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Regeneration method development for used alumina in the hydrogen peroxide process

Master's thesis in Innovative and Sustainable Chemical Engineering

Gandhi Rajamani Balasubramanian

MASTER'S THESIS 2020

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Department of Chemistry and Chemical Engineering
Division of Chemical Reaction Engineering
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden 2020

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Cover: Photo by the author. Upper Figure: Soxhlet Regenerated alumina for different solvents, Lower figure: Solvent Extracted liquid after Soxhlet extraction

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Abstract

Hydrogen peroxide is one of the majorly used bleaching chemicals in the pulp and paper industries worldwide. Among the various production process of hydrogen peroxide, Anthraquinone process (also known as autoxidation or AO process) is the widely used industrial route. The use of alumina as a catalyst is used in the AO process for the recovery of active quinones from the inactive anthraquinones [Chen, 2008]. However, this repeated usage of alumina results in loosing its ability to regenerate these inactive anthraquinones and hence limited by its short usage of time. Acid sites recovery for the alumina is the focus of this thesis. It has been a subject of studies in the pulp and paper industry in recent times.

Few proposed methods such as calcination and caustic treatment has been proposed by researchers for the regeneration of alumina which are discussed briefly later but there is very little knowledge on the washing of the alumina surface by organic solvents. Soxhlet extraction is chosen as a primary method for the regeneration in this thesis followed by caustic treatment. Methanol, acetone, acetonitrile and ethyl acetate is chosen as the solvents depending upon its properties. This is then followed by NH_3 -TPD to characterize the active sites and then titration by a method proposed by Nouryon is used to test the production of hydrogen peroxide in laboratory scale.

The results of the regenerated alumina using soxhlet extraction shows that the ethyl acetate maybe a better solvent on the basis of the color indication and caustic treatment shows strange results and hence neglected. NH_3 -TPD indicates that the acetone maybe a better solvent while the test for titration shows that the methanol maybe a better solvent. The result of these experiments does not give a clear picture of how well the alumina has been regenerated.

To summarize, this thesis work suggest that the methanol and ethyl acetate might have an impact on the regeneration of alumina surface but it requires more research work to give us a clear indication to be implemented in pilot and industrial scale.

Keywords: Regeneration, Used Alumina, γ -Alumina, Hydrogen peroxide, NH_3 -TPD.

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1

Introduction

The anthraquinone process is considered to be the major route for production of hydrogen peroxide worldwide. One significant step in the anthraquinone process is the regeneration of working solution.

Activated alumina is used in the hydrogen peroxide process for this regeneration has two roles:

- It is used as a catalyst for de-hydrogenation and de-epoxidation reactions.
- It is used to remove the degradation products obtained from the working solution.

The adsorption of degradation products on the activated alumina surface are typically due to carbon deposits. These carbon deposits are then responsible for losing alumina's ability to be re-used as a catalyst in the production process. The used alumina ends therefore up as a waste resulting in a production cost and not closing the loop in the circular economy making it a concern in terms of life-cycle perspective. It would be desired to regenerate the used alumina so that it could be reused in the production of hydrogen peroxide.

The thesis work is performed and done for Nouryon's bleaching chemicals department Process RDI, focusing on HP plants. Nouryon's HP plants are available in 5 different locations Norway, Venezuela, USA and two in Sweden with an annual production output of over 200,000 tonnes. This results in a substantial amount of used alumina that can be regenerated. Nouryon produces various grades of hydrogen peroxide which are available in concentrations of 30% to 70%. They can be used in a variety of applications and among them the 60% are used as bleaching agents in both mechanical and chemical pulps [Nouryon, 2019].

Regeneration of alumina has previously been studied by Nouryon showing some possibilities, i.e. to calcine the alumina and by using caustic treatment. The current objective is to evaluate the potential to use the technique of "Soxhlet Extraction" using various desired solvents. The alumina has also been treated with caustic as an after treatment for the regeneration of used alumina.

1.1 Goal

The thesis work aims to develop a method for regeneration of used alumina produced in the hydrogen peroxide process so that the aluminum oxide preferably could be reused in the production process. The intention is to find an effective regeneration method that will remove carbon deposits and reclaim active sites of the used alumina.

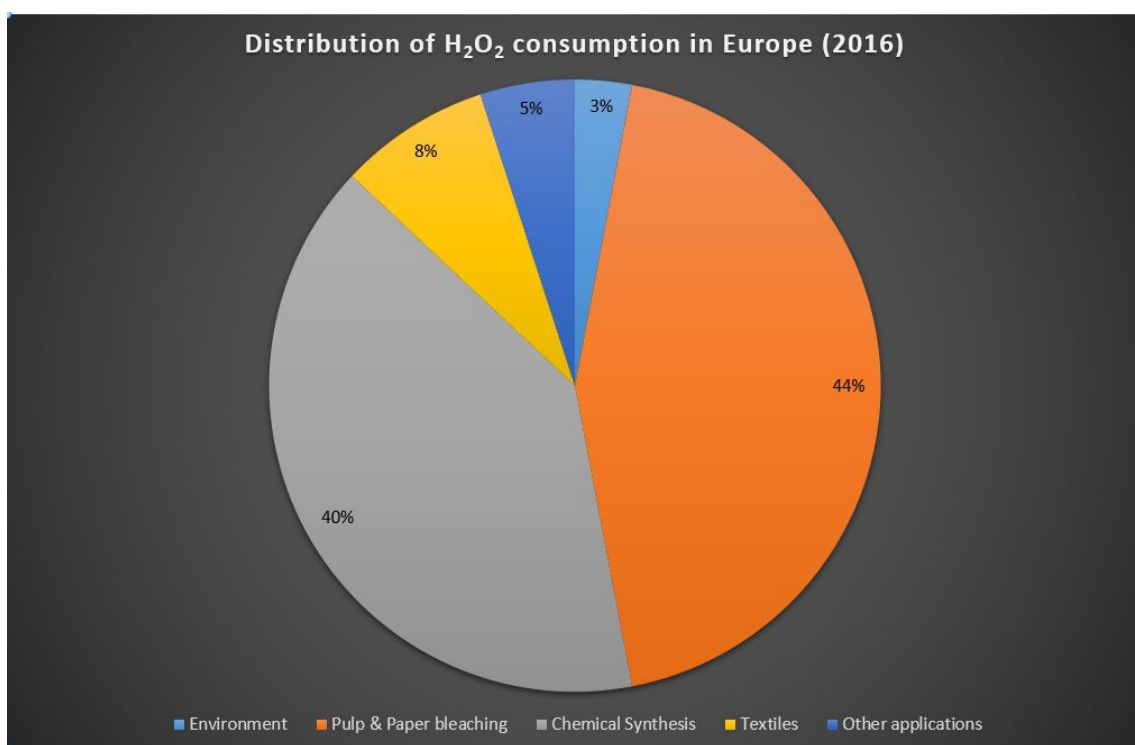
The work includes experimental work in laboratory scale, aiming to finally suggest a plant design for regeneration of used alumina. This includes treating the used alumina firstly with Soxhlet extraction using different solvents and eventually a caustic treatment in order to recover the active sites of the γ alumina. The regenerated alumina samples will eventually be analysed using NH_3 -TPD to characterize the different active sites encountered and also verifying the activity of the alumina by a lab test on working solution de-hydrogenation.

2

Theory

2.1 Hydrogen Peroxide

Hydrogen peroxide is a chemical widely used in various industries, mainly for pulp bleaching and production of percarbonate/perborate [Chen, 2008]. Hydrogen peroxide is used as an oxidant and is seen as a very environment friendly chemical since it decomposes only into water and oxygen [Campos-Martin et al., 2006].



*Figure 2.1: H₂O₂ consumption in various industries in Europe.
[Ciriminna et al., 2016]*

As of 2015, the annual world production of hydrogen peroxide reached 5.5 million metric tonnes and the production demand is expected to grow in the near future [Ciriminna et al., 2016]. Pulp and paper bleaching usage accounts for about 50% of the production. Other major usages are detergent bleaching, textile bleaching and water purification. Some interesting usage are as part of the chemical synthesis of hydrogen peroxide propylene epoxide (HPPO), usage as disinfectant in

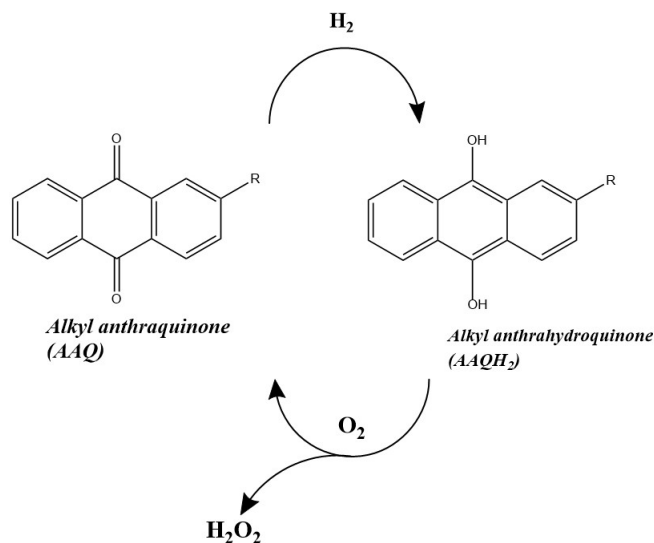


Figure 2.2: Schematic representation of Anthraquinone process
[Chen, 2015]

medical treatment and also used in the military and as a rocket propellant fuel [Edwards et al., 2009]. The usage of hydrogen peroxide mainly depends on the market regions. In Europe, as described in *Fig 2.1*, the major usage is for chemical synthesis of detergents (40%) and for pulp and paper bleaching (44%). Hydrogen peroxide may be produced by several different methods, e.g. hydrolysis of ammonium persulfate. However, the main industrial route is by the anthraquinone process.

2.2 Anthraquinone Autoxidation Process

In 1935, Reidl and Pfeleiderer in BASF found a method by using anthraquinone as an organic catalyst to produce the hydrogen peroxide. The anthraquinone process is currently the only production route for hydrogen peroxide in an industrial scale. It is often referred to as the Reidl-Pfeleiderer process or Autoxidation (AO) process (some also call it Anthraquinone autoxidation process).

The entire reaction is a cyclic process that involves four major steps: hydrogenation, oxidation, extraction and regeneration of the working solution. In the manufacturing process, anthraquinone is often considered as an organic catalyst for the reaction of AO process and the anthraquinone solvent mixture is called the working solution [Hess, 2000].

The cyclic anthraquinone process, as seen in *Fig 2.2*, includes the following steps as follows:

- The anthraquinone (AAQ) is hydrogenated to form anthrahydroquinone (AAQH₂) in the presence of a heterogeneous hydrogenation catalyst preferably a Pd catalyst.

- The formed AAQH₂ is oxidized with oxygen back to AAQ and simultaneously produces hydrogen peroxide.
- The formed hydrogen peroxide is extracted from the working solution into a water solution.
- The resulting working solution which holds the AAQ is recycled back to the hydrogenation stage to continue the production process.
- The extracted hydrogen peroxide is concentrated by distillation to obtain chemical and technical grades of hydrogen peroxide.
- Except from these steps the working solution also has to be regenerated since unwanted side reactions generates inactive quinones and other degenerated molecules. Also, the active quinone balance is shifted if regeneration is not performed. The regeneration is done by passing the working solution over an alumina catalyst where inactive anthraquinones are converted into desirable anthraquinones [Chen, 2008]. The alumina does also remove some unwanted by products from the working solution by deposition onto the alumina surface.

2.2.1 Over-Hydrogenation and Hydrogenolysis of anthraquinones

The catalytic hydrogenation of AAQ over the palladium catalyst in the hydrogenation step is subjected to a number of secondary reactions. The secondary reactions generate anthraquinones that are inactive in the AO process and therefore not wanted.

These secondary reactions occurs in two different ways:

- Over-hydrogenation of aromatic rings
- Hydrogenolysis of C-OH bonds

The over-hydrogenation changes the structure of the anthraquinones from aromatic rings to cyclic hydrocarbons. The catalytic hydrogenation of alkyl anthrahydroquinone, as seen in *Fig 2.3* results in the formation of 5,6,7,8- tetrahydro anthrahydroquinone (H₄AAQH₂) (active) and further reduction leads to octahydro anthrahydroquinone (H₈AAQH₂) (inactive). The hydrogenolysis of the C-OH bond generates the tautomers 9,10-anthrone (AAN) (active) by hydrogenation of the 9 and 10-hydroxyanthrones (inactive).

Experimental results conclude that the formation of over-hydrogenated anthraquinones [Chen, 2008] can be decreased due to the following measures:

- Use of a higher concentration of active anthraquinones in the working solution reduces the over-hydrogenation.
- Weakening of the basicity of the working solution prevents the active anthraquinones and their corresponding hydroxyanthrones to form anthrones (AAN).
- A lower H₄AAQH₂ content in the working solution prevents the hydrogenation of H₄AAQH₂ to H₈AAQH₂.

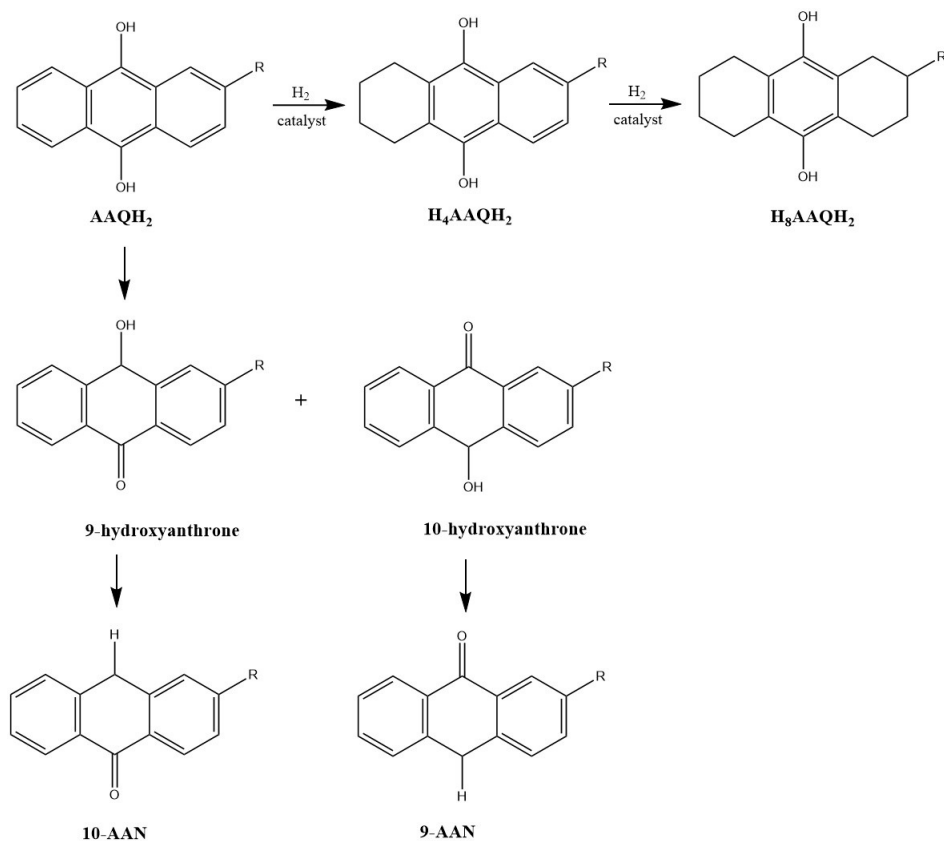


Figure 2.3: Hydrogenation scheme of alkyl anthrahydroquinone
[Hess, 2000]

H₄AAQH₂ can be oxidized in the presence of oxygenated atmosphere such as air to form the corresponding tetrahydro alkyl anthraquinones (H₄AAQ) and hydrogen peroxide [Hess, 2000].

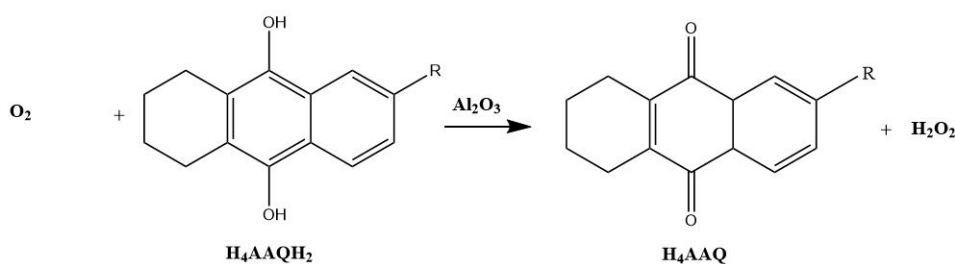


Figure 2.4: Formation of Hydrogen peroxide from oxidation of H₄AAQH₂

This tetrahydro alkyl anthraquinones (H₄AAQ) may further reacts with the hydrogenated alkylanthraquinone (AAQH₂) and this results in the active anthraquinones which could be used for the production of hydrogen peroxide [Aksela and Paloniemi, 2005]. Hence, these anthraquinones and tetrahydro anthraquinones are called "active quinones" [Chen, 2015]. The H₄AAQH₂ is thereby actively participating in the production of hydrogen peroxide. The balance between the H₄AAQH₂ and the AAQ is important

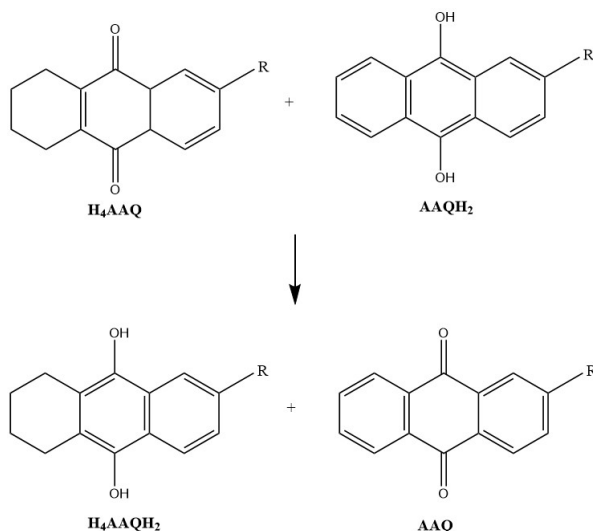


Figure 2.5: Possible reaction mechanisms of AQ derivatives
[Hess, 2000]

to maintain for keeping the desired production of hydrogen peroxide.

Although being considered an active component in the cyclic process, H_4AAQ in high concentration causes precipitation and selectivity issues in the production process of hydrogen peroxide, which both are undesirable. Activated alumina is used as catalyst to regenerate the H_4AAQ and the other over hydrogenated anthraquinone compounds to active quinones which is explained in detail later. The anthraquinones that cannot be recovered by the alumina will be accumulated in the working solution. These accumulated anthraquinones may hinder the solubility of the active anthraquinones and increase the density of the working solution which creates problems in extraction [Hess, 2000].

The so called "active quinones" AAQ , AAQH_2 , H_4AAQ and H_4AAQH_2 are degraded due to the repeated deep hydrogenation and thereby loses their ability to produce H_2O_2 . These degraded anthraquinones are referred to as the "irrecoverable inerts" [Shang et al., 2011] [Eller and Snyder, 1959].

2.2.2 Formation of epoxide

The epoxide is formed as a byproduct of the oxidation of the H_4AAQH_2 in the hydrogen peroxide production, see Fig 2.6. During the repeated cycles of the production, this is formed as a secondary reaction which are accumulated in the working solution and degrades the production process [Aksela and Paloniemi, 2005].

2.2.3 Formation of other degradation products

During the oxidation and hydrogenation in repeated cycles, there is also an alteration in the organic molecules of the working solution. A typical by-product that is formed during the hydrogenation-dehydrogenation process are ketones, among other by-

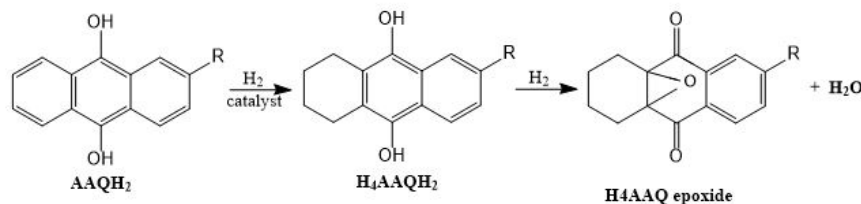


Figure 2.6: Formation of Epoxide
[Aksela and Paloniemi, 2005]

products. The ketones are formed of higher alcohols which are typical polar solvents in the working solution [Hasegawa et al., 2018]. Other degradation products include oxidized and decomposed parts of organic solvents. The by-products obtained are referred to as being inert. As a result, there is an accumulation of by-products during the production process of hydrogen peroxide [Hasegawa et al., 2018].

The degraded solvent molecules may lower the solubility of the active anthraquinones in the working solution [Eller and Snyder, 1959]. With a lower solubility active anthraquinones the production efficiency of the working solution is decreased [Hasegawa et al., 2018]. Thus, it is not just necessary to remove the irrecoverable inerts as they serve no purpose but also highly desirable. Aluminum oxide has been shown to adsorb some of these inert degradation products and remove them from the working solution.

2.2.4 Regeneration of working solution

The regenerate of the working solution has gathered a lot of attention over a period of time [Guo et al., 2011]. However, few processes have been proposed for the regeneration. The regeneration of working solution consists of two parts. First, it is to recover the active alkyl anthraquinones and secondly to remove the impurities from the working solution. The industrially used method for this regeneration is to use alumina as a catalyst and a surface for deposition.

Except for the usage of alumina *Eller et al.*, has suggested to do the separation of anthrahydroquinones from the reduced form of old working solution by extracting it with a metal hydroxide solution which results in anthraquinone salts which are further oxidized into anthraquinone. The product is then mixed with the new working solution and can be re-used in the synthesizing process of hydrogen peroxide. The main disadvantage of this process is that the laboratory process is expensive and hence the industrial scale will result in huge economic investment [Eller and Snyder, 1959]. Another method of treating the working solution in the presence of ozone and then with caustic soda and finally treating with active alumina at 70-75°C i.e., this process involves three major steps which itself is economically

demanding [Lee and Schwartz, 1969].

2.3 Alumina

Alumina, also known as Aluminum oxide, is a chemical compound with the molecular formula of Al_2O_3 . Activated alumina or trans alumina's are the forms of alumina between the alumina hydroxides and corundum ($\alpha\text{-Al}_2\text{O}_3$). Activated alumina is typically found in granular and spherical form. The fact that activated alumina has typically a high surface area, good chemical resistance, high abrasion resistance and its high efficiency in the drying gives concrete evidence for its use in the refining and industrial catalytic process [Zotov et al., 2012] [Zotov et al., 2018]. The surface properties are of high value and purpose because the catalytic reactions take typically place at the inner surface of the catalyst [Knözinger, 1968].

The preparation of alumina is obtained by the thermal decomposition of alumina hydrates i.e, hydroxides and oxyhydroxides. Typical Aluminum hydrates are Bayerite, Gibbsite and Boehmite. The porous structure of the alumina determines its physical nature and the chemical nature of surface area obtained due to the dehydration process.

2.3.1 Thermal decomposition of Aluminum hydroxides

A wide range of transitional alumina's may be obtained by the thermal dehydration process of the Aluminum hydrates [Misra, 1986]. Depending on the starting alumina hydrate and the thermal treatment different forms of transitional alumina are created see *Fig 2.7*. The final anhydrous form in the thermal treatment is corundum ($\alpha\text{-Al}_2\text{O}_3$) which is obtained at 1100°C . $\alpha\text{-Al}_2\text{O}_3$ is a thermally stable polymorphs with a rather small surface area. The oxide ions are hexagonally closely packed and Aluminum ions are octahedrally coordinated. The intermediate temperature range of $250\text{-}800^\circ\text{C}$ results in the transitional alumina.

The thermal decomposition of boehmite or bayerite in air (i.e calcination) has various applications in the field of catalysis. Our interest lies in the $\gamma\text{-Al}_2\text{O}_3$ phase which are obtained from the calcination of boehmite in air at the temperature range of $400\text{-}500^\circ\text{C}$ [Misra, 1986]. Boehmite, when thermally dehydrated, undergoes a sequential polymorphic phase transition from boehmite to $\gamma\text{-Al}_2\text{O}_3$ and then further increase in temperature results in δ and $\theta\text{-Al}_2\text{O}_3$ to finally become $\alpha\text{-Al}_2\text{O}_3$ [Busca, 2014], see *Fig 2.7*.

The commercial production of $\gamma\text{-Al}_2\text{O}_3$ starts with the preparation of (pseudo)boehmite (layered oxyhydroxide). (Pseudo)boehmite are referred to as the nanocrystalline hydrous oxyhydroxide. Calcination of (pseudo)boehmite at a temperature of 450°C yields $\gamma\text{-Al}_2\text{O}_3$ with BET surface area of up to $500\text{ m}^2/\text{g}$.

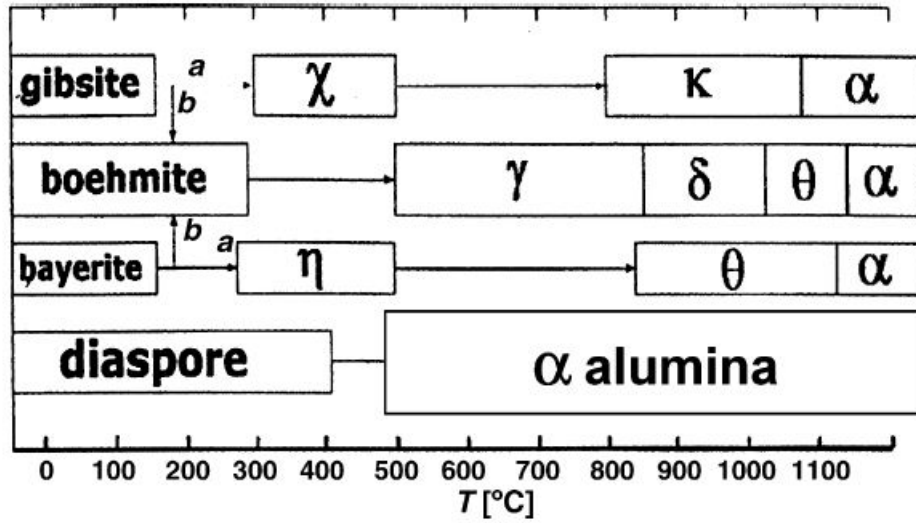


Figure 2.7: Decomposition sequence of Aluminum Hydroxide
[Huntz et al., 2007]

2.3.2 Crystal structure, Morphology of γ -Alumina

The structure of γ - Al_2O_3 is cubic defective or non-stoichiometric spinel in which the oxygen atoms are arranged in cubic close packing and the Al^{3+} ions occupying the tetrahedral (8a) and octahedral (16d) sites, see Fig 2.8 [Lippens and de Boer, 1964]. Al atomic positions are not fully occupied in the basic stoichiometry of AB_2O_4 , thus deviating from the chemical formula of a spinel structure [Samain et al., 2014]. Vacancies are spread over the tetrahedral (8a) and octahedral (16d) spinel sites while Zhou *et al.*, suggests that there is a possibility of the vacancies being occupied by Al atoms [Zhou and Snyder, 1991].

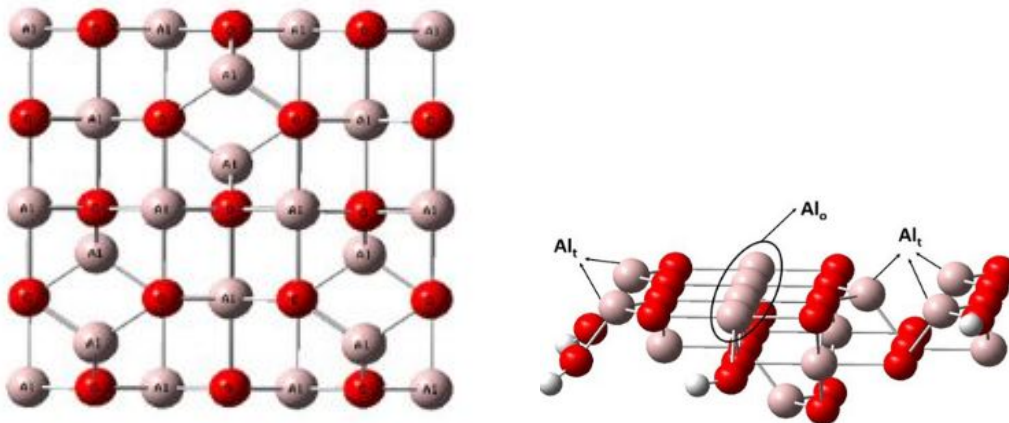


Figure 2.8: Structure of γ -Alumina
[Shimizu et al., 2016]

2.3.3 Acid sites of γ -Alumina

The surface of the activated alumina is a complex mixture of aluminum, oxygen and hydroxyl ion groups which combine to form acid and base sites of alumina. These sites have prominent importance in adsorption, chromatographic and catalytic applications because of their surface activity [Pearson, 2000]. A great deal of adsorption and catalytic properties of alumina can be governed by controlling the hydroxyl ion concentration. For example, the adsorption of hydrocarbons is very weak while the adsorption of non-ionic proton donors and proton acceptors such as hydroquinones and quinones are stronger due to the presence of hydrogen bonding with oxygen atoms.

The dehydration of alumina results in the simultaneous formation of Lewis acid sites and Brønsted acid sites as seen in *Fig 2.9*.

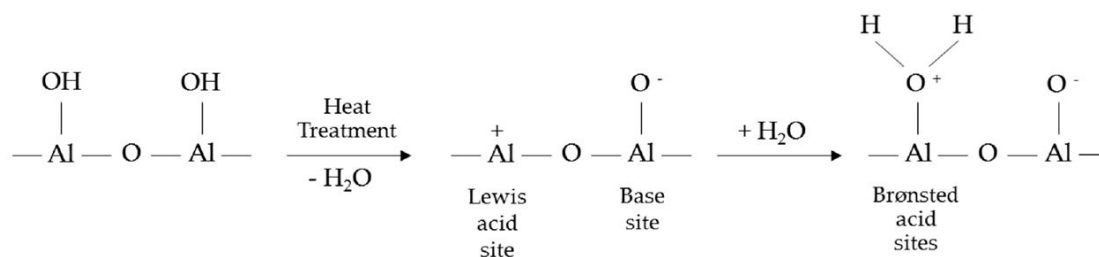


Figure 2.9: Different acid sites of γ -Alumina
[Mukhamed'yarova et al., 2019]

Lewis acid sites

Lewis Acid Sites (LAS) are any species, that can accept electron pair by coordination bond because of the presence of the incomplete electron grouping. The catalytic activity of the transitional alumina are related to the LAS that are related to small number of low coordinated surface Aluminum ions. Lewis acid sites, in general, are characterized by the adsorption of probe molecules, e.g. ammonia, and are associated with the ionic nature of the surface of Al-O bond [Busca, 2014]. In a non-spinel structural model of $\gamma\text{-Al}_2\text{O}_3$ proposed by *Digne et al.*, it is evident that the LAS are coordinated Al^{3+} ions can be penta, tetra and tricoordinated site [Digne et al., 2004]. Among them, tricoordinated Al^{3+} , see *Fig 2.10*, constitute the strongest LAS on alumina's. These are presented as metastable species on the (110)-face $\gamma\text{-Al}_2\text{O}_3$ particles, corresponds to the "defect" sites which are responsible for unique properties of activated alumina [Digne et al., 2004].

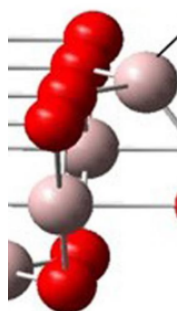


Figure 2.10: A typical three coordinated aluminum atoms on the surface of γ -Alumina

[Shimizu et al., 2016]

The surface density of very strong adsorption acid sites for ammonia of more than 200 kJ/mol is estimated to be around 0.1 sites/m². Due to the bulk density of γ -Al₂O₃, one out of 50-100 surface cation ions acts as a strong LAS outgassed at usual 400-500°C while the rest of the maximum are hydroxylated or highly uncoordinated. This is due to the fact that the surface density of the strongest Lewis acid sites is not proportional on the annealing temperature and time. The total number of strong acid sites decreases as the stability of the transformation of polymorphs occurs [Busca, 2014].

Brönsted acid sites(BAS)

BAS is an acid site which contains a hydrogen containing species able to release a proton and a base has the capability of combining with a proton. The evaluation of Brönsted acid strength shows typically medium to high acidity of the alumina acid hydroxyls. Typical analytical methods are the method "hydrogen bonding method" and the "base protonation method" proposed by Busca *et al.*, but also using of adsorption of probe molecules like ammonia should doable (no reference found for the method but some are referring to the drawbacks of NH₃-TPD measurements). The moderate acidity implies that the aluminas become more active only at high temperatures. The ionic properties of the alumina are responsible for the medium charge, due to which γ -Al₂O₃ are highly polar in nature. Oxide anions are also present in γ -Al₂O₃ apart from basic hard cations, thus a reason for surface basicity. The acidity of Al³⁺ ions responsible for basicity of anions but cation-anion pairs are actively accountable for dissociating molecules.

2.3.4 Interaction of activated alumina with the working solution

Activated alumina plays a significant role in the working solution in the anthraquinone process since it can regenerate the deactivated anthraquinones and accumulate the polar degradation products of the solvents and solutes. When the over-hydrogenated anthraquinones are regenerated it is done via the reaction of 3 moles of H₄AAQ in contact with Al₂O₃ at 50-100°C. The products will then be 1 mole of AAQ and 2 moles of H₄AAQH₂ to be used for the production of hydrogen peroxide

[Aksela and Paloniemi, 2005].

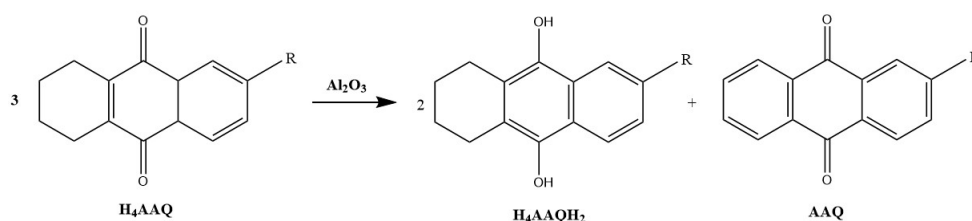


Figure 2.11: Disproportionation reaction
[Aksela and Paloniemi, 2005]

The oxidation degradation is done by reacting the H_4AAQ epoxide with H_4AAQH_2 producing H_4AAQ in the presence of gamma alumina at 50-140°C [Aksela and Paloniemi, 2005].

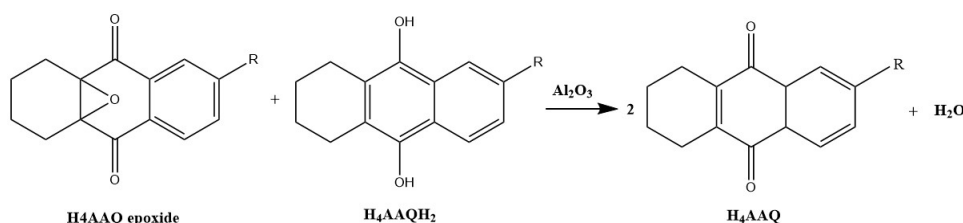


Figure 2.12: Conversion of "Epoxide" to "Tetra"
[Aksela and Paloniemi, 2005]

The most effective and commercially used method in the industries is when the degraded alkylanthraquinone solution is heated to a temperature of 55°C in the presence of activated alumina [Sprauer and Williams, 1956]. In parallel to the regeneration of the anthraquinones the gamma alumina does also remove inert material from the working solution, i.e. degenerated working solution and anthraquinones not possible to regenerate. The removal of these inerts are done by adsorption to the alumina surface. Several of the inerts are highly polar giving good adhesion to the alumina via the acid sites and the hydroxyl-groups. This adsorption of organics (fouling) on the alumina deactivates the alumina and activated alumina loses thereby its ability to regenerate the anthraquinones.

2.3.5 Regeneration of used alumina

The regeneration of the working solution demands huge amounts of activated gamma alumina as a catalyst. Since the activated gamma alumina used in the regeneration process is deactivated one would like to regenerate the alumina to its active form again.

There are a few methods proposed in regenerating the used alumina in the hydrogen peroxide process. A method of regeneration where the alumina is calcined at 300-400°C until organic matter is removed, then placed in contact with sodium

hydroxide and calcining again at 300-400°C until the alumina retrieves its active sites [Browning, 1974]. The disadvantage with this process is that it has a higher risk of losing the alumina durability (abrasion resistance) due to alteration of the crystalline structure and that the method is energy demanding. Eurecat is one such commercially facility that does this type of regeneration of alumina. They have proved that the used alumina from the hydrogen peroxide plant could be regenerated to about 90% in lab scale but has not been evaluated in full scale and it is expected to differ. One other method of regeneration is to remove the organics by washing with organic solvents and has been tested [Becker, 1999]. However, there is little knowledge on such regeneration. Hence, Soxhlet extraction is chosen as our primary method to regenerate our used alumina.

2.4 Soxhlet extraction

The conventional Soxhlet extraction is used for the removal of desired compounds from a heterogeneous material with the help of an appropriate solvent. The advantage of this method is that the heterogeneous material is washed with a pure solvent without using large amounts of solvent. Thus, the Soxhlet extraction is therefore interesting to use for the washing of used alumina.

The Soxhlet process of solid-liquid extraction of alumina is done by evaporation of a suitable organic solvent. The solvent passes the alumina in a parallel pipe and is condensated above the alumina. The condensated solvent is then flowing down over the alumina. The unit is constructed by a swan neck to submerge the alumina fully before draining the solvent back down to the distillation flask. The solvent will during the contact with alumina extract soluble organics from the alumina. The extracted organics is mainly large molecules and will stay in the distillation flask due to their high boiling point (assuming the solvent having low boiling point) [Anderson, 2015]. This process is repeated in a cyclic motion where the complete cycle refers to the start of the solvent evaporating until it returns to the distillation flask including the extract. This continuous process is followed until the complete extraction is obtained [Zygler et al., 2012].

Extraction Parameters

The choice of the extraction solvent is a key factor that can play a major role in influencing the optimum recovery of the target compound. However, several other parameters may impact the final recovery of the target compounds, e.g. type of solid sample, extraction solvent, target analytes, sample size, extraction time, temperature and the volume. Several factors should therefore be kept in mind in order to obtain the desired result because different solvents are capable of yielding the different extracts with varying composition [Zygler et al., 2012].

The three main properties the extraction solvent should have are the right polarity versus the organics that are to be extracted, the right polarity versus the alumina and it should have a lower boiling point than the extracted compounds. A trade-off between the extraction time and the boiling point of the extraction solvent is

under obvious consideration for better optimization. The polarity of the solvent needs to be similar to that of the target analytes for best results. In several historical cases a non polar solvents such as n-hexane, dichloro methane are employed for the extraction of non-polar target compounds such as poly brominated diphenyl ethers (PBDEs), poly chlorinated biphenyl (PCBs). Similarly, polar solvents (eg., methanol, acetonitrile and acetone) are used for the extraction of polar target analytes such as phenols, chlorinated phenols and triclosan [Zygler et al., 2012].

The alumina is highly polar due to the presence of both positive and negative species, it is therefore obvious to prefer an extraction solvent that is moderately or highly polar in nature. Meanwhile the low boiling point of the solvent are also taken into consideration. However, it is also important to observe the flash point, auto-ignition temperature, liquid and vapor density of the solvent to minimize the risks associated to be performed in a coming plant design and for the laboratory scale. Finally, it was decided to go ahead with acetone, methanol, ethyl acetate and acetonitrile. They all have a good history on extracting polar compounds from the solid matrix. For example, acetone and methanol are good for the removal of all polar compounds, while ethyl acetate is suitable for the removal of phenolic compounds.

Working Principle of a Soxhlet apparatus

The Soxhlet apparatus usually consists of the Soxhlet unit including the thimble (sample holder), condenser unit and the distillation flask (distillation flask) containing the extraction solvents

The basic soxhlet extractor apparatus is shown below and their basic components are explained with their function in order to gain a better understanding of the process.

Soxhlet unit: It is a glass container with a swan neck and a parallel distillation arm. The dried solid sample is packed inside the thimble to keep it in the glass container of the Soxhlet unit. The solvent is evaporated, traveling up through the distillation arm and condense above the solid sample. The condensed liquid solvent soaks the solid sample and thereby extract any organics. When the glass container is filled, filled up to the swan neck the solvent pores back down to the distillation flask by the siphon effect [Anderson, 2015].

Thimble: The function of the thimble or porous container as the name suggests is to hold the solid sample. The condensed solvent saturates the solid sample and thereby extracting the organics or active material. When the solvent returns to the distillation flask, the filter retains the insoluble components inside the glass container of the Soxhlet unit.

Distillation flask: It is used to hold the solvent, evaporate the solvent and act as a reservoir and storage for the extracted material. It is also referred to as the distillation flask.

Condenser: The purpose of condenser is to cool the solvent vapor and condense it back to the glass container in the Soxhlet unit.



Figure 2.13: Lab set-up of Soxhlet extractor

2.5 Caustic treatment

Caustic is known to dissolve organic material and may also dissolve alumina i.e., the alumina is not stable in too caustic environment. Caustic has previously been tested as a regeneration of alumina.

According to *Browning et al.*, the concentration of the aqueous sodium hydroxide solution for treating the alumina is 0.5-5 wt%. Usually a preferred caustic treatment is to use a concentration 1.5 wt% of the sodium hydroxide solution at room

temperature (25°C). It is important to have the concentration range as it will have an effect on the solid crystalline structure of γ alumina and might possibly disintegrate the structure. During the contact time, the sodium hydroxide is expected to be either adsorbed on to or reacted with the γ -alumina since the drained solution will contain a lower percentage of sodium hydroxide than the fresh alumina solution [Browning, 1974].

2.6 Ammonia-Temperature Programmed Desorption

The acidic properties of γ -alumina catalyst could be analyzed with ammonia temperature program desorption (NH₃-TPD). NH₃-TPD has been widely used for the characterization of heterogeneous catalysts [Berteau and Delmon, 1989] [Chen et al., 2019]. It works on the basic principle method that NH₃ is physisorbed / chemisorbed to a sample and thereafter is the NH₃ desorbed by a temperature increase. The release of NH₃ is analyzed with e.g. an FTIR detector. The generated desorption spectra show the amount of NH₃ released at different temperatures. The correlation between the amount of released NH₃ and temperature indicates the amount of acid sites and the strength of the acid sites [BOZBAĞ et al., 2018]. The amount of acid sites that are released can be determined from the peak area using the NH₃ TPD profiles but the re-adsorption or slow diffusion makes it hard for the interpretation of the peak shape and peak position [Katada et al., 1997]. NH₃-TPD profiles are usually deconvoluted in various peaks that could be identified as different Lewis and Brönsted acid sites which could be responsible for the catalytic activity of the γ -alumina [Chen et al., 2019].

A typical NH₃ TPD spectra can look like Figure 2.14 below, i.e. the full spectra of fresh γ -alumina. The spectra shows the temperature profile (red curve) used during the measurement and the concentration of ammonia in the gas passing over the alumina. As carrier gas is typically Ar used, in this case 300 ml/min at all time. The NH₃-TPD spectra shows typically several different regions, see figure 2.14:

1. Rinsing the equipment- Purging the alumina for 4200 sec with 300 ml/min of pure Ar at 100°C.
2. Absorption phase - Purging of the alumina during 3600 sec with 400 ppm of NH₃ in 300 ml/min of Ar at 100°C. During this stage is ammonia adsorbed i.e, physisorbed and chemisorbed to the alumina. The ammonia signal reaches therefore a plateau after some time indicating full absorption at this temperature.
3. Desorption of physisorbed ammonia – Purging of the alumina during 3600 sec with 300 ml/min of pure Ar at 100°C. During this phase is all physisorbed ammonia desorbed from the alumina. As shown, the ammonia signal decrease down from 400 ppm to 0 ppm.
4. Desorption of chemisorbed ammonia – Purging of the alumina during 3000 sec with 300 ml/min of pure Ar with a temperature increase from 100 to 500°C.

2. Theory

The temperature increase is done by 20°C/min. During this phase is the chemisorbed ammonia desorbed from the alumina generating different peaks. The peaks are correlated to the temperature indicating the strength of the binding between ammonia and the alumina surface.

5. After treatment – Purging of the alumina during 3600 sec with 300 ml/min of pure Ar keeping the temperature at 500°C and thereafter allowing the temperature to fall down to 100°C again.

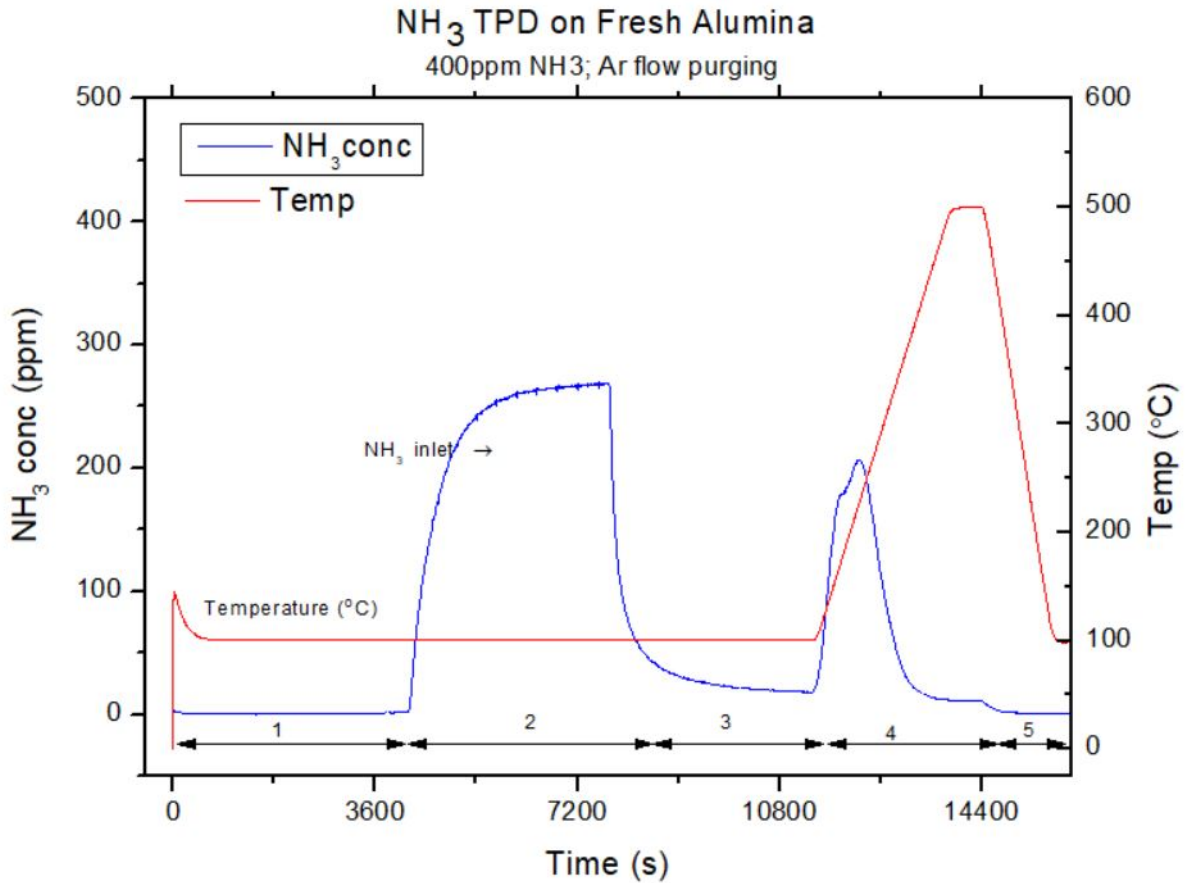


Figure 2.14: TPD Profile of Fresh Alumina

1. Rinsing the equipment, 2. Absorption phase 3. Desorption of physisorbed ammonia 4. Desorption of chemisorbed ammonia 5. After-treatment

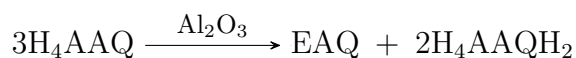
The NH₃-TPD was obtained and re-drawn with the help of software *Origin lab*. The desorption of NH₃ from the surface corresponds to the peaks obtained at a specific temperature. This temperature relates to the strength of the bonding. It is well known that low NH₃ desorption temperature corresponds to the weakly adsorbed acid-sites and the high desorption temperature corresponds to the strongly acid sites [Vierck and Leclerc, 2017]. The acid sites are classified as: weak (25-200°C), intermediate (200-400°C) and strong (> 400°C) [Maciver et al., 1963].

2.7 Quality control of Aluminum oxide

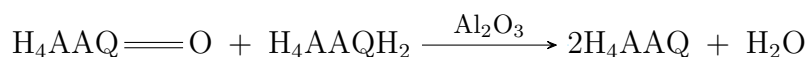
To understand if the active sites available on the regenerated aluminum oxide are capable of de-hydrogenating and de-epoxidizing quinones, a quality control is performed according to a method developed by Nouryon.

The main reactions occurring during these laboratory experiments are Dehydrogenation as seen in *Fig 2.11* and De-epoxidation *Fig 2.12* to produce "active quinones" and the consecutive oxidation to hydrogen peroxide.

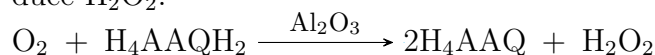
Dehydrogenation:- In dehydrogenation, H₄AAQ is first converted to EAQ and H₄AAQH₂ in the presence of Al₂O₃.



De-epoxidation:- The epoxide reacts with H₄AAQH₂ in the presence of Al₂O₃ to produce THEAQ.



Oxidation:- The repeated oxidation of H₄AAQH₂ in the presence of Al₂O₃ to produce H₂O₂.



2.8 Hydrogen peroxide in working solution by sodium thiosulphate

To determine the amount of hydrogen peroxide available in an aqueous sample, one method is to use titration with sodium thiosulphate, after extracting hydrogen peroxide from the working solution. The main reaction occurring during this laboratory experiments is as follows:



The detailed procedure of the experiment can be referred from Nouryon lab document- "*Hydrogen peroxide in working solution- titration by Na₂S₂O₃-LABINS02*"

Calculations and Reporting:- For calculations performed by Na₂S₂O₃ titration, the formula used are as follows:

$$\text{H}_2\text{O}_2(\text{g/dm}^3) = \frac{A.C.M_w}{V.2}$$

where: A = ml of Na₂S₂O₃ required for the sample

C = 0.1 (mol/dm³), concentration of Na₂S₂O₃

M_w = 34 g/mol, molecular weight of H₂O₂ V = Sample volume (ml)

3

Methods

In this work, the method that has been carried out to regenerate the used alumina is to use Soxhlet Extraction in order to extract organics from the used alumina and to treat the Soxhlet treated alumina with caustic. The used alumina used in all experiments comes from Nouryon's hydrogen peroxide plant located in Bohus. The Aluminum oxide type used in all trials is called DD-6 and is manufactured by BASF.

3.1 Soxhlet extraction

This section displays the procedure of the Soxhlet extraction. Polyethylene Glycol (PEG) of 1.5 dm^3 was filled in the heating bath to heat the distillation flask. PEG is chosen as the heating transfer chemical as it has low vapour pressure, $< 0.01 \text{ mm}$ of Hg (20°C) and high boiling point, $>250^\circ\text{C}$. It is therefore a good heat transfer liquid to be used for long hour experiments. The set temperature at the PEG bath depends on the boiling point (BP) temperature of the solvents used for the extraction.

Approximately 15-16 g of the used alumina sample was used taken as solid sample for the extraction. 200 ml of the solvent for each sample is used. A first heating set point is maintained at slightly above the boiling point of the solvent so that the evaporation and condensation starts up. The temperature set point for the PEG bath is thereafter changed as per the duration of the first cycle. The extraction of organics, i.e. carbon deposits and working solution is done when the solvent is in contact with the aluminum oxide and the extracts are carried down to the distillation

Table 3.1: Table of Soxhlet extraction for different solvents

	Solvents used	Sample wt [g]	Boiling point [$^\circ\text{C}$]	Set point [$^\circ\text{C}$]
Trial 1	Acetone	15.400	56	70
Trial 2		15.473	56	70
Trial 1	Methanol	16.047	64.7	90
Trial 2		16.047	64.7	90
Trial 1	Ethyl Acetate	15.040	77.5	100
Trial 2		15.152	77.5	100
Trial 1	Acetonitrile	15.425	82	110
Trial 2		15.042	82	110

flask with the solvent. The evaporation and the solvent returning to the distillation flask is referred to as a cycle and these cycles process for hours. Depending on the solvent used the time for each cycle differs. The extraction of the organic material is apparently visible as a red-brown color in the solvent around the thimble. The experiment was ceased when no color change could be detected around the thimble. The extraction process was left overnight to get as “complete” extraction of the alumina as possible. Each solvent is done as a double experiment.

3.2 Caustic Treatment

The fresh alumina, the used alumina as well as the samples treated with acetone, acetonitrile, methanol and ethyl acetate (the Soxhlet treated alumina samples) are also treated with caustic. Approximately 2.5g of alumina are immersed in 3.6 wt% concentration of sodium hydroxide solution. The caustic solution is formed by 18.75g NaOH diluted in 500ml of H₂O. During the treatment that takes place for about 2 hours, it is essential to maintain the temperature at 25°C and a stirrer was added to make sure the reaction between sodium hydroxide and alumina takes place uniformly. The alumina is then separated and washed using 200ml of water through a filter funnel. Later, the filtered alumina is placed in a porcelain dish and kept inside the dryer at about 110°C for about 2 hours.

3.3 Ammonia Temperature-Programmed Desorption

The different alumina samples were analyzed using NH₃-TPD. The alumina samples are kept in a micro-reactor, with one thermocouple measuring the catalyst temperature in the center placed in the middle of the catalyst and a second thermocouple positioned 10mm in front of the catalyst, which is used for controlling the temperature in the gas phase before the catalyst. The inlet gas temperature was controlled with a PID regulator (Eurotherm). The gas mixing system is used for feeding the gases using mass flow controllers (MFC) Bronkhorst Hi-Tech and the composition of the gases were analyzed using an FTIR spectrometer (MKS 2000). The measurement is done using the following steps:

Auto-tune

In prior to the separate series of experiments, pre-treatment is done to purify the unit. The auto-tune process is carried out using Ar flow of 1200ml/min, heating to 500 °C during 6.5 hours. The samples were pre-treated so as to clean the instrument and thus can provide a starting point for the measurements thereby constructing a similarity with the other sample series. The auto-tune is performed as per pre-defined script mentioned in *Appendix A- Auto-tune*.

Gas Calibration

For quantitative purposes, the apparatus was calibrated with an empty reactor flow-

ing 400 ppm ammonia in Ar . Gases are fed at the total flow of Ar at 300ml/min for 3.35 hours. The gas calibration is performed as per pre-defined script mentioned in *Appendix A- Gas Calibration*.

Activity Measurements

The experimental procedure for the further experiments in the reactor were conducted as follows: Fresh alumina, used alumina, the four samples from soxhlet extraction and the 6 samples of caustic treated sample was analyzed. The catalyst was exposed to flowing Ar at 300ml/min for 1.5 hours at 100 °C. Thereafter, 400 ppm of NH₃ fed by the Ar flow to the reactor at 100°C for 1 hour. The supply of NH₃ results in a saturated physisorption and chemisorption. The physisorbed NH₃ is thereafter removed by flowing pure Ar at 300 ml/min at 100 °C for 1 hour. This was thereafter followed by the desorption of chemisorbed NH₃ using a temperature ramp with a heating rate of 20 °C/min from 100 °C to 500 °C, that is for 40 minutes, while exposing the catalyst to an Ar flow at 300ml/min. Finally, the catalyst was exposed to an Ar flow of 300 ml/min for 1 hour. 12 samples were analyzed but in a sequence of 3 at 4 different batches. Different batches using the same set-up were performed as per pre-defined script mentioned in *Appendix A-TPD alumina*.

3.4 Aluminum oxide performance test

The activity of the alumina could be measured using a lab experiment including dehydrogenation/de-epoxidation and their consecutive hydrogen peroxide formation. This method was done to give additional information to the NH₃-TPD results to evaluate the different regeneration done.

3.4.1 Dehydration and De-epoxidation reaction

This section is performed according to Nouryon laboratory document "*Test av alumina kvalitet-LABINS16*"

To test the performance of Aluminum oxide by checking its ability to de-hydrogenate and de-epoxidize quinones, the first step is to prepare a synthetic working solution called "the standard epoxide solution" in which the Aluminum oxide stays for six days. Preparation of standard epoxide solution is done by mixing (*Confidentiality of information supplied by Nouryon and cannot be disclosed*).

The standard epoxide solution was used as a blank sample. The different samples were then prepared with a mixture of the standard epoxide solution of 25ml and 0.7g of regenerated used alumina sample from Soxhlet extraction and caustic treated samples using different solvents.

The alumina oxide performance test was done as a double sample. The test of the alumina quality is done as:

- 2-3g of each regenerated alumina is kept in the oven for 2hrs at 110°C for drying out the moisture of the alumina sample.



Figure 3.1: Sample mixtures of Fresh and used alumina immersed in standard epoxide solution

- The samples were then kept in the desiccator for cooling to room temperature.
- 0.7g of each alumina sample is immersed into 25ml of epoxide solution in a 50ml glass flask.
- Nitrogen purging is done to remove the air from the flask and from the pores to create an inert atmosphere in the glass flask to avoid oxidation of hydrogenated quinones that are formed during the reaction.
- The samples are then stored in the heating cabinet at 70°C along with the blank sample.
- The samples are shaken daily over the next 5 days.
- The samples are removed from heating cabinet and allowed to cool to room temperature.
- The samples are opened to air and stirred for 2 hours to allow oxidize hydrogen peroxide. No aluminum oxide is present during the oxidation.

3.4.2 Hydrogen peroxide in the working solution- titration by sodium thiosulphate

Titration with sodium thiosulphate is used to determine the amount of hydrogen peroxide each Soxhlet regenerated alumina quality had produced. The amount of hydrogen peroxide in each sample gives an indication on how many active sites have been obtained after the regeneration treatment.

Extraction of hydrogen peroxide from working solution

An extraction was performed for removing the water soluble hydrogen peroxide from the organic phase to a water phase using phosphoric acid to enhance the extraction. 10ml of the oxidized working solution was pipetted into a glass separation funnel and then 50ml of phosphoric acid was added to the glass funnel. After the addition of phosphoric acid, it was then shaken 8 times to get a uniform mixing of the both immiscible liquid and let the phases separate into two distinguished layers. The water phase is then filtered through a 005 filter paper into a 250ml E-flask. This procedure was repeated 2 times and the water phases were collected, giving 150ml, and taken further for the titration with sodium thiosulphate.

Titration with Sodium thiosulphate

(Confidentiality of information supplied by Nouryon and cannot be disclosed)

4

Results and Discussion

This chapter will show the results obtained from the regeneration experiments with the soxhlet extraction and caustic treatment using NH_3 -TPD and aluminum oxide performance test, accompanied by discussion.

4.1 Soxhlet Extraction

Fig 4.1 below shows the regenerated samples after Soxhlet extraction with different solvents. As *Fig 4.1* shows there is small difference of the color of the alumina samples after the Soxhlet treatment. This may be indicating that the solvents extract the organics from the used aluminum oxide equally good. However, the color of the external surface of the aluminum oxide grains may be deceiving since this may only be a result of the outer surface of the alumina grains and not a picture of how well the organics are extracted from the internal of the aluminum oxide grains.



Figure 4.1: Regenerated Samples from Soxhlet Extraction: (from the left)
a. Acetonitrile b. Ethyl acetate c. Methanol d. Acetone

The extraction liquid derivatives from the 4 different solvents can be seen in *Fig 4.2*. As *Fig 4.2* shows a clear color difference between the solvents after the Soxhlet treatment is seen. This difference of color is a clear indication that the extraction of the different solvents is differently effective. However, a darker color could be due to either a larger concentration of organics or possibly a larger concentration of colored organics. This difference should be further analysed to show the difference. Assuming that the color reflects the extraction power, the Soxhlet trials could possibly indicate an order of extraction power as Ethyl acetate > Methanol > Acetonitrile > Acetone.



*Figure 4.2: Extraction solvent after the Soxhlet extraction
(from the left) Acetone, Acetonitrile, Ethyl acetate and Methanol*

Observations from the Soxhlet extraction for the different solvents are as follows:

Methanol Extraction

- The 1st cycle of extraction for methanol as a solvent took around 50 minutes to occur. Hence, after 1 hour the initial set point temperature was increased from 79°C to 90 °C.
- During the initial extraction for methanol, the color around the thimble is in dark brown color indicating good extraction.
- The 2nd extraction cycle took around 20 minutes.
- Noticed is that the solvent was less colored in the top than in the bottom of the thimble at the first extraction cycle see *Fig 4.3*. This could indicate that the extracted components have a higher density or viscosity than the solvent.

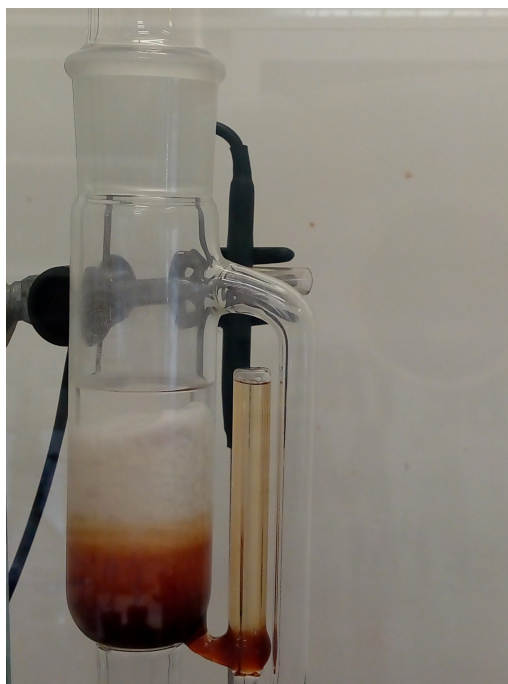


Figure 4.3: Visibility of layers in soxhlet extraction using methanol solvent

Acetone Extraction

- The 1st cycle of extraction for acetone as a solvent took around 90 minutes to occur. Hence, after 2 hours the initial set point temperature was increased from 70°C to 80°C.
- During the initial extraction, the color around the thimble is in light yellow color.
- The 2nd extraction cycle took around 45 minutes.
- No formation of layers was obtained with acetone.
- Further extraction cycles during the first day generated more and more colored liquid around the thimble.

Ethyl Acetate Extraction

- The set point temperature was at 90°C at the start of the cycle resulted in no condensation above the sample. The temperature was increased to 100°C which resulted in desired condensation above the sample. After 45 minutes, the 1st cycle took place.
- During the 1st cycle of extraction, the color became light yellow.
- The 2nd extraction cycle took around 12 minutes with a temperature setpoint of 100°C.
- Further extraction cycles during the first day generated more and more colored liquid in the thimble.

Acetonitrile Extraction

- The 1st cycle of extraction takes place after 1.12hrs when the set point temperature was at 110°C.

- During the initial cycle of extraction, there was no difference in color seen along the thimble as obtained in other solvents.
- After the 2nd cycle color started to show. The total duration for this cycle was 17 minutes.
- After a few extraction cycles, there was an equal distribution of yellow color obtained along the surface of the thimble. This could possibly be an indication that the extracted compounds from the alumina sample have similar density and hence, miscible with acetonitrile solvent.

The Soxhlet extractions showed some difference in the practical handling indicating that Methanol and Acetone are the better solvents. Methanol gave dark colored solvent earlier in the treatments indicating good extraction. Meanwhile, Ethyl Acetate and Acetonitrile gave light color in the beginning of the treatments but became darker with time as the extraction proceeds. The extraction solvents after finalized Soxhlet treatment shows on the contrary that the ethyl acetate color has the darkest color followed by acetonitrile and methanol indicating that the better solvent maybe ethyl acetate. Thus, definite conclusions cannot be made with the observations from Soxhlet extraction alone but would need further facilitation with the extraction technique and analytical methods to back up the results.

The total duration and the average number of cycles during the Soxhlet extraction for the different solvents are tabulated in *Table 4.1*. The average number of cycles for each solvent could be used to distinguish of how well the extraction had taken place. Assuming that the number of cycles is correlated to the amount of extracted organics (color of the extraction solvents) one can see that the fewer number of cycles have less color, i.e. less extracted organics. However, the total duration time was including the night between start and stop where no surveillance was done. The treatments were always finalized (no color around the thimble) in the morning.

Table 4.1: Total duration and Average number of cycles by Soxhlet extraction for different solvents

	Solvents used	Total duration [hrs]	Approx. Average No. of cycles
Trial 1	Acetone	20	64
Trial 2		24	77
Trial 1	Methanol	21	98
Trial 2		22	103
Trial 1	Ethyl Acetate	24.5	120
Trial 2		21	102
Trial 1	Acetonitrile	23.75	80
Trial 2		24	82

4.2 Ammonia- Temperature Programmed Desorption

NH_3 -TPD was used to show the amount and strength of different acid sites of the alumina, both fresh, used and regenerated alumina (both Soxhlet and caustic treated alumina). The NH_3 -TPD spectra was obtained and drawn with the help of the software Origin lab.

4.2.1 NH_3 -TPD profiles of commercial fresh and used alumina

The NH_3 -TPD spectra below shows only the desorption peaks of chemisorbed ammonia. The graphs are plotted with the NH_3 concentration ($\mu\text{mol/g}$) and temperature ($^\circ\text{C}$) versus the time. The correlation between the desorption peaks and the temperature is indicated by arrows. These arrows are positioned only by eyesight. No scientific correlation is used for this.

Fresh Alumina

As seen in *Fig 4.4*, there are two NH_3 peaks obtained with the fresh alumina sample one at a lower temperature, at 175°C , and one peak at a higher temperature, at 227°C . The peak at the lower temperature indicates ammonia that are not as strongly bound to the alumina sites compared with the ammonia shown by the higher temperature peak.

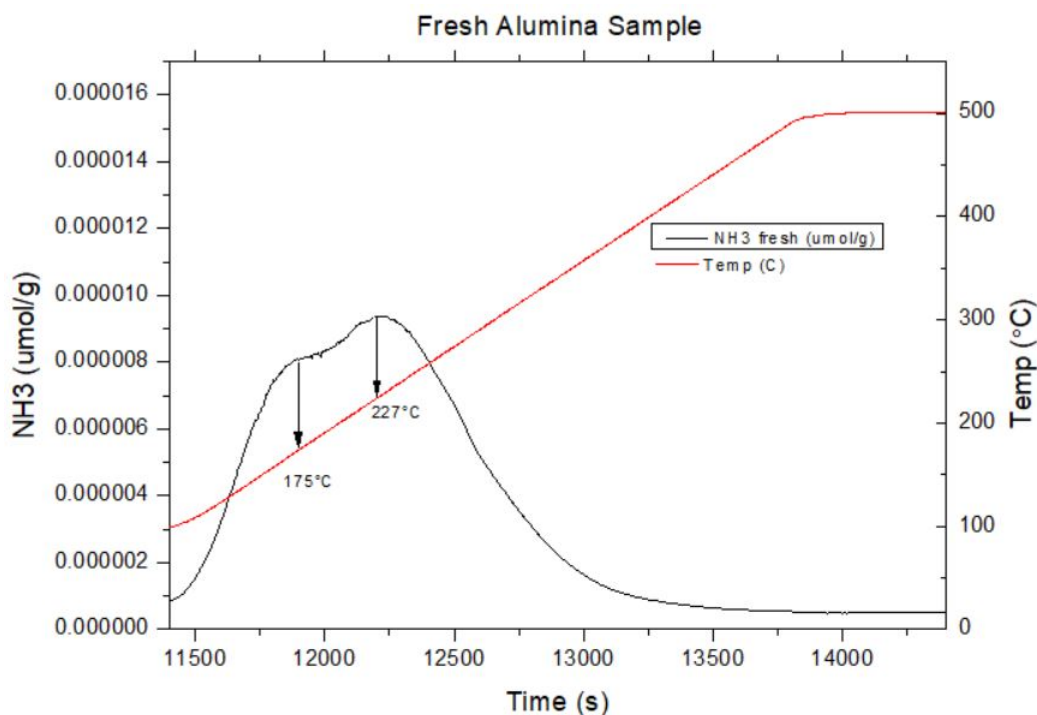


Figure 4.4: Temperature ramp-up profile of Fresh Alumina

The two peaks obtained for the fresh alumina could be due to either the presence of both Lewis acid sites (LAS) and Brönsted acid sites (BAS) or different strength of only one or both of these types. Even if both acid sites would have been visible it is difficult to predict which peak belongs to Lewis acid sites and vice-versa. This is considered as one of the shortcomings of the NH_3 -TPD as it can identify the presence of acid sites rather than as a method for site-specific.

Fresh and used Alumina

Fig 4.5 is the desorption peaks for both fresh and used alumina. As *Fig 4.5* shows, the first peak obtained at 175°C for fresh alumina is shifted to 188°C for used alumina. Also, the higher peak which is seen at 227°C for fresh alumina is shifted to 261°C for used alumina. Another interesting finding is the third peak in the used alumina spectra obtained at 380°C , while there is no such peak in the fresh alumina.

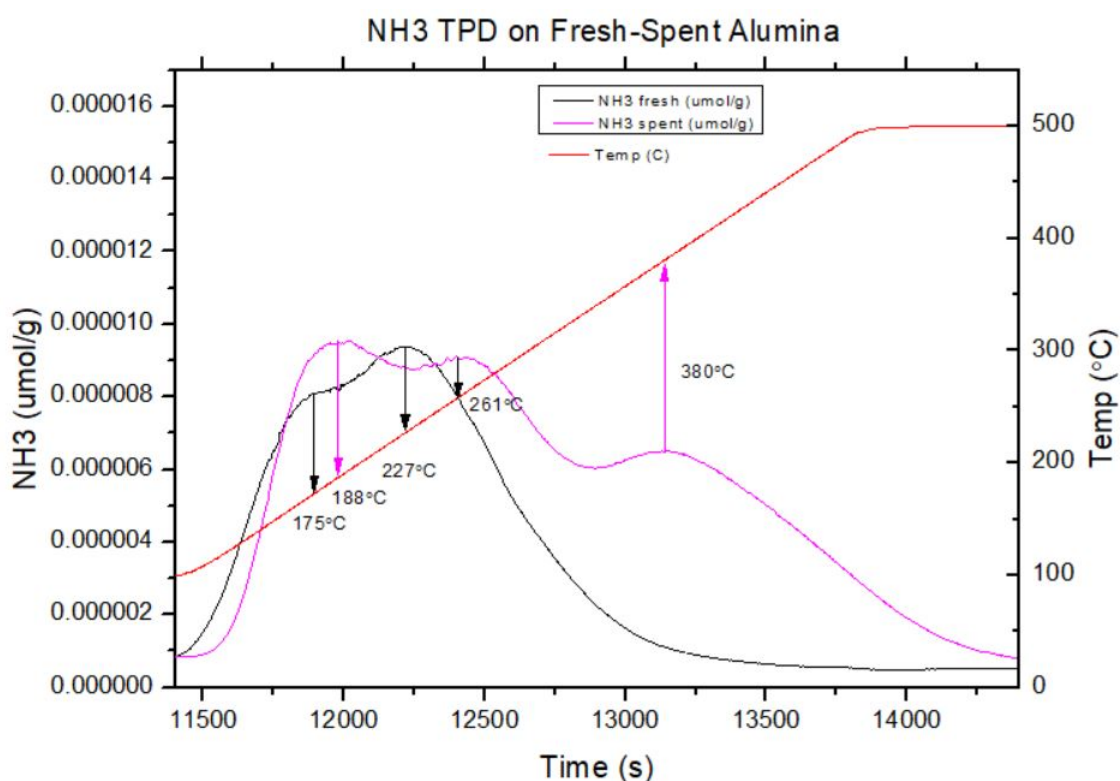


Figure 4.5: Temperature ramp-up profile of Fresh and used Alumina

The upwards shift of the first and second peak in the used alumina versus the fresh alumina has no clear explanation. The reason could be as indicated due to stronger acid sites even though organics normally should not be the cause of that. However, one other explanation could possibly be due to chromatographic effects due to the organic material in the used alumina. The mechanism of desorption to analysis (FTIR) are done by several steps; desorption from the aluminum surface, diffusion through the aluminum oxide pores, passage through the instrument with the Ar flow, analysis of the NH_3 . When NH_3 is desorbed one could possibly think that the organic material is making the pores more narrow and/or also provides adsorption

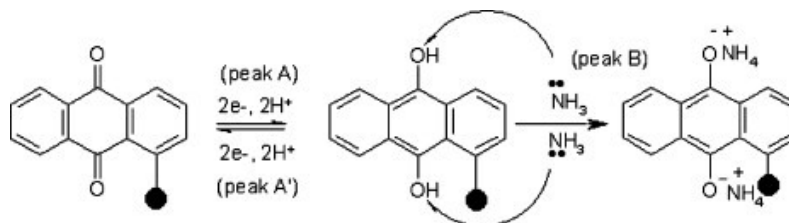


Figure 4.6: Reaction between Anthraquinone and Ammonia
[Ramakrishnappa et al., 2011]

sites for the NH_3 and thereby slow down the diffusion of NH_3 out of the aluminum grains and to the FTIR detector. We will therefore have a time delay due to the transportation leading to a temperature up-shift of the peaks.

The desorption peak at $380^\circ C$ of the used alumina could possibly be due to acid sites in the alumina. However, the organics should not be the cause of those. Another explanation could possibly be that the organics them self could bind NH_3 . One such example is that the anthraquinones could possibly bind ammonia, see Fig 4.6.

4.2.2 Regeneration samples from Soxhlet extraction

Soxhlet Extraction samples

The spectra for the different solvents treated alumina including the fresh and used alumina is seen in Fig 4.7. Other individual plots compared with fresh alumina will be discussed in Appendix B.

Fig 4.7 shows that Methanol and Acetonitrile treated alumina has one identically peak at $158^\circ C$. Fig 4.7 does also show that Ethyl Acetate treated alumina has a broad peak around the same area as the fresh alumina and that Acetone treated alumina has a spectra with large triple peak similar to the used alumina spectra.

It is expected that the NH_3 -TPD spectra differences between the different Soxhlet solvents should be a difference of how well the the solvents have removed the deposited organics from the alumina. However, there is a risk that the solvent may affect the NH_3 -TPD spectra. If there still are solvents left in the alumina structure this may react with ammonia and thereby give strange signals. This risk was neglected since the alumina samples were treated with flowing Ar at $100^\circ C$ for 4200 sec which should remove any traces of the solvents (boiling point 56 to $82^\circ C$).

The Methanol/Acetonitrile treated alumina spectra shows a single peak at $158^\circ C$. This could possibly indicate that the Soxhlet treatment with Methanol/Acetonitrile removes most of the acid sites from the alumina. Acetonitrile is known to bind to Brönsted acid sites where they may be hydrolyzed [Barbosa and van Santen, 2000] and Methanol is also known to bind (as metanota, HCO_2^-) to alumina [Greenler, 1962]. These two solvents may therefore affect the NH_3 -TPD spectra.

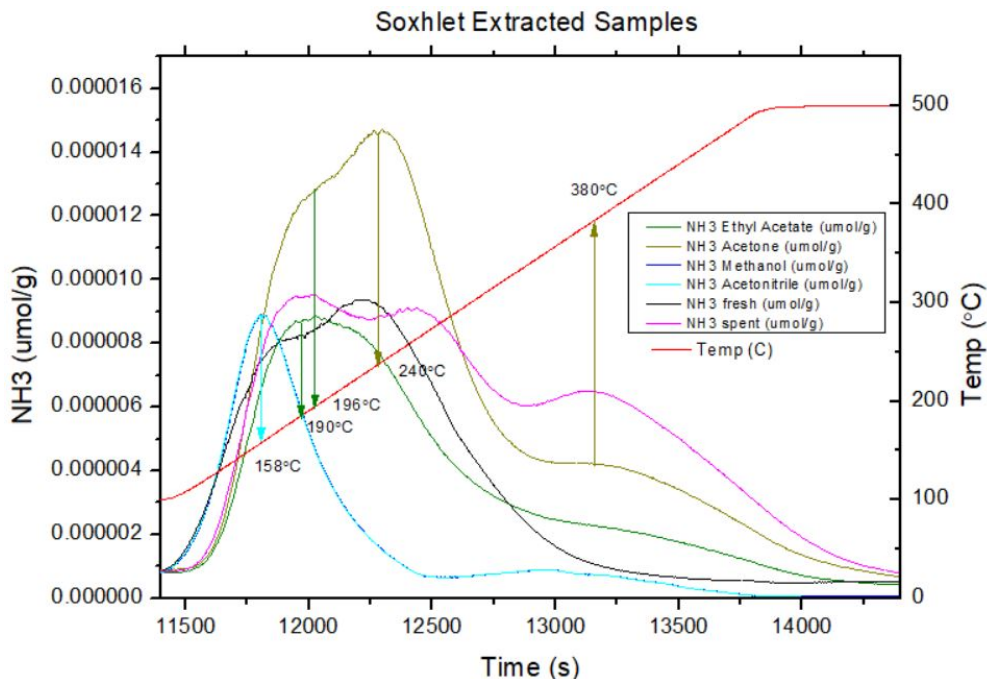


Figure 4.7: Soxhlet extracted samples for different solvents where yellow represents Acetone, green for ethyl acetate, Dark Blue for methanol, Light blue for Acetonitrile, black for the fresh alumina and purple for the used alumina. The peaks of the Soxhlet spectra's has been indicated by an arrow to the temperature profile, but not the fresh and spent alumina spectra

The large spectra peak of the Acetone treated alumina sample is surprising. It indicates that we have much more acid sites in the Acetone treated alumina than what we have in the fresh alumina. Also the acetone is known to adsorb to alumina which should affect the NH_3 -TPD covering acid sites giving a smaller signal [Pavlenko et al., 1985]. If Acetone is present in the alumina when treating the alumina sample with NH_3 there is also a risk that Ammonia reacts with Acetone making imines. The imines would not be seen in the NH_3 -TPD spectra. The NH_3 -TPD spectra of the Acetone treated alumina seems to be similar to the fresh and used alumina, only much higher signal, see Fig 4.8. A normalization of the spectra for the Acetone treated sample and the fresh alumina, see Fig 4.9, shows that the Acetone spectra is similar to the fresh alumina spectra regarding the first two peaks if they are normalized by the highest peak, see Fig 4.9. This could possibly indicate that the a Soxhlet treatment with Acetone would give an alumina that has a similar activity regarding regeneration. However, there is still a peak at 380°C which most probably is from the organic material which may block acid sites of the alumina. One other possible explanation for the large peak for the Acetone Soxhlet treated alumina is that the instrument has been differently calibrated since the acetone treated alumina was run in a later batch of the NH_3 -TPD analysis compared with the other analysis.

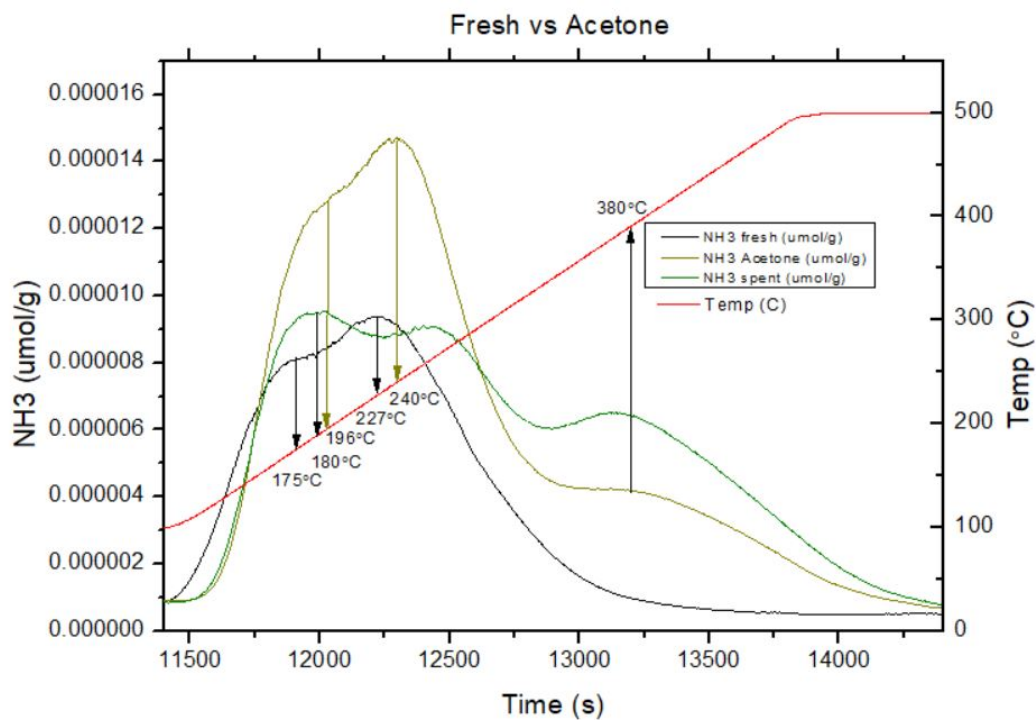


Figure 4.8: Comparison of Fresh, Used alumina and Regenerated sample using Acetone

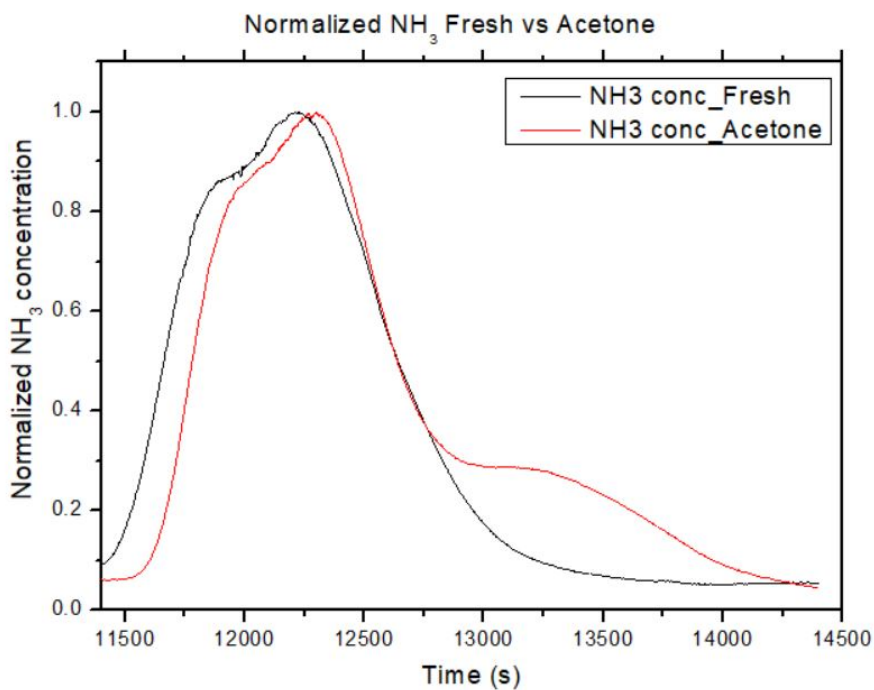


Figure 4.9: Comparison of Fresh and Regenerated sample using Acetone with normalized NH₃ signal.

Ethyl Acetate is not to our knowledge known to react with alumina and bind to the acid sites. The NH_3 -TPD spectra of the alumina Soxhlet treated with Ethyl Acetate should therefore show the amount of acid sites available on the alumina after treatment. The NH_3 -TPD spectra of the Ethyl Acetate treated alumina does show a spectra with slightly more low acid sites and less strong acid sites than the fresh alumina. The functionality of these acid sites are to be proven in the performance test. The desorption peak temperature of different solvents along with the fresh and used alumina are tabulated in *Table 4.2*. This gives an indication on how the desorption temperature (the acid site strength) is influenced by different solvents during Soxhlet extraction in comparison with the fresh and used alumina. According to *Maciver et al*, peak 1 refers to the weak acid site and peak 2 and 3 refers to the intermediate acid site strength [Maciver et al., 1963].

Table 4.2: Comparison of the desorption peak temperature of different solvents with fresh and used alumina

Samples	Peak 1 temperature (°C)	Peak 2 temperature (°C)	Peak 3 temperature (°C)
Fresh alumina	175	227	-
Used alumina	188	261	380
Acetone	196	240	380
Acetonitrile	158	-	-
Methanol	158	-	-
Ethyl acetate	190	-	-

4.2.3 Regeneration samples from Caustic treatment

Fresh vs Caustic Fresh

Fig 4.10 compares the fresh alumina and the caustic treated fresh alumina. As *Fig 4.10* shows there are two peaks for the caustic treated alumina but at higher temperature (up-shift) and with a higher concentration. The caustic treatment is expected to give a larger amount of acid sites and thereby larger peaks. However, this difference (the double amount) in concentration does not feel to be reasonable due to more acid sites done by the caustic treatment. The difference in concentration of ammonia is more probably due, or partly due, to the same error as the previous acetone treated sample. The up-shift of the peaks to higher temperature due to the caustic treatment could be due to a larger amount of acid sites. The temperature up-shift of the desorption peaks could be due to re-adsorption to the acid sites and thereby prolongs the diffusion of ammonia out of the aluminum oxide pores.

Caustic Used vs Fresh and Used Alumina

Fig 4.11 shows the spectra of caustic treated Used alumina. As *Fig 4.11* shows, the caustic treated used alumina has two peaks at 235 and 365 °C and there seems to be a small shoulder to the left of the 235 °C peak. These peaks are at temperatures similar to the spectra of the used alumina. However, the sizes of the peak are different to the spectra of the used alumina, i.e. the first peak(the shoulder) is

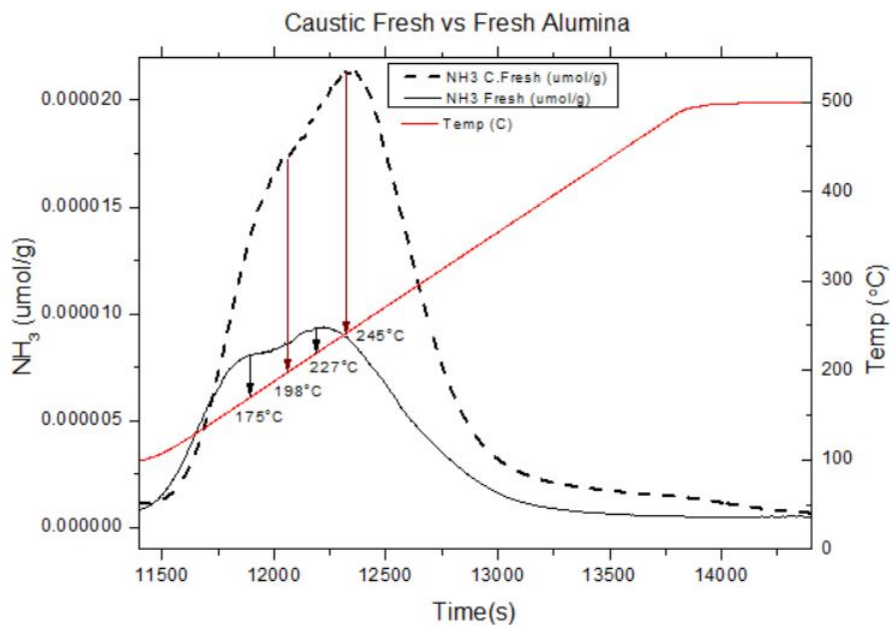


Figure 4.10: Comparison of Fresh alumina and Caustic Fresh Alumina

smaller and the last peak are larger and a totally larger concentration than the spectra from the fresh and the used alumina. The totally larger may be due to the same reason as before.

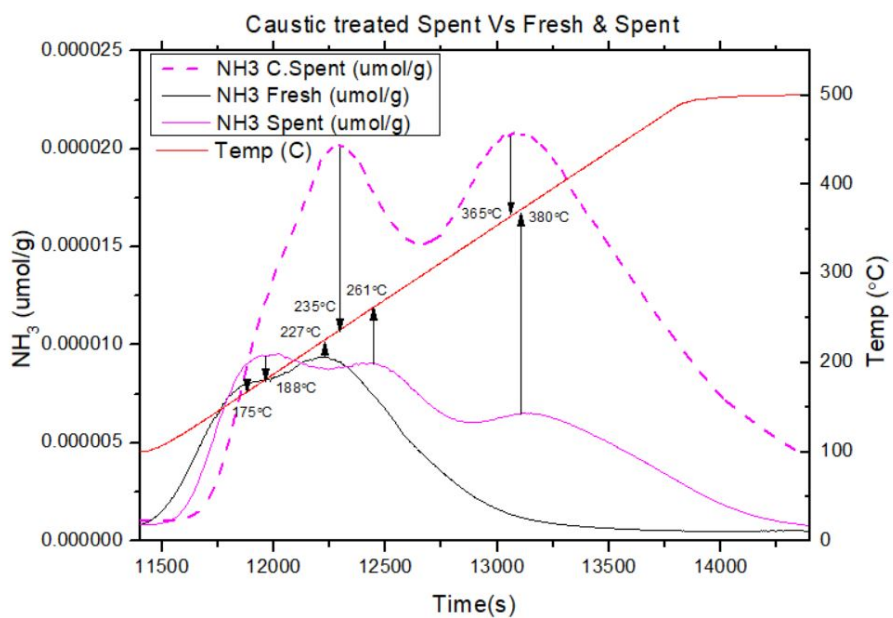


Figure 4.11: Comparison of Caustic Used alumina with Fresh & Used Alumina

Caustic treated samples

The spectra of all the alumina samples treated with both Soxhlet and caustic are shown in *Fig 4.12*.

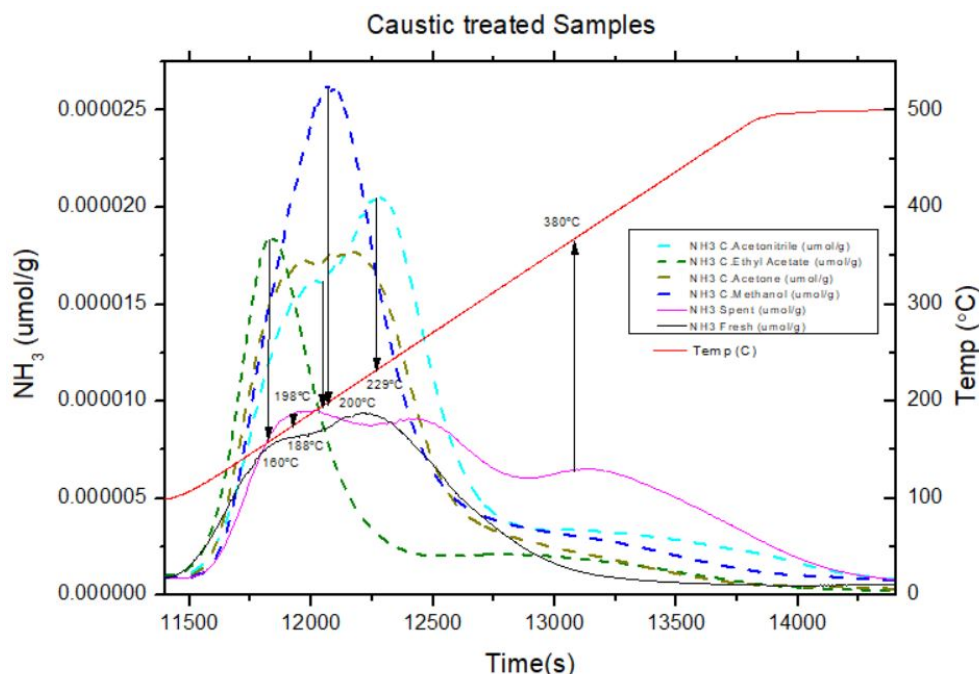


Figure 4.12: Caustic treated samples for different solvents

As *Fig 4.12* shows all the alumina sample treated with solvents and thereafter caustic shows a higher concentration than the fresh and used alumina. This may be due to a higher amount of acid sites but could also be due to the same problem of calibration as discussed previously. When comparing these spectra of the caustic and Soxhlet treated alumina (*Fig 4.12*) with the alumina with just Soxhlet treatment *Fig 4.7* the result is puzzling. Ethyl Acetate changes from a broad peak at 190°C to a narrower peak at 160°C, Acetone changes from three peaks at 196, 240 and 380°C to a broad peak at 200°C, Methanol changes from a narrow single peak at 158°C to a single peak at 200°C and Acetonitrile changes from a single peak at 158°C to two peaks at 198 and 229°C. These changes are strange since the caustic treatment seems to both shift the desorption peaks downwards in temperature, i.e. Ethyl Acetate and Acetone, and upwards, i.e. Methanol and Acetonitrile. It does also change the structure of alumina surface giving different acid sites, i.e. Acetone shifts from three peaks to a single peak and Acetonitrile changes from single peak to two peaks. This result seems to be strange and are therefore questioned. One should therefore not draw any conclusions from this part of the material.

The strange result of the NH_3 -TPD of the caustic treated alumina may also be an effect of that solvents may react with caustic. Ethyl Acetate may react with caustic making sodium acetate and ethanol, acetone may react with caustic making enolate which is a strong nucleophile, methanol may react with caustic making the methyl

base and the Acetonitrile may react with caustic making amide. All these reactions will most probably affect the analysis with NH_3 -TPD giving different results making it even harder to understand the NH_3 -TPD result.

Table 4.3: The desorption peak temperature of different alumina treated with different solvents at the Soxhlet treatment and with caustic

Samples	Soxhlet treatment (°C)	Soxhlet and Caustic treatment (°C)
Ethyl Acetate	Broad peak at 190°C	Single peak at 160°C
Acetone	Three peaks, 196–380°C	Broad peak at 200 °C
Methanol	Single peak at 158°C	Single peak at 200°C
Acetonitrile	Single peak at 158°C	Two peaks at 198 and 229°C

It is also worth noting that the caustic treatment gave alumina that had less strength than the not caustic treated alumina. This was shown after the drying of the caustic treated samples when handling the alumina for the analysis. The reason for the lost crush strength is most probably due to that caustic has dissolved part of the alumina creating thinner walls in the pore structure. This could have happened due to too high caustic concentration or insufficient washing of the alumina after the caustic treatment.

4.3 Aluminum oxide performance test

4.3.1 Dehydrogenation and de-epoxidation reactions

The fresh alumina, the used alumina, the four Soxhlet treated and the six caustic treated samples were tested for their ability to dehydrogenation and de-epoxidation. After a 6 days heat treatment with a standard epoxide solution the samples did show a color difference already when taken out of the oven indicating on a difference in activity, see Figure *Fig 4.13*. The fresh alumina gave a darker color than for used alumina which is due to that more H_4AAQ has been hydrogenated to H_4AAQH_2 than for the used alumina. The different Soxhlet treated and caustic treated samples had a color somewhere between the fresh and the used alumina. This indicates that those samples are better than the used but not as good as fresh alumina in regenerating the working solution. Unfortunately, there are no pictures of the other epoxide solutions.



Figure 4.13: Used and Fresh alumina (double sample) after aluminum oxide performance test

4.3.2 Hydrogen peroxide in working solution by sodium thio sulphate

The alumina quality was finally checked by allowing the standard epoxide solution to be oxidized and the amount of hydrogen peroxide formed was analyzed. The hydrogen peroxide analysis was done using thiosulphate. Previous to the analysis of the hydrogen peroxide is the formed hydrogen peroxide extracted with a phosphoric acid/water solution. Results from the titration experiments from the hydrogen peroxide in the working solution are tabulated in *Table 4.4*.

Table 4.4 shows that the fresh alumina creates about 1.26 g/dm^3 of hydrogen peroxide. It does also show that all the Soxhlet extractions gave less hydrogen peroxide, best was the Methanol treated alumina with 1.13 g/dm^3 and the Ethyl Acetate is the least good. The Caustic treated samples gave a higher conversion to hydrogen peroxide with the caustic treated fresh alumina as the best with almost double amount compared with fresh alumina.

The result of Ethyl Acetate is a bit surprising as it gave less activity of the alumina since the Ethyl Acetate seemed to have extracted more organics than any other solvent, see *Fig 4.2*.

This result indicates that the Soxhlet extraction will give a positive effect of how well the alumina can regenerate the working solution and that a caustic treatment will increase the regeneration even more. However, there are some doubts about the result from the titration. During the titration one are assumed to add a small amount

Table 4.4: Results from Hydrogen peroxide in working solution titration for Soxhlet treated samples. Density of H_2O_2 is taken as 0.9 g/dm^3

Sample name	Amount of solvent used (g)	Total consumption (ml)	H_2O_2 (g/dm^3)
Fresh alumina	20.5	16.85	1.40
Used alumina	18	8.55	0.81
Methanol	15.42	11.42	1.26
Acetone	18.04	9.50	0.90
Acetonitrile	17.89	12.46	1.18
Ethyl acetate	17.46	6.54	0.64
Caustic Fresh alumina	18.35	25.73	2.38
Caustic Used alumina	19.07	11.84	1.06
Caustic Methanol	16.944	14.25	1.59
Caustic Acetone	18.24	18.17	1.69
Caustic Acetonitrile	18.10	9.84	0.92
Caustic Ethyl acetate	17.99	19.88	1.88

of (*Confidentiality of information supplied by Nouryon and cannot be disclosed*). The amount is defined as a pinch. All the analysis resulted in a pale blue color while the end titration are expected to be colorless. The color was due to that a too large addition of the (*Confidentiality of information supplied by Nouryon and cannot be disclosed*) was used. It has been agreed that no conclusions from the titrations should be made regarding how well the alumina was regenerated.

4.4 Final Discussion

The result of this work does not give a clear picture of how well Soxhlet extraction regenerates the alumina ability to dehydrogenate and de-epoxidate the working solution. The color of the extraction solvents indicates that Ethyl Acetate is the better solvent, the test of the alumina oxide performance test indicates that Methanol may be the better solvent and the NH_3 -TPD does indicate that Acetone would be the better solvent. Without better knowledge, we conclude that the solvent color and the performance test is the better measurements of the regeneration since the NH_3 -TPD seems to generate contradictory result possibly due to adsorption of solvents to the alumina and reactions with ammonia with the solvents. Also, the knowledge of the NH_3 -TPD does not differentiate of which acid sites that does the dehydrogenation and de-epoxidation. It is therefore suggested that more Soxhlet regeneration work should be done using Methanol possibly Ethyl Acetate to answer the aim of this work.

4. Results and Discussion

The caustic treatments indicate that a higher ability to regenerate is achieved when comparing the performance test. It is therefore suggested that caustic treatment is tested as an after treatment for Soxhlet trials. However, the crush strength has to be followed closely since caustic may change that.

5

Conclusion and Future work

5.1 Conclusion

Soxhlet extraction with Methanol, Ethyl Acetate, Acetone and Acetonitrile has been tested for extraction of organics from used alumina from the hydrogen peroxide plant. The measurements after the Soxhlet trial has shown conflicting results where some of the result may be due to measuring errors.

The result indicate that Methanol and possibly Ethyl Acetate may be used as extracting solvent of the organics from the used aluminum oxide.

5.2 Future Work

Some thoughts on how to improve the work came to my mind. A future work is therefore presented below:

- Amount of organics present in the recovered working solution can be done by Gas chromatography method.
- More trials on Methanol and Ethanol acetate can be done. This can be carried over by varying the time for a uniform average number of cycles for both solvents.
- NH_3 -TPD did not give any major indication on the different acid sites. Thus, it is better to use titration results as a function test.

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A

NH₃-TPD Scripts

Auto-Tune

The following section involves the pre-defined script for Auto-Tune done during NH₃-Temperature Programmed Desorption.

	Gas-MFC (%)																	
Gas name:	N2O	N2	NO2	NO	NH3	CO	CO	CH4	O2	Ar	Liquid HC				Water			
Gas conc (%)	0.05	100	0.5	3	4	10	10	2	100	100	Ar HC (ml/min)	HC (g/h)	HC conc (%)	Switch 1	Ar H2O (ml/min)	H2O (g/h)	H2O conc (%)	100
MFC #:	G	A	C	D	E	H	I	K	J	N	A	A		OFF:0/ON:1	C	B		OFF:0/ON:1
	Gas	Gas	Gas	Gas	Gas	Gas	Gas	Gas	Gas	Gas	Gas	Liq	Conc	Sw	Gas	Liq	Conc	Sw
	1	0	1	1	1	0	1	0	1	1	1	1	1	1	1	1	1	1
	0.000	0.00	0.000	0.00	0.00	0.00	0.00	0.00	0.00	100.00	0	0	0	0	0	0	0	0
	0.000	0.00	0.000	0.00	0.00	0.00	0.00	0.00	0.00	100.00	0	0	0	0	0	0	0	0
	0.000	0.00	0.000	0.00	0.00	0.00	0.00	0.00	0.00	100.00	0	0	0	0	0	0	0	0
	0.000	0.00	0.000	0.00	0.00	0.00	0.00	0.00	0.00	100.00	0	0	0	0	0	0	0	0
	0.000	0.00	0.000	0.00	0.00	0.00	0.00	0.00	0.00	100.00	0	0	0	0	0	0	0	0
	0.000	0.00	0.000	0.00	0.00	0.00	0.00	0.00	0.00	100.00	0	0	0	0	0	0	0	0
	0.000	0.00	0.000	0.00	0.00	0.00	0.00	0.00	0.00	100.00	0	0	0	0	0	0	0	0
	0.000	0.00	0.000	0.00	0.00	0.00	0.00	0.00	0.00	100.00	0	0	0	0	0	0	0	0
	0.000	0.00	0.000	0.00	0.00	0.00	0.00	0.00	0.00	100.00	0	0	0	0	0	0	0	0
	0.000	0.00	0.000	0.00	0.00	0.00	0.00	0.00	0.00	100.00	0	0	0	0	0	0	0	0
	0.000	0.00	0.000	0.00	0.00	0.00	0.00	0.00	0.00	100.00	0	0	0	0	0	0	0	0

Figure A.1: Script for Auto-Tuning

Script for NH₃-TPD

The following section involves the pre-defined script for sample catalyst activity done during NH₃-Temperature Programmed Desorption

											Gas-MFC (%)																		
											Gas name:	NO2	N2O	H2	NO	NH3	Ar	NO	H2	O2	Ar	Liquid HC					Water		
			Target temp (°C)								Gas conc (%):	0.50	1.000	4.000	3.068	3.994	100.00	3.068	4.000	100.000	100.000	Ar HC (ml/min)	HC (g/h)	HC conc (%)	Switch 1	Ar H2O (ml/min)	H2O (g/h)	H2O conc (%)	100
Time (s)	Total flow (ml/min)	Ramp (°C/min)	Reactor	IM heater	Pre-heat	By-pass	To FTIR	Vent heat	Liquid HC	Water	MFC #:	G	A	C	D	E	H	I	K	J	N	A	A		OFF:0 /ON:1	C	B		OFF:0 /ON:1
	ID:	Ramp	RegRE	RegE	Reg E	Reg E	RegE	RegE	RegD	RegD		Gas	Gas	Gas	Gas	Gas	Gas	Gas	Gas	Gas	Gas	Gas	Liq	Conc	Sw	Gas	Liq	Conc	Sw
	Used?	1	1	1	1	1	1	1	1	1		1.00	0	0.000	1.000	1.000	0	0.000	0.000	1.000	1.000	1	1	1	1	1	1	1	1
600	300		100	191	191	191	191	191	20	110											100								
3600	300		100	191	191	191	191	191	20	110											100					700	3.068	5	0
3600	300	20	100	191	191	191	191	191	20	110						0.04					99.96					700	3.068	5	0
3600	300	20	100	191	191	191	191	191	20	110											100					700	3.068	5	0
2400	300	10	500	191	191	191	191	191	20	110											100					700	3.068	5	0
600	300	20	500	191	191	191	191	191	20	110											100					700	3.068	5	0
3600	300	20	100	191	191	191	191	191	20	110											100					700	3.068	5	0
900000	300	20	100	191	191	191	191	191	20	110											100					700	3.068	5	0

Figure A.3: Script for TPD Alumina

B

NH₃-TPD Profiles for various solvents

The following section involves the profiles obtained from NH₃-Temperature Programmed Desorption for different solvents using *Origin Lab*.

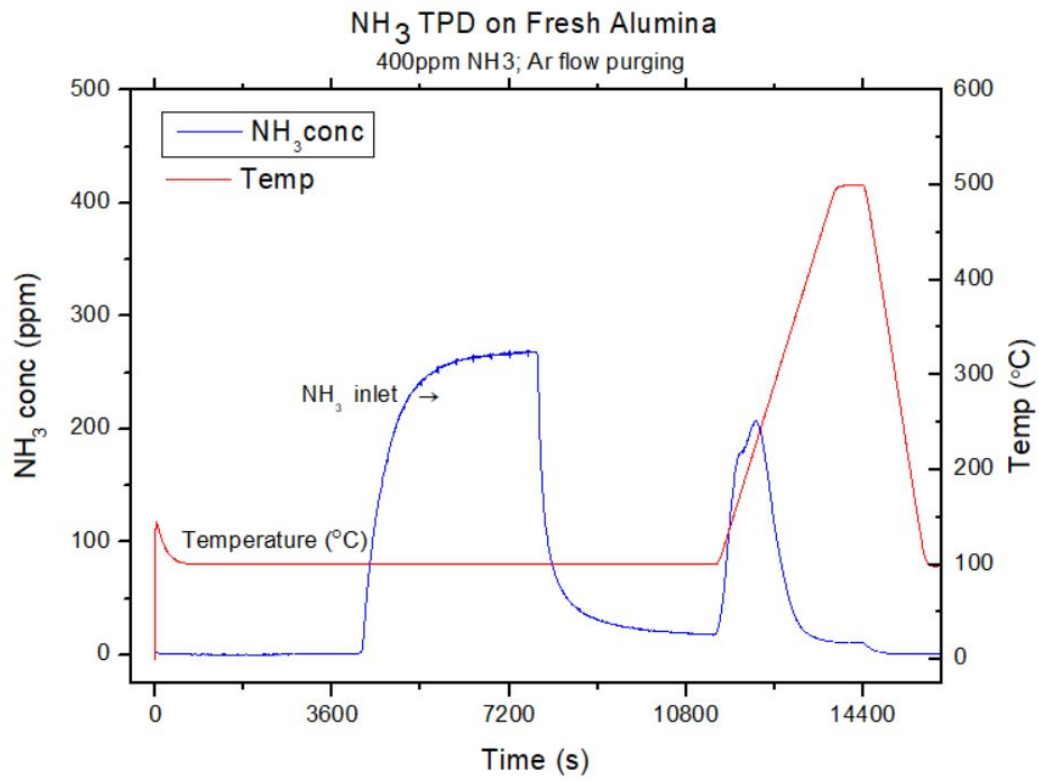


Figure B.1: Profile of Fresh alumina

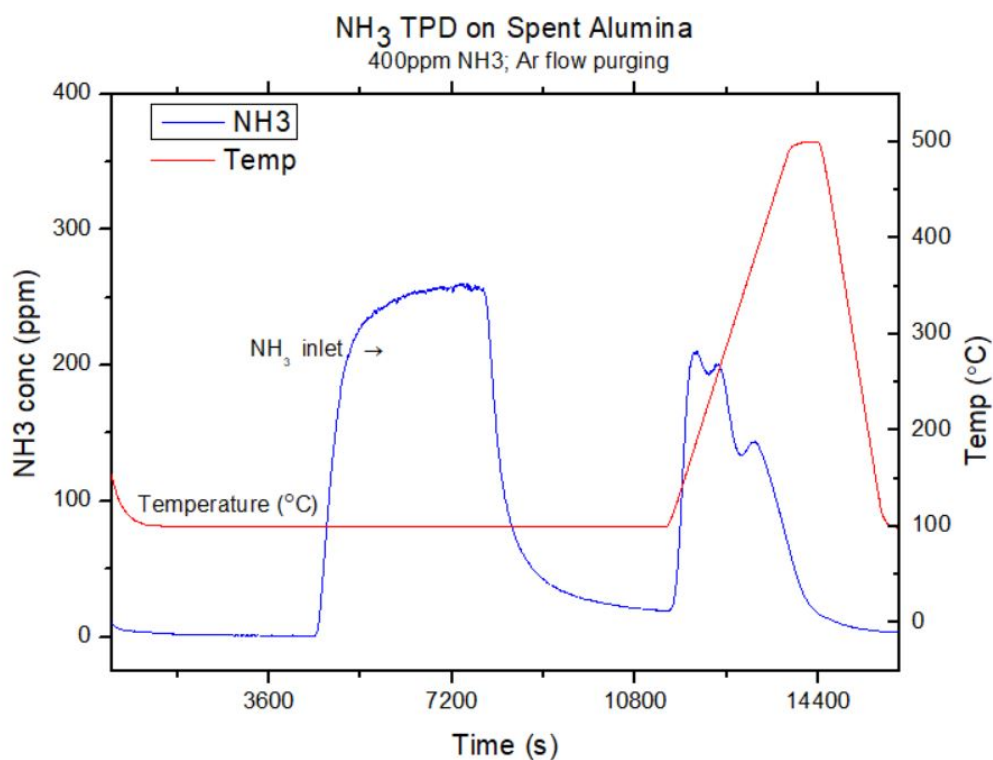


Figure B.2: Profile of used alumina

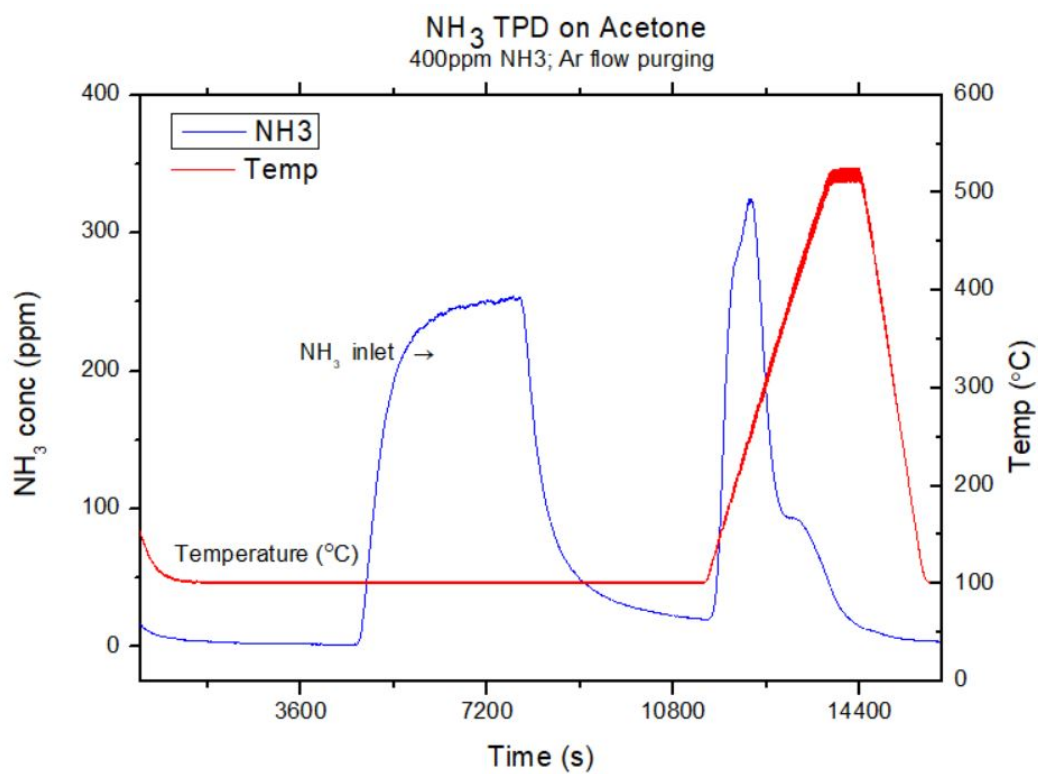


Figure B.3: Profile of Acetone from Soxhlet extraction

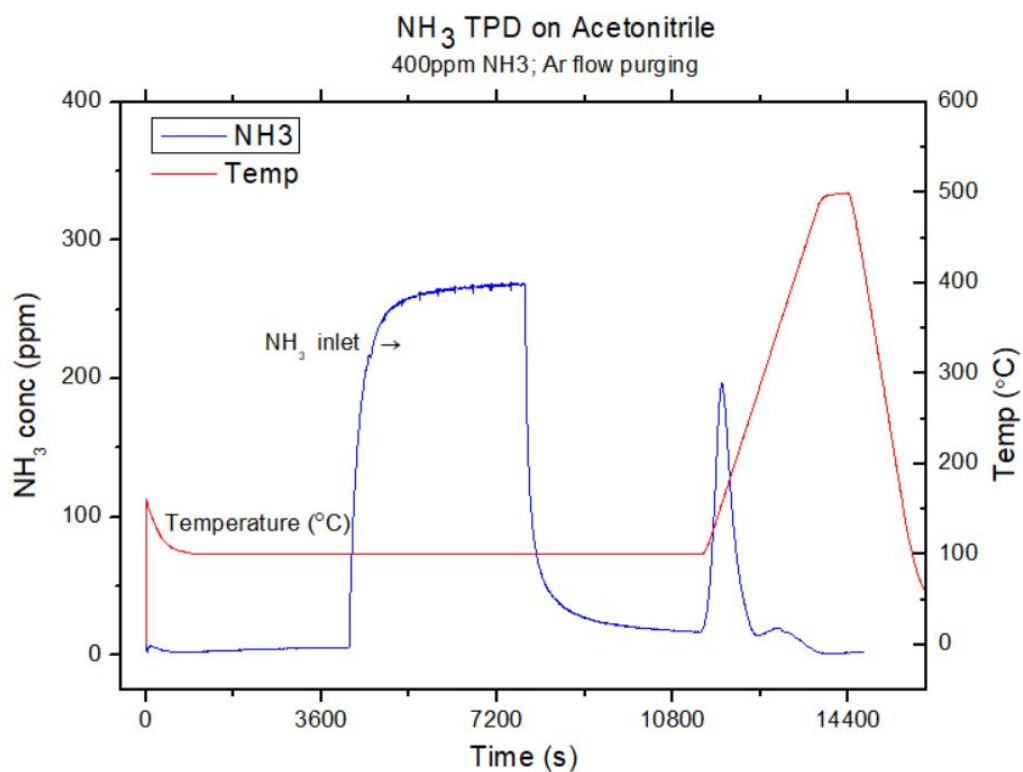


Figure B.4: Profile of Acetonitrile from Soxhlet extraction

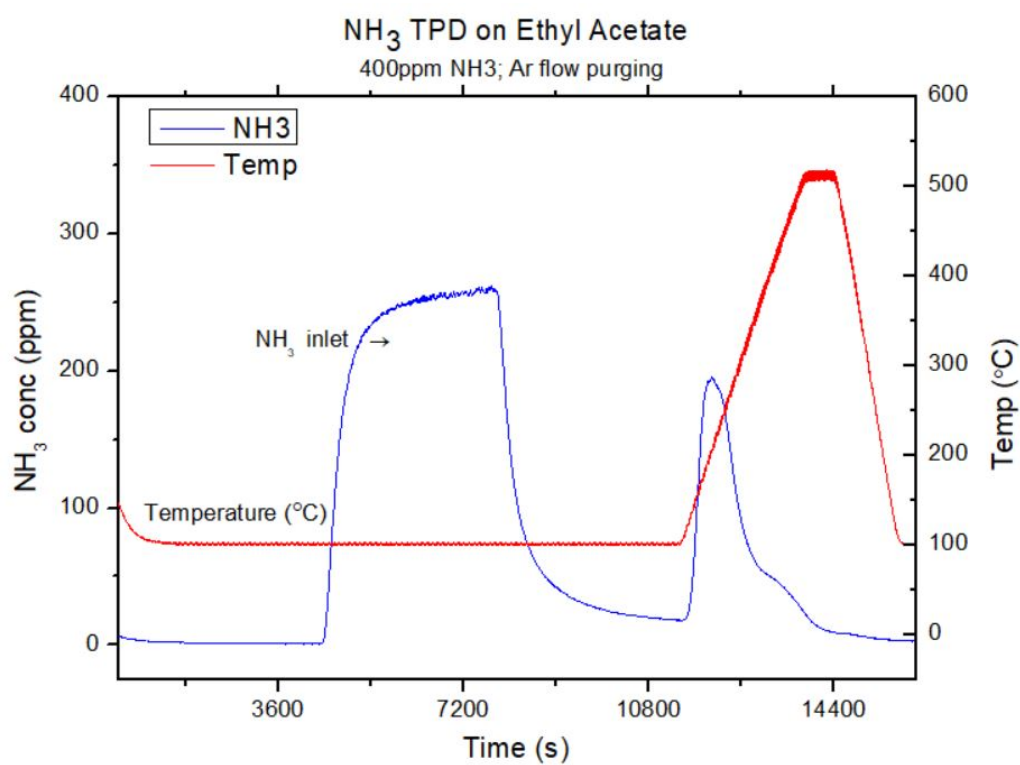


Figure B.5: Profile of Ethyl Acetate from Soxhlet extraction

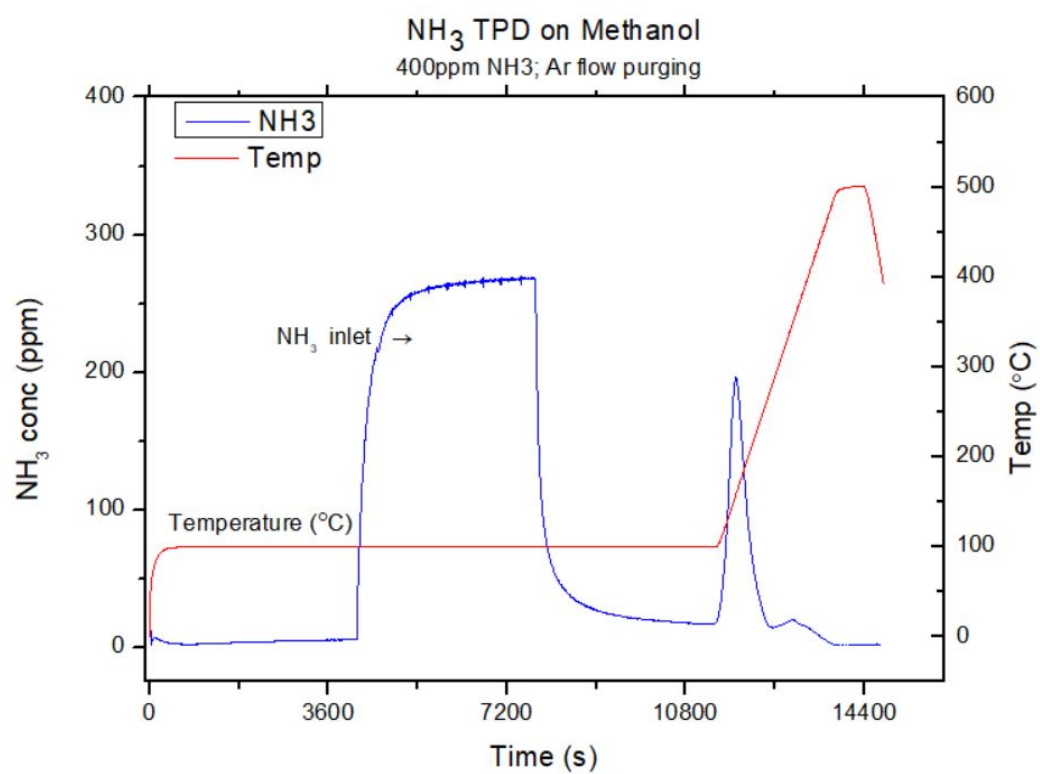


Figure B.6: Profile of Methanol from Soxhlet extraction

Temperature ramp-up profile for individual solvents

The following section involves the profiles obtained by temperature ramp-up profile for different solvents when compared with the base case i.e., fresh and used alumina using *Origin Lab*.

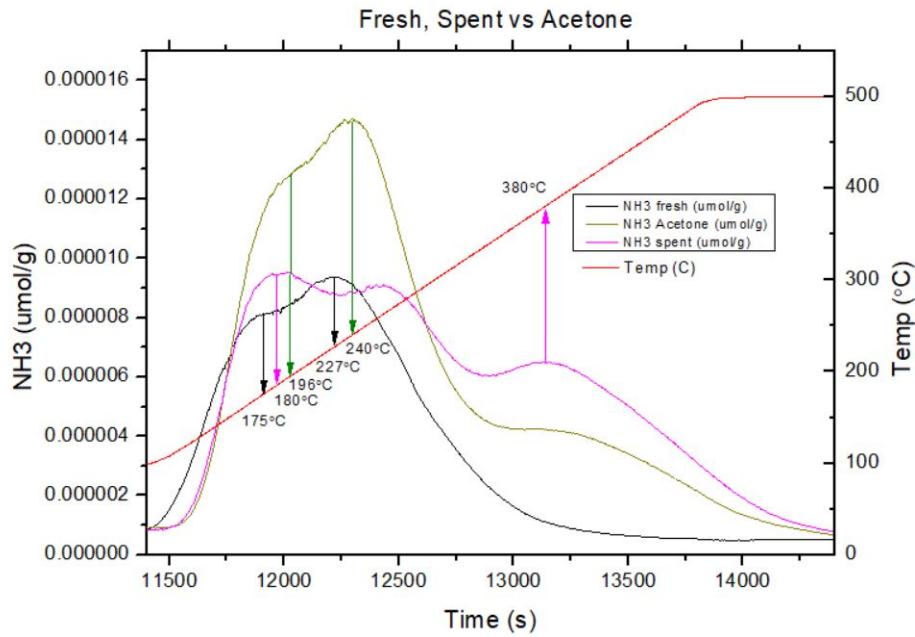


Figure B.7: Temperature ramp-up of Fresh, used and Acetone

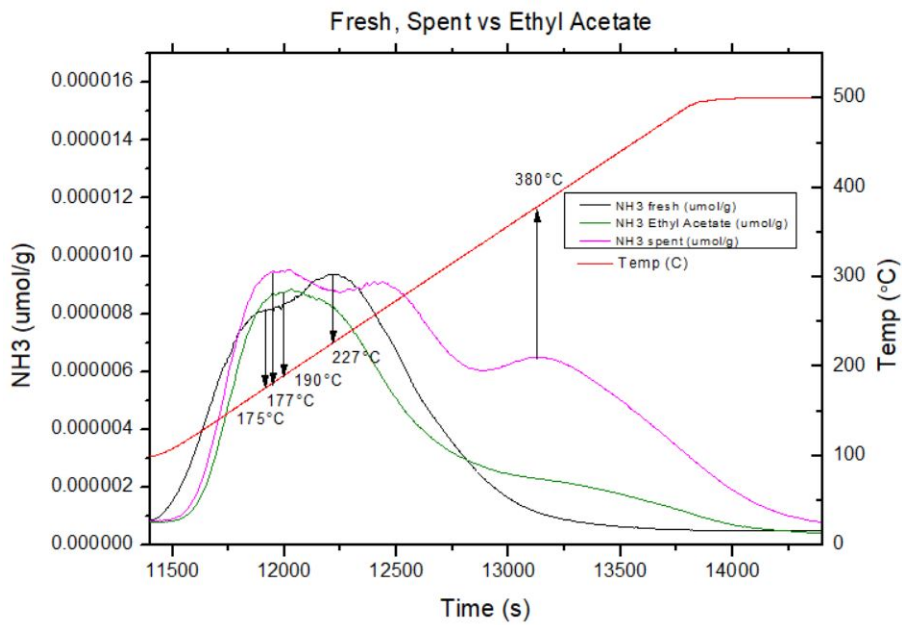


Figure B.8: Temperature ramp-up of Fresh, used and Ethyl acetate

B. NH_3 -TPD Profiles for various solvents

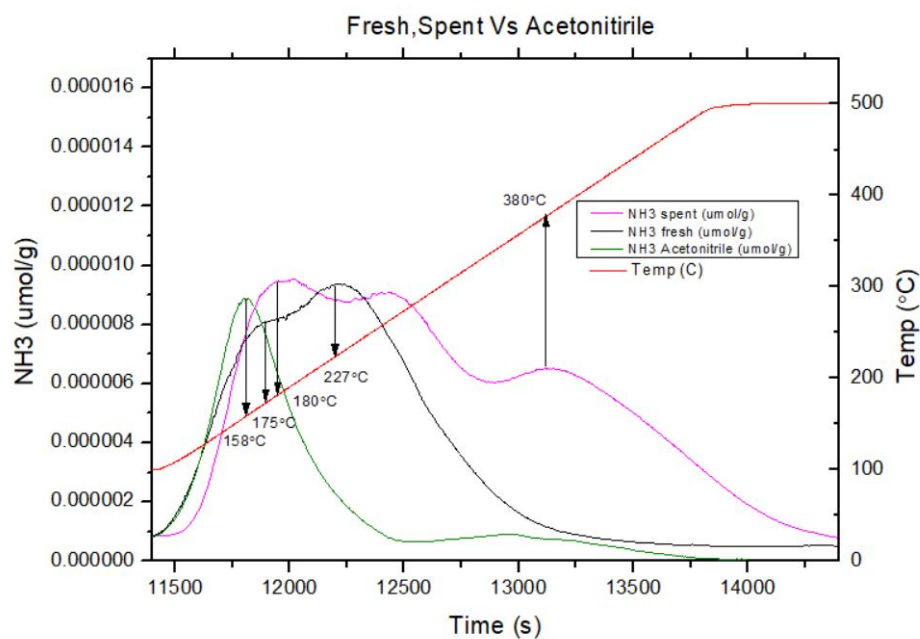


Figure B.9: Temperature ramp-up of Fresh, used and Acetonitrile

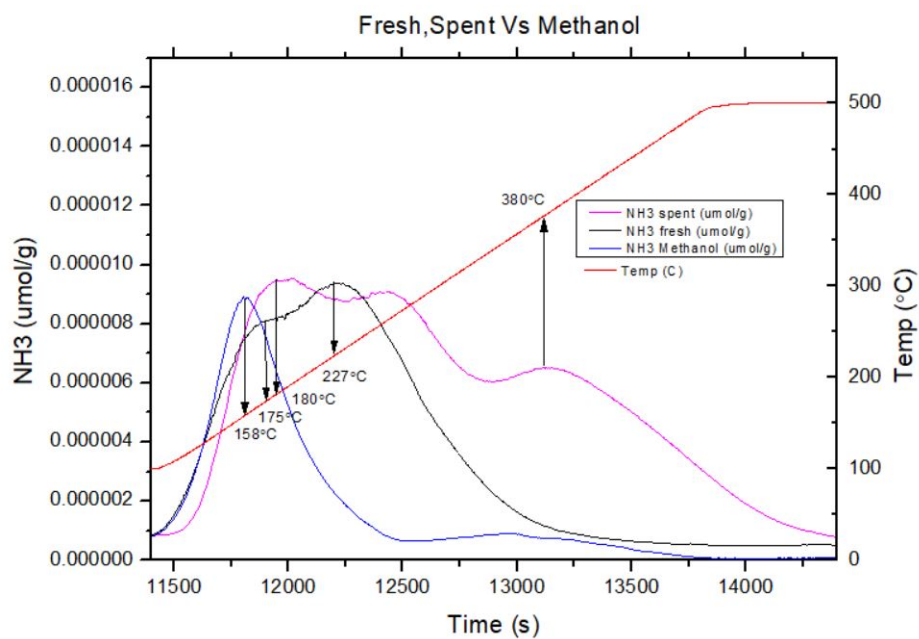


Figure B.10: Temperature ramp-up of Fresh, used and Methanol