Lappeenranta – Lahti University of Technology LUT
School of Engineering Science
Master's Programme in Chemical and Process Engineering

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CHEMICAL RECYCLING OF MAGNETIC TAPE

Master’s thesis

Examiners: Associate professor Eveliina Repo
D. Sc. Sami Virolainen

TIIVISTELMÄ

Lappeenrannan – Lahden teknillinen yliopisto LUT
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Magneettinauhan kemiallinen kierrättätys

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Tarkastajat: Associate professor Eveliina Repo
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hakusanat: Polyetyleenitereftalaatti hydrolyysi emäs depolymerisaatio rauta koboltti

Työn tarkoituksena oli tutkia magneettinauhojen kierrätysmahdollisuuksia. Tällä hetkellä lukematon määrä magneettinauhoja päätyy kaatopaikoille.

Kirjallisuusosuudessa pyrittiin löytämään kierrätystapa magneettinauhan kahdelle tärkeimmälle osalle; muoviselle pintakerrokselle ja metallipigmentille. Kirjallisuuden perusteella muovikerrokselle, joka koostuu polyetyleeniterefalaatista, sopivimmaksi osoittautui muovipullojen kierrätystekniikka; hydrolyysi emäsliuoksessa. Metallipigmentille, joka sisältää suurimmaksi osaksi rautaa, mutta myös kobolttia, soveltuvimmaksi menetelmäksi voitiin ehdottaa typpihappoliuotusta, joka on koboltille selektiivinen. Kirjallisuusosan lopuksi prosessista piirrettiin lohkokaavio.

Kokeellisessa osuudessa testattiin kirjallisuudesta löytyneitä prosesseja. Muovikerroksen polymeeri hajosi monomeereiksi helposti suhteellisen alhaisissakin lämpötiloissa; 170 ja 150 ^{o}C ja 7 barin paineessa. Reaktion nopeutta rajoittavaksi tekijäksi todettiin emäksenä käytetyn NaOH:n konsentraatio, minkä pitoisuuden ollessa 0,1 M, reaktio ei tapahtunut loppuun, mutta pitoisuuden ollessa 0,25 M tai enemmän samoissa olosuhteissa depolymerisaatio oli täydellistä.

Depolymerisaation jälkeen metallipigmentti kerättiin harmaana jauheena. Jauheen massasta 55% saatiin liukenemaan rautana ja 3% kobolttina, 1 tai 3 M rikkihappoon 30 minuutin aikana. Liuotusta jatkettiin 24h, jolloin systeemin oletettiin päässeen tasapainoon liuoksen konsentraation ollessa raudalle 5,5 g/L ja koboltille 0,3 g/L . Koboltille selektiivinen liuotus saatiin aikaiseksi käyttämällä 1 M typpihappoa, jolloin suuri osa raudasta saostui rautanitraatiksi, jättäen raudan konsentraatioksi 0,24 g/L .

Elektrolyysi suoritettiin liuotuksessa saaduille metalliliuoksille. Liuoksen pH:n ollessa alle 5, metallien talteenotto ei tuottanut tulosta. Kun liuoksen pH nostettiin arvoon 5 tai sen yli ja lämpötila pidettiin alle numerona vaan, kobolttia saatiin pelkistymään. Kun liuoksen pH oli 5 tai yli ja liuoksen lämpötilaa nostettiin 40 ^{o}C:een rautaa pelkistyi koboltin sijaan.

ABSTRACT

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Chemical recycling of magnetic tape

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This work aimed to study a recycling path for magnetic tapes. Magnetic tapes at the time of writing have no recycling processes and end up in dump despite their massive volumes.

In the literature review composition of magnetic tapes was studied and possible recycling solutions for the two main layers; plastic and metal pigment layers were proposed. It was concluded that the plastic layer consisting mainly of polyethylene terephthalate (PET) a hydrolysis process, a common plastic bottle recycling process, done in alkaline conditions was the most suitable for magnetic tapes. For the remaining metallic pigment, it was suggested that while the pigment mainly consist of iron a selective cobalt leaching could be possible by using nitric acid. Finally, a block diagram overlying the whole process was produced.

In the experimental part experiments were done on the unit processes described in the literature review. PET was easily depolymerized under relatively mild conditions of 175 and even 150 ^{o}C with 7 bars of pressure. The limiting condition for reaction rate was found to be the alkaline concentration where when NaOH concentration was set to 0.1 M the tape did not completely depolymerize but at 0.25 M and above depolymerization was complete.

After depolymerization a dark grey powder containing metals was collected. From the powder, 55 m-% of the powder was leached as iron and 3 m-% as cobalt into 1 or 3 M sulphuric acid within 30 minutes. The leaching was continued for 24 hours and therefore it was assumed to be in balance with iron concentration of 5,5 g/L and cobalt concentration 0,31 g/L. Selectivity for cobalt was achieved using 1 M nitric acid where after iron was precipitated as iron nitrate, iron concentration was reduced to 0,24 g/L.

The leaching solutions were subjected to electrolysis. When solution pH was below 5 and temperature at around 0 ^{o}C no metals were recovered. When pH was risen to 5 or above and temperature kept at below room temperatures, cobalt was recovered. When temperature was risen to 40 ^{o}C and pH to 5 or above iron was recovered instead of cobalt.

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Simo Pöntynen

Lappeenranta (Finland) 16th of October 2019

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1 Introduction

Magnetic tapes were one of the most commonly used media storage devices from 1980 to 2010 before other optical and digital media storing devices replaced them. Mainly, the magnetic tape was used in VHS tapes which was eventually superseded by disc type devices such as the DVD. This has left us with innumerable amount of magnetic tape junk which as of today ends up in landfills. Various types of magnetic tapes are shown in Figure 1.

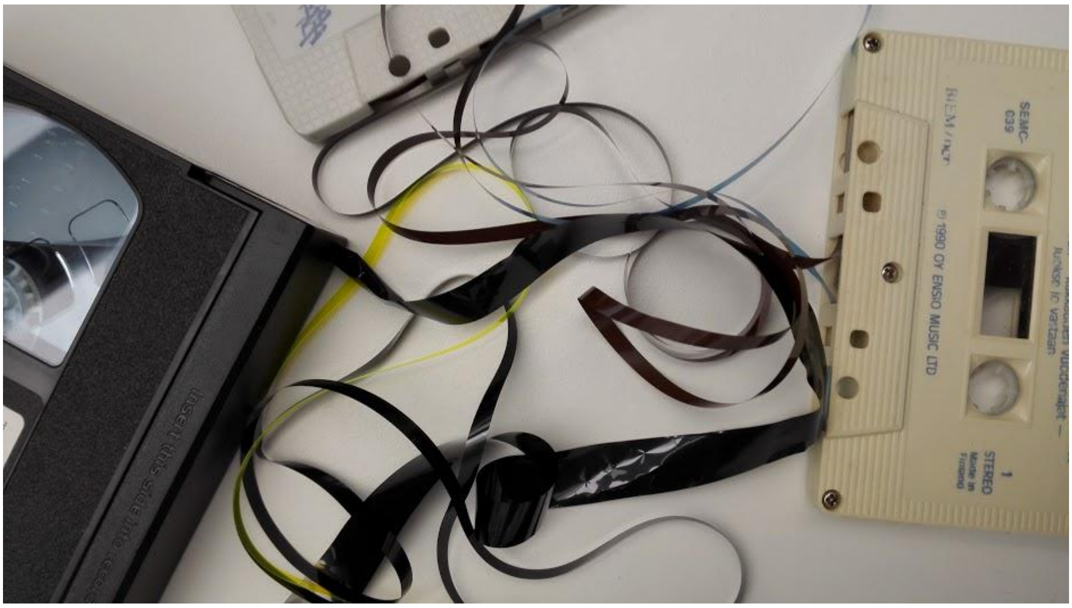

Figure 1 Magnetic tape media storages; brown and blue tape as well as thin black and yellow tape are from audio casettes and the wide black tape is from a VHS tape

The goal of this work is to find a possible recycling route for used magnetic tapes using chemical recycling methods. Recycling of magnetic tapes has not been studied previously and therefore there is inherent novelty value in the subject. Other motivation behind the study is the use and possible recovery of precious metals such as cobalt in magnetic tapes. Cobalt is in the list of EUs critical raw materials and namely possesses high economic significance. When a suitable process would be found the copious amount of raw material with the possible recovery of other materials such as valuable chemicals from the recovery process could prove to be an economically viable process. As with all research done on recycling previously unrecyclable product there is an environmental incentive as well.

This study is done in two parts. First, a literature research is done to find a suitable processing route for the magnetic tape. Secondly, an experimental research is carried out according to the process suggested on the literature part.

Literature review

Background

Magnetic tape commonly consists of a thin base layer and a thin layer of magnetic pigment containing magnetic particles on top of the base layer. The magnetic layer also contains binder chemicals which binds the two layers together. Tapes come in different widths and lengths according to numerous media recording and playing devices and their corresponding standard tape sizes. Most commonly magnetic tapes are used in VHS tapes and audio cassettes as the media storage. There is surprising amount of variation in different magnetic tapes, not only on the size but also in the materials used. As magnetic tape media storage technology gained popularity, so did the development and improvements in it such that more data could be fitted in the same volume. Earliest magnetic tapes used only iron oxides in the magnetic layer. Due to this magnetic layer is sometimes called oxide layer. Later, cobalt induced iron oxides, chromium and elemental metals were used to improve on the tape's performance.

2.1 Materials in magnetic tapes

The base layer is apart from a few exceptions made up of polyethylene terephthalate (PET). Earliest iterations of produced magnetic tapes were created during 1930 and they used cellulose acetate as the plastic layer. This was soon replaced by polymers due to celluloses problem with hydrolysis that led to so called vinegar syndrome causing deformation or loss of plasticiser that led to structural weakness. PVC (polyvinyl chloride) was also used as the plastic layer but its use was mostly limited to Germany during 1930. PET replaced cellulose acetate and PVC as the plastic layer from 1940 onwards and is still used as the plastic layer. PET has significant downside, however, when compared to cellulose acetate, as it stretches before snapping leading to unrecoverable damage in the data. This mandates precise handling and sizing from the media device using the tape (IASA - International Association of Sound and Audiovisual Archives 2019). The tape is commonly wound up on a roll and encased in a PVC cartridge. In addition to PVC the cartridge often contains some metal parts such as hinges and screws.

The base material; PET is otherwise commonly used in textiles and example plastic bottles. According to Ji approximately 60% of global PET production is consumed by textile industry and 30% by production of plastic bottles. All together PET makes up 18% of global polymer production (Ji 2013).Thus its properties and life cycle including recycling potential is well researched. In textile industry PET is more commonly known as just polyester. PET can appear as amorphous or semi crystalline structure both being transparent or opaque. Its structural formula is shown in Figure 2.

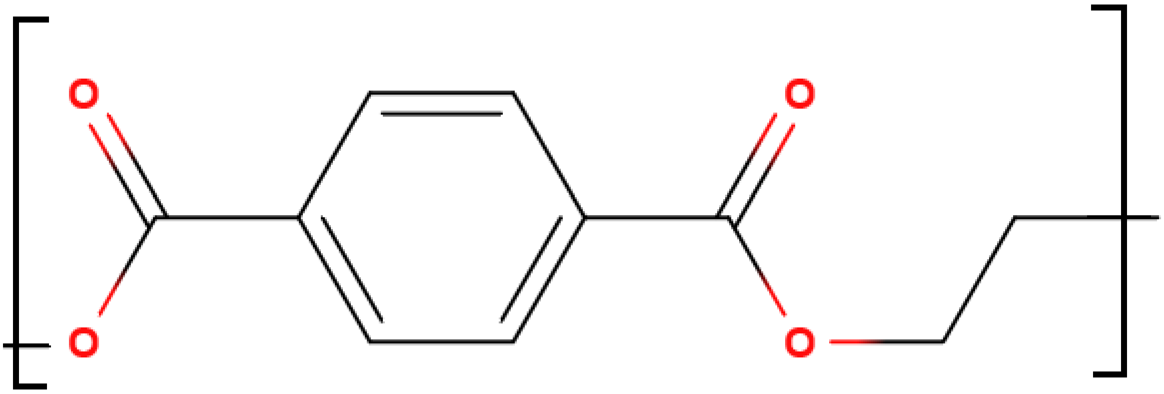

Figure 2 Structural formula of polyethylene terephthalate polymer. Brackets notes the monomeric structure of the polymer

Notable physical properties of PET are its Young's modulus of 2800-3100 MPa, tensile strength of 55-75 MPa, Glass transition temperature of 67-81 °C, melting point of around 250 to 260 °C and being practically water insoluble.

PET can be polymerized by either direct esterification from terephthalic acid and ethylene glycol or by transesterification using ethylene glycol and dimethyl terephthalate (DMT). Transesterification produced methanol as the by-product where direct esterification leaving only water as the by-product. The polymerization reaction used is polycondensation. Under elevated temperatures and, in the case of direct esterification, pressures where the by-product either water or methanol is continuously removed from the system via distillation allowing the reaction to proceed. In transesterification the reaction is done in two steps with excessive amounts of ethylene glycol. In the first step both methylene groups are replaced by ethylene glycol and methanol is removed from the system. In the second step one of the ethylene groups is removed via distillation and a second monomer group is joined in the place of now removed ethylene group while ethylene glycol is continuously removed from the system. As such, reaction consumes two times the amount of ethylene glycol molecules than what is left in the polymer. The benefit of transesterification polymerization is that it can be done under normal atmospheric pressures whereas direct esterification is done under pressures between 2.5 – 5.5 bars (Köpnick, et al. 2000). Transesterification has been more popular method in the past as the reaction proceeded faster than with direct esterification but direct esterification gained popularity during and after 1980 with developments in direct esterification process (Kemes 1969) (W. Wang 2016) (Yamada 1996). Most noteworthy difference between the esterification processes, however, is the different raw material used; transesterification uses DMT and direct esterification uses terephthalic acid. This becomes especially important when considering the recycling cycle of PET using chemical recycling. PET can be recycled into either DMT or terephthalic acid depending on the method used. Different recycling methods for PET are discussed in following chapters.

One of the defining properties of PET polymer is its high intrinsic viscosity. Intrinsic viscosity (IV) is a measure of a component's partial contribution to solutions viscosity. It is calculated using equation shown below.

$$[\eta] = \lim_{\phi \to 0} \frac{\eta - \eta_0}{\phi \, \eta_0} \tag{1}$$

Where, η is component's viscosity, η_0 is solution's viscosity in absence of the component and ϕ is the volumetric fraction of the component in solute. Thus, intrinsic viscosity is extrapolated to relative viscosity 0 decilitre per gram. It is also called limiting viscosity number for this reason. Intrinsic viscosity is also known as the Staudinger's index. It is strongly related to the length of the polymer chains. Longer polymer chains lead to more entanglement of the chains resulting in increase in solution viscosity. Due to its value being taken at zero concentration it technically has no unit even though IUPAC demands its unit to be specified. PET has an intrinsic viscosity range from 0.4 to 1 depending on the method it was prepared and what it is used for. For example, PET for textile industry has IV values commonly in the ranges from 0.4 to 0.7 whereas PET for bottles has IV values from 0.7 to 0.8 (Gupta and Bashir 2002). For comparison, Haiyang et al. calculated IV values for PVC in different solvents and got values closely around 0.7 (Haiyang, et al. 1999).

Specifically, in magnetic tapes the polymer used is BoPET (biaxially oriented PET) also sometimes known as mylar or hostaphan. BoPET is different to regular semi crystalline PET in that it is stretched mechanically at high temperatures and kept in tension as it cooled down to prevent BoPET from shrinking back to its original length. This gives BoPET superior strength compared to PET. BoPET has Young's modulus in the ranges of 4GPa compared to 3 GPa of regular PET. This is beneficial in magnetic tapes to prevent data corruption caused by stretching of the tape. Also, BoPET crystalline structures that are created during the settling after high temperature stretching are smaller than the wavelength of visible light and thus BoPET has excellent clarity property, which is mandatory for magnetic tapes. BoPET has an intrinsic viscosity commonly between 0.6 to 0.7 (Gupta and Bashir 2002). Other than being used in magnetic tapes BoPET can be used in food packaging. BoPET can be coated with aluminium by vapor deposition, which results in a thin film that is impermeable by gases and reflects almost all light wavelengths including those in the infrared spectrum. This is useful for the food packaging applications.

More recently, polyethylene naphthalate (PEN) has been used in magnetic tapes as a base layer. PEN is closely related to PET but has naphthalene rings in place of the benzene ring in PET. Structural formula of PEN is shown in Figure 3.

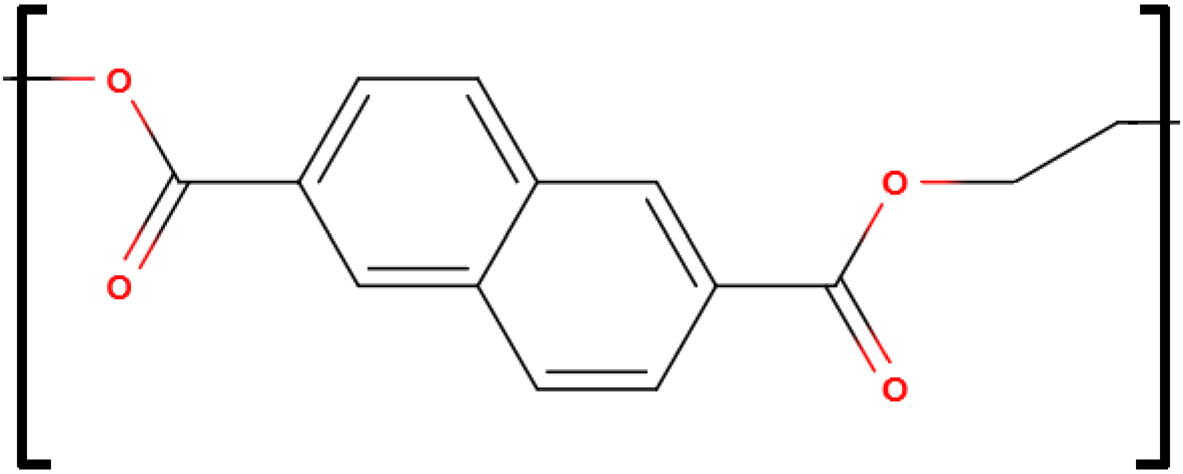

Figure 3 Structural formula of polyethylene naphthalate (PEN).

Compared to PET, PEN has higher modulus (around 5 to 5.5 GPa), glass transition – (113 - 117 °C) and melting temperatures (270 °C) (GoodFellow 2019). Similarly, to PET, PEN can be generally produced using two different methods that utilize two different raw materials one being diacid – and other being diester compound containing naphthalene group.

Magnetic part of the magnetic tape comes from the metal pigment on top of the base layer. First iterations of magnetic tapes used ferric oxide (γFe_2O_3) powder. Iron oxide is still used in large majority of magnetic tapes. Ferric oxide is brownish in colour, which makes the tapes brownish in colour too. This can easily be seen in old audio tapes and cassettes seen in Figure 1. Ferric oxide particles pose a limitation to the tape’s performance potential due to the size of the particles. Ferric oxide particles used are generally around 0.3 to 0.4 µm long and have a width to length ratio of 4 to 6 (Kresilermaier 1985). Particle size limits how intensely data can be stored on the tape. Therefore, in order to increase the performance different magnetic particles were needed. Chromium dioxide (CrO_2) coated tape was developed to increase the performance of the tape. This iteration of tape used only chromium dioxide as the magnetic particles. Cobalt induced iron(II,III) oxide (Co- Fe_3O_4) was also created for the same purpose. The amount and method of induced cobalt varied between manufacturers, however, amount of cobalt is generally between 1 to 10 w-%. Additionally, different combinations of nickel-cobalt-iron alloys were tried and researched but nickel never gained much success. Comparing to the ferric oxide cobalt induced particles are less than 0.1 µm long and therefore give significant increase in tape performance (Kresilermaier 1985). Both chromium and cobalt induced iron(II,III) (magnetite) are black powders that have a greyish shine on the magnetic tape. An improvement on the chromium dioxide tapes were double layer tapes in which chromium dioxide layer was laid on top of the ferric oxide layer. Latest iteration magnetic tapes may contain elemental iron particles as the magnetic particles. These give the greatest performance but are prone to oxidation.

Magnetic tape iterations are categorized by the IEC(international electrotechnical commission) in four types. First type magnetic tapes are tapes using ferric oxide layer. Some cobalt coated ferric oxide tapes also belong in the first type category. IEC type II magnet tapes are tapes using chromium dioxide particles or cobalt induced magnetite particles. There is a lot of variation and development in the IEC type II with companies such as BASF and TDK racing to create the best available magnetic tape. Type III magnetic tapes are tapes utilising chromium- and ferric oxides together in dual layer fashion. Type III tapes were soon outdone by type IV tapes and therefore are not as common as type I and II. Type IV tapes are the tapes using pure – or elemental metal particles often abbreviated to MP-tapes. While type IV tapes do give the best performance in terms of output signal, they also have the most noise and their production is difficult due to the oxidation. Oxidation of these extremely small iron particles can be so rapid that it results in an explosion. Therefore, they must be produced in a controlled environment such as nitrogen environment.

In addition to plastic and magnetic layers, magnetic tapes have binders and other additives that are at least in the case of type I and II tapes mixed with the metal particles. These additives are added for varying reasons such as holding the structure together and help spreading the magnetic particles uniformly on the tape. Other additives are added to reduce wear and improve corrosion resistance. Later iterations of magnetic tapes may have a matted back side. This is added to increase the packability and ease of handling of the tape. Black matting agents also increase the conductivity of the tape. All together additives make up roughly 30w-% of the metal pigment layer (Kresilermaier 1985).

Additives that are binding the magnetic particles on the plastic layers are called binders. Binders may be a combination of polymers such as polyvinyl chloride, polyesters, polycarbonates, polyurethanes, polyamides, epoxies, and some of related copolymers. For example, Hercules used polyester – and vinyl chloride/vinyl acetate copolymer resins as binders for their audiotape (Kresilermaier 1985). Binder reagents make up majority of additives on the final tape after solvents used in pigments have been mostly evaporated out in their manufacturing process.

The top layer of magnetic layer often contains lubricant. The lubricant may be added into the pigment or added on top of the layer. Its purpose is to reduce wear on the tape caused by friction between the tape and tape head. Tape head is the device that transfers the magnetic fluctuations caused by the tape moving by the tape head to electric signals. Or tape head can also transfer electrical signals into magnetic writing on the tape. Lubricants also aid in preventing layer-to-layer adhesion that binder chemicals may cause. Kresilermaier says that while silicones have been reported to possess great performance their use is limited due to the cost of silicone and thus cheaper options such as different esters and fatty acids are used more often (Kresilermaier 1985). Back side of the base layer may have black matting agent commonly elemental carbon to add converse properties to lubricants. Back matting eases in handling of the tape especially in studio applications where magnetic tapes are lengthier than in consumer products.

To make the metal pigment applicable to the base layer, they are dissolved to a paint-like liquid. For this, solvents are needed. Common solvents include toluene, methyl ethyl ketone, methyl isobutyl ketone and cyclohexane. Sometimes more active solvents such as tetrahydrofuran or dimethyl-formamide are used when more common solvents cannot be used. The pigment is dried in an oven after being applied on the base layer and therefore not much of the solvent remains in the tape. Wetting agents may be added in the solvent system to aid complete wetting of the metal particles in the solution. Main benefit of wetting agents is reduced milling and mixing time of the pigment solution. In his report Kresilemaier names exemplary wetting agents for iron oxides such as zinc naphthenate, dioctyl sodium sulfosuccinate, oleic acid esters and lecithin.

Demonstrative figure of magnetic tape composition is shown in Figure 4

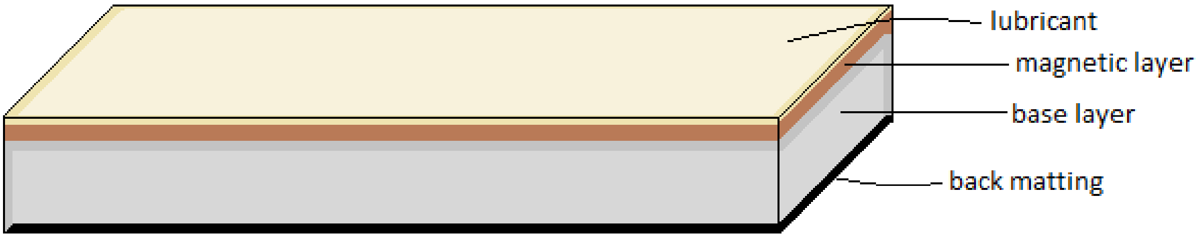

Figure 4 Composition of a magnetic tape

As can be seen from Figure 4, majority of the tape volume is made up by the base layer. Actual thickness of the base – and magnetic layers vary with different tape types and standards. Commonly thickness of the base layer is roughly two to three times the thickness of the magnetic layer. For example, open reel consumer audio tape designed for long play is overall 36 µm thick of which 24 µm is made by the base and 12 µm by the magnetic layer and back coated studio tape has 30 µm of base layer, 13 µm of magnetic layer and additionally 7 µm of back matting making 50 µm in total thickness.

2.2 Current relevance, market and handling

From the year 2000 onwards disc type media storage devices started to replace magnetic tape media on consumer markets. More recently, streaming services have emerged to the audio and video entertainment markets. Even though consumer grade video and audio tapes have become obsolete magnetic tape still has a place as a data storage. Magnetic tape technology such as linear tape-open (LTO) is being developed and produced by numerous companies including Hewlett Packard, IBM, DELL, Sony and Lenovo. The market for magnetic tapes is forecasted to rise at around 7.6% compound annual growth rate (CAGR) and to reach 6.5 billion dollars in 2022 (Infoholic Research 2018). A report done by wan et al. (Wan, Cao and Xie 2014) compares the prices and capabilities of three data storage methods; HDD (Hard disc drive), magnetic tape and blue-ray discs. The report shows magnetic tapes being competitive with the other two data storing technologies. Magnetic tape has one big downside of being extremely slow compared to disc type storages but otherwise has equal or better data storing capabilities. However, with the extremely rapid growth of available data, data storing technologies are being developed constantly to account for the demand created by the growth of available data and therefore reports dated back to 2014 are not necessarily relevant anymore. For example, Hajirahimova & Aliyeva predicted the amount of global data to increase ten times during the time period between 2013 and 2020 from 4.4 zettabytes to around 44 zettabytes (Hajirahimova and Aliyeva 2017). The report by Wan et al. uses LTO6 as the magnetic tape technology as it was at the time the best available magnetic tape technology. As of now, early 2019, LTO8 is the current technology with LTO9 being under development. LTO8 was released on December of 2017 and has almost 5 times the capacity of LTO6. Other storage technologies have too seen developments and more up to date comparisons are needed to make design decisions.

Amount of magnetic tape that has been sold over the years is hard to estimate but it is safe to assume that it is massive. Just one format; VHS, was produced in such a massive scale that video players playing them were produced from 1983 to 2016. The last known VCR (video cassette recorder) producer Funai Electric produced VCR systems for 30 years and at its peak sold up to 15 million units annually (Nikkei 2016). Even VHS systems competitor, Betamax, that lost a format war against VHS during 1980s had its tapes still being produced on 2016 even though the players for it had not been produced since 2002 (Sony 2015). In the audio market, C-cassettes were the dominant format for a similar time period until CD took its place during early 2000’s.

In the data storage applications, Ultrium LTO reported that during 2017 the sold data storage exceeded all previous years. LTO manufacturers Hewlett Packard, IBM Corporation and Quantum sold a little over 108 000 petabytes (PT) which is 12.9 % more than in the previous year (Ultrium LTO 2018). Assuming most of the sold capacity was using LTO7 format, which was the best available technology for most of the year, would mean that in total 720 000 units were sold as LTO7 has 15 terabytes (TB) of compressed capacity.

Currently magnetic tape is not recycled at large volumes. Old unusable VHS and C cassettes are for the most part thrown away amongst other waste. Small quantities are used for crafting and the cartridge may be used as a storage but other than that no recycling done. Environmental educator from Finnish waste disposal company Jätekukko Anja Räsänen confirms that unwanted VHS or C cassettes may be thrown in mixed waste bin and that no extensive recycling path exists for them (Muhonen 2016). Environmental expert from YTV, Olli Linsiö, agrees with Räsänen (Yleisradio Oy 2008). However, even though magnetic tape is not recycled the PET plastic used in them is recycled at a large scale. Recycling of

PET bottles is promoted in many countries across the globe via the container deposit legislation program. Therefore, PET recycling process is well researched, and the infrastructure is already in place.

3 Chemical recycling of polyethylene terephthalate

Polyethylene terephthalate can be recycled either mechanically or chemically to generate new PET plastic products. It is possible to also recycle PET to energy via combustion, but that recovery path is controversial due to the release of toxic flue gases and will not be explored in this research. Mechanical recycling of PET means forming PET into new product by cutting waste PET into granules and then melting and extruding waste granules into new products. Mechanical recycling is fast and cheap method, which generally yields lower quality PET plastic. It attempts to not alter the polymer chains however due to melting, extrusion and aqueous or acidic residuals that may cause chain scission, each cycle reduces length of the chains reducing the product quality. Therefore, its use may be limited especially on food grade products. Chemical recycling of PET means the use of solvolysis to depolymerize the polymer chains into monomers that can be used to create new high-quality polymer. Multiple methods and reagents can be used to achieve depolymerization and generally it must be performed under high temperatures and sometimes high pressures. The most used chemical recycling methods are glycolysis, which uses glycols such as ethylene glycol, and methanolysis, which uses methane to achieve depolymerization.

In the case of magnetic tape, mechanical recycling is unfeasible due to magnetic pigment layer and its adhesives heavily contaminating the product. However chemical recycling has potential to work yielding PET monomer fraction and a metal pigment fraction as products. As of now, metal recovery from magnetic tapes has been deemed unfeasible due to low concentration of valuable metals and difficulty of recovering said metals from the tape (Dobransky 2016).

Other than methanol and glycols, chemical recycling can be done using hydrolysis. The hydrolysis process can be done in acidic, alkaline or neutral solutions each with slightly varying reaction but resulting in similar products. Chemical recycling using amino- or ammonolysis and even depolymerization using ionic solvents has been researched.

3.1 Glycolysis

Glycolysis is chemical recycling of PET using glycols such as ethylene glycol, diethylene glycol, propylene glycol or dipropylene glycol in the presence of a catalyst, most commonly metal acetate catalyst. It depolymerizes PET into Bis(2-Hydroxyethyl) terephthalate (BHET) that can be processed into new PET plastic by polycondensation. Depolymerization reaction using ethylene glycol (EG) is shown below.

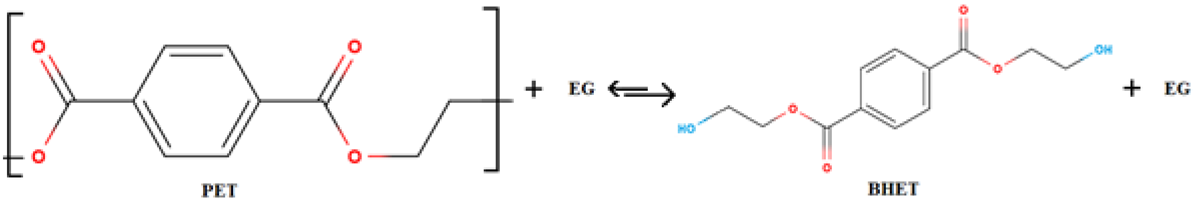

Figure 5 Depolymerization of polyethylene terephthalate using ethylene glycol.

Use of glycols in depolymerization of PET has been known for a long time. Korshak et al. carried out glycolysis and acidolysis experiments on PET degradation on 1959 (Korshak, Bekasova and Zamiatina 1959). Specifically, Korshak et al. used ethylene glycol to produce depolymerization. Abdel Azim carried out glycolysis experiments with diethylene glycol and propylene glycol using manganese acetate as catalyst (Azim 1996). However, for a complete depolymerization ethylene glycol seems to be the most used reagent. Other than the type of glycol used, the reaction kinetics are affected by multiple factors such as PET to EG ratio, reaction temperature, - pressure, - time and the type and amount of catalyst used. As the depolymerization reaction is reversible, it is critical to find optimal reaction conditions not only to maximize efficiency but to also minimize backwards reaction reducing product yield. Without the use of a catalyst, complete depolymerization is unreachable and the partially depolymerized oligomers make the separation of BHET monomers difficult. Therefore, the use of catalyst is mandatory for a recycling process and different catalysts have been the subject of multiple researches (Chen and Chen 1998). Ghaemy and Mossaddegh on 1998 experimented with different metal acetates; namely zinc, lead, manganese and cobalt acetates (Ghaemy and Mossaddeh 2005). They found zinc acetate to have the greatest activity of the catalysts used followed by manganese and then cobalt leaving lead as the least active catalyst according to their results. Their result was confirmed by the experiment done by Baliga and Wong on 1989 where they also found zinc to be the most active catalysts of the four tried catalyst acetates (Baliga and Wong 1989). Both experiments were done at below 200 °C (Baliga & Wong at 190 °C and Ghaemy &

Mossaddeg at 198 ^oC) temperatures under nitrogen atmosphere. Goje and Mishara on 2003 found optimal conditions for glycolysis using zinc acetate as catalyst to be 197 ^oC temperature and reaction time of 90 minutes for 127.5 micrometres long fibres. Optimal amount of catalysts was found to be 0.002 moles of catalyst per 10 g of PET and 40 g of ethylene glycol (Goje and Mishra 2003). Nitrogen atmosphere is often applied to prevent inhibiting glycol oxidation reactions.

Zinc and lead catalysts have the downside of being heavy metals and therefore their excessive use may cause environmental problems. Research has been done to find an eco-friendlier replacement for heavy metal catalysts. Shukla & Kulkarni on 2002 used sodium carbonate and – bicarbonate to achieve comparable results to zinc – and lead acetates with reaction temperature of 190 ^oC and – time of 8 hours (Shukla and Kulkarni 2002). Zinc – and lead acetates had BHET yield of only around 0 to 4% more than sodium carbonate or – bicarbonate all being between 60 and 70% with varying raw materials. Shukla et al. on 2006 used sodium sulphate as a catalyst with similar reaction conditions as Shukla & Kulkarni earlier and achieved similar 60% BHET yields (Shukla, Harald and Jawale 2008). Another significant drawback of these catalysts is that they are soluble in ethylene glycol and therefore their separation from products can be challenging. Catalysts that are not soluble in EG such as zeolites or silica nanoparticles have also been studied. Imran et al. on 2011 used silica nano- and – microparticles that had been doped with different metal oxides to catalyse glycolysis of PET. Their conditions greatly differ from the other studies described earlier as they used significantly higher temperature of 300 ^oC and pressure of 1.1 MPa but used a reaction time of only 40 to 80 minutes. They did achieve over 90% monomer yield with manganese oxide doped silica nanoparticles (Imran, Lee, et al. 2011). At temperatures over 254 zinc acetate reportedly loses its ability to catalyse glycolysis and thus other catalysts are needed at high temperatures (Campanelli, Kamal and Cooper 1994). Imran et al. studied the use of even more novel porous metal oxide structures to catalyse glycolysis on 2013. Their glycolysis was again proceeded at around 300 ^oC temperature for 40 to 80 minutes. They found that metal oxide spinels provided better catalytic activity than plain oxide structures due to their increased specific surface area. Amongst all used metal – and mixed metal oxide spinels (cobalt, manganese and zinc) tetragonal zinc manganese oxide ($ZnMn_2O_4$) gave the best performance (Imran, Kim, et al. 2013).

Zhu et al. (2013) investigated use of solid acids as catalysts on PET glycolysis (Zhu, et al. 2012). Solid acids offer significant advantages over conventional catalysts and acids such as being easily filtrated out and generating less waste products. Solid acids used by Zhu et al. were sulphated oxides; zirconia and titania. With reaction temperature of 180 ^{o}C and – time of 3 hours they achieved around 91 wt% BHET yield. Ionic liquids have alsobeen studied as the catalyst in glycolysis. Ionic liquids are liquid salts that have a low melting point, generally below 100 ^{o}C temperature, due to their large size and unsymmetricality. Ionic liquids have been at the center of attention for a while now due to their seemingly endless solvent applications with excellent thermal – and electrochemical stability. Wang et al. used six different ionic liquids to catalyse glycolysis (Wang, et al. 2009). The ionic liquids used were four different 1-butyl-3-methylimidazolium (bmim) salts; chloride, bromide, hydrogen phosphate and hydrogen sulphate, and two different (3-amino-propyl)-tributyl-phosphonium salts; glycine and alanine. It was found that out of the four bmim salts, only bromide was effective under the used 160 to 190 ^{o}C reaction temperature for 5 to 10 hours. However, both tributyl salts were found effective. Yue et al. used a different set of four bmim salts; chloride bromide, hydroxide and bicarbonate (Yue, Wang, et al. 2011). They found, that with reaction temperature of 190 ^{o}C and – time of two hours, hydroxide – and bicarbonate salts were most effective and unlike Wang et al.’s research bromide was the least effective. Notable difference is that Yun et al used significantly more ionic liquid than Wang et al, and that Wang et al found optimal ionic liquid dosage to be 5wt%, which is much less than 1 to 5 g / 5g of PET that Yun et al used. Other ionic liquids such as bmim-$FeCl_4$, bmim-$ZnCl_3$ and bmim-acetate have been used to similar effect (Yan, et al. 2012) (Yue, Xiao, et al. 2013)

Production of unsaturated polyester resins (UPR) from PET waste using glycolysis is an intriguing possibility that has had positive impact on the development of glycolysis. Unsaturated polyester resins have a multiple possible uses such as production of paints and composite materials like fibre glass (Polynt 2016) produced by dissolving and reacting generated PET degradation products with various chemicals. One of the earliest reports on PET waste use on UPR production was done by Ostrysz on 1969, that dissolved glycolysis products from polyester fibres in styrene and then stabilized them with hydroquinone (Ostyrsz 1969). Ostrysz used (1,2) propylene glycol to produce partial glycolysation creating polyethylene terephthalate oligomers in the report done on 1969 and again in another experiment where he used maleic acid to alter the resin product (Ostrysz 1970). Partial glycolysation was achieved using 1:4 to 1:1 molar ratios of propylene glycol to PET fibres at 200 °C and a reaction time of 2 hours under presumably atmospheric pressure. Reacting PET degradation products with maleic acid and then dissolving the product in styrene became the standard process for UPR production using PET waste. Vaidya and Nadkarni carried out an experiment testing propylene with varying ratios to PET with number average molar weight of around 20 000 in the presence of zinc acetate catalyst. The experiments were carried out in a nitrogen atmosphere with atmospheric pressure and 200 °C temperature for 8 hours. Weight ratios used were 62.5% 50% and 37.5% which all resulted in oligomers with number average molar weights of 480, 399 and 276 respectively (Vaidya and Nadkarni 1987). The glycolysis product BHET has a molar mass of 254.2 g mol^{-1}, which means that with 62.5% weight ratio the PET waste was nearly completely depolymerized. The experiments done by Azim on 1997 were aiming to produce UPRs for polymer concrete production. Similarly to earlier experiments, the conditions used were 200 °C temperature, nitrogen atmosphere at atmospheric pressure and reaction was ran for 4 hours or 3 hours using 210 to 220 °C temperature.

3.2 Methanolysis

PET can be depolymerized using methanol under elevated temperatures and pressures. Similar to glycolysis, the PET polymer chain is polymerized into terephthalate monomer, but the hydroxyl groups are replaced with methyl groups from methanol. The reaction is shown below.

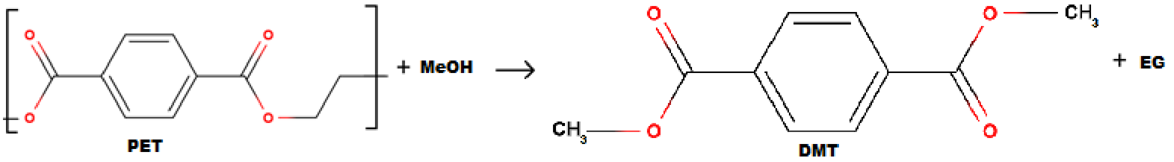

Figure 6 Depolymerization of polyethylene terephthalate (PET) using methanol (MeOH) leaving dimethyl terephthalate (DMT) and ethylene glycol (EG) as products.

DMT has been conventionally used to create new PET polymer but a trend to switch from DMT esterification to direct synthesis from terephthalic acid (TPA) to PET has been seen for many years now. This may create the need to convert produced DMT into TPA, which increases the operation costs. Methanolysis commonly has greater ethylene glycol yields than other recycling methods, which is one of its greatest advantages. Also, separation and purification of products are easier due to lesser generation of potentially problematic side products such as diethylene glycol (Yoon, et al. 1993).

Methanolysis is performed generally at 160 to 300 ^{o}C, 2 to 4 MPa for 30 to 60 minutes and a catalyst may be used. Even higher pressures may be used. Yang et al. on 2002 used 250 to 270 ^{o}C temperatures with 8.5 to 14 MPa for 40 minutes to perform methanolysis on various PET waste sources (Yung, et al. 2002). In conditions this extreme, methanol is in supercritical state as its critical point is around 240 ^{o}C and 8 MPa. Supercritical methanol is an attractive reagent in methanolysis as it theoretically should be much better in solvolytic reactions than vapor or liquid methanol are. Goto et al. on 2002 used supercritical methanol to perform methanolysis on waste PET (Goto, et al. 2002). They used 270 ^{o}C and 20 MPa for 2 to 120 minutes and achieved 80% yield of DMT after 2 hours and 60% EG yield after 1 hour. As PET conversion was 100% and DMT yield 80% some oligomers were left in the product. Genta et al. also studied the use of supercritical methanol on methanolysis (Genta, et al. 2005). They used reaction pressures from 0.9 MPa to 15 MPa with 250 to 270 ^{o}C temperatures. With pressure of 0.9 MPa methanol does not reach its supercritical state and stays in vapor phase. Genta et al. compared methanolysis using methanol vapor at 0.9 MPa and supercritical methanol at 14.9 MPa and found supercritical methanol to reach better DMT yields. During 5 minutes at the specified temperature, methanol vapor did not have any DMT formation while supercritical methanol had already reached over 80% DMT yield and DMT yield of 98% was reached at 30 minutes. Vapor methanol reached 40% DMT yield at 30 min and 60% at 100 minutes. The results show supercritical methanol being clearly superior to vapor methanol but vapor methanol still being capable of depolymerizing PET without the addition of catalyst.

Although unlike glycolysis, the use of catalyst is not mandatory due to otherwise unfeasible reaction rates, using catalysts the reaction temperature and or pressure can be lowered from the usual values. Mishra & Goje on 2003 used methanolysis to depolymerize PET waste with zinc acetate in the presence of lead acetate as a catalyst (Goje and Mishra 2003). They used 120 to 140 ^{o}C temperatures and 5 to 7 atm pressure. They achieved 98% conversion of PET using 120 ^{o}C, and 100% using 130 and 140 ^{o}C temperatures with reaction time of 2 hours. The motivation to use lower than 150 ^{o}C temperatures was to limit oxidation and carbonization of reagents. Kurowaka et al. used Aluminium triisopropoxide (AIP) to catalyse methanolysis of PET (Kurowaka, et al. 2003). They used an autoclave that was heated to 160 to 200 ^{o}C temperatures. Pressure measurement or regulation was not mentioned; however, the pressure naturally builds up when the autoclave is heated. Therefore, it is safe to assume that the pressure used would have been multiple bars. Kurowaka et al. found that by using a methanol toluene mixture both DMT and EG yields could be improved. They got DMT and EG yields of 64% and 63% respectively with methanol and 88% and 87% respectively using 80vol% methanol 20vol% toluene mixture. They mentioned that the reaction rate is related to the solubility of PET in the solvent, which also explains the benefit of using supercritical methanol. They also found that the AIP catalyst significantly improved their yields and that without catalyst the reaction proceeded at a very slow pace. Catalyst was found to be especially effective in the last step of the depolymerization; from oligomers to monomers.

3.3 Hydrolysis

Hydrolysis of PET depolymerizes the polymer into terephthalic acid (TPA) and ethylene glycol. This technology has gained interest due to direct synthesis of PET from TPA and EG replacing the conventional DMT and EG process. Hydrolysis can be done using acidic –, alkaline – or neutral solutions but almost always requires high temperatures and pressures and commonly is slower than competing technologies.

3.3.1 Acidic hydrolysis

Acidic hydrolysis is most often done using sulphuric acid but other acids such as nitric – or phosphoric acid can be used as well. The depolymerization reaction from PET to TPA using H_2SO_4 is shown below as an example.

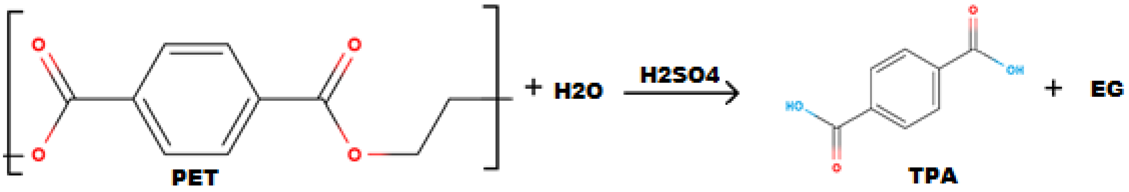

Figure 7 Depolymerization of polyethylene terephthalate (PET) to terephthalic acid (TPA) and ethylene glycol (EG) using acid hydrolysis.

Usually, TPA product needs to be reacted with aqueous alkaline solution such as ammonia or KOH to produce terephthalic salt, which is then precipitated in acidic solution. The requirement for high temperatures and pressures can be alleviated by using concentrated sulphuric acid with concentration of 14 M or more as described in US patents from around 1980 (Brown and O'Brien 1974) (Pusztaszeri 1981). The patents describe the use of very low temperatures; below 100 °C and atmospheric pressure for 72 hours. Other than extremely long reaction times Yoshioka et al. notes that the problem with using concentrated sulphuric acid is that it makes the separation and recycling of sulphuric acid impossible as it becomes contaminated with EG (Yoshioka, Motoki and Okuwaki, Hydrolysis of Waste PET by Sulphuric Acid at 150°C for a Chemical Recycling 1994). A process, which consumes large amounts of sulphuric acid that cannot be recycled, becomes costly. Yoshioka et al. tackled this problem by using sulphuric acid with concentrations below 10M, which allows sulphuric acid to be separated from EG product using for example dialysis. They found that with reaction temperature of 150 ^{o}C and sulphuric acid concentrations above 3M the degradation ratio quickly rose from 20% with increased acid concentration reaching 95.5% at 6M and at 10M degradation was 100%. Yoshioka et al. used reaction times of 1 to 6 hours and found that similarly to concentration, degradation ratio quickly rose from 20% at 3 hours to above 70% at 4 hours and above 90% at 5 hours using 7M acid solution. Yoshioka et al. do not mention the pressure but they used sealed Pyrex tubes so some pressure build-up can be assumed. Mehrabzadeh et al. carried out similar experiment using sulphuric acid at concentrations from 0 to 10M at 130 to 170 ^{o}C for 1 to 6 hours (Mehrabzadeh, Shodjaei and Khosravi 2000). Again, sealed Pyrex tubes were used. Mehrabzadeh et al. found that with acid concentrations from 0 to 5M PET degradation was not seen during 5 hours at 150 ^{o}C. Increasing the acid concentration to 6M and beyond quickly increased the PET degradation rate and at 9M 80% PET degradation ratio was reached. The results is in agreement with earlier results by Yoshioka et al. Similarly, results in agreement with Yoshioka et al.'s previous experiments were found on degradation ratios' relation to reaction time. In addition, reaction temperature was found to have a significant effect on the degradation where 130 ^{o}C was found to be ineffective, 150 ^{o}C achieved around 60% degradation and 170 ^{o}C almost complete degradation during 5 hours with 7M acidic solution. The results clearly show that with sulphuric acid concentrations below 6M higher temperatures are mandatory to achieve reasonable depolymerization rates and to achieve decent depolymerization with temperatures below 100 ^{o}C it is suggested to use very concentrated solution with concentration at or above 12M or 70 wt%.

Yoshioka et al. showed in another experiment how nitric acid could be used similarly to the US patents; using temperature of 100 ^{o}C or lower and a reacting time of 72 hours under atmospheric pressure (Yoshioka, Okayama and Okuwaki 1998). They used nitric acid concentrations from 7 to 13M and found that the concentration had a significant effect on the degradation ratio of PET: After 24 hours at 100 ^{o}C 13M nitric acid achieved 91.3% degradation. Similarly, temperature had a significant effect on the reaction rate. With the results they calculated the activation energy of depolymerization reaction to be 101.3 kJ/mol. Interestingly, the recovered EG was oxidized into oxalic acid which, while not used in PET synthesis, is more valuable than EG. Kumar & Rao conducted experiments with 13M nitric acid on PET depolymerization with temperatures from 80 to 100 ^{o}C (Kumar and Rao 2003). Again, temperature was proven to have significant effect on the depolymerization rate. Kumar & Rao calculated the activation energy of the depolymerization reaction to be 135 kJ/mol, which is more than what Yoshioka et al calculated earlier.

3.3.2 Neutral hydrolysis

Neutral hydrolysis uses water or steam in high temperatures and pressures generally again at 200 to 300 ^{o}C and 1 to 4 MPa. The depolymerization reaction is akin acidic hydrolysis with end products being TPA and EG but the reaction is not promoted by an acid. Instead, the reaction is often promoted by a transesterification catalyst. A benefit of not using acidic or alkaline solution is to avoid generating problematic inorganic salts along with obvious safety and ecological advantages.

Zope and Mishra studied kinetics of non-catalysed neutral hydrolysis (Zope and Mishra 2008). They used temperatures from 100 to 250 ^{o}C and pressures from 0.1 to 3.1 MPa. It was found that with temperatures 100 and 150 ^{o}C very little depolymerization took place over 2 hours. Increasing temperature to 200^{o}C gave drastic improvement to PET conversion rate, from below 5% at 150 ^{o}C to 60% at 200 ^{o}C. Increasing the temperature to 250 ^{o}C further improved the conversion rate to 88%. As the reactions used autogenous pressure, the pressure was also increased when temperature was risen. At the temperatures of 150, 200 and 250 ^{o}C the pressure was 0.55, 1.59 and 3.1 MPa respectively. Melting point of PET is at around 250 ^{o}C and thus increasing the temperature over 250 could drastically increase reaction rate but could also make purification of products more challenging. Zope and Mishra found the reaction kinetics to be of the first degree with velocity constant in the order of 0.01 min^{-1}. They also calculated the activation energy of neutral hydrolysis to be 99.6 kJ/mol. Mancini and Zanin got even more polarized results with temperatures at 200 ^{o}C and below (Mancini and Zanin 2004). They used temperatures of 205, 170 and 135 ^{o}C and got depolymerization ratios of 99%, 8.2% and 1.7% after 6 hours. Similarly to Zope and Mishra, Mancini and Zanin used autogeneous pressure, which were 4 atm, 7.5 atm and 13.5 atm for 135, 170 and 205 ^{o}C respectively. The main difference between experiments done by Zope and Mishra versus experiments done by Manicini and Zanin is that the PET to water ratio was much less on the experiments done by Manicini and Zanin.

Liu et al. used microwave irradiation to enhance hydrolysis (Liu, et al. 2004). They used 220 ^{o}C temperature and 20 bars pressure for 90 to 120 minutes with water:PET mass ratio of 10:1. They found that the temperature and pressure used affected TPA yield and depolymerization the most and that raising the power used to induce microwave irradiation from 200 to 800 W did not significantly influence either of those. However, they showed that by using microwave irradiation it is possible to achieve complete depolymerization significantly faster than previous experiments.

3.3.3 Alkaline hydrolysis

In alkaline hydrolysis PET is recycled back into TPA and EG monomers using alkaline aqueous solution under high temperatures and pressures. Temperatures are usually around or above 200^{o}C at 1.4 to 2 MPa. Alkalinity of the aqueous solution is commonly produced using sodium – or potassium hydroxide but other hydroxides such as ammonium hydroxide can be used (Lamparter, Barna and Johnsrud 1983). The reaction differs from the acidic or neutral process in that where acidic – and neutral processes after depolymerization is done the TPA need to be separated from the solution it can be done by introducing alkaline reagents into the solution. This generates TPA salts that can be then precipitated out by lowering the solution pH back to acidic range. In alkaline hydrolysis, the depolymerization product is TPA salt, which can be then precipitated out by lowering the solution pH. Ammonium hydroxide can be converted to TPA by heating the TPA ammonium salt to 225 to 300 ^{o}C as demonstrated in US patent US6723873B1 by Murdoch (Murdoch 2000). The depolymerization reaction is shown below.

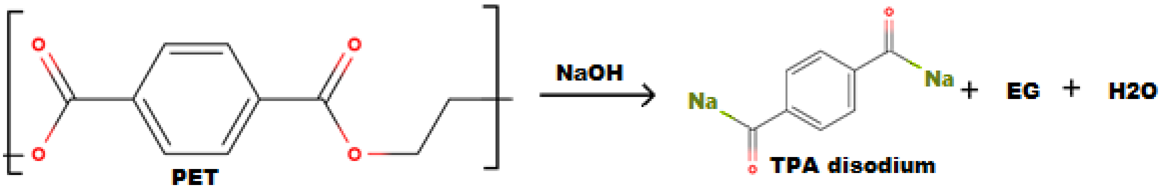

Figure 8 Depolymerization of PET using alkaline hydrolysis into terephthalic acid (TPA) disodium salt and ethylene glycol (EG).

What makes alkaline hydrolysis particularly interesting is its tolerance to contaminated raw materials such as magnetic tapes.

Wan et al. used KOH to depolymerize PET flakes using temperatures 120, 140 and 160 ^{o}C and respective pressures 1.7, 2.9 and 4.6 atm for up to 2 hours (Wan, Kao and Cheng 2001). Purpose of the relatively low temperatures were used to study the reaction kinetics. After 2 hours only 160 ^{o}C temperature reached 100% PET conversion with PET: KOH molar ratio of 1:4. They found that according to their supposed reaction mechanism, temperatures above 230 ^{o}C should be used to enhance reaction. They also calculated activation energy to be 69 kJ/mol, lower than that of neutral – or acidic hydrolysis. Karyannidis et al. used NaOH to depolymerize PET flakes in temperatures 120, 150 and 200 ^{o}C under autogenous pressure for up to 8 hours (Karayannidis, Chatziavgoustis and Achilias 2002). Their PET: NaOH ratio was 1:2.2 produced with 1.125 molar NaOH solution. They found that with 200 ^{o}C temperature 98% yield was achieved after 1 hour of reacting and 40 minutes of preheating. With 150 or 120 ^{o}C temperatures over 90% yield was not reached even after 7 hours when 84% and 33% yields were collected respectively. Using their results, they calculated activation energy of 99 kJ/mol. The resulted disodium terephthalate was reacted with sulphuric acid to generate 98% pure TPA according to their NMR analysis with 2% isophthalic acid impurity.

Use of phase transfer catalyst may be applied to allow the use of lower temperatures and or pressures. Kosmidis et al. studied the kinetics of alkaline hydrolysis in the presence of trioctylmethylammonium bromide (TOMAB) (Kosmidis, Achilias and Karayannidis 2001). They used temperatures from 75 to 90 ^{o}C notably lower than that of uncatalyzed alkaline hydrolysis. Molar PET to NaOH ratio was also kept low; from 1:30 to 1:90. The solution was allowed to react for up to 6 hours. Phase transfer catalyst TOMAB concentration was varied from 0 to 1.5 mol(TOMAB) / mol(PET) but for most of the tests kept at 0.1 mol/mol. It was found that with no catalyst, TPA yield was only 7% after 5 hours. With TOMAB/PET ratios of 0.01/3, 0.01/1 and 0.01/0.05 mol/mol very similar TPA yields were gained at all times, reaching 90% after 5 hours at 80 ^{o}C temperature. Furthermore, at 90 and 95 ^{o}C TPA yield of 90% was reached after 3 and 1.5 hours. From the results activation energy was calculated to be 83 kJ/mol.

Paliwal and Mungray tried to intensify the alkaline hydrolysis by using a phase transfer catalyst and ultrasound (Paliwal and Mungray 2013). They used 190W power to produce 20 kHz frequency ultrasound waves to a 10% by weight NaOH solution, which had tetrabutyl ammonium iodide (TBAI) as a catalyst. Temperature and pressure used on the reactions were

90 ^{o}C and atmospheric pressure. They found that with TBAI:PET ratio of 0.03:1 and 10% weight NaOH solution TPA yield reached 100% after 40 to 60 minutes. They also found that the catalyst affected the reaction more than ultrasound. Khalaf and Hasan used TBAI with microwave irradiation to enhance alkaline hydrolysis of PET (Khalaf and Hasan 2012). They found results very similar to Paliwal and Mungray. The best TPA yield at nearly 100% after 60 minutes was given by 10% by weight NaOH solution with catalyst loading ratio of 0.03:1 TBAI to PET. As with ultrasound, the power used to induce microwave irradiation did not have much impact on the TPA yield. Experiments done with 200 and 400W both reached around 90% TPA yields. Increased power did influence the temperature of the water from 90 ^{o}C at 200W to 98 ^{o}C at 400W. As the experiments were done under atmospheric pressure 98 ^{o}C is already close to the boiling point of water, which prevented any further increase in power.

Alkaline hydrolysis in contrast to the other two hydrolysis processes does not involve water in the reaction. Therefore, it is possible to perform alkaline hydrolysis in non-aqueous solutions such as ethylene glycol. When EG is used, the product EG can be collected with the rest EG used as solvent. Oku et al. used alkaline hydrolysis in non-aqueous solution to depolymerize PET pellets (Oku;Hu ja Yamada 1997). They used nitrogen atmosphere with atmospheric pressure and temperatures from 150 to 180 ^{o}C. They got very good TPA yields, close to 100% with every temperature after 15 to 80 minutes depending on temperature. They also found that ethereal solvents like dioxane gave further increase on reaction rates. 20/80 vol% solution of dioxane/EG increased the reaction rate twelve times. Ruvolo-Filho and Curti conducted similar experiments than Oku et al. using alkaline EG NaOH solution to depolymerize PET (Ruvolo-Filho and Curti 2006): They used atmospheric pressure, PET:NaOH ratio of 1:4 at temperatures from 150 to 185 ^{o}C. They got 100% TPA yields after only 15 minutes using various NaOH concentrations and 170 ^{o}C. With very thin, 0.5 mm thick, PET flakes 100% TPA yield was achieved in just 30 seconds. Temperature was again proven to have a big impact on the reaction rate. They also calculated activation energy of 172 kJ/mol, which is high. They explained that the high activation energy is compensated by activation enthalpy and – entropy.

3.4 Other chemical recycling methods

Ammonolysis is a PET depolymerization method into terephthalamides using anhydrous ammonia in ethylene glycol solution. US patent US4973746A describes the use of ammonolysis under 120 °C temperature and 8.6 bars pressure for up to 7 hours (Blackmon, Fox and Shafer 1988). Formed terephthalate amides are insoluble in ethylene glycol and can therefore be filtered out. The inventors mention that ammonolysis may be performed in temperature from 80 to 250 °C. Yields of over 90% with purity of 99% or more are promised with this method. The patent however does not describe how the diamide terephalatic acid can be converted to pure TPA but does cover other modifications such as conversion to terephthalonitrile.

Another process capable of producing terephthalamides is aminolysis. Aminolysis is a process that is conventionally used to modify PET fibres colour or other quality properties. Fukushima et al. carried out PET aminolytic depolymerization expermients on PET using various amines catalysed by 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) (Fukushima, et al. 2013). The catalyst TBD was chosen as it was proven to be an effective catalyst in methanolysis and glycolysis and it has been used to depolymerize other ester polymers (Sabot, et al. 2007). It was seen that with simple amides such as ethylenediamide and relatively mild reaction temperatures after 1 hour, 80% to 90% yield was achieved. However, as the amide remains as a part of the product it might be beneficial to use more complex amides such as aniline compounds. This yields terephthalamide that has aniline groups at both ends of terephthalate core. Pingale and Shukla were able to improve on Fukushima et al.'s test by using microwave assisted aminolysis in the presence of a sodium containing catalyst (Pingale and Shukla, Microwave-assited aminolytic depolymerization of PET waste 2009). They used ethanolamine for which Fukushima et al. found optimal conditions to be 120 °C for 2 hours to produce bis(2-hydroxyethyl) terephthalamide yield of 93%. Pingale and Shukla found that with 700W microwave assistance 94% yield was achieved with just 4 minutes using sodium sulphate on PET fibre waste and 91% yield after 7 minutes using sodium acetate on PET bottle waste. Tawfik and Eskander also used ethanolamide to depolymerize PET but used dibutyl tin oxide as catalyst (Tawfik and Eskander 2010). They used 190 °C temperature to conduct the reactions. However, they reached only 60% yield after 1 hour using catalyst loading of 1w-% of PET. Previous studies used catalyst loading of 3 to 5 w-% but lower temperatures, which may cause the variation in results. It is also possible that the chosen catalyst was not as effective as the ones used in previous studies.

Bioprocesses and enzymatic reactions have been proposed as a green alternative in many applications and are used widely in waste management. Müller et al. reported on enzymatic hydrolysis of PET using hydrolase from actinobacteria *thermobifida fusca* (Müller, et al. 2005). Enzymatic processes are not capable of competing with commercial processes due to their slow nature but would be in a big scale extremely economic. They also conducted parallel experiments using enzymes generated by bacteria *Candida Antarctica* and *Pseudomonas ps.* but they did not show similar PET degradation ability. They observed 15% weight loss during 8 weeks of incubation at 55 ^{o}C. For comparison Pingale et al observed 78% weight loss on glycolysis, which was determined to be the result of complete degradation of PET material (Pingale, Palekar and Shukla 2009). Yoshida et al. reported on a different bacterium capable of producing PET degrading enzymes (Yoshida, et al. 2016). They found that *Ideonella sakaiensis* 201-F6 was producing two enzymes that were converting PET into TPA and EG when it was grown on PET.

3.5 Metal recovery

Metals contained within magnetic tapes potentially could also be recovered. The metal content in the tape varies from pure ferric oxide to cobalt or chromium doped magnetite to elemental metal particles. After the removal of the plastic layer, metal powder with various organic contaminants can be collected. Various pyro– and hydrometallurgical methods to separate cobalt chromium and iron from the collected metal fraction are utilized in the industry. As an example, Bulong nickel-cobalt plant removes iron and chromium contaminants in one step by pH and Eh adjustments (Fett 2004). In this process the contaminant is most likely discarded as waste.

Ferric oxide can be removed even from highly contaminated matter with low metal content. Reduction roasting and magnetic separation has been used to recover iron and chromium from various sources like slags with as low as 5 w-% metals (Liu, et al. 2016) (Long, et al. 2015). Pyrometallurgical methods such as reduction roasting are attractive methods since they can at the same time remove organic contaminants and reduce ferric oxide back to elemental iron. In reduction roasting ferric oxide reacts with carbon to generate carbon oxides and iron. Problem with roasting is high energy requirement and pollution, latter of which could be even worse due to the organic contaminants releasing toxic sulphur –, chlorine – and nitrogen compounds. Sintering can also be used similarly to roasting (Li, et al. 2009).

Hydrometallurgical methods such as leaching and solvent extraction or electro winning could also yield good quality metals. However, many times the process involves calcination, which would release the organic contaminants as potentially toxic oxides, akin to roasting or sintering. Temperature used for calcination is commonly at around 700 ^{o}C for iron compounds, same that Liu et al. found to be the optimal roasting temperature for ferric iron (Cui, et al. 2015) (Liu, et al. 2016). Ferric oxide can be leached with various acids such as hydrochloric acid resulting in water soluble ferric chloride. Use of organic acids such as oxalic acid has been studied as an effort to find feasible environmental alternative to more common inorganic acids (Lee, et al. 2006). After leaching and removal of insoluble impurities, iron can be precipitated out as a hydroxide by pH adjustment.

When notable amounts of cobalt or other valuable metals are present it may not be attractive to leach iron together with the other metals. Önal et al. demonstrated a method to leach rare earth elements (REE) from NdFeB magnet waste (Önal, et al. 2015). Selective recovery was done by roasting and leaching the sample in the presence of sulphuric acid then roasting a second time and finally leaching the REEs into demineralized water leaving the iron as solid sulphide compound. REE yield of 95% was gained by Önal et al. Zhang et al. demonstrated the use of sodium chlorate, – sulphate and calcium hydroxide to selectively precipitate unwanted ferric and silica compounds from sulphuric acid leachate (Zhang, et al. 2010). The process involves multiple reactions from ferric oxide to ferrous sulphite to ferric sulphite to finally natrojarosite ($NaFe_3(SO_4)_2(OH)_6$) precipitate. Calcium hydroxide is used to turn silica into gel and is not involved in the iron precipitation. Li et al. demonstrated the use of phosphoric acid to selectively leach cobalt and nickel from limonitic laterite ore (Li, et al. 2018). Limonitic laterite is a nickel containing ore, which contains high amounts of iron. Leaching the laterite ore with phosphoric acid resulted in leaching the nickel and cobalt into solution while simultaneously reacting the iron into ferric phosphate precipitate achieving selective nickel and cobalt leaching. Phosphates of nickel or cobalt were not generated similarly to iron due to regulation of the leaching solution’s pH. It was found that with phosphoric acid concentrations of 1 to 6 M, the pH of the solution should be kept between 1 to 2 so that ferric phosphate would precipitate, and cobalt and nickel stay in solution. Li et al also proposed that the generated ferric phosphate is a high value byproduct that could be used for example in intercalation electrodes. North and Wells previously had noted similar behavior in cobalt iron system where nickel is not present (North ja Wells 1942). They found success with pH value of 3.5.

The pH value 3.5 is used in conventional iron precipitation due to iron precipitating as insoluble ferric hydroxide in normal conditions. Conventional iron precipitation is carried out using ammonium hydroxide to control the pH of solution and promote hydroxide formation. In theory cobalt requires much more alkaline solution, pH around 11, to precipitate as hydroxide (Ma, et al. 2013) but often some loss of cobalt is seen during iron precipitation. Degray and Ritterhausen carried out experiments on iron cobalt separation using conventional ferric hydroxide precipitation trying to lessen the loss of cobalt with addition of oxalic acid (Degray ja Ritterhausen 1943). They found that with addition of oxalic acid precipitation of cobalt was prevented and only iron was precipitated as hydroxide. This was thought of resulting from cobalt forming oxalic complex that is unaffected by the addition of ammonium hydroxide. Precipitation separation of cobalt from aqueous iron solution can be done using ferrocyanide or potassium cobalticyanide as demonstrated by Evans et al (Evans, et al. 1943).

Cobalt can be extracted from aqueous solutions using ion exchange. More commonly ion exchange is used in cobalt nickel separation due to the difficulty of the operation but is easily applied to cobalt iron separation. Hazan and Korkisch used Dowex 1-X8 anion exchange resin in 9:1 acetone to 6M HCl medium to selectively pull the cobalt and nickel ions from the solution leaving iron into the solution (Hazan ja Korkisch 1965). They then extracted cobalt and nickel into 7:1 acetone to 2M HCl solution. Korkisch and Ahluwalia did similar experiments using Dowex 50-X8 resin in an 8:1 tetrahydrofuran to 3M HCl medium to separate cobalt, nickel and aluminium from iron (Korkisch ja Ahluwalia 1966). They noted that separation was occurring simultaneously by ion exchange as well as by liquid-liquid extraction. Retained ions were recovered from the resin into 9:1 tetrahydrofuran to 6M HCl solution.

Solvent extraction of iron and cobalt can be done using alkyl phosphonic acid such as Cyanex 272. Gandhi et al. studied the separation of cobalt, iron and nickel from nitric acid using Cyanex 272 with chloroform as diluent. They found that iron and cobalt were selectively extracted at different pHs; iron at pH 3 and cobalt at pH 8, while nickel was not extracted at all. Therefore iron and cobalt extracted into Cyanex 272 could be stripped selectively by lowering the solution pH below 8 for stripping cobalt and then below 3 for stripping iron (Oliver 2011). Chloroform was chosen due to beneficial interactions on the extraction such as dipole-dipole and hydrogen bonding, but similar effectiveness was found with for example benzene, toluene and xylene. In industrial processes kerosene is often used due to economic and environmental feasibility. Lanagan and Ibana studied how chromium behaves during cobalt and nickel leaching using Cyanex 272 (Lanagan ja Ibana 2003). They found that chromium is extracted to organic phase from aqueous solutions at various degrees at pH range of 3 to 7. However the stripping of chromium from Cyanex 272 can be challenging and therefore extraction has to be done with caution. Dong et al. conducted experiments on carrollite leach solution containing various metals like cobalt, nickel, iron, zinc, and copper. Good extraction rate of cobalt was found using 35% P507 (2-ethylhexyl phosphonic acid mono 2-ethylhexyl, HEH(EHP)) in sulfonated kerosene.

Chromium is mainly leached from chromite ore by oxidizing the chromite or ($FeCr_2O_4$) in the presence of lime or soda ash into water soluble chromium salts. Lime roasting process is problematic due to the high amount of carcinogenic chromium (VI) containing process residue. Soda-ash roasting is suitable only for chromite that is rich in chromium. Liquid oxidation method utilizing potassium hydroxide was developed to improve the short comings of soda-ash roasting. Liquid oxidation process uses high temperatures and requires long processing times but is capable of converting chromite into potassium chromite salt leaving iron as insoluble slag. A demonstration plant in Henan province, China was built utilizing liquid oxidation process to separate chromium from chromite (Zheng, et al. 2006). The plant uses 320 ^{o}C temperature and 8h reaction time with 80 wt% KOH solution during which 99% of chromium is converted into the soluble salt form. Chen et al. further optimized the process by introducing pressure leaching. They found optimal reaction conditions to be 220 ^{o}C and 2 MPa using 50 wt% KOH solution for 5 hours. With these parameters 98% or better conversion of chromium was achieved. This also eliminated a dilution step needed for processes using higher than 50 wt% KOH solution.

Chromium separation from iron in aqueous solution can be done by precipitating the iron using similar ammonium precipitation to cobalt resulting in some loss of chromium. Liu et al. demonstrated the use of oxalic acid to separate multiple metals such as iron and cobalt from chromium using precipitation (Liu, et al. 2014). They showed that Fe, Co, Mn, Ni all precipitated at pH 3 at 30 ^{o}C using a small excess of oxalic acid while Cr started to precipitate only after pH was risen above 3. The result is interesting since it partly contradicts previous knowledge of cobalt oxalic acid interaction on precipitation demonstrated by Degray and Ritterhausen in 1943.

4 Recycling steps and – process

4.1 pretreatment

Magnetic tape is often wound up in a tight reel. This is ideal for storing and maintaining but is not ideal for chemical recycling. The tape is also often in a casing made from metal or PVC, which must be removed before magnetic tape could be processed. Historically, one of the most common magnetic tape media was VHS tapes, in which the magnetic tape is encapsulated in a PVC cartridge. It is possible to pull the magnetic tape as a single strip out of the cartridge but as the tape is between 50 and 500 m long depending on the type it seems unattractive. Crushing the cartridge is possible, however, crushing the cartridge generates PVC scrap that if not properly removed from the tape could cause problems later in the process. US patent 6349457B2 describes apparatus for removing VHS style cartridge into three parts; closure flap and top – and bottom cartridge parts, exposing the reels connected to the bottom part. This would significantly reduce PVC scrap that would be generated from just crushing the cartridge without separating the three pieces.

The tightly wound reel should be significantly loosened if not broken completely. Many of the depolymerization experiments showed that thickness of the PET layer is an important factor. Multiple layers are stuck together preventing solvent flow between the layers, which could have a significant impact on reaction speed. Additionally, when multiple magnetic tape layers are stuck together the metal layer could further inhibit depolymerization. Therefore, some mechanical layer dispersion is advised. Removing the tape by pulling it out as a long strip achieves this. Crushing may also achieve this depending on how the crushing is carried out.

PVC has a melting point at around 200 ^{o}C while PETs melting point at above 250 ^{o}C. This would allow melting separation of PVC cartridge from PET. This is, however, made more challenging by the fact that PETs glass transition temperature is at 80 ^{o}C giving PET plastic amorphous properties when it might be removed with the molten PVC or PVC trapped between PET layers. Drelich et al. experimented froth flotation separation of PVC from PET (Drelich, et al. 1999). They achieved good separation efficiency by using 2 wt% alkaline solution at 70 to 80 ^{o}C. Froth flotation could be used due PET losing its hydrophobicity in alkaline conditions. PVC is affected similarly but to a much lesser degree. Therefore, on froth flotation hydrophobic PVC particles would float to the top while modified PET particles would sank to the bottom. They noticed that PVC behaves unpredictably and may sometimes lose its hydrophobicity completely like PET. To combat this, they proposed an additional stage in which plasticizer is added restoring the hydrophobicity of PVC. A process similar to Drelich et al.'s proposal is described in US patent 5120768A (Sisson 1991). The patent differs from Drelich et al.'s process in that it uses a non-ionic surfactant with alkaline aqueous solution to modify PET and PVC particles. After modification, froth flotation is used to collect PVC from the top and PET from the bottom.

4.2 depolymerization

Magnetic tapes separated from their possible casings and purified from other matter such as dust can be depolymerized dissolving both EG and PET monomers while leaving metal particles as a solid fraction. Binders and other additives such as elemental carbon have to be addressed separately prior or after the depolymerization reaction. Most polyester and polyurethane compounds used as binders can be depolymerized in similar conditions. For example, glycolysis is used to turn polyurethane into polyols at temperatures around 200 ^{o}C. This could theoretically occur as a side reaction in any PET depolymerization method as ethylene glycol is generated as a product during depolymerization. Polyurethane may also undergo a hydrolysis or methanolysis similar to PET yielding polyols and amides.

As depolymerization of PET can be done using various methods, an evaluation of the different methods and their applicability to depolymerize magnetic tape is needed. Novel methods such as enzymatic depolymerization or aminolysis are not considered due to the slow reaction speed and relatively low scientific maturity level. The main chemical recycling methods of PET are glycolysis, hydrolysis and methanolysis. Experimental results from different methods are collected in tables below.

Table I Collection of Polyethylene terephthalate glycolysis experiments

glycolysis	**t, min**	**T, ^{o}C**	**p, bar**	**catalyst**	$\frac{w_{PET}}{w_{solvent}}$	$\frac{mol_{cat}}{mol_{PET}}$	**PS, µm**	**Yield, %**
(Goje and Mishra 2003)	90	197	1	ZnAc	1:4	1:25	127	98
(Goje and Mishra 2003)	130	220	2	ZnAc	1:4	1:25	127	94

(Shukla et al., 2002)	480	190	1	ZnAc	1:2	1:200	~2000	62,5
(Imran, Kim, et al. 2013)	80	300	110	Mn_3O_4 SNP	1:3,6	1:100 w/w		
(Zhu, et al. 2012)	180	180	1	solid acid	1:5,55			01
(Yue, Xiao, et al. 2013)	120	190	-	BMIM (OH)	1:10	1:25	~2000	71,2
(Yue, Wang, et al. 2011)	480	180	1	BMIM (Br)	1:4	1:4,3	2500	78

Where PS means particle size and SNP means silica nano particles. As the manganese oxide was infused on top of the SNPs the catalyst load is given in catalyst weight ratio.

Table II Collection of polyethylene terephthalate methanolysis experiments

Methanolysis	**t, min**	**T, ºC**	**p, bar**	**catalyst**	$\frac{w_{PET}}{w_{solvent}}$	$\frac{mol_{cat}}{mol_{PET}}$	**PS, µm**	**Yield, %**
(Yung, et al. 2002)	30	250	100	-	1:6	-	3000	95
(Goto, et al. 2002)	30	300	145	-	1:5	-		100
(Mishra and Goje 2003)	120	120		ZnAc-PbAc	1:2,3	1:0,84	127	98
(Kurowaka, et al. 2003)	120	200		AIP	1:16	1:0,89	3000	67

Table III Collection of polyethylene terephthalate acidic hydrolysis experiments

Acidic hydrolysis	**t, min**	**T, ºC**	**p, bar**	**acid**	$\frac{w_{PET}}{w_{solvent}}$	**Acid conc. M**	**PS, µm**	**Yield, %**

(Yoshioka, Motoki and Okuwaki 1994)	60	190	1	H_2SO_4	1:200	3	125	99
(Mehrabzadeh, Shodjaei and Khosravi 2000)	360	170	1	H_2SO_4	1:15	7	200	100
(Yoshioka, Okayama and Okuwaki 1998)	1440	100	1	HNO_3	1:33	13	100	90
(Kumar and Rao 2003)	300	100	1	HNO_3	1:300	13	550	90

Table IV Collection of neutral polyethylene terephthalate hydrolysis experiments

Neutral hydrolysis	**t, min**	**T, ºC**	**p, bar**	**catalyst**	$\frac{w_{PET}}{w_{solvent}}$	$\frac{mol_{cat}}{mol_{PET}}$	**PS, µm**	**Yield, %**
(Zope and Mishra 2008)	120	250		-	1:25	-	150	88
(Mancini and Zanin 2004)	360	205	13,5	-	1:8,5	-	150	99
*(Liu, et al. 2004)**	90		20	-	1:10	-		99

*Liu et al used microwave irradiation using 600W power to promote depolymerization

Table V Collection of polyethylene terephthalate alkaline hydrolysis experiments

Alkaline hydrolysis	**t, min**	**T, ºC**	**p, bar**	**catalyst**	$\frac{w_{PET}}{w_{solvent}}$	$\frac{mol_{cat}}{mol_{PET}}$	**alkali con., M**	**PS, µm**	**Yield**
(Wan, Kao and Cheng 2001)	60	160	4,6	-	1:6	-	3,5M KOH	390	90
(Karayannidis, Chatziavgoustis and Achilias 2002)	60	200		-	1:10	-	1,125M NaOH	6000	98
(Kosmidis, Achilias and Karayannidis 2001)	300	80		TOMAB	1:130	1:300	2M NaOH	6000	90

*(Paliwal and Mungray 2013)**	45	90		TBAI	1:15	1:55	2,5M NaOH	500	>99
*(Khalaf and Hasan 2012)**	60	90		TBAI	1:33	1:33	2,5M NaOH	500	98
Non-aqueous Alkaline hydrolysis*									
(Oku, Hu and Yamada 1997)	40	160		-	1:10	-	2,5M NaOH	1000	95
(Ruvolo-Filho and Curti 2006)	10	170	1	-	1:20	-	1,1M NaOH	2700	100

*Paliwal and Mungray used ultrasound with 20 kHz and 190 W and Khalaf and Hasan used microwaves with 200 W to promote depolymerization. Both the non-aqueous alkaline hydrolysis experiments used ethylene glycol as the solvent.

As can be seen from the above tables good yields can be achieved using every method. Glycolysis with cheap and reusable catalysts such as zinc acetate or solid acids can be used to achieve over 90% BHET yields from PET waste. However, magnetic tapes being roughly 30 to 40 w-% of non-PET materials, even if depolymerization could be done without hindrances from the non-PET materials, especially, the separation and purification of products such as ethylene glycol from organic additives, can be challenging. Therefore, glycolysis process becomes expensive with high S-L ratios as high volumes of ethylene glycol would need to be purified with for example distillation. Also, recycle of used catalyst becomes more challenging due to the presence of metal pigment particles. On the other hand, when metal particles are a desirable product, catalyst being left in the metal particle yield provides additional challenges. Methanolysis suffers from similar problems as glycolysis. While methanol distillation is easier than ethylene glycol distillation, methanolysis product; DMT requires further processing to be used in modern PET production. Also, non-catalytic methanolysis is not competitive with other methods without using supercritical methanol, which in turn requires very high temperatures and pressures further increasing the process costs. It is worth noting that most of these experiments were done using either PET bottle scarp or PET pellets straight from a manufacturer. These materials have much greater thickness than magnetic tape meaning that potentially much better reacting speeds can be expected with magnetic tapes.

Considering the downsides of glycolysis and methanolysis, hydrolysis seems the most promising chemical recycling method for magnetic tapes. Good yields have been achieved with acidic hydrolysis using relatively mild conditions. The downside of using acids is that when metal product is desired, the separation might be challenging due to some or all of the product being leached into the acid. This requires the removal of metals from the acid solution prior to TPA precipitation as iron and other metals would precipitate as hydroxides during TPA precipitation. This might also hinder the depolymerization reaction requiring greater acid concentrations or volumes than for exclusive PET depolymerization. This stresses the always present environmental and safety concerns of using concentrated acids. Other problem with highly concentrated acids is that it makes the separation of ethylene glycol difficult. Alkaline hydrolysis is reportedly tolerant of highly contaminated PET material, which is an obvious benefit given the high non-PET content of magnetic tapes (Scheirs 1998). They also do not possess similar problems than acidic hydrolysis does with metal particles as metal particles do not dissolve into alkaline solutions easily. One exception to the rule is chromium being potentially oxidized to a water-soluble salt. Relatively low volumes of ethylene glycol can be separated using for example dialysis as described by Yoshioka et al (Yoshioka, Motoki and Okuwaki 1994). Therefore, alkaline hydrolysis is chosen for the process.

Possibility to use microwaves or ultrasound is also an intriguing option. Liu et al. proved that microwaves could be used to induce hydrolysis in otherwise really mild conditions of 90 ^{o}C and atmospheric pressure in plain water to achieve 99% TPA yield. Ramopoulos et al. designed an industrial scale reactor for microwave assisted alkaline hydrolysis of PET at high temperatures (Ramopoulos, et al. 2018). The vessel was designed to handle a range of different solutions and reactants and produce a reaction temperature in the range of 150 to 220 ^{o}C. The system operates in a continuous fashion utilizing an Archimedean screw.

4.3 Separation

Following depolymerization; solid metallic - and liquid monomer fractions can be separated using a simple filtration step. The solid fraction might require additional washing step with hot alkaline solution to release organic contaminants such binder additives from the metal fraction. Some additives such as back matting agents may still persist in the solid fraction after washing, which could be released by high temperature treatment converting them into gaseous oxides.

Obtaining the depolymerized TPA from the filtrate is done by simply lowering the filtrates pH down to 2.5. This precipitates the terephthalate acid as small white crystals, which can be filtered again to gain TPA as powder leaving a liquid filtrate containing salt from the alkaline neutralisation and ethylene glycol from the depolymerization. Ethylene glycol could be distilled from the aqueous solution or collected using for example dialysis. Hopefully, most additives and other unwanted organic materials are retained in final liquid filtrate leaving TPA and metal fractions as pure as possible. Obtained TPA could be washed with acidic solution or recrystallized to purify it.

During conventional TPA production, crude TPA from p-xylene oxidation often contains organic impurities such as benzaldehydes. They are removed using hydrogenation catalysed by a metal catalyst such as palladium. Hydrogenation is done under high pressures and temperatures usually in the ranges of 270 to 290 ^{o}C and 70 to 90 bars. US patent 4791226A describes the use of catalytically activated palladium to catalyse hydrogenation of TPA (Puskas ja Cerefice 1984). The hydrogenation is done under high pressure and temperature autoclave that is loaded with water, TPA and hydrogen at 14 bars pressure. The autoclave is then heated up to 270 ^{o}C and reacted for 3 hours and 15 minutes. US patent 4892972A describes a similar process in which palladium or rhodium containing catalyst is used to catalyse hydrogenation purification of crude TPA (Schroeder ja James 1989). TPA, water and hydrogen were loaded into an autoclave that was then heated to 277 ^{o}C temperature generating 63 bars of pressure and reaction was ran for 4 hours. Harsh conditions of conventional crude TPA purification can be alleviated by using an organic solvent tailored to selectively dissolve impurities from the TPA (Chemical Engineering 2007). Such TPA purification processes are available commercially by for example GTC technologies (GTC Technology ei pvm). Obvious downside of using hydrogenation or its alternative methods is the cost associated with it.

After purification steps valuable metals; cobalt and chromium can be collected using hydrometallurgical methods. Due to the high iron content, selective leaching of valuable metals from the metal fraction leaving the iron seem attractive. Therefore, methods such as liquid oxidation using KOH to selectively leach chromium should be investigated. For cobalt such method is not easily found, and some iron is likely to be leached with cobalt. Therefore, selective extraction of cobalt is more commonly practiced. Selective extraction could be achieved using solvent extraction using for example Cyanex 272 or P507 extractants or ion exchange using Dowex 1-X8 or Dowex 50-X8. Extraction could be achieved also by precipitating the iron as hydroxide or phosphate. Precipitation separation could be used for the whole metal fraction as Liu et al demonstrated (Liu, et al. 2014). Finding out the best available method requires additional investigation. Furthermore, the behaviour of chromium during alkaline leaching has to be investigated potentially allowing simultaneous alkaline chromium leaching and PET depolymerization.

4.4 Overall process and a block diagram

Chemical recycling process for magnetic tapes requires in total around 6 to 9 unit processes yielding PET monomers TPA and EG and metals: iron, cobalt and chromium. A suggestion for a magnetic tape chemical recycling process is displayed below.

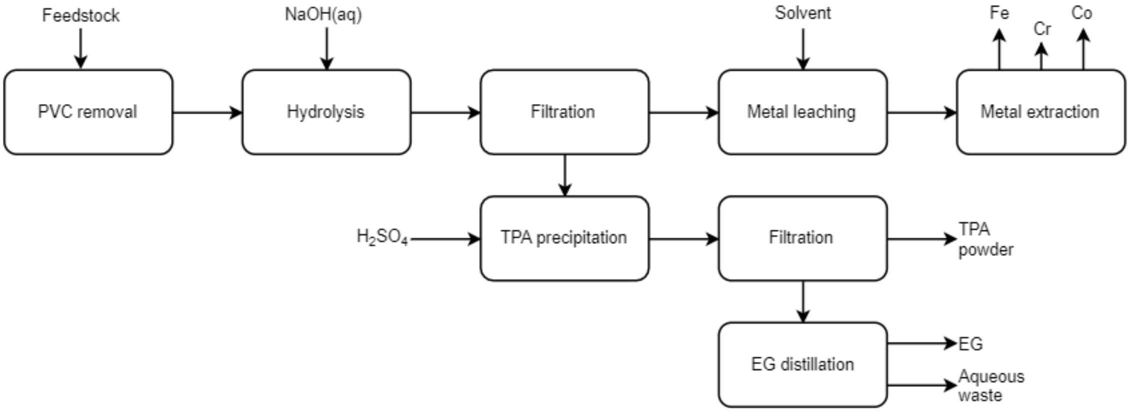

Figure 9 Suggested block diagram for a chemical recycling process of magnetic tape.

Metal extraction step generally would include two to three unit processes depending on the methods being used. Using oxalic acid, it may be done even in a single step as shown by Liu et al. If it is found that chromium is easily leached during alkaline hydrolysis, a separate chromium separation step is needed after TPA filtration.

Final aqueous waste contains $NaSO_4$ in addition to possible organic contaminants. EG can be left in the aqueous waste if the distillation or similar separation process is not found to be economically feasible. All of the unit operations with a possible exception of metal extraction and PVC removal steps are simple well-known industrial processes.

Experimental part

5 Materials and methods

The experiments were conducted on used VHS tapes made by SONY. Analytical grade NaOH from Sigma Aldrich was used to prepare aqueous solutions to depolymerize the VHS tape. Analytical grade sulphuric acid from Sigma Aldrich was used to obtain TPA from depolymerization product. Sulphuric -, phosphoric -, and oxalic acids from Sigma Aldrich were used as solvents in metal leaching. Hydrogen peroxide from Sigma Aldrich was used to aid electrolysis.

5.1 Depolymerization

The depolymerization was done using alkaline hydrolysis in an autoclave. Autoclave was fitted with a mixer and a heating jacket. Mixing speed and vessel temperature was controlled during the experiments. The autoclave, shown in Figure 10, was pressured autogenously, and the generated pressure was monitored during the experiments. Ten grams of VHS tape was measured and cut into random small pieces using scissors (Figure 10). Cut VHS tape pieces were loaded into 500 ml stainless steel vessel. After the tape, the vessel was loaded with 200 ml of aqueous NaOH solution.

The vessel was heated to the target temperature after which the temperature and mixing were maintained for a set duration. The heating took a significant amount of time, as the vessel reached 200 ^{o}C after roughly 30 minutes, which has an obvious effect on the depolymerization time. The vessel was allowed to cool before the vessel was emptied and the depolymerization product was filtered to separate liquid and solid fractions. The solid metal containing fraction was washed two times with cold aqueous NaOH solution. Pure water was not used to prevent any TPA precipitation into solid phase.

A few of the metal fractions were chosen to be processed again in a small autoclave capsule under similar conditions. This was done to analyse the amount of TPA and possible other organic contaminants that were remaining on the metal fraction and could have been removed using the autoclave.

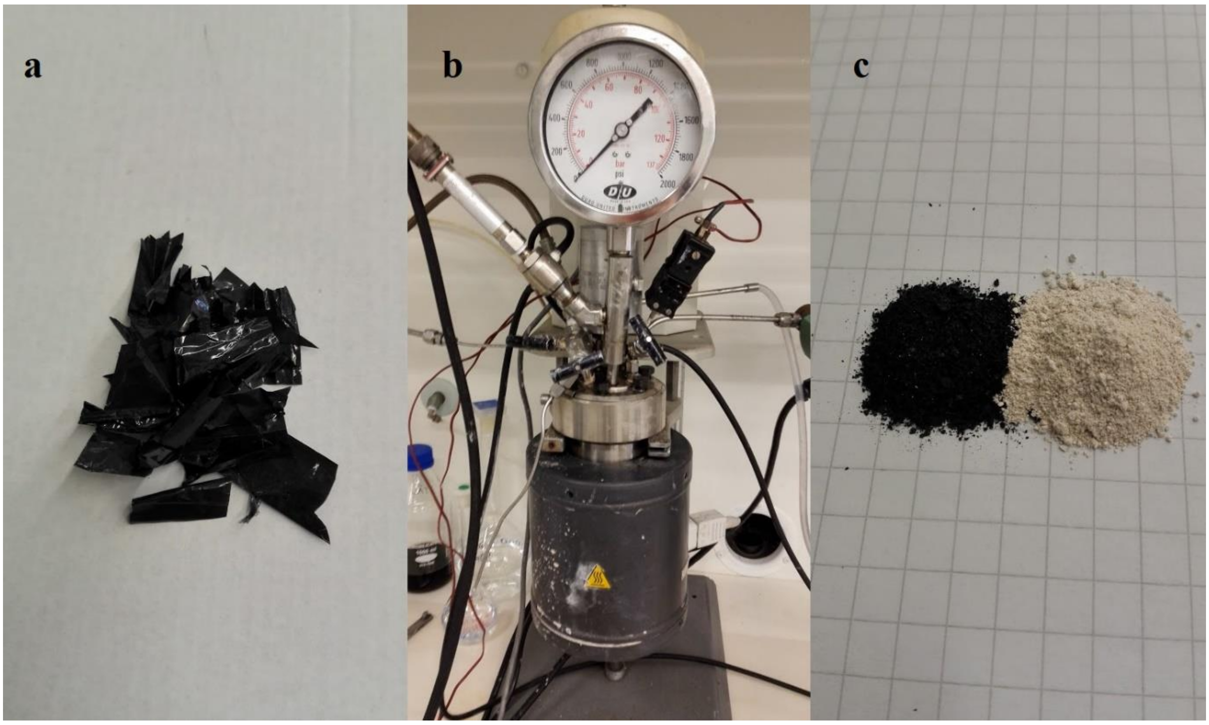

Figure 10 Experimental setup for depolyemerization reactions. The raw material is shown in section “a”. In section “b” the autoclave which served as reaction vessel is shown. In section “c” the two depolymerization products; black metal containing fraction and white terephthalic is shown. Additionally, a liquid fraction not shown in the figure was collected.

5.2 Monomer recovery

Terephthalic acid was precipitated out from the liquid fraction using sulphuric acid. The pH of the liquid containing TPA was reduced from initial 14 to around 2.5. This was done in a glass beaker aided by a magnetic stirrer. Terephthalic acid was crystallized to small white powder that was then filtered out from the remaining liquid. The collected terephthalic acid and metal containing solid fractions can be seen in Figure 10.

5.3 Metal leaching

The solid fraction after depolymerization was dried and stored in a container. For the leaching the multiple solid fractions from depolymerization experiments were combined in order to form a uniform solid dark grey powder. The leaching was done in a 250 ml jacketed glass vessel. First, 100 ml of acid was heated to a target temperature of 80 ^{o}C in the vessel after which one gram of the grey powder was weighted and placed in the vessel along side a magnetic stirrer. A small aliquot of a sample was taken at minutes 1, 5, 15, 30, 60 and 120. The leaching was left to run for a 24h after which a final aliquot was taken, and leaching was ended. All of the samples as well as the final leaching product was filtered to remove any remaining solids. The filtered solids were dried and stored for analysis.

5.4 Metal recovery

Aqueous product from the leaching experiments were subjected to electrolysis in order to attempt metal recovery. Electrolysis experiments were conducted in a glass vessel using copper cathode and graphite anode, which were connected to an adjustable power supply. Most samples were treated with sodium hydroxide to adjust the solution pH and hydrogen peroxide to promote precipitation of ferrous iron into ferric iron hydroxide. Generated iron hydroxide was filtered off before electrolysis experiments. Roughly 40 ml of aqueous solution was placed in a 100 ml glass vessel alongside a magnetic stirrer. The electrodes were placed in the liquid sample at a specific height so that the electrode surface area in the liquid was known. The electrolysis was ran with a specified current for a maximum duration of 3 hours during which aliquots were taken periodically. Due to the brittle nature of graphite, during the electrolysis? graphite anode was releasing graphite powder into the solution and therefore all of the samples had to be filtered to remove any solid graphite particles. Temperature control during the electrolysis was achieved by placing the glass vessel in a water bath to vent excess heat generated during the electrolysis. For the experiment requiring heating the glass vessel was placed in a larger jacketed vessel for which the temperature could be controlled.

Initially, a simple leaching process where depolymerization step was not used was attempted. The initial testings consisted submerging a piece of magnetic tape in hydrochloric, nitric, and sulphuric acid in 1 to 3 molar concentration for duration of 3 days. Additionally, an experiment where 10g of magnetic tape was leached with 100g of sulphuric acid at 100 ^{o}C for 1 hour. None of the initial testings provided yields above 5% of the raw material mass and therefore a depolymerization step prior to leaching was deemed necessary.

5.5 Analysis

Initially, a small piece of VHS tape was cut and completely dissolved with Milestone Ultrawave microwave digestion system using a solution of 67% nitric and 37% hydrochloric acids in 1:4 HNO_3:HCL volumetric ratios. The dissolved VHS tape sample was then analysed using Agilent 7900 inductively coupled plasma mass spectrometer (ICP-MS) to gain understanding of the metallic content in a VHS tape. The same ICP-equipment was used for other samples where metal concentration was analysed. The samples and products from depolymerization were analysed using Parking Elmer spotlight 200 FTIR infrared spectroscope (IR). IR scans were done both the recovered TPA powder, dried solid metal containing fraction and liquid fraction from which TPA had been removed. For the metal containing fraction from depolymerization, a thermo gravimetric analysis using Netzsch TG 209 was done in order to find possible organic contaminants that were left from the depolymerization. Metal fraction was additionally analysed using X-ray diffraction (XRD) with Bruker D8 Advance and Cu Kα irradiation. Samples from leaching were analysed using ICP-MS. The residue from leaching was analysed with XRD. Additionally, crystal particles formed in an oxalate leaching product were analysed with XRD. For the electrolysis, a cyclic voltammetry was used on the aqueous leaching products Samples taken during electrolysis were analysed with ICP.

6 Results and discussion

After initial simple leaching experiments proved unsuccessful, it was deemed necessary to remove the plastic layer prior metal leaching. Therefore, the starting point was chosen to be depolymerization experiments.

6.1 Depolymerization and TPA recovery

Depolymerization of VHS tapes was tried at different temperatures and NaOH concentrations. The conditions used in the experiments are displayed in Table VI.

Table VI Reaction conditions used in VHS depolymerization experiments.

EXP#	c(NaOH), mol	t, min	T, C	p, bar
1	1	45	200	13,8
2	1	30	200	13,8
3	1	30	175	7,9
4	1	30	150	6,9
5	1	30	150	4,1
6	0.5	30	200	13,8
7	0.5	30	175	17,9
8	0.25	30	200	13,8

9	0.25	30	175	8
10	0.1	30	200	13,8

The experiments resulted in different masses of TPA and metal products. Some water was found to be left on the TPA product as the combined masses of TPA and metal fractions nearly accounted for all of the used raw material. Measured masses are shown in Table VII

Table VII Mass measurement results from the depolymerization of magnetic tape. Masses of the tape and TPA were measured and the three other values were derived from those measurements. EG THEO means the theoretical mass of formed ethylene glycol, and non-DEP means the mass of non-depolymerized material assuming the formed TPA was pure.

EXP#	TAPE, G	TPA, G	NON-TPA, G	EG THEO., G	NON-DEP., G
1	9.95	4.921	5.029	1.839	3.190
2	10.09	5.424	4.666	2.027	2.639
3	11.74	7.181	4.559	2.683	1.876
4	11.14	7.661	3.479	2.862	0.617
5	10.6	7.098	3.502	2.652	0.850
6	10.67	7.098	3.572	2.652	0.920
7	10.22	7.065	3.155	2.640	0.515
8	9.88	5.76	4.12	2.152	1.968
9	9.83	5.518	4.312	2.062	2.250
10	9.84	2.258	7.582	0.844	6.738

As can be seen from Table VII, The measured masses for TPA are too large to be pure TPA. This is especially true for the experiments from 3 to 7 where the mass of TPA was measured to be above 7 grams, making up almost 70% of the tape mass. The table also shows values derived from the mass measurements. Theoretical mass of generated ethylene glycol assuming that the generated TPA was pure was calculated using molecular masses, as the PET chain breaks into equal parts of ethylene glycol and TPA. Non depolymerized material was calculated by subtracting both theoretical EG and measured TPA values from mass of the tape. Even on the first experiment, where the non-depolymerized mass was 3.2 g, the mass was still greater than expected as the measured mass of the metal fraction was 3.754 g, which equals to 10.5 g of products.

However, despite the moisture skewing the results it can be concluded that the tape is depolymerized even at temperatures generally below those used in PET depolymerization. Only the 0.1 M NaOH solution was showing significantly worse TPA yield than the other experiments. It can be speculated that it is possible to use even lower temperatures and that the time it takes for the depolymerization to occur is less than 30 minutes, which was used during experiments due to how nearly all of the experiments succeeded to completely depolymerize the tape. It should be noted that the heating and cooling times add some time when the solution is still depolymerizing, which while being similar for all the experiments, has an effect on the results.

The formed TPA was analysed with infrared spectroscopy. An IR scan of the TPA from Experiment 1 is shown in Figure 11

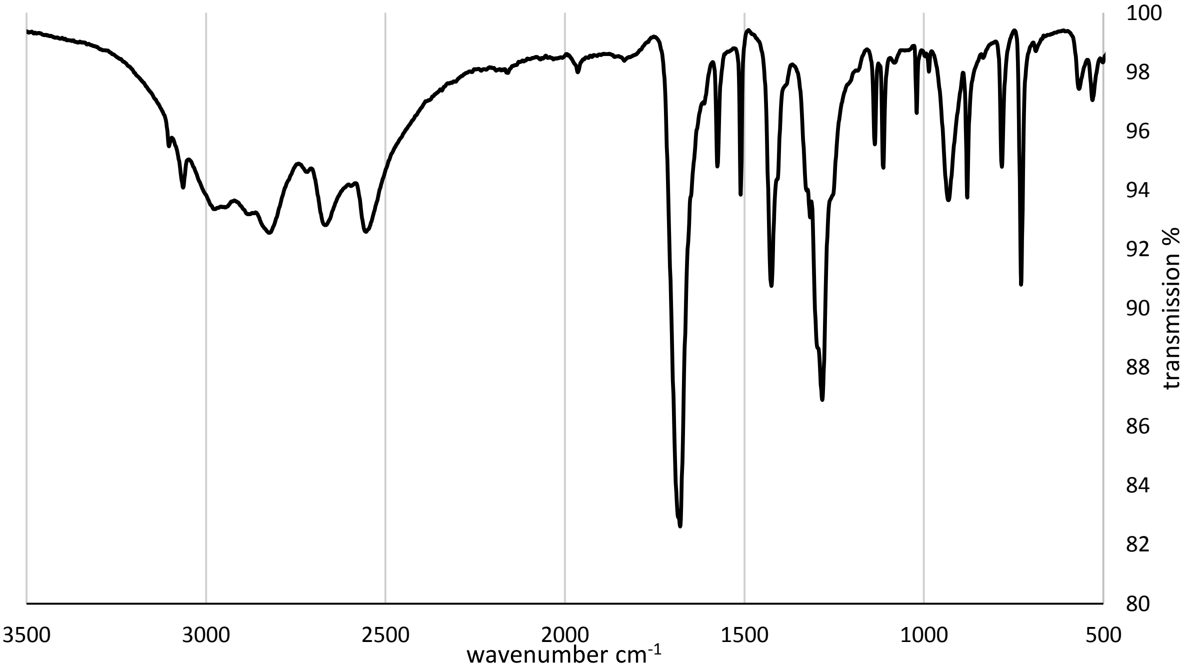

Figure 11 IR scan of terephthalic acid from depolymerization reaction. Reaction conditions were T = 200 °C, p = 13.8 bars, t = 45 min, c(NaOH) = 1 M

From the IR scans some of the suspected water content can be seen as O-H stretch between wavenumbers of 3000 and 2500 cm^{-1}. Terephthalic acid has peaks before and after 1500 cm^{-1} which is seen on the scan as well as smaller peak just above 1000 cm^{-1} and three peaks between 1000 and 500 cm^{-1}, which can all be found in Figure 11 (National Institute of Standards and Techonolgy 2018). Additionally, three smaller peaks can be found between the TPA peaks and three peaks at around 1200 and 1000 cm^{-1}. Ethylene glycol has two peaks between 1100 and 1000 cm^{-1} and a third peak between 1000 and 750 cm^{-1}, which is a possible contaminant in the solid TPA fraction as ethylene glycol is present in the liquid phase TPA is precipitated from. This explains the additional peaks after the two TPA peaks around 1500 cm^{-1} but the three additional peaks around 1500 cm^{-1} cannot be explained by either TPA or EG. It is possible that an organic solvent or adhesive used in the tape is retained in the product. Peaks around 1500 cm^{-1} commonly signify existence of aromatic carbon double bonds, primary amines and carboxylates. TPA contains both aromatic and carboxylate groups, which due to the existence of multiple unidentified peaks suggest that there may be some amide impurities present. Various polyamides can be used as a binder additive on magnetic tapes.

The scans on all of the TPA products had peaks at identical wavenumbers. Main difference that can be found is a stretch peak at 2100 cm^{-1}, which is not found on most of the scans such as in Figure 11. The stretch at 2100 cm^{-1} is only found on scans from experiments done at lower temperature; specifically, the stretch can be found on both of the 150 ^{o}C experiments and one of the 175 ^{o}C experiment. The IR scan from Experiment 5 is shown on Figure 12.

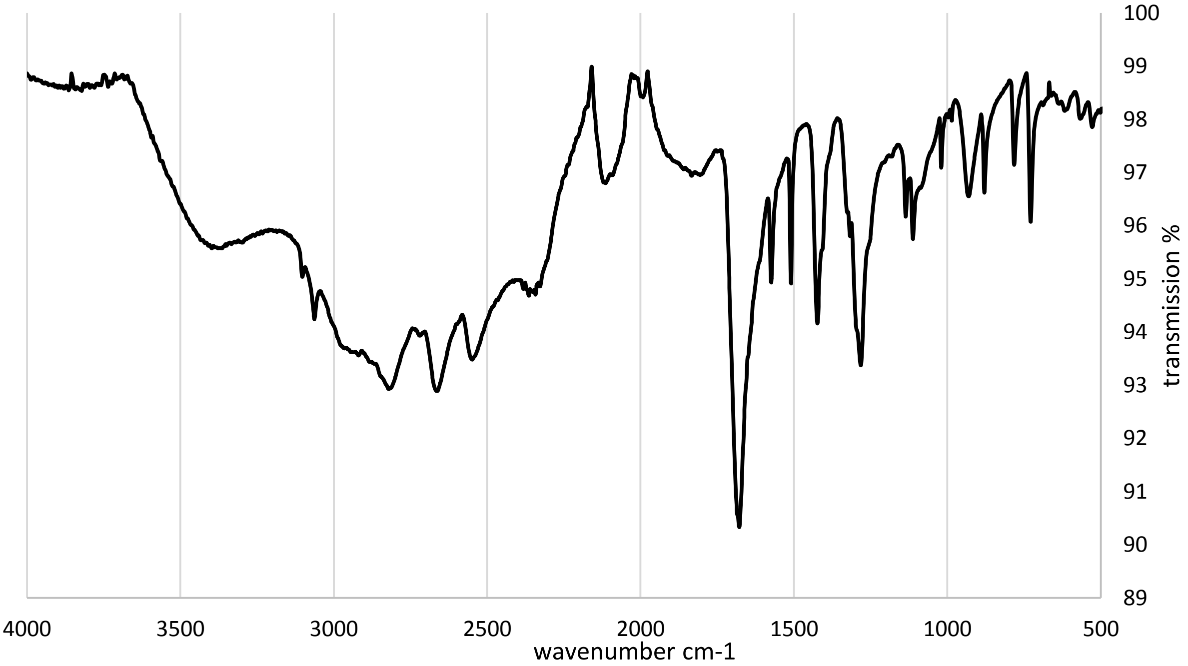

Figure 12 IR scan of terephthalic acid from depolymerization reaction. Reaction conditions used were T = 150 ^{o}C , p = 4.1 bar c(NaOH) = 1 M

The peaks seen in Figure 12 are notably less well defined than in Figure 11 but the peaks are found on identical wavenumbers. Only exception is the aforementioned peak at around 2100 cm^{-1}. Peaks at 2100 may indicate the presence of carbon triple bond but the peaks are usually weak. More likely, the peak at 2100 indicates an isocyanide group. Due to the peak not appearing in scans done to depolymerization products at higher temperatures it is possible that the compound showing a peak at 2100 cm^{-1} is completely dissolved during the higher temperature experiments.

Similarly to TPA products, the metals containing? solid fraction was also analyzed with IR but also with TG and XRD in order to find out possible contaminants. Additionally, the solid fraction gained from Experiment 5 and Experiment 3 were processed again to see whether any TPA could be obtained from the once processed metal fraction.

IR scans from the solid fractions show at times widely different spectra as the amount of organic matter within the mostly metallic fraction was rather small. Some of the samples had significant amount of moisture in them and thus the scan mainly shows the resulting O-H stretch. IR scan from the solid fraction from Experiment 3 is shown Figure 13.

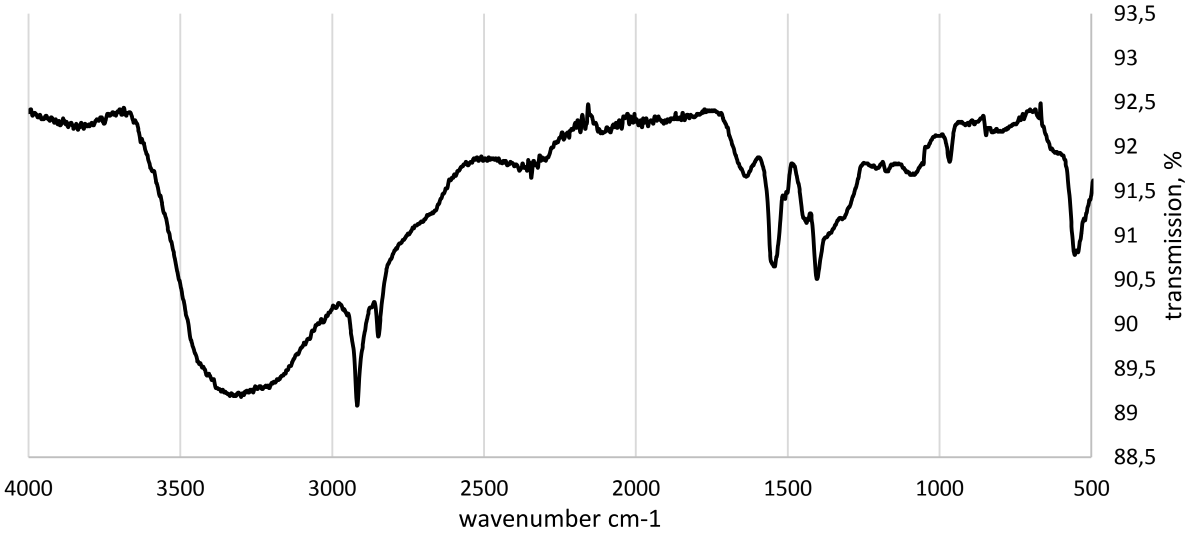

Figure 13 IR scan from solid fraction from magnetic tape depolymerization. Reaction conditions were T = 175 °C, p = 7.9 bars, c(NaOH) = 1 M.

From Figure 13 few defined peaks can be seen alongside the O-H stretching at around 3500 to 2500 cm^{-1} wavenumbers. Notably, two significant peaks can be seen just above and below 1500 cm^{-1} and a third one at 500 cm^{-1}. The two peaks around 1500 cm^{-1} are similar to the ones found in Figure 11 and Figure 12 which strongly suggest that some TPA is being retained in the solid fraction, most likely in liquid form or adsorbed on the solid particles. The peak which can be seen at 500 cm^{-1} most likely signifies the presence of carbon metal bond, which would indicate that the TPA is in a salt form as TPA forms TPA-Na salt during depolymerization. A peak can be seen at 3000 cm-1, which signifies a carbohydrate group such as methylene group, which makes a peak at 2920 cm^{-1} mark. Interestingly, such a peak was not seen on all of the IR scans of solid fractions from different experiments. IR scan from Experiment 6 is shown in Figure 14

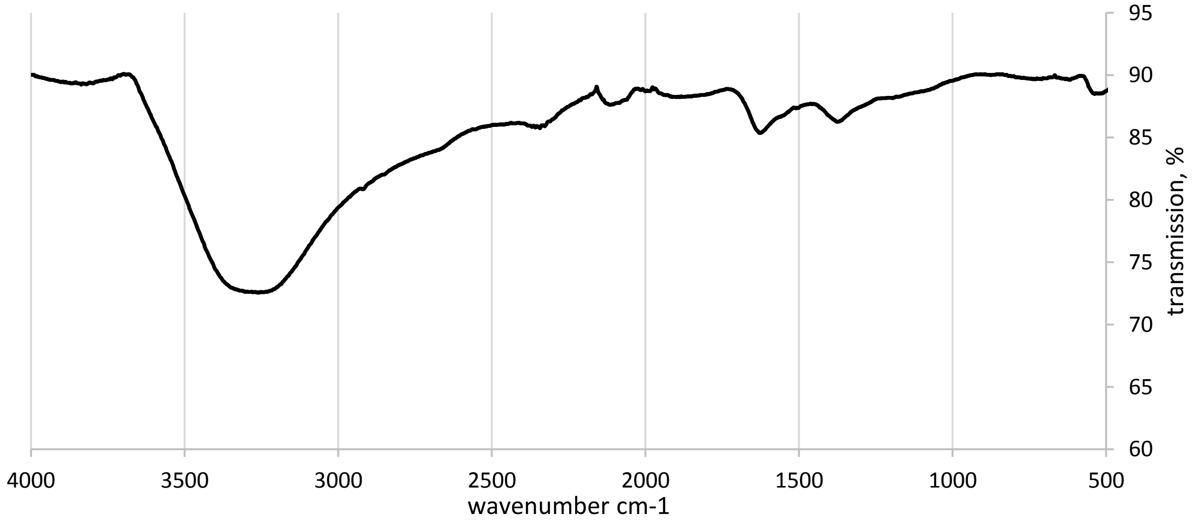

Figure 14 IR scan of a solid fraction from a magnetic tape depolymerization. Reaction conditions were T = 200 °C, p = 13.8 bars, c(NaOH) = 0.5 M.

A significant difference between IR scans from Expeiment 3 (Figure 13) and Experiment 6 (Figure 14) is the amount of moisture in the sample. The same two peaks around 1500 cm^{-1} and the one at 500 cm^{-1} can be seen on both figures. The peak at 500 cm^{-1} is also weaker on Experiment 6 (Figure 14), which has a lower concentration of NaOH. This is consistent with all of the scans where the peak is not really noticeable anymore at experiments done in 0.25 and 0.1 molar solutions even though the two peaks at around 1500 cm^{-1} are still significant. Interestingly, the unidentified wide peak at 2000 cm^{-1} is also seen. The ethylene glycol peaks that are visible on TPA samples are mostly missing on the solid fraction samples. Some resemblance of the glycol peaks found on TPA samples can be seen Figure 12 Figure 13 but is not a clear indication of ethylene glycol.

The unidentified peak at around 2000 cm^{-1} can be seen more clearly on samples where moisture content is low. Most likely the wide peak caused by the O-H stretching from the moisture is masking peaks in the range from 3500 to 2000 cm^{-1}.

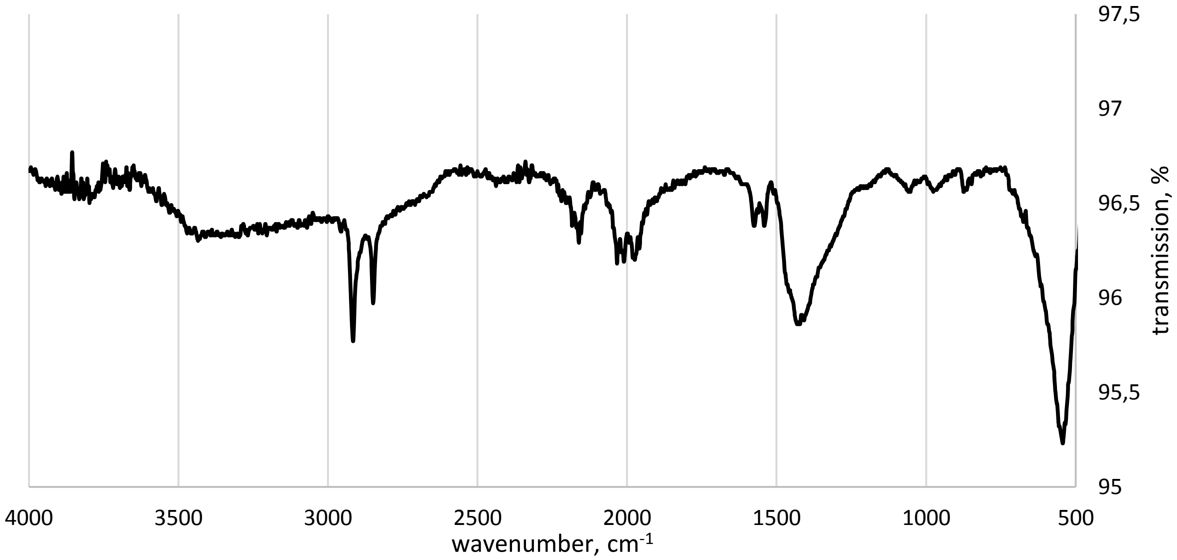

Figure 15 IR scan of a solid fraction from depolymeization of a magnetic tape. Reaction conditions were T = 200 °C, p = 13,8 bars, c(NaOH) = 1 M.

IR scan from experiment 1 is shown in Figure 15. In Figure 15 it is immediately clear that wide O-H stretch is missing. Due to this, peaks in the range from 3000 to 2000 cm^{-1} are clearly seen. Peaks other than the ones around 1500 cm^{-1} and 500 cm^{-1} indicating TPA are almost identical to the ones seen in IR scan from Experiment 3 (Figure 13). Two peaks at around 2950 cm^{-1} and multiple at around 2000 cm^{-1}. Three small peaks around 1000 cm^{-1} can also be found which correspond to the ethylene glycol peaks in TPA samples. The peak at around 3000 cm^{-1} might also originate from ethylene glycol as methylene group produces a strong peak at 2925 cm^{-1}. The multiple peaks at around 2000 cm^{-1}, which were also found in some of the TPA samples, again suggest a presence of an amine or multiple different amine groups.

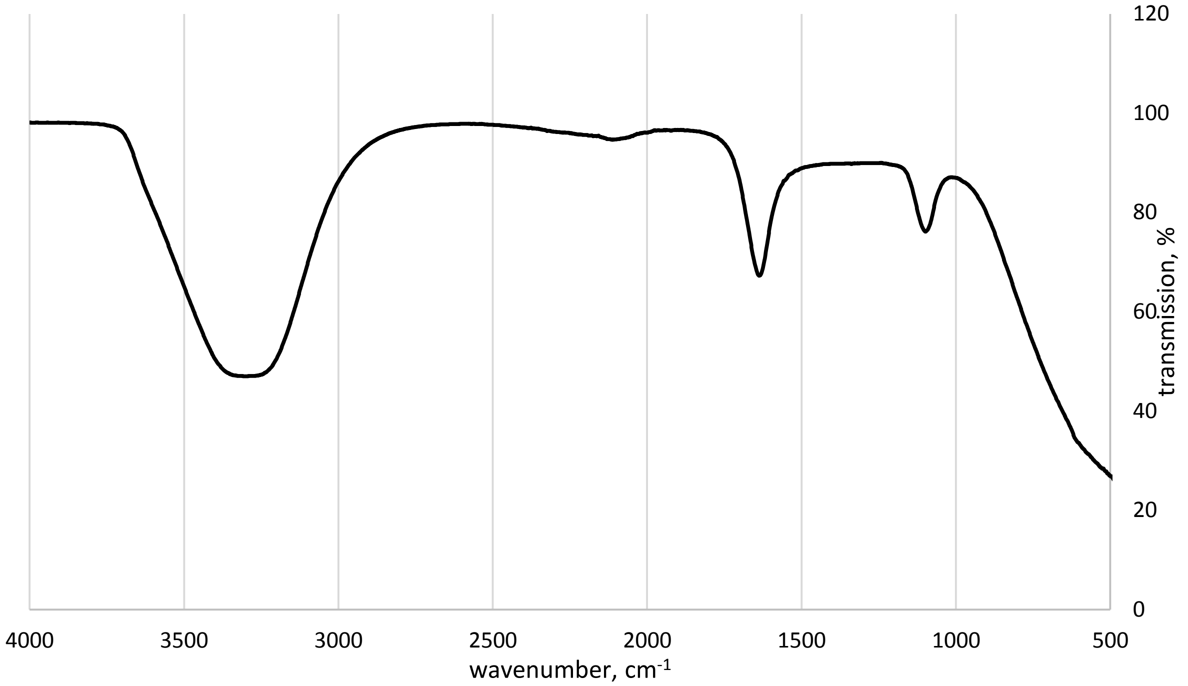

Figure 16 IR scan of a liquid fraction from a magnetic tape depolymerization from which TPA has been removed. Reaction conditions were: T = 200 °C, p = 13.8 bars, c(NaOH) = 1 M.

IR scans were also done for the liquid fraction. Liquid fraction from experiment 1 is shown in Figure 16 which shows three distinct peaks. The O-H stretching at around 3500 to 3000 cm^{-1} and the one at 1600 cm^{-1} belong to water as most of the liquid is water. The peak at around 1200 cm^{-1} belongs to either ethylene glycol or sodium sulphate as they both could be present in the liquid. $NaSO_4$ originates from the TPA precipitation where sulphuric acid is added to NaOH solution containing dissolved TPA in order to lower the pH of the NaOH solution. A strong unidentified peak at 500 cm^{-1} is also seen.

The 1600 cm^{-1} peak that is seen in Figure 16 is seen on all of the IR scans done to liquid fractions. The difference between the scans is the height of the peak. IR scan of the liquid fraction from Experiment 10 is shown in Figure 17

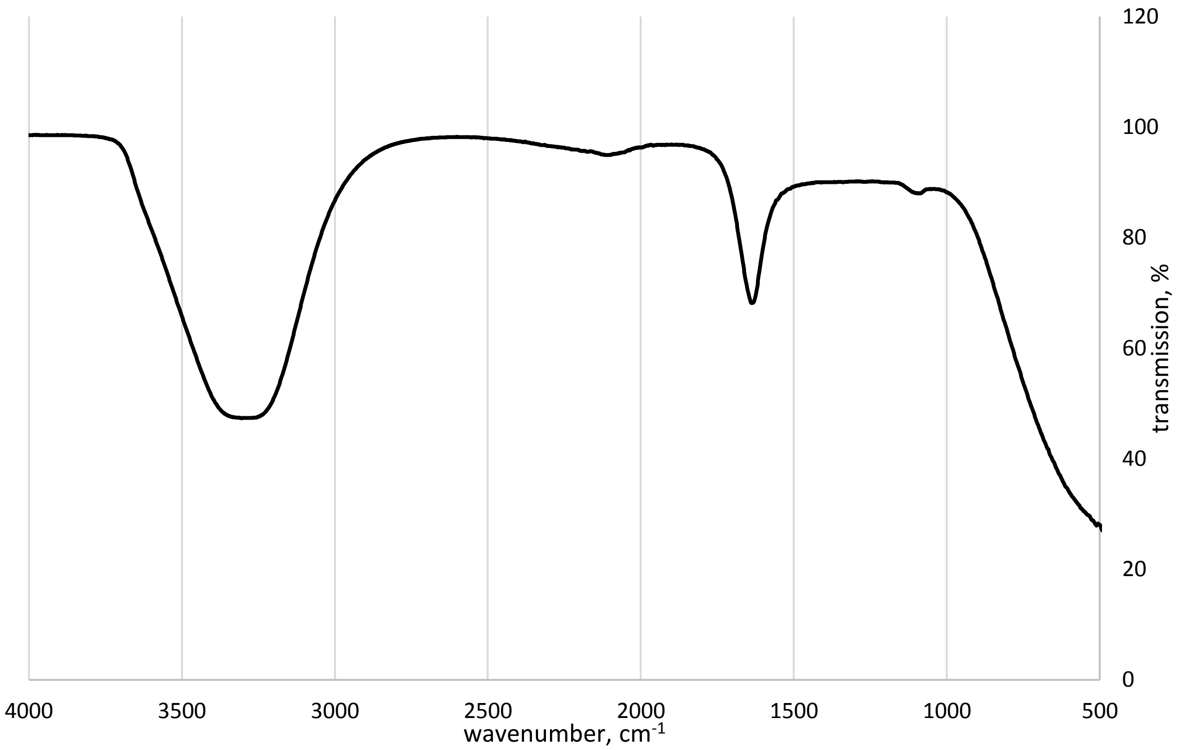

Figure 17 IR scan of a liquid fraction from a magnetic tape depolymerization from which TPA has been removed. Reaction conditions were T = 200 °C,p = 13,8 bars, c(NaOH) = 0,1 M.

In Figure 17 a graph very similar to Figure 16 is seen and the only notable difference is the height of the peak at 1200 cm^{-1}. The peak height follows a trend where the peak height is lower in experiments done at lower NaOH concentrations and is barely noticeable in experiment done on 0.1 M concentration as seen in Figure 17. Interestingly, the height of the unidentified peak at 500 cm^{-1} stays the same suggesting it is unrelated to the NaOH concentration or other reaction conditions.

Peak height at 1600 cm^{-1} strongly relating to the concentration of the solution suggest that the peak seen originates from $NaSO_4$ rather than ethylene glycol as the amount of ethylene glycol should not be so strongly affected by the NaOH concentration used. As was seen in Table VII the mass of TPA product was not significantly lower in experiments done with 0.5 or 0.25 M solutions, however, the height of the peak at 1600 cm^{-1} observed for liquid fractions is. Therefore, it can be assumed that ethylene glycol is not seen on the IR scans of liquid fractions. $NaSO_4$ might also appear in the TPA samples amplifying the visible ethylene glycol peaks, however, it should not be found on solid fraction as the addition of sulphuric acid is done after solid fraction is collected. Even though no ethylene glycol is found on the IR scans of the liquid fraction, it is highly likely remaining liquid fraction contains most of the formed ethylene glycol.

No correlation of reducing temperature from 200 to 175 ^{o}C or pressure from 13 to 7 bars leading to less complete depolymerization and therefore leaving ethylene glycol in the TPA product was found and therefore it is assumed that ethylene glycol found in TPA samples results from a liquid impurities, which could be washed off, rather than from a poor depolymerization.

6.2 leaching of metals

In order to recover the metals from magnetic tapes a leaching process was applied on the metal containing solid fraction from the depolymerization step. Metal leaching was tried with sulphuric and phosphoric acids in one and three molar concentrations as well as with 0.1 molar oxalic acid. The used acid concentrations were chosen according to values found in the literature. Leaching was done at 80 ^{o}C at 1:100 solid – liquid ratio. The leaching was carried out for a duration of 24 hours taking samples periodically. The solid fractions not dissolved during alkaline depolymerisation experiments were combined and mixed together to form a uniform powder for the leaching experiments.

Results from ICP analysis are shown in figures below. Figure 18 shows the leaching of iron from the powder sample into different acidic solutions over time.

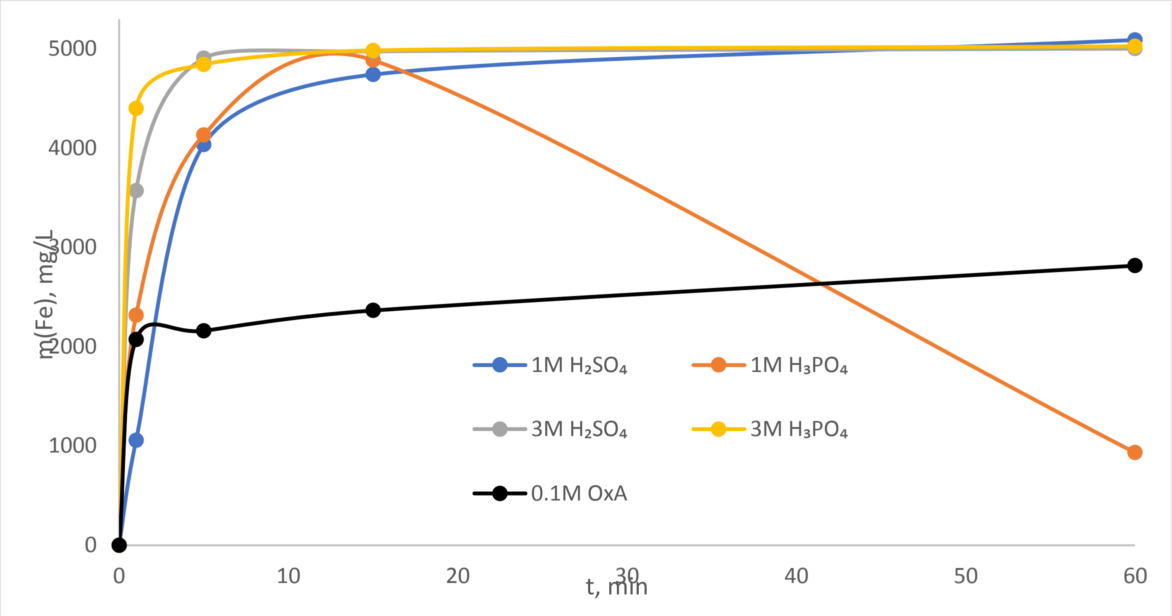

Figure 18 Concentration of leached iron in different acids as a function of time. Leaching was done at 80 °C at 1:100 solid to liquid ratio and at atmospheric pressure.

From Figure 18 it is clear that shortly after 10 minutes nearly most of the leachable iron was dissolved into the solution at the given conditions. After an hour concentration of dissolved iron reached more than 5 grams per litre in both of the sulphuric acid solutions and in three molar phosphoric acid solution. After 3 hours the concentration of iron reached 5.1 to 5.2 grams per litre in sulphuric acid solutions and was fluctuating around 5 g/L in 3 M phosphoric acid solution. After 24 hours the concentration reached around 5.5 grams per litre further displaying the significant decrease in the rate of dissolution. It can be assumed that most of the leachable iron was dissolved at that point meaning that when the original sample was 1 gram and the amount of acid used in leaching was 100 mL, from it 55% could be leached using this method.

One molar phosphoric acid behaved differently from the other acids as over time iron concentration in the solution was seen to decrease. At 15 minutes the iron concentration was 4.9 g/L, close to those of sulphuric acid solutions and 3 molar phosphoric acid solution. However, after an hour the concentration was decreased to 0.9 g/L and was further decreased to 0.6 g/L after two hours and 0.4 g/L after 3 hours. After 24 hours the iron concentration was 0.24 g/L. Additionally, instead of the black coloured powder distinct light grey particles were formed after 10 minutes during the leaching process indicating the formation of a new solid powder. The former grey solid particles were confirmed to be ferric phosphate using XRD. Phosphoric acids tendency to precipitate iron as ferric phosphate was previously described by Li et al (Li, et al. 2018). Interestingly at 3M phosphoric acid similar behaviour was not seen. Three molar phosphoric acid had a slight fluctuation in iron concentration after one hour as the iron concentration at one hour was 5 grams per litre after which the iron concentration fell to 4.96 and 4.92 grams per litre during subsequent hours. However, after 24 hours the iron concentration reached 5.47 g/L similarly to sulphuric acid leachings. Even after the solution cooled down to room temperature iron was not precipitating at a notable rate like it was in the one molar solution. This is likely caused by the decrease in pH on 3M phosphoric acid solution compared to 1M being able to dissolve formed iron precipitate.

Oxalic acid initially seemed a good solvent for iron as the solution was quickly coloured to bright green, however, iron concentration after 24 hours remained at 2.99 g/L clearly showing inferiority to the other acids at the given conditions.

Cobalt concentrations during the leaching are shown in Figure 19

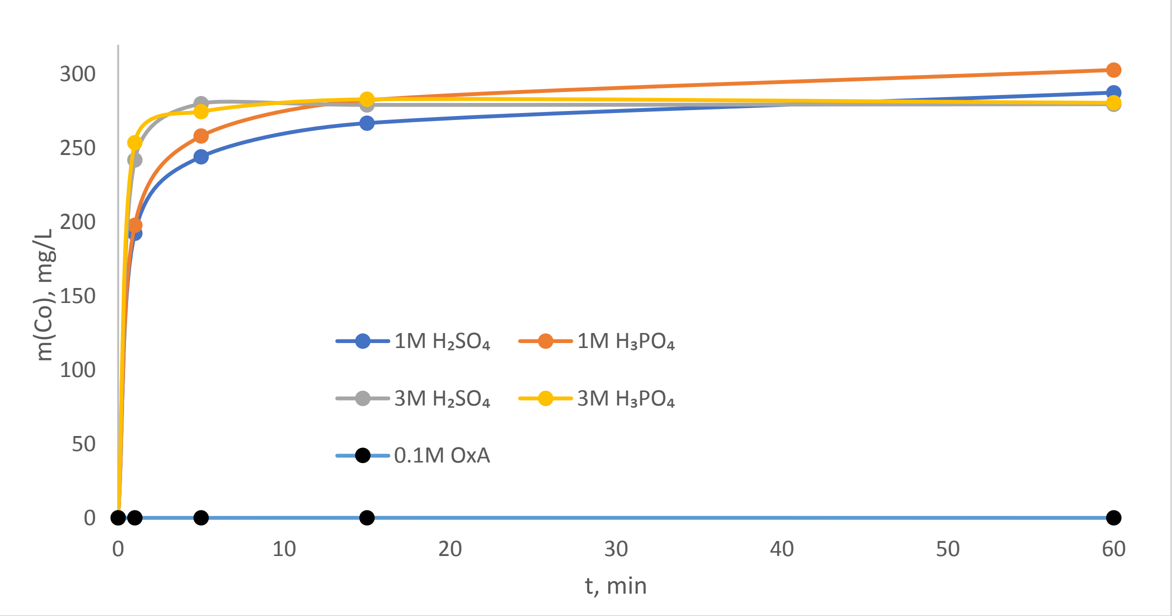

Figure 19 Concentration of leached cobalt in different acids as a function of time. Leaching was done at 80 °C at 1:100 solid to liquid ratio and at atmospheric pressure.

Like iron, most of the cobalt can be leached within the first minutes in the given conditions. At 5 minutes both of the 3 molar acid solutions reach 0.28 g/L concentration after which the cobalt concentration stayed the same for the following three hours and only after 24 hours a small increase to 0.31 g/L was seen. More steady increase after the initial 5 minutes was seen with 1 M solutions and 1 M phosphoric acid solution had a cobalt concentration higher than the three molar solutions. However, after 24 hours one molar solutions also had a cobalt concentration of 0.31 g/L, which is probable all of the leachable cobalt in the sample. This means that from the original sample around 3.1% could be leached as cobalt. From the one molar acids phosphoric acid performed slightly better than sulphuric acid, with three molar solutions noticeable difference was not found. Oxalic acid was not able to leach any cobalt from the sample.

Both iron and cobalt were leached faster into phosphoric acid than sulphuric acid. In three molar solutions the difference was not meaningful as most of the available metals were leached within the first 5 minutes. In one molar solutions the difference was more noticeable. Additionally, given the formation of ferric phosphate precipitate in one molar phosphoric acid, the solution contained more cobalt than iron with cobalt concentration of 0.31 g/L compared to 0.24 g/L of iron after 24 hours. Both one and three molar sulphuric acid solutions and 3 M phosphoric acid solution contained mostly iron with concentrations of 5.5g/L and cobalt with concentrations of 0.31 g/L. Therefore, it is likely easier to obtain cobalt from one molar phosphoric solution with less iron affecting the recovery. When leaching of iron together with cobalt is desired using sulphuric acid is preferable. Using 3M acid solutions at the given conditions seems excessive and could cause problems such as corrosion and additional costs in later steps for example when pH control is required. Oxalic acid was not proficient at leaching iron and did not leach cobalt at all. One interesting property of oxalic acid solution is that once the solution cooled down and was allowed to settle, small neon yellow crystals were formed in the solution. The crystals were separated and analysed using XRD alongside the solid residue left over from the leachings.

Other than iron and cobalt leaching, the leaching of chromium was a point of interest. Chromium was thought of as possible contaminant that would cause problems in the metal recovery steps. However, chromium was not found at significant quantities in any of the samples. This means that either the sample did not contain any chromium, or that it was not leached into the solution. Also, neither copper nor nickel was found, which according to literature are occasionally used in magnetic media storages.

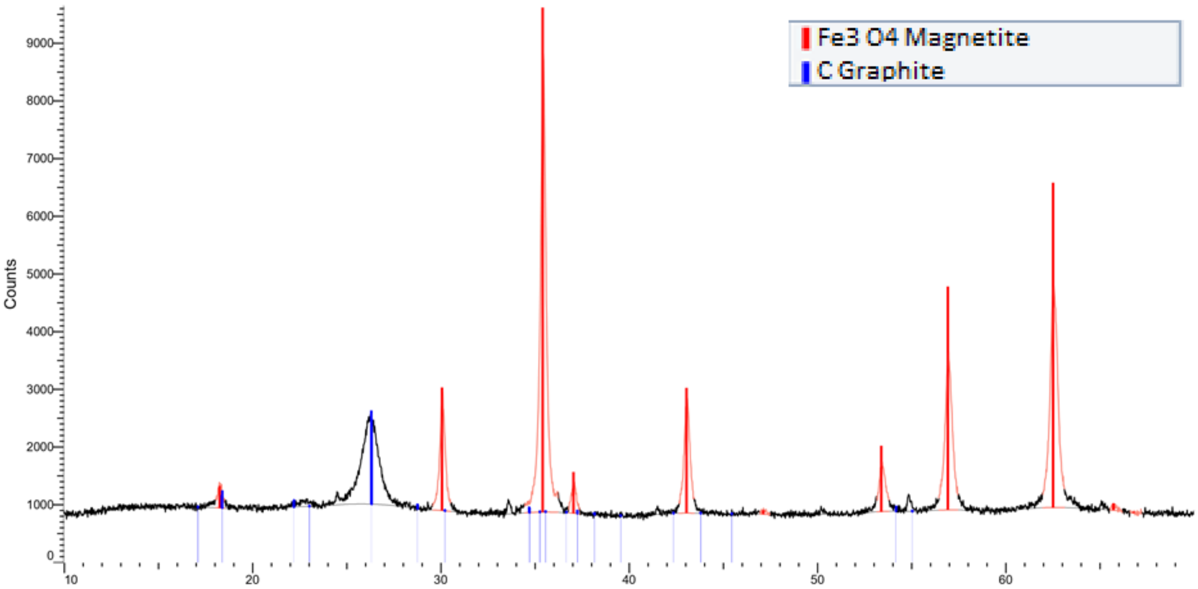

Figure 20 XRD analysis of a solid, metal containing, residue from a VHS tape depolymerization. XRD was taken using 2theta (Coupled TwoTheta/Theta) WL=1.54060

An XRD image from the original metal sample is shown in Figure 20. The XRD image clearly shows spikes indicating a strong presence of magnetite, which was expected. Cobalt oxide, which is not seen in the image, would shows peaks at similar points; at 37 and 45 according to XRD analysis done by Raza et al.(Raza, et al. 2016). Likely, the cobalt concentration is too show and is being by the magnetite.

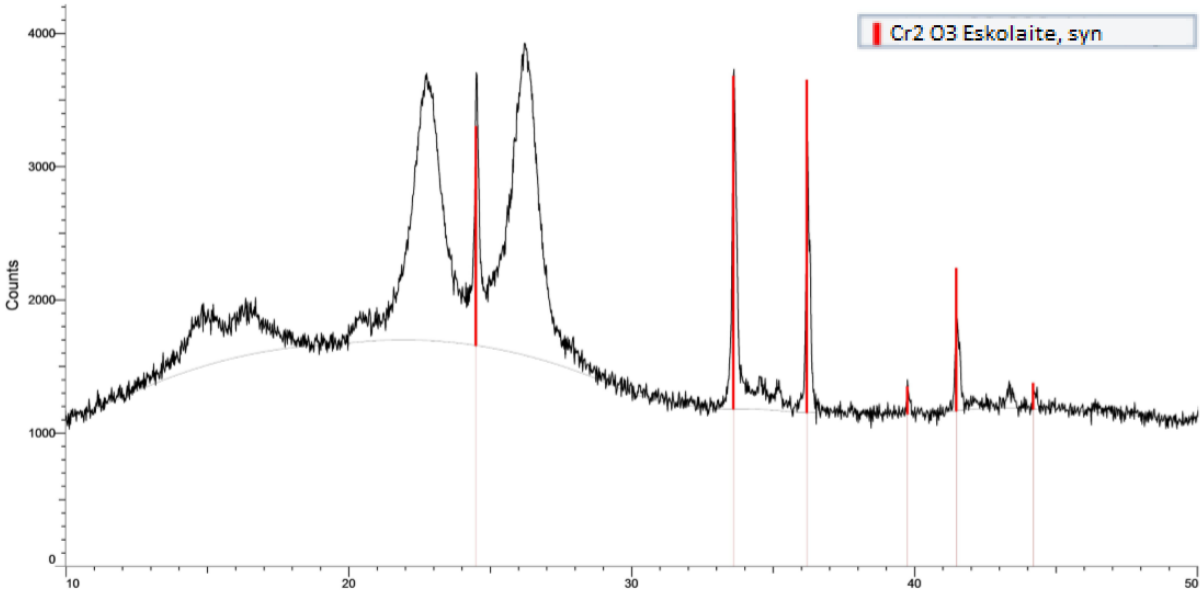

Figure 21 An XRD image of a leaching residue from 1 molar sulphuric acid leaching. XRD was taken using 2theta (Coupled TwoTheta/Theta) WL=1,54060

XRD of the leaching residue from 1 molar sulphuric acid solution is shown in Figure 21. From the Figure 21, peaks around 34 and 36 can be seen indicating chromium oxide. Large wide peak at 26, which corresponds to the peak in Figure 20 indicating graphite, is seen. A peak at 22 can also be found, which was also found in other XRD images at varying peak heights but was not identified during the analysis. It is unlikely that the peak is formed during leaching due to it being present in phosphoric acid as well as in sulphuric acid leaching residues. The presence of chromium oxide in the leaching residue reveals that chromium oxide was indeed not dissolved during the leaching as it was not found in the ICP results of the same leaching at quantities similar to cobalt or iron. Therefore, the handling of chromium is not strictly necessary during the metal refining process. Also, when obtaining chromium is desired, it could be separated from the leaching residue using hydro – or pyrometallurgical methods without interference of other metals. Considering that other than chromium oxide the residue contains mainly graphite, pyrometallurgy is appealing. The XRD of the leaching residue from 3 molar sulphuric acid leaching is similar to that of 1 molar sulphuric acid leaching shown in Figure 21. The main difference between the images is the peak height of the graphite, which for 3 molar leaching is roughly twice as high comparatively. Main cause for the difference in graphite peak heights is likely due to uneven sampling. As the metal powder was combined from different depolymerization reactions, even after thorough mixing particles of different sizes were visible. The particle size varied from dust to sand sized particles. Graphite in particular was found as coagulated matte black colored lumps. This could cause some disparity in XRD images as for XRD analysis only a pinch of the sample material is needed. This is most noticeable in 3 molar phosphoric acid leaching residue XRD image where graphite is by far the highest peak. The XRD of the 3M sulphuric acid leaching residue is not shown as it is otherwise identical to the 1M sulphuric acid leaching residue.

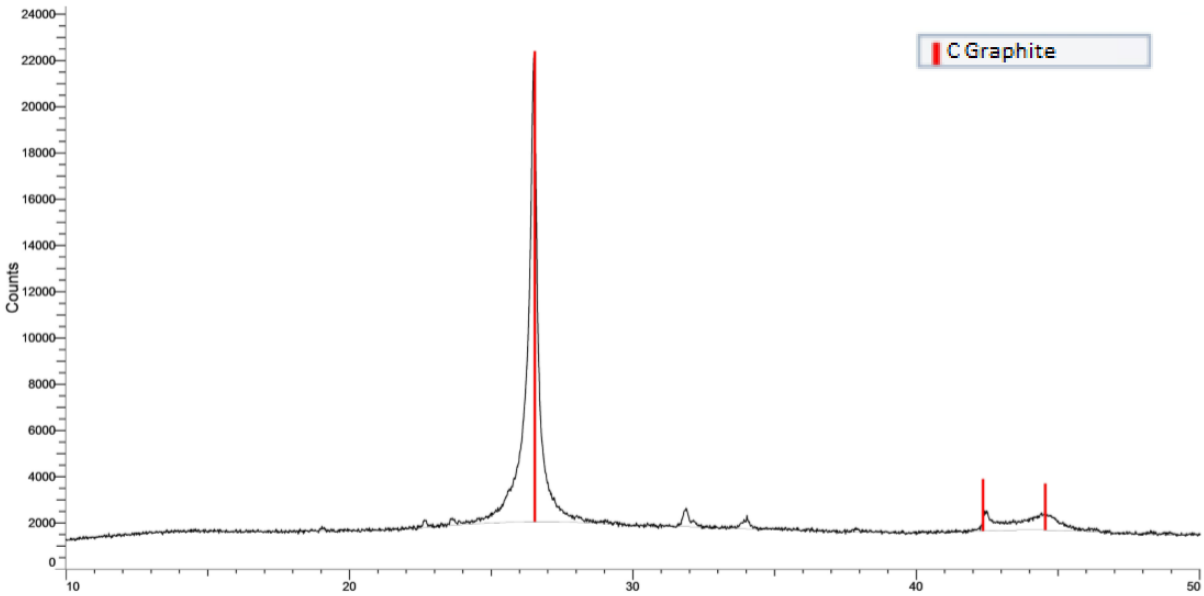

Figure 22 An XRD image of the leaching residue from 3 M phosphoric acid leaching. XRD was taken using 2theta (Coupled TwoTheta/Theta) WL=1,54060

XRD of the 3 M phosphoric acid leaching residue is shown in Figure 22. The XRD from 3 M phosphoric acid leaching residues clearly shows a large peak at 26 where graphite is found in other samples. However, the smaller peaks at around 41 and 42 are not as high as they are expected and therefore it can be assumed that the peak height is additionally increased by an another unidentified component. Additionally, chromium that is present in other XRD images is not found and instead two peaks at similar distance from each other are found at 32 and 34. It is possible that chromium oxide peaks are shifted slightly to left in the residue from 3 M phosphoric acid leaching. The peak heights of the two smaller peaks are of similar height to the ones found in other samples. Perhaps, the presence of graphite affected the peaks similar to doping, which is known to have an effect on the XRD images (Kramakar, et al. 2012).

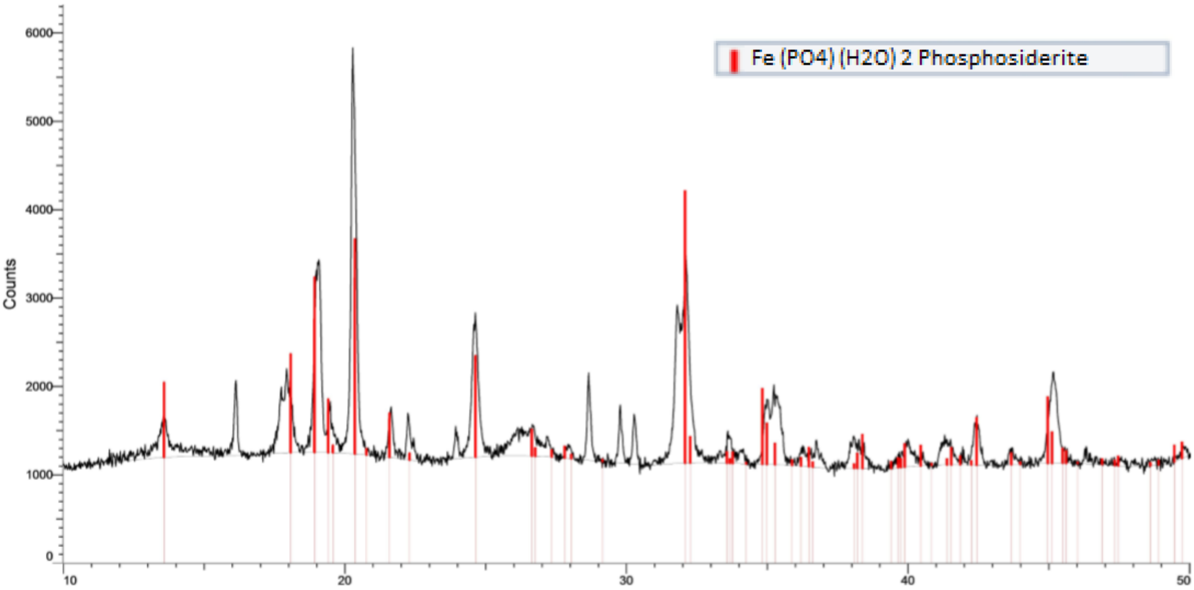

Figure 23 An XRD image of a leaching residue from 1M phosphoric acid leaching. XRD was taken using 2theta (Coupled TwoTheta/Theta) WL=1,54060

The XRD image of 1M phosphoric acid leaching residue is shown in Figure 23. XRD image of 1 M phosphoric acid leaching residue clearly shows substantially more peaks than any of the previously shown XRD images. The peaks reveal the presence of ferric phosphate in the residue, which was seen as grey solid particles during the leaching and as a decrease in the iron concentration over time. Other than ferric phosphate a wide peak can be seen at 26, where graphite is seen in other XRD images. There are three unidentified peaks at 29 and right before and after 30. Any decrease in cobalt content was not seen in the ICP results and therefore it is unlikely that the peaks are caused by cobalt. More likely, the peaks could be caused by the chromium content, which similar to ferric phosphate is mostly insoluble in water. The two unidentified spikes found in 3 M phosphoric acid leaching residue are not present in the 1 M equivalent. A peak at 32 is seen but the one at 34, which is seen on Figure 22, is missing from Figure 23. Additionally, peaks corresponding to chromium oxide found in sulphuric acid leaching residues at 34 and 36 are missing too. As chromium is not found in the ICP results of phosphoric acid leachings it can be assumed that it should be present in the XRD images similar to how it is present in the sulphuric acid leaching residue images. It’s probable that some of the points in figure 23 are caused by chromium compounds but the compounds were not be identified. As the spikes corresponding to chromium oxide is not found in 1 M phosphoric acid and only partly found in 3 M phosphoric acid leaching residue, it is possible that it is partly or fully converted to chromium phosphate during the phosphoric acid leachings. The difference between the two leachings results could be caused by the difference in pH similar to difference in iron phosphate formation.

6.3 electrolytical recovery of cobalt

In theory, cobalt should be obtainable from a solution of cobalt and iron due to their reduction potential as cobalt has reduction potential of -0.28 which is higher than that of iron which is -0.44 (Atkins 1997) (Haynes 2012).

Metal leaching solutions were processed further using electrolysis in order to recover metals from the leaching solutions. Electrolysis was tried in different solutions and conditions i.e. solution pH, current densities and reaction temperature was varied between experiments. In most solutions, the initial iron concentration was reduced by increasing the solution pH, which precipitates iron as a hydroxide.. Hydrogen peroxide was also added in order to convert ferric iron to ferrous iron, which further aids the iron hydroxide precipitation. Prior to electrolysis the solution was filtered to remove the iron hydroxide precipitate. Iron concentration after the hydroxide precipitation was between 0.01 and 0.05 g/L. As a side effect the cobalt was co-precipitating resulting in cobalt concentration of 0.9 to 1 g/L.

Initial electrolysis experiments resulted in no visible yields on cathode and rather mainly hydrogen was evolved. This is mainly seen as an increase in solution pH as water molecules are splitting on cathode leaving hydroxide ions in the solution rising the pH. When a metal is obtained on cathode however, the solution pH is decreasing due to the anode reaction where oxygen is evolved, leaving hydrogen ions in the solution.

Initial reactions consisted of 1 and 3 M sulphuric and phosphoric acid solutions with pH around 3.2 using current densities of 1, 5, 10 and 20 A/cm^2. However, due to hydrogen evolution the pH of the solution increased, which resulted in iron precipitation. As an example, 1M sulphuric acid leaching under the electrolysis with 10 A/cm^2 current density lost 15% of its iron content after 15 minutes and 67% after 60 minutes. Cobalt was not affected by increase in pH as the precipitation pH of cobalt hydroxide is significantly higher. Similar occurrence was seen using 5 A/cm^2 current density where iron concentration was reduced by 62% after 60 minutes. With current density 1 A/cm^2 hydrogen evolution was not intense enough in order to significantly affect the iron concentration in one hour. Phosphoric acid leaching solutions behaved similarly to sulphuric acid solutions with no notable metal recovery occurring on the cathode.

Improvements were seen when initial pH of the solution was raised above 5. One molar sulphuric acid leaching solution, which was raised to pH 5.68 using NaOH saw a decrease in pH during electrolysis using 10 A/cm^2 current density. The solution pH after one hour was decreased to 3.15. During the electrolysis iron concentration was not reduced but remained at 0.01 g/L, however, cobalt concentration was reduced by 29% as cobalt was deposited on the cathode. During the experiment the reaction temperature was controlled using an ice bath which achieved in keeping the solution temperature below 5 ^{o}C throughout the experiment. An experiment using similar initial conditions but with no ice bath to act as a heatsink saw similar decrease in solution pH after one hour; from 5.87 to 4.16 and similarly cobalt was found on the cathode surface. A reaction where the initial pH was 4.96 saw an increase in pH to 5.85 after one hour, which suggests that the defining reaction was hydrogen evolution and thus the initial solution pH should not be lower than 5 in order to obtain cobalt on the cathode.

In all but the one experiment done with no heatsink, an ice bath was used to keep the solution temperature low near 0 ^{o}C. This experiment was done to see how temperature affects the electrolysis where the solution temperature was being maintained at 45 ^{o}C using a heat controllable vessel. A 3 molar sulphuric acid solution, which had pH of 2.01, was processed similarly to the above successful attempts with 10 A/cm^2 for a duration of one hour. After electrolysis solution pH was 2.05, which suggest that hydrogen evolution was the dominating reaction on the cathode. However, such a small change in pH did not cause any noticeable decrease in iron concentration. Cobalt concentration saw a small decrease of 8% after one hour. An experiment using similar reaction conditions 45 ^{o}C and 10 A/cm^2 but with initial solution pH of 5.0 was also tried. After the reaction, solution pH was decreased to 2.55 suggesting a metal reduction reaction on cathodic side which was visibly confirmed as metal was deposited on the cathode surface. However, unlike the reactions done at low temperatures the cobalt concentration saw no significant reduction and instead iron was reduced by 10% after one hour. This suggest that for the electrolysis solution pH is more important than reaction temperature and that when the recovery of cobalt is desired the reaction temperature should be kept low in order to limit iron interference.

7 Conclusions

The aim of the work was to find and study a recycling process for magnetic tapes and subsequent recovery method for precious metals such as cobalt from magnetic tapes. Magnetic tapes consisting of two main layers; plastic and metal pigment layers were processed separately. It was quickly seen after initial experiments that dealing with the plastic layer of the magnetic tape is necessary prior to metal leaching. It was also found in literature that magnetic tapes are easily depolymerized using alkaline hydrolysis process. Depolymerization of PET using alkaline hydrolysis has been studied for bottles and fabrics before and the hydrolysis was expected to work for the magnetic tapes also. What was found was that the depolymerization was easily done and that it could be done using temperatures and pressures lower than with other PET material such as plastic bottles. Mainly the limiting condition for depolymerization was found to be alkaline concentration. Magnetic tape could be depolymerized during 30 minutes at temperatures as low as 175 and 150 ^{o}C with autogenous pressure from 4 to 14 bars as long as NaOH concentration was kept above 0.25 M. Main difference magnetic tapes have to bottles and fabrics is the high amount of non-polymeric content. Magnetic tapes are particularly challenging due to the use of adhesives that may be behaving similarly to polyethylene terephthalate and therefore end up contaminating the monomer product. As an example, IR scans from the TPA samples revealed unidentified amine compounds most likely were used as additives in the magnetic tape. Therefore, it may be necessary to include additional TPA purification steps. Also, the recovery of ethylene glycol, which was not studied, might be more challenging and require additional purification due to the additives used in magnetic tapes.

Separation of the different fractions; metal containing powder, TPA product and remaining liquid fraction was simple and easily achieved using filters. Metal containing fraction was obtained after the depolymerization reaction had occurred and similarly TPA after precipitation was done. Metal containing fraction contained in addition to metals, organic compounds such as residue PET monomers and graphite which was seen on XRD scans. The purity of the metal containing fraction was not seen as crucial as the TPA fraction since metals were leached out from the solid fraction leaving solid residue containing organic matter graphite and unleached metals such as chromium. Metal leachings proved that the metals; mainly iron but also some cobalt were simple to leach, and almost complete recovery was achieved after 20 to 30 minutes. It was also seen that iron leaching was affected by the choice of solvent. Therefore, selectivity on leaching of iron and cobalt was achieved as iron concentration was reduced from 5,5 g/L to 0,24 g/L when using 1M phosphoric acid compared to 1 or 3M sulphuric acid or 3M phosphoric acid which while cobalt concentration remained at 3,1 g/L. Additionally, the XRD scans of the leaching residues revealed that chromium was found in the residue.

Recovery of metals from the leaching solutions were attempted using electrolysis. No metal recovery was achieved when solution pH was below 5. Iron concentration was declining due to hydrogen evolution rising the solution pH which resulted in iron precipitation. When solution pH was risen above 5 but the solution temperature was kept at around 0 ^{o}C, cobalt was precipitating on cathode. Iron concentration was not affected during electrolysis at above 5 pH and 0 ^{o}C. When solution pH was set to above 5 and the solution temperature was heated to 40 ^{o}C instead of cobalt, iron was reduced on the cathode and cobalt was not significantly affected. Therefore, selective recovery of cobalt and iron can be achieved by controlling the solution temperature during electrolysis.

8 Recommendations for future research

For future research more work need to be done on solving the optimal processing conditions as the conditions used in this study were found to be possibly excessive. Bringing the processing time, - temperature, - pressure and alkaine or acid consumption down significantly affects its economic feasibility. Possibility to use more environmental solvents such as organic acids is also a topic of interest.

More research needs to be done on the purity of products especially TPA. Various types of organic and polymeric substances are used as additives on magnetic tapes. Therefore, it’s important to know how these substances are affected by the depolymerization process and do they end up in the product yields. Finally, the metal recovery process should be optimized further and other metal recovery methods besides electrolysis, such as ion exchange and solvent extraction should also be considered to gain higher yields and purities.

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