18	0,7089	0,5245	95	100
LMP	**12200**	2011-05-24	0,7017	0,5171	95	100
LMP	**12201**	2011-05-19	0,7084	0,6362	117	120
LMP	**12203**	2011-05-24	0,7269	0,4148	73	70
LMP	**12207**	2011-05-25	0,7118	0,4773	86	90
LMP	**12213**	2011-05-26	0,7418	0,4798	83	80
LMP	**12216**	2011-05-26	0,7146	0,4957	89	90
LMP	**12226**	2011-05-26	0,7087	0,4957	90	90
LMP	**12231**	2011-05-26	0,7041	0,5288	97	100
LMP	**12233**	2011-05-26	0,7127	0,4698	85	90
LMP	**12235**	2011-05-26	0,7361	0,4812	84	80
LMP	**12237**	2011-05-25	0,7146	0,4504	81	80
LMP	**12238**	2011-05-25	0,7167	0,4706	84	80
LMP	**12243**	2011-05-20	0,7109	0,4435	80	80
LMP	**12244**	2011-05-20	0,7253	0,4686	83	80
LMP	**12245**	2011-05-20	0,7112	0,4514	81	80
LMP	**12246**	2011-05-20	0,7283	0,4778	84	80

Appendix B – Analysis Result 1st chlorination and 2nd chlorination reactor, HMP samples

Quality	Batchnr.	Date of analysis	Amount of sample (g)	Absorbance	P % in FA (1st Chl.reac) (ppm)	Shown result
HMP	**12147**	2011-05-02	0,3384	0,4683	1792	1800
HMP	**12148**	2011-05-02	0,3319	0,3446	1344	1300
HMP	**12149**	2011-05-02	0,3176	0,3325	1355	1400
HMP	**12154**	2011-05-06	0,3007	0,2354	1012	1000
HMP	**12155**	2011-05-06	0,3095	0,3171	1326	1300
HMP	**12156**	2011-05-09	0,3225	0,4694	1885	1900
HMP	**12163**	2011-05-09	0,3209	0,2622	1057	1100
HMP	**12164**	2011-05-12	0,3177	0,385	1569	1600
HMP	**12165**	2011-05-12	0,3187	0,4029	1636	1600
HMP	**12166**	2011-05-12	0,3297	0,3865	1517	1500
HMP	**12174**	2011-05-25	0,3262	0,3545	1406	1400
HMP	**12175**	2011-05-25	0,3641	0,4072	1448	1400
HMP	**12196**	2011-05-17	0,3123	0,356	1475	1500
HMP	**12197**	2011-05-17	0,321	0,4157	1676	1700
HMP	**12230**	2011-05-26	0,3101	0,3962	1654	1700
HMP	**12239**	2011-05-26	0,3211	0,4751	1916	1900

Quality	Batchnr.	Date of analysis	Amount of sample (g)	Absorbance	P % in FAC (2nd Chl.reac) (ppm)	Shown result
HMP	**12147**	2011-05-03	0,7319	0,6589	117	120
HMP	**12148**	2011-05-03	0,7293	0,4495	79	80
HMP	**12149**	2011-05-03	0,7019	0,4062	74	70
HMP	**12154**	2011-05-06	0,733	0,4077	71	70
HMP	**12155**	2011-05-06	0,7074	0,3514	63	60
HMP	**12156**	2011-05-11	0,7373	0,362	62	60
HMP	**12163**	2011-05-11	0,7072	0,4356	79	80
HMP	**12181**	2011-05-25	0,7128	0,3904	70	70
HMP	**12189**	2011-05-24	0,7076	0,4309	78	80
HMP	**12190**	2011-05-19	0,695	0,3991	73	70
HMP	**12191**	2011-05-19	0,7002	0,4227	77	80
HMP	**12205**	2011-05-26	0,7158	0,3703	65	70
HMP	**12211**	2011-05-24	0,7086	0,4606	83	80
HMP	**12212**	2011-05-25	0,7158	0,3884	69	70
HMP	**12221**	2011-05-24	0,7057	0,4871	89	90
HMP	**12223**	2011-05-24	0,7209	0,5549	100	100
HMP	**12229**	2011-05-25	0,7253	0,3421	59	60
HMP	**12241**	2011-05-24	0,7176	0,3884	69	70

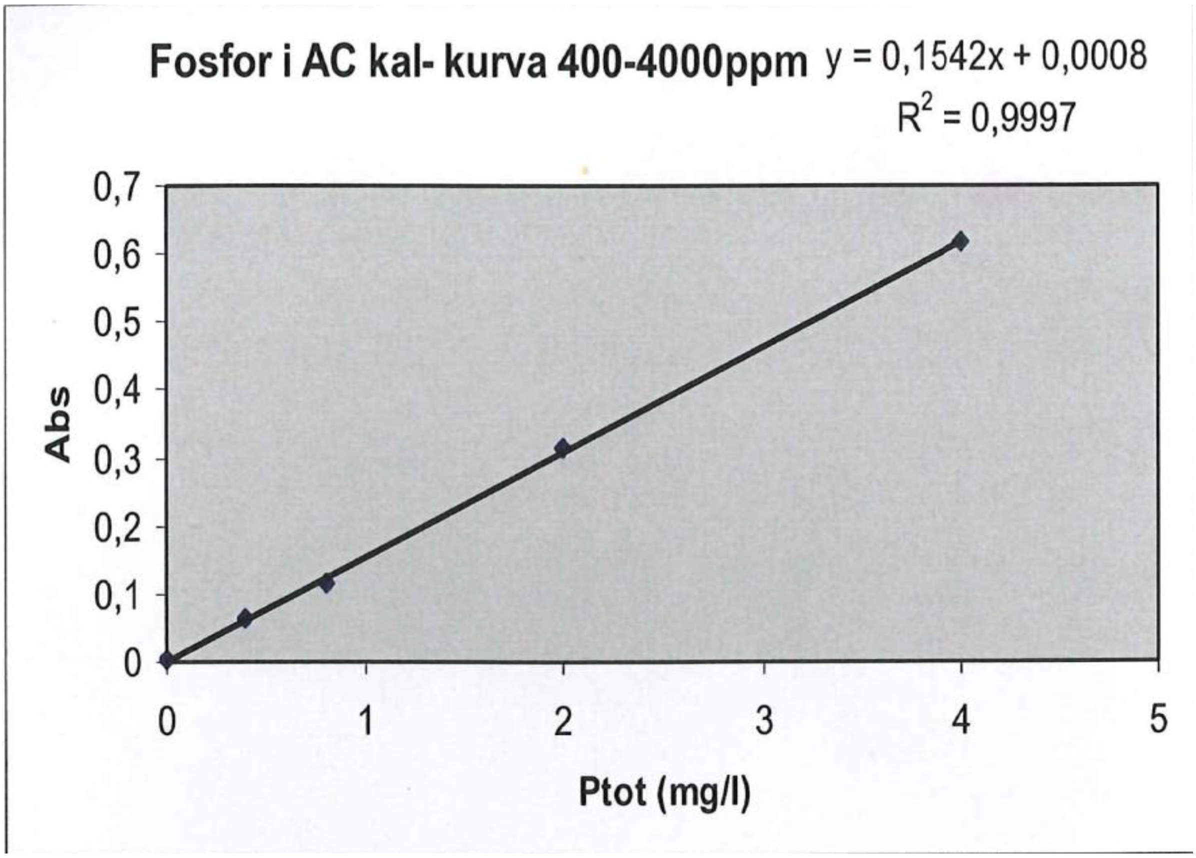
Appendix C – The Parameters the Samples were compared to.

Quality	Batchnr.	1st separation 6301	2nd separation 6303	3rd separation 6303	Total amount Phosphor 63-syst.	% FA (1st chlorination reactor)	% FA (2nd chlorination reactor)
LMP	**12142**	825	20	24	869	**9,42**	0,11
LMP	**12143**	815	20	17	852	**9,25**	0,14
LMP	**12144**	826	22	19	867	**9,25**	0,12
LMP	**12145**	821	21	22	864	**9,25**	0,04
LMP	**12146**	821	26	26	873	**8,97**	0,13
LMP	**12150**	831	20	23	874	**9,26**	0,08
LMP	**12151**	821	30	23	874	**9,05**	0,09
LMP	**12152**	826	20	24	870	**9,27**	0,09
LMP	**12153**	815	3	44	862	**9,15**	0,07
LMP	**12157**	808	9	59	876	**9,42**	0,07
LMP	**12158**	814	25	43	882	**9,46**	0,1
LMP	**12159**	814	12	32	858	**9,35**	0,12
LMP	**12160**	815	22	30	867	**9,03**	0,09
LMP	**12161**	809	23	24	856	**9,02**	0,1
LMP	**12162**	819	26	24	869	**9,05**	0,11
LMP	**12168**	815	15	35	865	**9,71**	0,1
LMP	**12169**	821	16	30	867	**8,98**	0,16
LMP	**12170**	821	22	31	874	**9,22**	0,1
LMP	**12171**	809	20	33	862	**9,08**	0,11
LMP	**12172**	809	21	37	867	**9,26**	0,07
LMP	**12178**	819	22	27	868	**9,53**	0,09
LMP	**12192**	815	24	27	866	**9,51**	0,07
LMP	**12193**	819	11	32	862	**9,42**	0,09
LMP	**12194**	809	11	42	862	**9,52**	0,1
LMP	**12200**	815	22	26	863	**9,38**	0,06
LMP	**12201**	814	26	20	860	**9,46**	0,07
LMP	**12210**	810	23	32	865	**9,40**	0,07
LMP	**12213**	815	9	31	855	**9,32**	0,09
LMP	**12216**	814	7	34	855	**9,51**	0,12
LMP	**12218**	809	9	26	844	**9,38**	0,16
LMP	**12225**	819	19	48	886	**9,67**	0,29
LMP	**12231**	815	13	33	861	**9,21**	0,15
LMP	**12243**	821	32	26	879	**9,01**	0,14
LMP	**12244**	815	36	38	889	**9,25**	0,1
LMP	**12245**	814	25	31	870	**9,34**	0,07
LMP	**12246**	810	24	30	864	**9,30**	0,13

Quality	Batchnr.	1st separation 6301	2nd separation 6303	3rd separation 6303	Total amount Phosphor 63-syst.	% FA (1st chlorination reactor)	% FA (2nd chlorination reactor)
HMP	**12147**	809	10	16	835	**10,03**	0,1
HMP	**12148**	819	12	13	844	**9,88**	0,07
HMP	**12149**	788	10	43	841	**10,03**	0,06
HMP	**12154**	798	15	30	843	**9,41**	0,07
HMP	**12155**	814	17	13	844	**9,71**	0,05
HMP	**12156**	809	10	31	850	**9,94**	0,05
HMP	**12163**	814	10	30	854	**9,95**	0,08
HMP	**12164**	809	12	24	845	**10,00**	0,08
HMP	**12165**	798	13	22	833	**9,83**	0,06
HMP	**12166**	814	10	17	841	**9,94**	0,11
HMP	**12174**	798	9	25	832	**9,80**	0,11
HMP	**12175**	809	10	29	848	**9,75**	0,11
HMP	**12196**	804	8	33	845	**10,12**	0,07
HMP	**12197**	798	14	32	844	**10,10**	0,08
HMP	**12230**	756	12	61	829	**10,25**	0,11
HMP	**12239**	793	17	36	846	**10,15**	0,08

Appendix D – Calibration Curve with equation for estimation of the amount of phosphorous in the samples.

1st chlorination reactor:



The Equation:

The amount of phosphorous in acid chloride and AKD (400 – 4000 ppm)

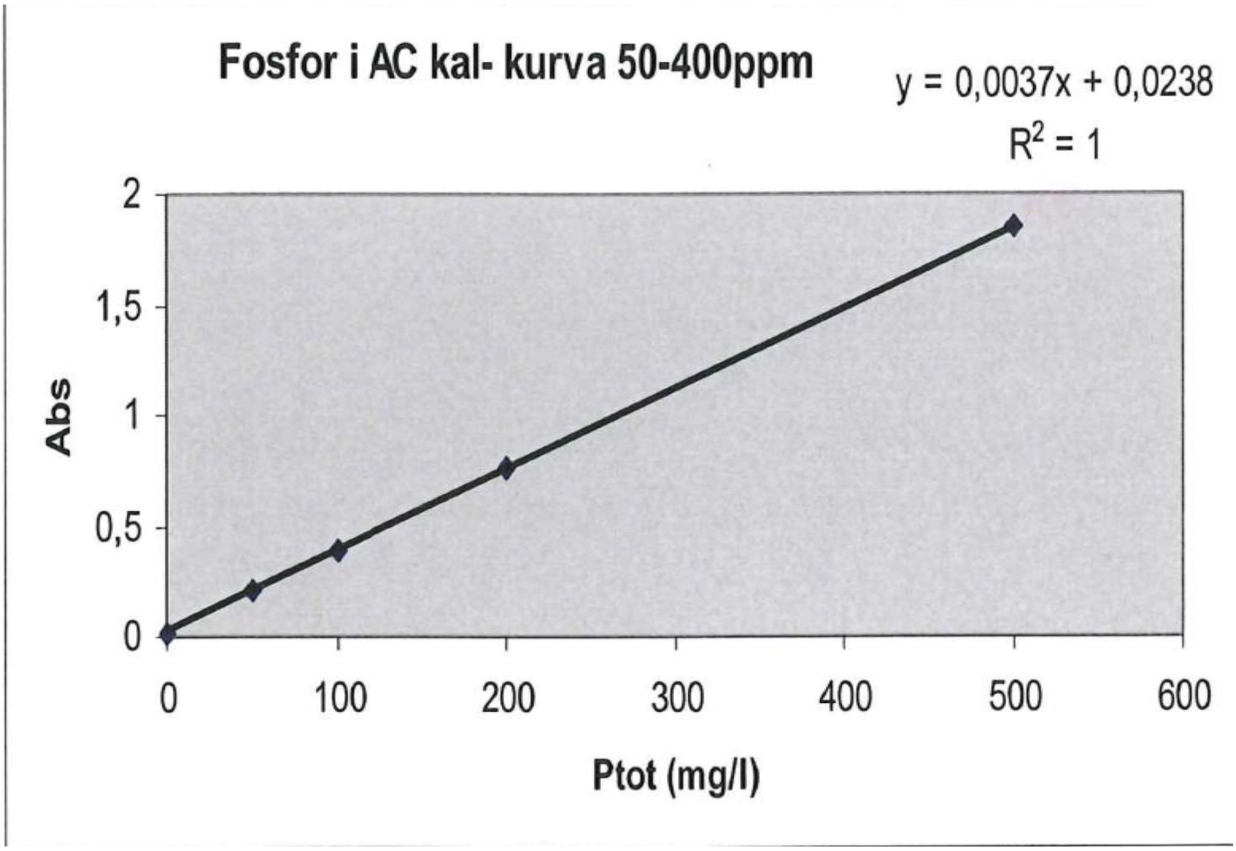
P (sample) = (A – I) / L

A = Absorbance
I = Interception (Intersection with the x-axis)
L = The slope of the calibration curve

P / AC (ppm) = (P (sample) *1000) / (5*m (AC))

P (sample) = the Amount P in the calibration curve
m (AC) = the weighed amount of sample (g)

2^{nd} chlorination reactor:



The Equation:

The amount of phosphorous in acid chloride and AKD (50 – 400 ppm)

P (sample) = (A – I) / L

A = Absorbance
I = Interception (Intersection with the x-axis)
L = The slope of the calibration curve

P / AC (ppm) = P (sample) / (2*m (AC))

P (sample) = the Amount P in the calibration curve
m (AC) = the weighed amount of sample (g)