



# A Comparison of the Rates of Destruction by Reactive Milling of Functionalised Long Chain Hydrocarbons

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## Abstract

Soil is composed of various minerals with variable amounts of organic matter that absorb many pollutants, which can be difficult and expensive to remove. High energy ball milling is an effective and cheap way of remediating contaminated soil. Research has shown that the initial step in the process is predominantly the ionization of the polluting organic molecules to form a radical. This radical initiates a chain reaction, thus destroying the organic pollutant.

The site(s) of ionization on the organic molecule has yet to be identified. Initial studies using diesel and some small molecules suggested that the ionization potential of the molecule is important, but the volatility of these small molecules had made these results uncertain. In this study, a range of large organic molecules with low volatilities has been investigated. These molecules contained a range of functional groups and were milled in quartz to determine their destruction rates. This enabled the investigation of whether destruction rates are dependent on the functional group or the main carbon chain in the organic compounds. Whether ionization is the major initiator was investigated as well.

It was found that the functional group does in fact play a major role in the destruction rates of the compounds. In order of destruction difficulty: The most difficult to destroy was found to be the alkene hexadecane then in order of increasing ease of destruction: hexadecanone, hexadecanol, methyl hexadecanoate, hexadecanoyl chloride, propyl hexadecanoate, ethyl hexadecanoate, hexadecanoic acid, hexadecylamine, decyl hexadecanoate, hexadecane and the fastest was n-ethylhexadecanamide.

Comparison of the destruction rates with the ionization energies of the functional groups showed, a modest relationship. While the ionization of the functional group does play a part, destruction is clearly a more complicated process.

## Declaration

“I hereby declare that this submission is my own work. To the best of my knowledge and belief, it contains no material which has been previously published or written by another person (except where explicitly acknowledged), nor material which has been accepted for the qualification of any other degree or diploma of a university or other institution of higher education.”

Date            01/12/2016

A handwritten signature in black ink, appearing to read 'Rugh', written over a horizontal dotted line.

Signed.....

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## 1.0 Introduction

### 1.1 Overview of Research

Reactive Ball Milling (RBM) is a mechanochemical destruction method that is very effective at removing organic pollutants from soil. This has been proven by research previously done in this industry. However, one of the limitations of the research carried out until now is that full-scale mills have lacked the ability to efficiently predict and regulate mill performances in terms of destruction efficiency.

Apart from the classic “dig and dump” approach, most soil remediation technologies are considered complicated and expensive, whereas RBM is a simple and relatively cost effective approach. For many countries that lack the funding and resources to carry out advanced soil remediation procedures, RBM is a promising method for removing organic pollution from soil.

Past research on how RBM works and how it destroys organic pollutants investigated chlorinated organic compounds such as the pesticide dichlorodiphenyl trichloroethane, better known as DDT, other persistent organic pollutants (POPs), polycyclic aromatic hydrocarbons (PAHs), petroleum hydrocarbons and aliphatic hydrocarbons. This thesis investigates RBM of a selection of functionalised linear C-16 compounds chosen for their low volatility.

### 1.2 Pollution

Pollution is defined as the presence in or introduction into the environment of a substance which has harmful and poisonous effects (Oxford University Press, 2016). There are many environments where pollution is a concern including soil, water, farmlands, forests, air and space.

Pollution can result from many factors including naturally occurring activity or through anthropogenic activity. Though pollution is one of the major issues in the environment and has been for a while, ways to reduce and eliminate pollution has been researched thoroughly over past decades and many of the systems designed have been utilised and have been relatively effective.

This project specifically looks at the pollution in soil. One major contributor to soil pollution is industry. This has been a big contributor to the problem in the last century especially due to the increase of mining and manufacturing. Most the industries do

not have a 100% efficient way of disposing material such as by-products, for example coal or iron ore from mining. Thus, all the industrial waste remains on the soil surface for a long time and sometimes seeps through the lower layers of soil, thus making it unsuitable for use.

Acid rain results when pollutants like sulphur dioxide and nitrogen oxides in the air react with water molecules and fall onto the ground (Wei, Liu, Zhang, & Qin, 2016). The polluted water could dissolve away some of the important nutrients found in soil and can also alter the structure of the soil. In terms of pH, soil has the ability to neutralise pH changes, which this is known as a buffering capacity. Soil exposed to acid rain can be harmful to the plantation. Whilst the acid rain will not kill the trees directly, it does weaken the trees by damaging their leaves, limiting the nutrients available to them, or poisoning them with toxic substances that is slowly released from the soil (Nie, Kuboda, Inoue, & Wu, 2013). Scientists theorise that acidic water dissolves the nutrients and other helpful minerals in the soil and then wash them away before the plants can utilise them. Some minerals such as aluminium is dissolved into the soil through acid rain and can be very toxic to plants. With damaged leaves and plants there can be a domino effect as less photosynthesis will occur and less energy for the plant will be available which will make the plants weak and ultimately kill them (Sun, et al., 2016).

Agricultural activity with the utilisation of chemicals has increased since technology provided us with modern pesticides and fertilisers. These pesticides and fertilisers are full of non-natural occurring compounds, and although most of it can be degraded, there are cases in which they cannot. Overtime, they seep into the ground after mixing with water and slowly reduce the fertility of the soil. The composition of the soil is affected by these chemicals thus making it easier to erode by water and air (Wei, Liu, Zhang, & Qin, 2016). For pesticides, many plants associated with this soil absorb the pesticides and when it comes to the plant decomposing, they cause soil pollution since they become part of the land (Kukreja, 2009).

Accidental oil spills from oil leaks or even petroleum compounds being spilt mostly occur near petrol stations due to storage or transportation. These compounds present in the fuel deteriorate the quality of the soil and make them unsuitable for cultivation. These chemicals can enter groundwater through the soil and drains and

make the water undrinkable creating a much larger issue environmentally and socially (Kukreja, 2009). A study performed by Ekundayo and Obyekwe investigated the effect of an oil spill on soil physicochemical properties of a spill site in Nigeria (Ekundayo & Obuekwe, 2000). They found that the top layers of the soil had a total hydrocarbon contaminant concentration of around 20 ppm and that the oil had penetrated to a depth of 8.4 metres into the soil with the concentration of the hydrocarbons increasing as depth increased (Ekundayo & Obuekwe, 2000). The major contributors to soil pollution are the oil wells, oil storage facilities, refineries and transport hubs as they deal in large volumes of oil (Ramadass, Megharaj, Venkateswarlu, & Naidu, 2015).

Pollution from waste disposal is a major growing area of concern. The waste that is dumped on the soil contains a vast number of compounds which are not environmentally friendly and can seep into the soil. Biological waste from sewers or from diapers etc. can also contaminate the soil. This occurs as waste from faeces and urine can potentially contain many compounds of concern, which cannot be broken down naturally (Kukreja, 2009). For the most of it, once the sewage contamination source is eliminated then the remaining contaminants usually breakdown however, there is the possibility of having toxic material in the waste.

A major form of pollution in soil is inorganic pollution. Heavy metals are the biggest problems when looking at inorganic pollution in soil. Heavy metals are elements that have high density and are considered toxic and poisonous at low concentrations. Some examples of these are mercury (Hg) and lead (Pb), arsenic (As), cadmium (Cd) etc.

With these heavy metals being of concern in the environment, they cannot be destroyed as such (they are elements) and there are not many ways of removing them cheaply. The most common solution used with soil containing heavy metals is the dig and dump method. Whilst this is giving a temporary solution, it is not removing the pollutants completely. It is however just using up space.

To remove inorganic pollutants, trees, plants and microorganisms are being used to sequester inorganic compounds for later removal. This is known as bioremediation. Although in the long term it can take years to complete which for commercial

reasons is not usually thought to be fast enough. Bioremediation is generally better suited to removal of organic pollutants.

Solvent washing is also being used to remove inorganics but has proved to be very costly and there is also the question of what to do with the contaminated solvents after completion.

Inorganic soil pollution can alter the pH of soil (Reijonen & Hartikainen, 2016). Heavy metals have positive ions which react with soil thus altering the pH of the soil. It is found that the relationship between heavy metals and pH are that the higher the pH of soil, the higher the concentration of the heavy metals will be (Bellingham, 2005). Higher pH allows more metals to be dissolved in the soil and immobilises the metals. This in turn keeps increasing the pH of the soil (Wuana & Okiemen, 2011). This change in pH as discussed above can have concerning effects on an ecosystem. Heavy metals are very mobile and so the area of contamination can increase easily. To allow metals to move in the soil, low pH must be obtained.

A plausible solution to soil pollution could be to use minerals like soil and sand which are polluted with both inorganic and organic contaminants and use them in the mixture of concrete. These pollutants will be trapped within the concrete for years and give a temporary solution. This concrete application could be used in driveways, roads, carparks etc. where the quality of the concrete is not required to be high. There are other soil remediation techniques, however, these will be discussed in depth in section 2.3.

### 1.3 Organic Chemical Pollution

Though there are inorganic and organic pollution in soil, this study looks specifically at organic pollution. Organic chemical pollution is one of the major forms of pollution in this world (Alvarez, Carral, Hernandez, & Almendros, 2016). As noted before, the removal of organic chemical pollution is very expensive and most countries just do not have the funds or materials to be able to carry them out. This will be further explained in section 2.2.

One of the major pollutants in the world are persistent organic pollutants, better known as POPs. POPs are chemicals that's are toxic to the environment because they can reside in the environment for several years before breaking down

(UNEP/GPA, 2006). They include 12 major chemicals, aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene, mirex, polychlorinated biphenyls, polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans, and toxaphen (Pariatamby & Kee, 2016). Many of these are no longer in use anymore however it is found that some developing countries continue to do so. Now, additional substances such as carcinogenic polycyclic aromatic hydrocarbons (PAHs) and certain brominated flame-retardants, as well as organometallic compounds such as tributyltin (TBT) have been added to the list of POPs (Caribbean Environment Programme, 2015).

The other major type of pollutant in soil is petroleum. It is found that soil due to oil spills are heavily contaminated. It is also found that soil near places like gas stations have polluted soil. This in turn is very harmful to the environment and must be removed to provide a cleaner and greener environment.

Though the major form of pollution are POPs and hydrocarbons from fuels, lubricants and other similar compounds. If something as such as milk was spilt in large quantities, that can also create concerns of becoming a form of pollution.

The major areas that can be polluted organically, both naturally and due to human activities are soil, water, built spaces, farmlands, forests and air. While there is a whole lot of work being done on the pollutants, soil pollution is an area that has been looked at quite extensively and has been a major concern for a long time. Though there are current remediation techniques which do work, it is essential that a cheaper and more efficient remediation technique is used so that it can be performed on a larger scale more frequently.

#### 1.4 Past Research – Students

There has been quite a lot of research done on RBM particularly at AUT University. Robertson has been looking at RBM over the past decade and has been looking at how it works including its mechanisms. Many students have worked with Robertson and have researched how milling various minerals differ, how altering the milling conditions differ and how various types of compounds behave (Robertson, 2013).

In 2004, Tristan Bellingham did his doctoral research in RBM. Bellingham had looked at a large number of soil matrices. Soil samples from two contaminated sites in New

Zealand were taken, quartz sand, crushed glass, river sand, beach sand, top soil, clay from a building site and slag were all used in this research (Bellingham, 2005).

DDT, DDD, DDE, DCB, inorganic chloride, diphenyl methane, charcoal, chlorobenzene, bromobenzene and naphthalene were the compounds used in the research. Each of those compounds were milled with the various minerals along with changing milling parameters such as ball size, milling time, ball to mineral ratio and contaminant concentrations. The intermediates and headspace analysis of the gases formed during milling were analysed with each mill run.

Bellingham concluded that the grinding of inorganic soil matrices resulted in the formation of reactive species on the freshly formed surfaces which react and destroy the organic compounds. It was found that all compounds are destroyed using the ball mill and just like Magoha, increasing the milling time gave higher destruction (Magoha, 2004). Bellingham recommended that mechanochemical destruction should be used for the remediation of contaminated soils rather than the destruction of pure pesticides.

It was also concluded that using too many balls can result in no movement from the balls within the milling jar and therefore contaminant destruction was limited. The ratio of balls to mineral is important. Bellingham found that using a low number of balls with a high volume of mineral resulted in destruction taking longer and therefore recommended for a laboratory scale ball mill with a 500 mL jar, 50 g to 100 g of mineral with 20 balls with a diameter of approximately 20 mm was ideal (Bellingham, 2005).

Happy Magoha in 2004 worked with Robertson on RBM and looked at the destruction of polycyclic aromatic hydrocarbons (PAHs) and aliphatic hydrocarbons in soil. The PAHs that were investigated were naphthalene, phenanthrene and anthracene and the aliphatic hydrocarbons were n-eicosane and n-octosane. Magoha used different minerals to test them with including scoria, clay, silica and slag. Milling condition like number of balls and milling time was also varied in some experiments. The addition of butylated hydroxytoluene (BHT) and paraffin wax was also looked at to see if they could catalyse the destruction. Ultimately, the aim of the study was to determine the destruction efficiency of the compounds using RBM.

What Magoha found was that changing operation parameters such as ball to soil ratio, milling duration, mineral type and the contaminant properties affect the rate and amount of contaminant destruction. When more balls were used, Magoha obtained higher destruction. Likewise, increasing milling time did the same.

The PAHs were found to be easier to destroy compared to the aliphatic hydrocarbons. Magoha concluded that because the PAHs experimented with acted similarly, other PAHs would be expected to behave the same. The aliphatic hydrocarbons were however destroyed at a slower rate. No intermediate products were observed for all the compounds even though there was an expectation of intermediates for the 28, 25 and 20 carbon containing compounds. By adding butylated hydroxytoluene (BHT) and paraffin wax, the destruction only slowed down. It was found that the hydrocarbons were simply competing for the radicals (Magoha, 2004).

In 2006, Niko has looked at the destruction efficiency of RBM on naphthalene and pyrene. Niko looked at the exchange nature of deuterium oxide ( $D_2O$ ) on naphthalene and pyrene and the intermediate products of both during the milling process.

Niko found that after 5 minutes of milling, naphthalene was completely destroyed where pyrene was completely destroyed after 15 minutes.  $D_2O$  exchange between the two molecules occurred. The naphthalene M+1 peak (one  $D_2O$  exchange on the molecule) had shown an increase in intensity as milling duration increased. Pyrene showed an increase in the M+1 peak too but was not as intensified as naphthalene. Quantitatively, naphthalene showed around 60%  $D_2O$  compared to pyrene which only showed around 35%.

The effect of the milling duration on the  $D_2O$  exchange on the molecules showed that as milling time increased, energy levels increased too therefore Niko concluded that H radicals or D radicals, must have been forming in the reaction and that D/H exchange was quite extensive (Niko, 2006).

In 2008, Zheng Xi Zhang used lead oxide, cupric oxide, magnesium oxide, zinc oxide and sodium hydroxide with quartz in the ball mill. The primary aim was to investigate the trapping of metals using two extraction methods. The two extraction methods that were compared were the acid digestion of sediments, sludge and soil, EPA

method EPA3050B. The second was the exhaustive HF digestion method based on ASTM C146-94a which is a test for chemical analysis in glass sand. Using the two analyses, the total recovery of metals was determined (Zhang, 2008).

Zhang found that the elements extracted by the EPA3050B method decreased in a negative exponential way with milling time. Zhang concluded that the metals were strongly sequestered into the fractured quartz. Total HF digestion of the insoluble matrix gave ideal results as the “lost” elements were detected in this method (Zhang, 2008).

In 2009, Shu Zhou focussed primarily at the headspace analysis. Zhou used specific gas detector tubes to determine the concentration of CO<sub>2</sub> and H<sub>2</sub>. The breakdown of the compounds was analysed and found the compounds were being broken down when being destroyed in the ball mill.

Zhou found that aliphatic compounds were broken down to small fragments such as methane, ethane and propane along with the other alkane gases. This is better shown in the figure below. Within 5 hours of milling, they were mainly converted to CO<sub>2</sub>, H<sub>2</sub>, elemental carbon and methane (Zhou, 2009). This work helped to answer one major question about where all the carbon went to.

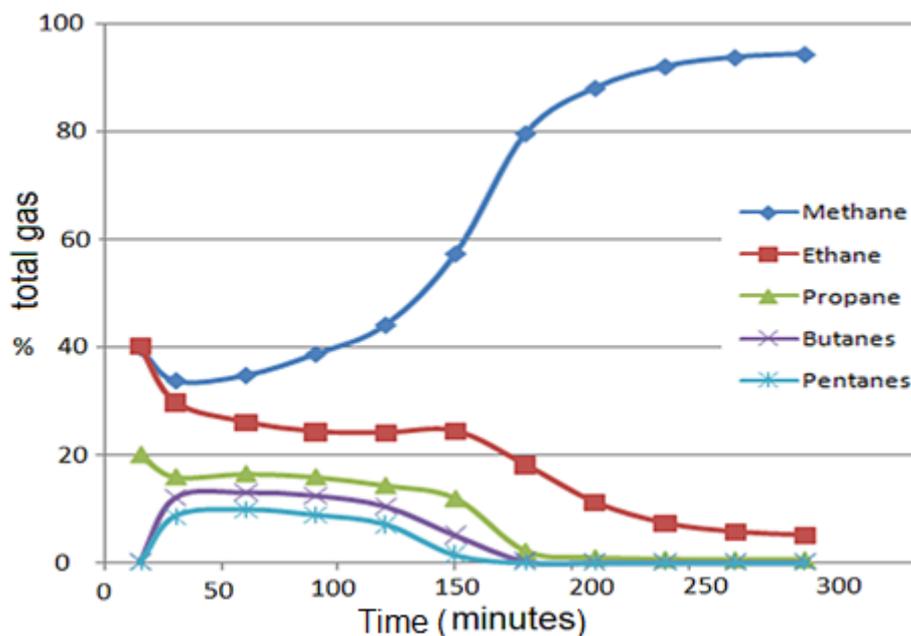


Figure 1 – Graph showing % total gas versus milling time of dodecane (Zhou, 2009)

In 2011, Ali Anwar had looked at the effect of soil type, water and organic materials on RBM destroying organic compounds. This study looked at the destruction rates of naphthalene, chloronaphthalene and diesel in various soil types. As past studies showed that water was reducing the efficiency of the destruction, the reason behind it was investigated. The effect of organic matter on the destruction of naphthalene was also investigated by the addition of cellulose powder in the soil samples. Anwar looked at how RBM effected the soil health by seeing if it can sustain plant life and if bacteria in the soil would survive the milling conditions (Anwar, 2011).

Anwar found that quartz had the highest overall destruction rate followed by scoria, limestone, subsoil, greywacke, china clay then terracotta clay. The effect found on the destruction was that the water reacted with the radicals generated on the reactive surfaces, therefore reducing the total number of radicals available to destroy the contaminant compounds.

The addition of cellulose powder in the soil decreased the destruction efficiency of the milling process. Finally, the soil health test found that the plants could not sustain life in the milled soil however if mixed with clean soil then the plant was able to sustain a healthy life. The bacteria, however did not survive the conditions in the ball mill due to the heat and friction produced inside the jar while milling (Anwar, 2011).

Also in 2011, Kelvin Soo looked at the rates of formation of carbon and other gases from RBM of organic compounds. The research proved to be harder than when it was initially proposed and though it was possible to measure the formation of carbon and show it was a mixture of both graphitic and amorphous carbon, the quantification of the results deemed unsatisfactory as the data was too random (Soo, 2011).

The investigation into other gases formed gave results as expected from previous research done by Zhou. Soo concluded that the radicals formed reacted with the carbon dioxide to give methane or methyl radicals. Which then formed methane and other longer hydrocarbons along with water. Therefore, the major products formed from milling were carbon, methane, carbon dioxide, hydrogen gas and water. Traces of nitrous oxide were detected during analysis when milling xanthine, however, due to being at such low amounts, it was not investigated further.

Nitrogen containing cyclic hydrocarbons like xanthine and imidazole delayed the formation of methane from carbon dioxide. Though, milling of other organic

compounds in nitrogenous environments only increased the rate of methane formation, there were no traces of nitrogen oxides. Soo recommended from his results that when doing RBM in a full-scale mill test, it is necessary for a pressure venting system and the formation of flammable gases at low concentrations should be taken into consideration. A part of the research was to look at any organic compounds that were resistant to mechanochemical destruction. The compounds that showed slow destruction were the long chain fatty acids (Soo, 2011).

Kapish Gobindlal looked at the mechanochemical destruction of diesel constituents via RBM in 2013. This study investigated the relative destruction rates of the hydrocarbon components in diesel and compared it to destruction rates of PAHs. Gobindlal also looked at the suitability of using diesel as a standard test compound for the regulation of full scale mill applications. Gobindlal also tried to compare the relative rates of destruction of linear and branched hydrocarbons.

The results showed that diesel gave consistent quantitative results to use diesel as a standard test compound. The relative rates of destruction of diesel were very similar to small PAHs, small linear hydrocarbons and small branched hydrocarbons (Gobindlal, 2013).

In 2014, Ethan Creighton looked at the relationship between ionization energy and the rate of destruction of organic compounds during RBM. Naphthalene was used as a standard in this study for comparison with the results as it was used in most past research. The other compounds milled were aniline, propyl acetate, decane, phenanthrene, tetraphenylporphyrin (TPP).

Creighton found that there is a relationship between ionization energies and destruction rates. The results it was concluded that overall, as ionization energy increased, the amount of destruction decreased. The TPP was not able to destroy completely however there was a colour change from blue to purple which gave indication that there was some form of chemical change (Creighton, 2014).

Also in 2014, Franko Schrupf looked at the radical detection during RBM of organic compounds. Schrupf focused on the specific rate and the detection methods of the production of quartz radicals using RBM but primarily tried to prove the existence and rate of production of radicals.

The specific rate of formation was measured by neutralization using 2,2-diphenyl-1-picrylhydrazyl (DPPH) which is a radical scavenger. The DPPH was dissolved in ethanol to be used as an extraction solvent. The colour change of the quartz sample in DPPH ethanol solution was analysed on the UV-Visible Spectrophotometer at a maximum wavelength of 520 nm.

The results showed that there was a relationship between the energy, number of collisions and duration of milling with the development of quartz radicals (Schrumpf, 2014).

## 1.5 Research Rationale

It is evident from past research that ball milling destroys organic molecules. Certain types of molecules are faster to destroy compared to other ones is but this has only been assumed.

The research carried out was to look at how different functional groups on organic compounds are destroyed from the ball milling process. Past researchers have come up with data and results which indicate that the ionization potential of compounds plays a major role in how long it takes to be destroyed. This is because they believed that ionization is the major initiator in the breakdown of the compounds therefore this was also researched.

An issue that most researchers have found, is that as soon as the lid of the jar was opened, a “puff” of sample was released meaning the compounds used in the experiments were volatile. It can be assumed that some contaminant sample was lost when this occurred.

To avoid the issue of sample loss, this project looked at large organic compounds, which are less volatile due to their higher boiling points, unlike organic compounds used in the past. The large organic compounds selected for this research were 16 carbon-containing compounds.

In addition, the ionization potential of the compounds was looked at to determine if there is a relationship between ionization and destruction rates.

The idea that the functional group plays a major role in the destruction of the compounds seems obvious but exactly how was not clear. The idea that ease of ionization may be important has its origins in early work by Tristan Bellingham when

it was noticed that the fragmentation of the parent compounds was a lot like the fragmentation seen in electron impact ionization mass spectrometry. More recently Gobindlal and Creighton investigated the relationship between ionization energy and destruction rates but were somewhat hampered by having to use fairly volatile compounds which can be lost during sampling and could significantly affect the results.

Considering these findings, whether ionization is the major initiator and where it could possibly occur on the compound was important to investigate to complete the “picture”. Ultimately, with all the data in this research and with future research, a “look up” table can be constructed where the composition of the matrix (usually the soil) and the molecules being destroyed can be looked up and the operating conditions for the mill calculated.

Specifically, this project did the following:

1. Obtained or synthesised a series of low volatility molecules with near identical structures differing only by functional groups. The C-16 molecule was selected with functional groups on the C-1 position. An exception to this was the ketone as it cannot be on the C-1 position.
2. The compounds were milled and sampled under identical conditions, attempting to make the sampling losses as minimal as possible.
3. Investigated the data to confirm if there was a measurable difference between the destruction and whether the hydrocarbon chain or the functional group was the primary starting point of destruction.
4. Determine if ionization is the major initiator in the breakdown of the compounds and where it could possibly occur on the compounds.

## 2.0 Literature Review

This review will give an insight into pedology, contamination issues, current remediation techniques, mechanochemistry and ionization energy.

### 2.1 Pedology

Pedology is generally defined as the study of soil. The study of soil has been around since the late 1800's and started with the work of Vasily Dokuchaev. Dokuchaev's approach to evolution of soils enabled him to determine all the complex connections between the soil forming factors, including the factors of time and human activity. Pedology provides essential information in real world applications. Areas like modern application of soils, agriculture, environmental issues, land use planning and agroforestry. Currently, research on pedology is branching out to see things, like how climate change effects soil and the interactions of water with soil (Brevik, Weindorf, & Stiles, 2015).

The figure below highlights the textural triangle. It shows the different types of soil that exist and how different combinations of sand, clay and silt can provide the type of soil. This triangle can be used to provide information on what percentage of sand, silt and clay make up a specific type of mineral. It can also assist in the make-up of synthetic soil. For RBM, this can influence the time it takes for compounds to be destroyed as past research has found that destruction in clay is a lot harder than destruction in sand (Magoha, 2004). Following this concept, knowing the composition of the mineral being milled can provide a clear indication of how long the samples should be milled for.

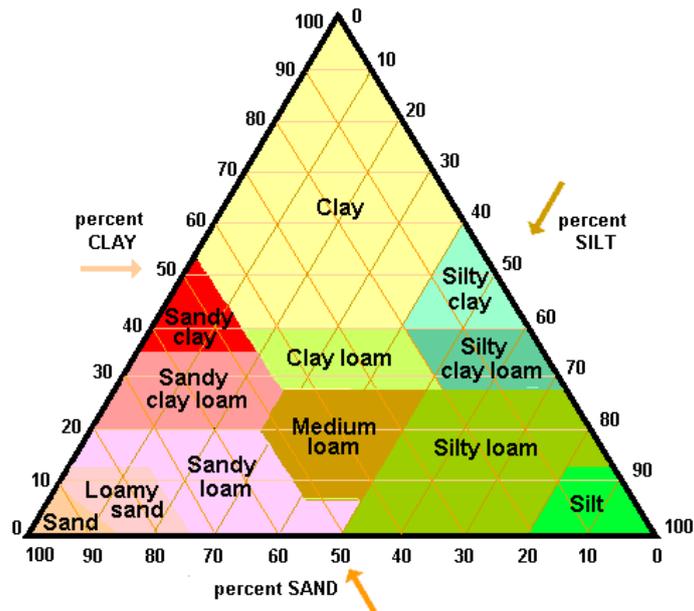


Figure 2 - The Textural Triangle of Soil used to describe soils (Gobindlal, 2013)

With anthropogenic activity heading towards soil becoming more contaminated with a range of different pollutants, it is necessary to understand what degree of impact we have on the soil ecosystem.

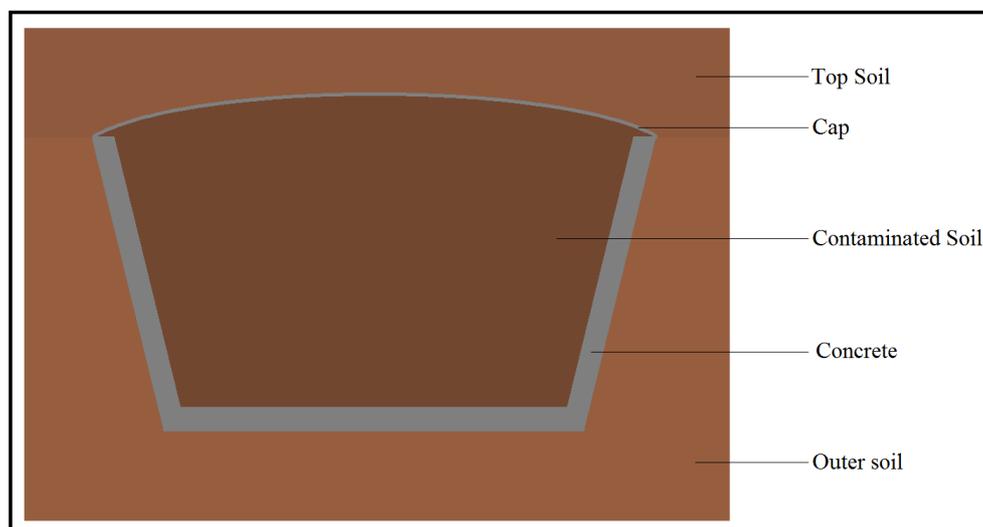
## 2.2 Current Remediation Techniques

There is a vast range of remediation techniques. These methods are used in various countries, however, can be costly both financially and to the environment. Taking that into consideration, it is good that these methods do work to satisfactory standards with each of them having positive and negative aspects.

RBM is an alternative to these methods discussed below. While RBM cannot remove inorganic pollutants, it can be targeted to be used for organic pollutants specifically. This section will discuss the methods currently out there in the market for all types of soil pollution.

### 2.2.1 Excavation and Isolation

The method better known as 'Dig and Dump' is one of most utilised methods as it is cheap and is simple to carry out. This method can be classified as being passive, as the soil is not treated but rather just transported to another area. The only major cost involved with this method is transporting the contaminated soil to the location it is to be dumped in. This method involves containing the contaminated soil in a capsulated area usually made of cement on the sides and bottom to prevent leakage into the outer soil and a suitable cap at the top with top soil above.



*Figure 3 – Dig and Dump encapsulation diagram*

There are benefits with this method as stated before, it is very cheap to carry out. The materials required are of low cost and does not require any advanced machinery. It is the most common way of getting rid of contaminated soil. This

method is very similar to how many countries use digging and dumping for other types of waste disposal.

The disadvantages with this application is that it does not get rid of the contamination in the soil. Overtime some of the pollutants may degrade but does not make a major difference. This can cause an issue if this land was to be used for other purposes besides a disposal site in the future.

There are now more advanced designs to this application.

### 2.2.2 Low Temperature Thermal Desorption (LTTD)

Low temperature thermal desorption (LTTD) can be used to remediate some soil. The process uses steam as the major mechanism to remove the contaminants. As shown in the figure below, the process is quite simple. The waste is heated to temperatures between 90°C to 320°C (Williams, 1998). This application has proven to be successful for remediating petroleum hydrocarbon contaminated soils. All types of soil can be put through LTTD and this process proves to have minimum 95% efficiency at removing contaminants (Anderson Environmental Consulting, 2012). Though contaminants with higher boiling points may not be removed, if using this method with the lower end of the temperature, this method does not harm the organic components in the soil which enables the treated soil to retain the ability to support future biological activity (Williams, 1998).

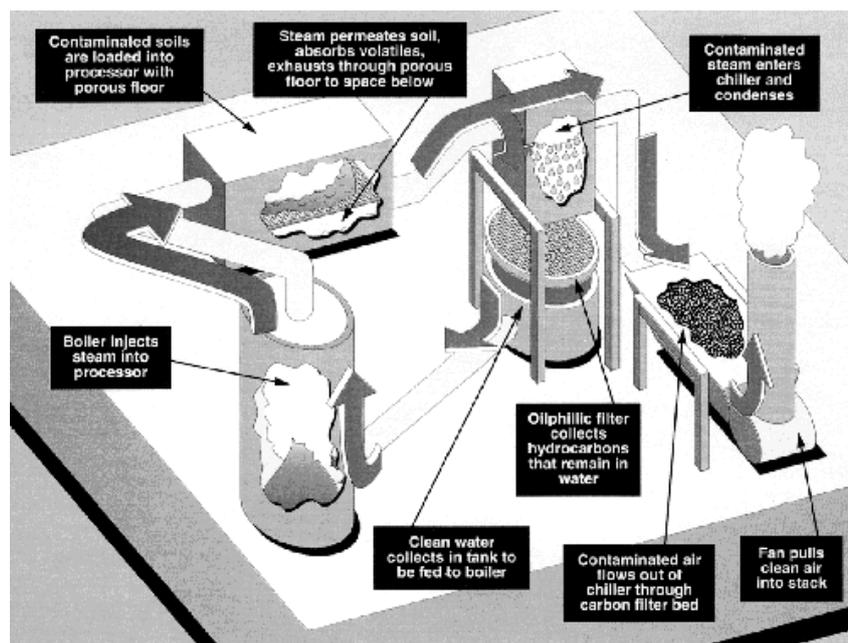


Figure 4– Flow chart of low temperature thermal desorption (LTTD) (Anderson Environmental Consulting, 2012)

### 2.2.3 High Temperature Thermal Desorption (HTTD)

High temperature thermal desorption (HTTD) is like LTTD however using more sophisticated technology along with higher temperatures. This full-scale technology allows soil to be heated between 320°C to 560°C. This method is usually combined with incineration, solidification/stabilization or dechlorination but is site specific dependant (Canning, 1999). This technology has proven to produce a final contaminant concentration under 5 mg/kg which is very low (Williams, 1998).

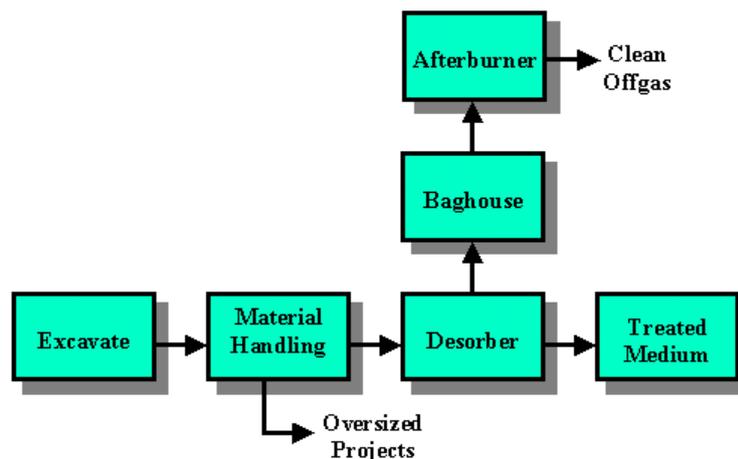


Figure 5 – Flow chart of high temperature thermal desorption (HTTD) (Williams, 1998)

HTTD produces gas which needs to be treated. A study conducted in U.S.A showed that citizens living in a 7km radius of a plant may be exposed to carcinogenic material in the air due to the gases produced during the incineration (Williams, 1998). With such serious risks, engineers and scientist are working to provide more efficient ways to avoid having such an effect on the community and environment.

### 2.2.4 Vitrification

Vitrification is a high temperature treatment of contaminated soil where the final product formed is glass. This process uses such high heat, that most organic contaminants either vaporize or are destroyed. Vitrification may be performed ex-situ (off site) or in-situ (in the reaction mixture) although in-situ processes require lower energy to perform and the cost is lower.

In-situ vitrification involves passing an electric current through the soil using an array of electrodes inserted vertically in the soil. A group of four electrodes is referred to as a melt. If the soil is too dry, it may lack conductivity. To overcome this, flaked

graphite or a glass frit is placed between the electrodes to provide an initial flow path for the current. Once initiated, the soil begins to melt and the melt grows outward and down as the molten soil usually provides additional conductance. A single melt can usually treat up to 1000 tonnes of contaminated soil with a depth of 20 feet at typically 4 tonnes per hour (Allahbadia & Gandhi, 2015).

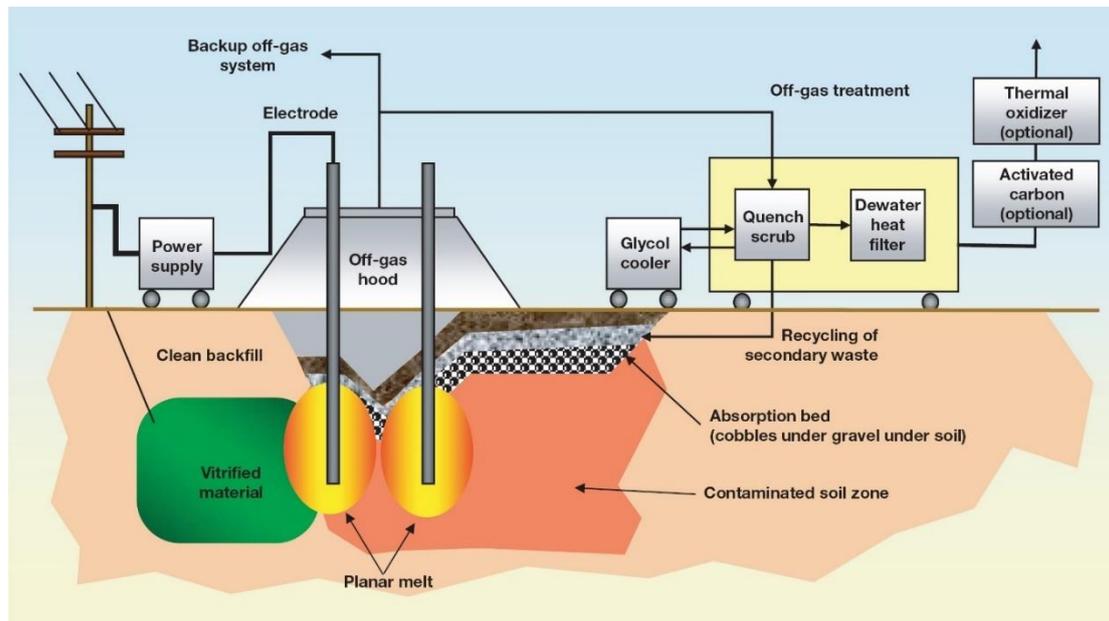


Figure 6 – In-Situ Vitrification diagram (Allahbadia & Gandhi, 2015) (EURSSEM, 2009)

With ex-situ vitrification, costs such as excavation, pre-treatment, melting and mixing is required prior to vitrification. The cost involved with melting is high and this is where the ex-situ becomes more expensive. Only after the pre-treatment, electrodes can be used to carry out the vaporization and destruction.

### 2.2.5 In-Situ Plasma Vitrification (ISPV)

Due to the limitations of vitrification using electrodes, a team at Georgia Tech Research Institute (GTRI) developed a modified vitrification method for soil remediation. They developed it to use a plasma in place of electrodes. Plasma vitrification was originally developed by NASA around the 1960s but was never used for remediation purposes.

Plasma is one of the four states of matter (i.e. solid, liquid, gas and plasma) and consists of highly ionised gas at high temperatures usually 2,000°C to 20,000°C. A plasma torch is used in this technology which converts electrical energy into thermal energy. The benefit of using a plasma over the traditional electrode is that it can

eliminate many of the limitations in terms of soil environment, depth, and volatility observed in other traditional in-situ vitrification technologies (Harjanto, Kasai, & Nakamura, 2000).

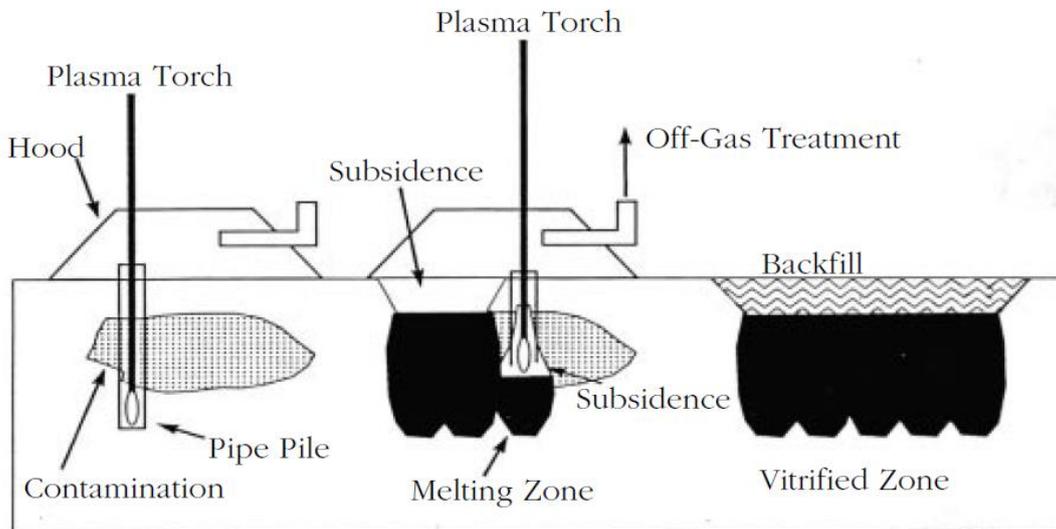


Figure 7 - Schematic Illustration of In-Situ Plasma Vitrification (ISPV) of Contaminated Materials (Fox, Circeo, & Martin, 2001)



Figure 8 - One-Megawatt Plasma Torch Prior to Insertion into Borehole in the Test at the Savannah River Site (Fox, Circeo, & Martin, 2001)

Thus, far the remediation techniques discussed are thermal remediation techniques. Biological remediation techniques have also been developed including phytoremediation, bioremediation and mycoremediation.

## 2.2.6 Phytoremediation

Phytoremediation is soil remediation using plants to absorb the contaminants in the soil. With conventional soil clean up techniques like soil washing costing around \$250 per cubic yard and incineration costing about \$1,020 per cubic yard, phytoremediation proves to be less costly and is approximately about \$80 per cubic yard (Black, 1995). Over the past decade, phytoremediation has gained a lot of attention because of its simplicity. Phytoremediation is applicable to a broad range of contaminants including many metals and organic pollutants (Schwitzguebel, 2001).

The mechanism of phytoremediation involves rhizofiltration (absorption or adsorption of soluble contaminants into plant roots from water), phytostabilization (immobilization of soil contaminants through absorption by plant roots), phytodegradation (break down of contaminant molecules by plant enzymes) and phytoextraction (the process of plants absorbing the broken-down contaminants). Subsequently, the decomposed molecules from the pesticides are released in the air in the process known as phytovolatilization. Phytostimulation occurs at the plant root zone known as the rhizosphere where microbes break down the organic contaminants (Wong, 2004).

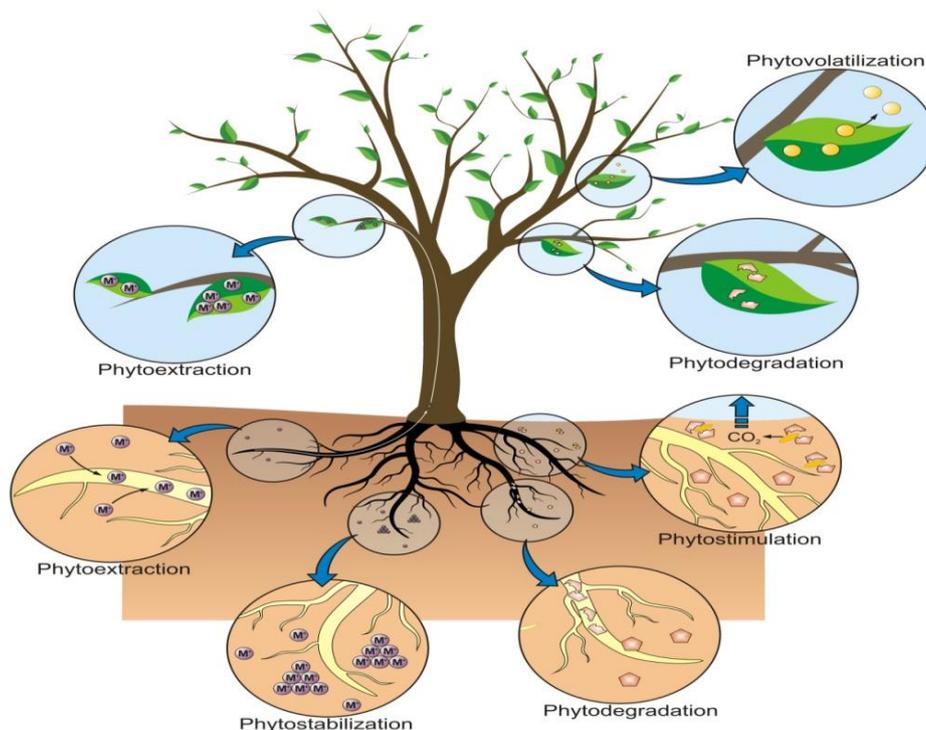


Figure 9 – Diagram of phytoremediation (Paulo, João, Mayank, Rohan, & Paul, 2014)

No special training required for phytoremediation. Trees are simply planted in the polluted soil area. While trees like willows can be used, the more common methods use fast growing plants like mustard in the early stages (Choudhury, Islam, Ahmed, & Nayar, 2016). Another benefit of this approach is that it reduces the volume of contaminated material necessary for disposal as areas with heavy metals commonly are treated by removing the soil to certain depth and depositing that soil in a hazardous landfill (Economic Research Service, 1996). Another major benefit of phytoremediation is that it decreases the risk of exposure of potentially toxic compounds via wind erosion (Wong, 2004).

Along with the advantages of phytoremediation, there are also disadvantages. One major disadvantage is that several crops may need to be grown to cleanse the soil when there is a large amount of contaminant (Wong, 2004). This requires time and it may therefore take years to remediate the soil. This is not practical for in many circumstances. Another disadvantage is that plants that absorb heavy metals and metalloids may be eaten by wildlife, leading to metals in the food chain affecting human health (Wong, 2004). However, in many cases, plants have shown to not absorb the pollutants, but in turn stabilize the soil surface which is just as important with the pollutants being under the top layer of soil (Wong, 2004).

### 2.2.7 Bioremediation - Bacteria

Bioremediation is the use of microorganisms to break down hazardous organic material to harmless compounds like water and carbon dioxide gas. The degradation activity changes the chemical and physical properties of soil including pH, moisture content and aeration properties (how air is passed through soil).

With the addition of specially adapted microorganisms, the treatment is enhanced. Bioremediation with bacteria can be carried out in two major ways (Foght, April, Biggar, & Aislabie, 2001). Most commonly in-situ treatment is used where the microorganisms like bacteria are added and left alone for the breakdown to occur (Hilberts, Eikelboom, Verheul, & Heinis, 1985). The microorganisms are usually added to the saturated zone of the soil. In addition to the microorganisms being added, nutrients are also added, an oxygen source such as hydrogen peroxide. Aerobic bacteria are most commonly used, however genetically modified anaerobic bacteria have also been used (Wilson & Jones, 1993).

The other method involves using a bioreactor. The contaminated soil is excavated and moved to a specific reactor for treatment. The soil is made into a slurry by adding water and then treated in the reactor where the bioremediation conditions are enhanced. A major advantage of this method is that there is a lot of control over the conditions and it is therefore usually the fastest method to remove soil contaminants. Bacteria are introduced in batches to enhance the degradation rate. After each batch, the soil is passed through a water separation system and the water is recycled (Wilson & Jones, 1993).

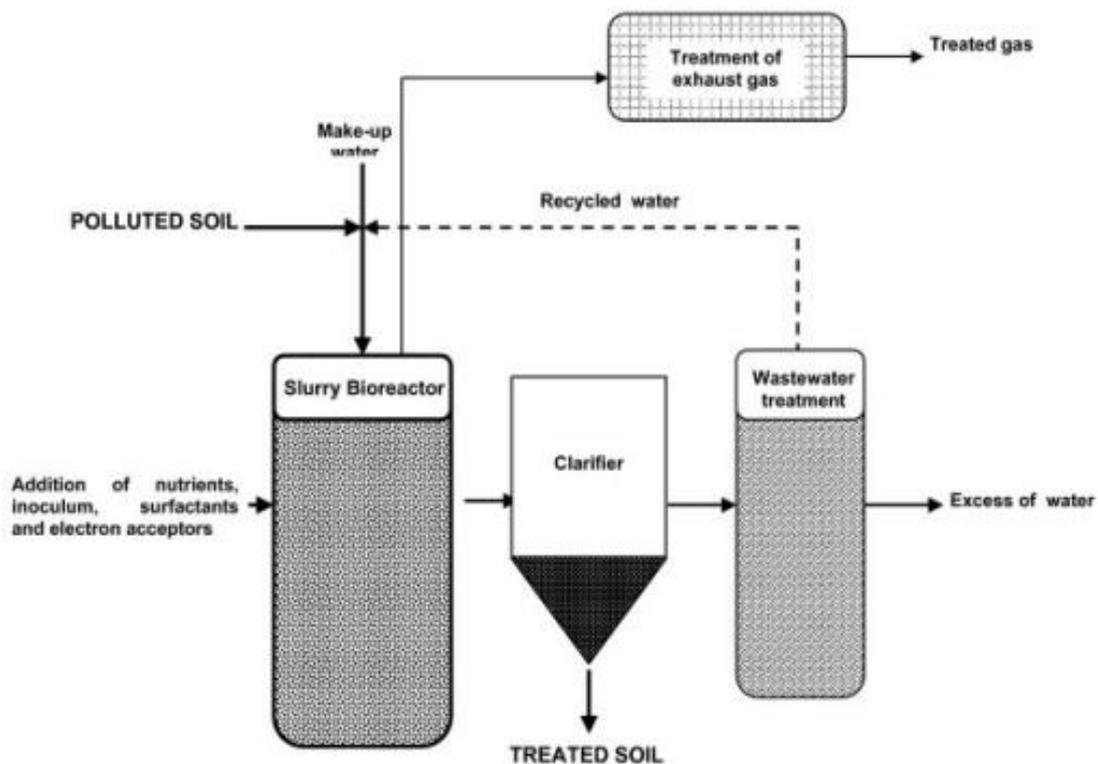


Figure 10 – Diagram of how a bioreactor works in soil remediation (González & Varaldo, 2008)

A major advantage of using bioremediation is that it is cost effective when compared to thermal and chemical remediation (González & Varaldo, 2008). Furthermore, the contamination is not transferred to another location, whereas this can occur for a dig and dump. Despite several advantages stated, the extent to how efficient it is at removing contaminants is not yet fully known. (Jesus & Muniz-Hernandez, 2014).

### 2.2.8 Mycoremediation

Mycoremediation is a form of bioremediation where fungi are used to remediate soil. This was first discovered in 1985 when white rot fungus *Phanerochaete*

*chryso sporium* was found to can degrade some harmful environmental pollutants (Kaur, Sharma, & Parihar, 2015). Since then, remediation using *P. chryso sporium* has been explored. In recent years, it was found that two white rot fungi, *Irpex lacteus* and *Pleurotus ostreatus*, are very effective at degrading organic contaminants in soil (Bhatt, Cajthami, & Sasek, 2002).

Other species used involve mycelia of oyster mushrooms which have been shown to be very effective at removing organic contaminants in soil. Lately, research has focussed on determining which fungus is best for each contaminant type (Valentin, et al., 2013).

### 2.2.9 Soil Washing

Soil washing is used to remediate soil contaminated with both organic and inorganic constituents. This involves a large amount of energy between the contaminated soil and an aqueous based washing solution (Gang, Guo, & Hu, 2016). Soil washing involves chemical and/or physical processes which lead to the separation, segregation and volume decrease of hazardous material and the chemical alteration of contaminants into non-hazardous material and substances.

The process involves five major steps. Firstly, the contaminated soil is excavated. Here the large debris or soil particles larger than around 2 inches are separated out before treatment. Then the soil is treated by entering a soil scrubbing unit. Soil with sand only requires a rinsing treatment as the contaminants do not adhere to the sand particles strongly. If soil is mixed with silt or clay, a more extensive remedial treatment as the contaminants are easily absorbed and therefore are harder to separate. Next, the solid and liquid components of the contaminants are separated. This is followed by the treatment or disposal of all residues and the wastewater being recycled. At this stage, the contaminants are either destroyed or isolated and have been removed. Finally, the soil is deposited in a new site or same site it came from (Semer & Reddy, 1996).

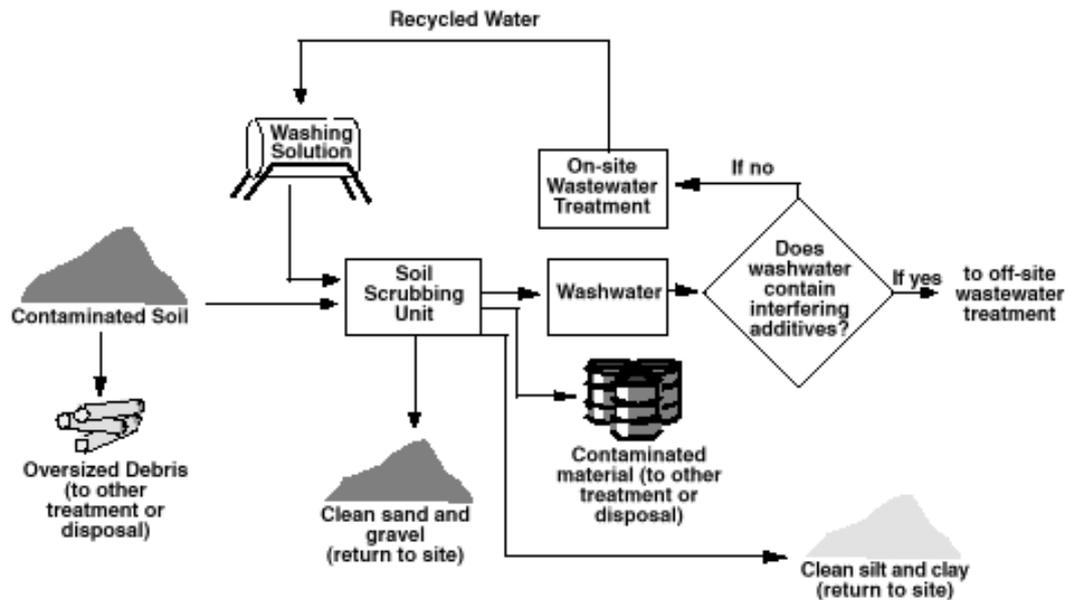


Figure 11 – Steps involved with soil washing (NCEPI, 1996)

The type of chemicals used to wash the soil is dependent on the contaminant type. Usually, water washing with a basic or surfactant agent is used to remove organic contaminants. The types of basic aqueous solutions used as extracting agents include caustic lime, slaked lime or industrial alkali based washing compounds. Acidic aqueous solutions used as extracting agents include sulfuric acid, hydrochloric acid, nitric acid, phosphoric acid and carbonic acid. Oxidising agents are also used and are normally agents like hydrogen peroxide and sodium hypochlorite which chemically change the contaminants and help with the washing process. For the hydrophobic organics and PCBs, organic solvents are used (Semer & Reddy, 1996).

There are a number of advantages to soil washing as a soil remediation technique. Firstly, the entire process is carried out in a closed system which allows all conditions to be controlled. Secondly, the completion of remediation can lead to having a reduction in the volume of contaminant mass. Thirdly, soil washing can remove a large number of contaminant types (Gang, Guo, & Hu, 2016). Another advantage is that the hazardous material can remain on site preventing contamination of additional sites. Lastly, the cost involved is lower than using thermal remediation techniques (Semer & Reddy, 1996).

Alongside the advantages, there are some disadvantages. When only physical processes are used, it is typically found that there is only a small reduction in

contaminant concentration (Gang, Guo, & Hu, 2016). If extremely hazardous contaminants are being removed, then the chemicals that have extracted must be treated. The problem can arise what to do with the extracted. The effectiveness of soil washing is also limited by complex waste mixtures, inhibiting solvent soil reactions, high humic content and high fine grained content (Trellu, et al., 2016).

### 2.2.10 Fenton's Reagent

Many organic molecules are readily oxidised. One of the most effective ways of removing organic contaminants from material is by using Fenton's reagent (Bigda, 1995). Fenton's reagent consists of hydrogen peroxide and iron salts.

It has been found that by modifying Fenton's reagent so it has a high concentration of hydrogen peroxide can enhance contaminant desorption and destruction. The iron present in the soil catalyses the decomposition of hydrogen peroxide to generate  $\bullet\text{OH}$  which is an even more powerful oxidant than  $\text{H}_2\text{O}_2$ . This treatment can occur both in-situ and ex-situ; however, in-situ treatment is more cost effective (Goi & Trapido, 2004).

Once contaminants are oxidised, the compounds can often be taken up by bacteria or even plants. Figure 12 shows the species involved in Fenton chemistry.

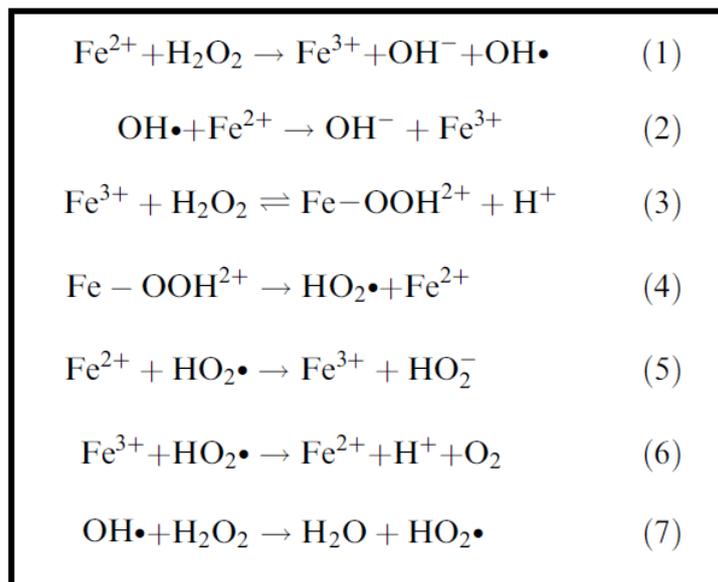


Figure 12 – Reactions involved in Fenton chemistry (Chamarro, Marco, & Esplugas, 2001)

### 2.2.11 Electrochemical Remediation Technology (ECRT)

Electrochemical remediation is carried out on soil contaminated by either organic or inorganic contaminants or with a mixture of both organic and inorganic molecules in the soil. A direct current (dc) electric field is used. The contaminants are transferred using electroosmosis, electrophoresis and/or electromigration (Moreira, et al., 2016). A dc electric field is effective in driving fluid through soil grains and so electrochemical remediation is suitable for fine grained soils with low conductivity.

ECRT works by extracting mobile contaminants from soil particles. Contaminants can be absorbed on the soil particle surfaces or on the soil pore fluid. If the contaminants are solid within the soil particles, only contaminants dissolved in the soil pore fluid or within the soil particles can be extracted.

Electrolytic decomposition of electrolytes occurs at the electrodes where  $H^+$  ions are generated at the anode and  $OH^-$  ions are generated at the cathode. These ions are transferred to the contaminated soil which alters the pH of the soil (Yeung & Gu, 2011).

The electrical signals mineralize organic compounds (e.g. volatile organic compounds VOCs) and mobilize metal contaminants (Moreira, et al., 2016). Low voltage, low amperage electrical fields are used that polarize the soil particles. This initiates redox chemistry within the soil. The ECRT can be carried out in-situ or ex-situ, with again in-situ treatment being considerably cheaper (CPEO, 2010).

There are some limitations associated with ECRT. The rates of reaction are inversely proportional to grain size. Clay and silt containing soil is therefore faster to remediate than soil containing sand and gravel. The working depth of the application is limited by the availability of drilling technology to install the electrodes. Acidic conditions and corrosion of the anode may create difficulties. Species close to the electrode may precipitate leading to the process slowing down. Also, using ECRT alone is not sufficient to remove adequate amounts of contaminants; therefore, it is normally coupled with soil washing procedures (Yeung & Gu, 2011).

## 2.3 Mechanochemistry

Mechanochemistry is the study of chemical reactions that occur when induced by kinetic and mechanical energy. The mechanical energy in RBM is from grinding and impact (Gilman, 1996).

### 2.3.1 History

Mechanochemistry was first discovered by a student of Aristotle who was known by Theophrastus of Eresos, who lived from 371-286 BC. His study was titled "De Lapidibus" which translates to "On Stones". His research deduced that when native cinnabar was ground up with vinegar using a brass mortar and pestle, metallic mercury is acquired.

Although mechanochemistry was discovered prior to this, it is Wilhelm Ostwald who is commonly referred to as the founder of mechanochemistry. Ostwald discovered that displacement of internal structures in matter cause elastic deformation and internal friction. After the 1950's, ideas on the mechanism of mechanochemistry was researched, however, it was found it is most likely due to the immense build-up of heat. In other words, a reactive plasma is formed (Bellingham, 2005).

Mechanochemistry is an ideal method for mining metal. It is also used in the agricultural field. In the last 25 years, the use of mechanochemistry for soil remediation has been increasing and substantial research has been put into this to make it a permanent and well known soil remediation application.

### 2.3.2 Mechanisms

High energy can provide an enormous force that is required to initiate and carry out chemical reactions. This results in deformation and interactions both intermolecular and intramolecular within a compound. (Gobindlal, 2013).

RBM three main interactions occur from collisions. Firstly, ball-ball collisions occur at high forces. Secondly, the ball jar collisions. Finally, ball material collisions which help grind up the material. The collisions fracture the surface and generate immense energy that initiates chemical reactions (Bellingham, 2005).

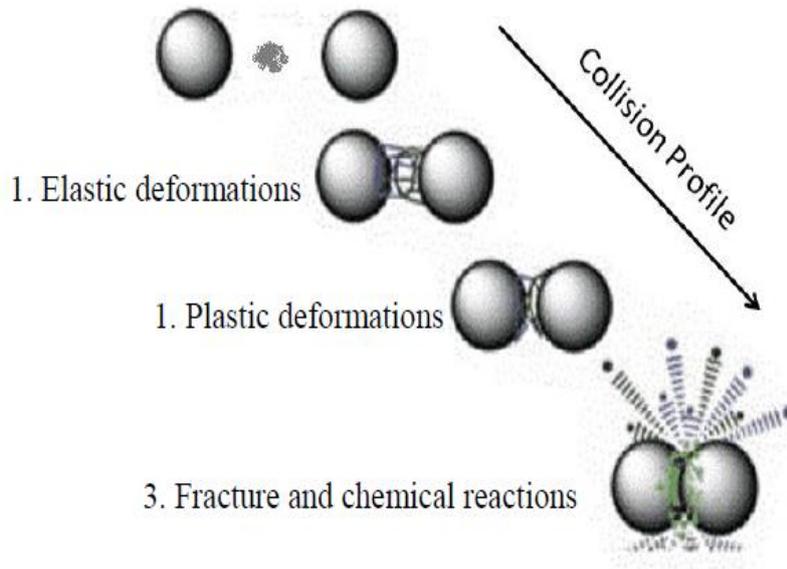


Figure 13 – Collision profile of two balls with alterations in matter (Balema, 2006)

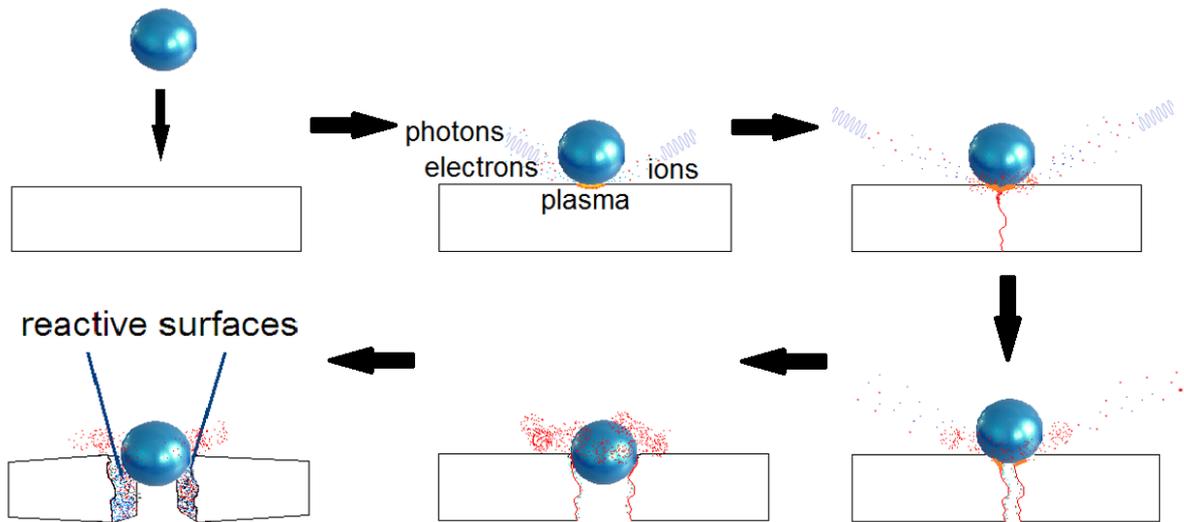


Figure 14 – Basic theory of the mechanism (Robertson, 2013)

When a fracture occurs of the material, radical formation, electron transfers and electron sharing which can destroy chemical bonds are induced. The intense burst of particles and photons can cause bond excitation and rupture within the blast radius. It is assumed that the effect is on a nanosecond scale, so the effectiveness is a function of the energy and the number of impacts per second.

The surface reaction sequence is assumed to be as follows. First, the molecules settle onto the surface. Then the electrons are transferred forming energetic ions and radicals. These radicals are very unstable and initiate the degradation of the

molecules as the energetic ions and radicals fragment smaller ions, radicals and neutral species.

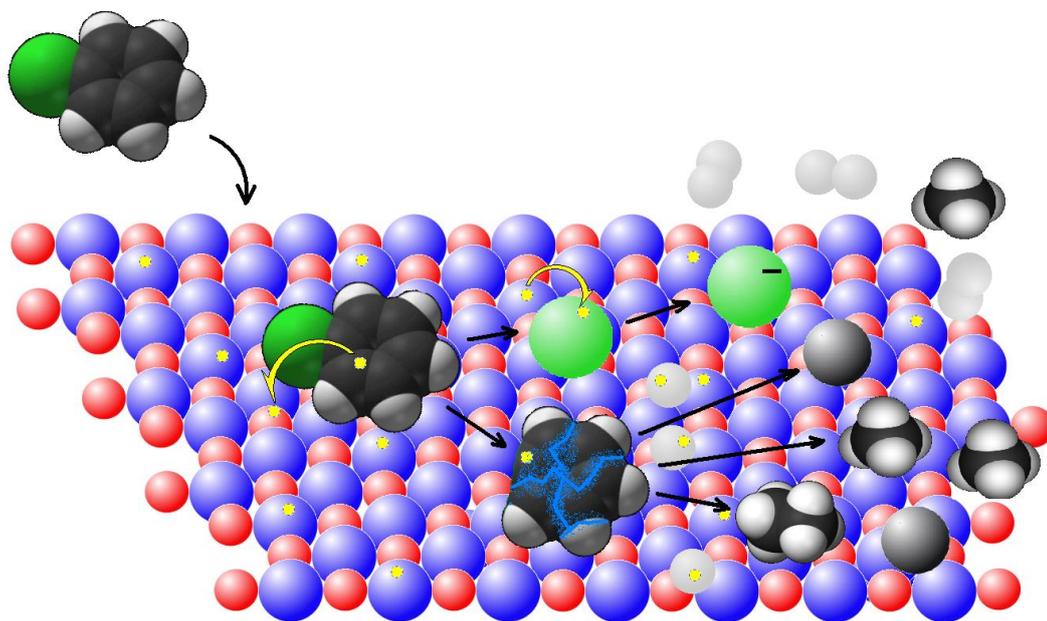
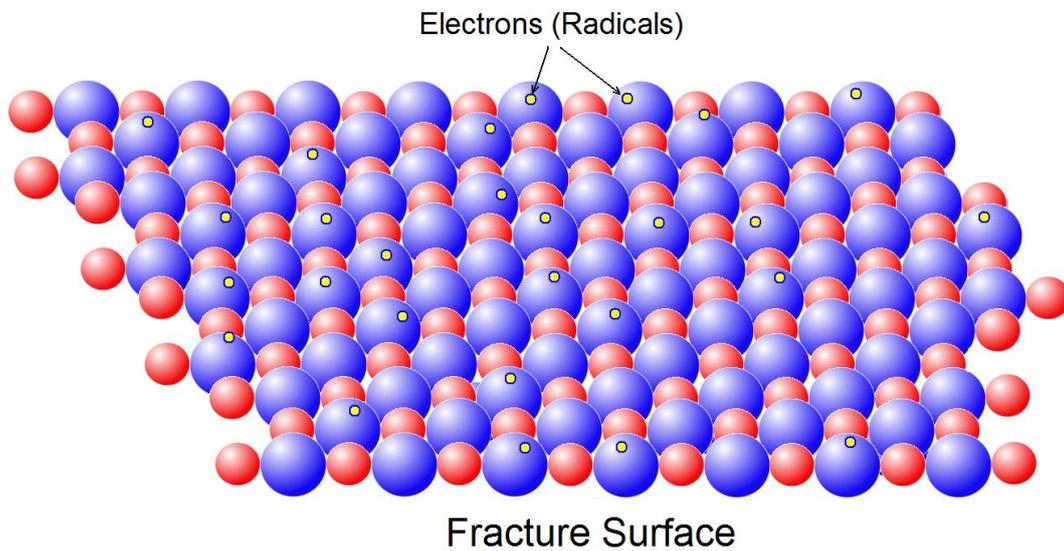


Figure 15 – Image showing how the radicals fragment other species (Robertson, 2013)

There are two basic initiation mechanisms. Electron ionization and photon ionization. Both of these leads to the formation of radicals and the breakdown of the compounds. The radical and ion reactions involved include free radical reactions



Table 1 – Table of ionization potentials of 3 carbon compounds (Industrial Scientific, 1996) (NIST, 2016)

<b>Compound</b>	<b>Ionization Potential for 3-Carbon Compounds (eV)</b>
Propane	11.07
Propanoic Acid	10.41
Methyl Propanoate	9.86
Ethyl Propanoate	10.00
Propyl Propanoate	10.21
Propanol	10.59
Propanone	9.69
Propanamide	9.50
Propanamine	8.78
Propene	10.73
Propanoyl Chloride	10.78

#### 2.3.4 Reactive Ball Milling – Planetary Ball Mill

Ball milling in its simplest form can be thought of as small hammers (the balls) hitting things (the soil particles). Its primary function is to grind material into fine powder. Ball mills are used extensively for the industrial preparation of fine solids such as paint pigments.

The mill consists of metal balls normally made of steel which come in various sizes and quantities. These balls are put in a steel jar along with the material to be ground and the jar is rotated at high speeds in a planetary motion. This type of ball mill is called a planetary ball mill.

The ball mill jar is rotated anticlockwise and has a supporting disc which rotates clockwise creating a planetary motion. The balls move around the rim and fly to the opposite side colliding with each other and colliding with the contaminant absorbed sediments (Montinaro, Concas, Pisu, & Cao, 2012).

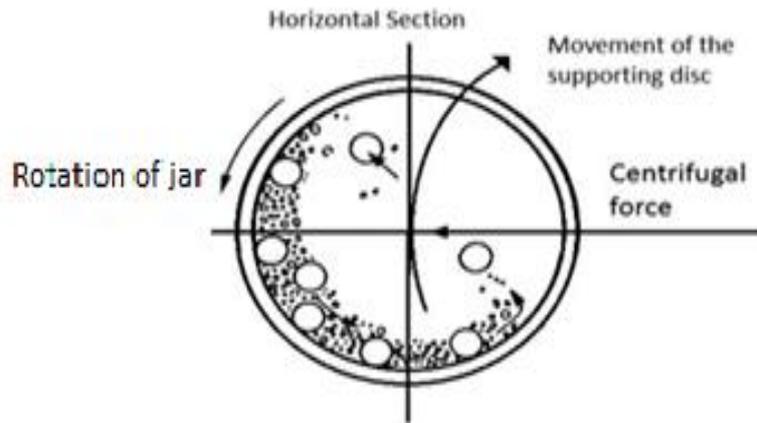


Figure 17 - Cross section of ball mill jar showing how particles are crushed and therefore upon collision molecules are destroyed (Faryna, 2006)

## 2.4 Full Scale Successful Applications

Planetary ball mills are ideal as research tools; however, they lack the capacity, continuous flow capability and energy densities required for practical and effective ongoing environmental decontamination. The EDL MCD™ Reactor was developed in collaboration with AUT University for full scale mill applications and is a modified attritor mill. The reactor was patented and contained a vertically stacked horizontal ball mill arrangement (Robertson, 2013). The stacked mill design allows the mills to run in series, parallel or in combinations depending on how demanding the destruction of the molecules is.

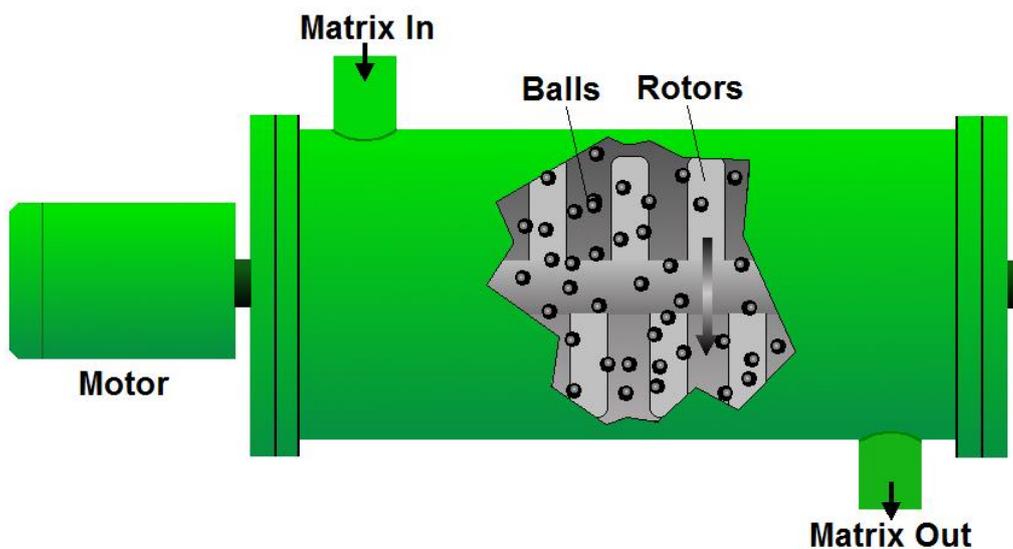
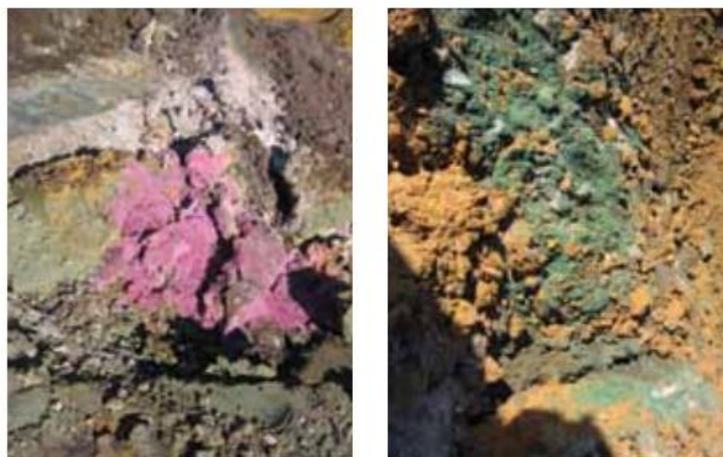


Figure 18 – Diagram of the EDL MCD™ Reactor (Robertson, 2013)



*Figure 19 – Image of the EDL MCD™ Reactor (Robertson, 2013)*

For many years, the Fruit Growers' Chemical Company (FCC) site in Mapua, Nelson, was recognised as New Zealand's most contaminated soil site. In 2007, the site was remediated using the EDL MCD™ Reactor. The compounds which were of most concern was dichlorodiphenyltrichloroethane (DDT), dichlorodiphenyldichloroethane (DDD), dichlorodiphenyldichloroethylene (DDE) and aldrin, dieldrin, lindane (ADL).



*Figure 20 – Contaminants in soil at the old FCC site (Ministry for the Environment, 2011)*

After remediation, the soil was tested and it was found to have little to no contaminants remaining. In fact, the remediation of this soil was so effective that the land is now being used by the public and involves a recreational park. 40% of the site is for the public and 60% of the site is privately owned residential areas. This

was now New Zealand's first major successful soil remediation project (Ministry for the Environment, 2011).



Figure 21 – Old FCC site after remediation (Ministry for the Environment, 2011)

In 2008, a trial of the EDL MCD™ Reactor in the US Naval Dockyard in San Francisco was carried out. This trial proved to be successful in remediating the entire dockyard. The soil initially contained various mixed hydrocarbons and PCB.

Whilst using the EDL MCD™ Reactor, the soil samples were extensively tested and emissions were monitored. Both EDL and US Navy project managers confirmed the successfulness of the project (Robertson, 2013).



Figure 22- Site from the US Navy Dockyard (Robertson, 2013)

In 2009 the EDL MCD™ Reactor was taken to Japan. The sites that were to be milled was the old Tokyo markets which contained inorganic and organic contaminants. The project specifically evaluated decontamination capabilities along with noise emissions (Robertson, 2013). Once again successfully remediating the site and the noise levels were to the standards that were aimed for.

In 2010, the EDL MCD™ Reactor was flown to Alaska by the United States Air Force to clean up and demonstrate the technology at an abandoned DEW Line (Distant Early Warning Line) site which contained radars. This site was operational from 1957 to 1985. The site was an abandoned Active Relay Station (ARRS) in an inaccessible terrain (Robertson, 2013). Research suggested that off road vehicles had damaged vegetation and organic matter. The transportation of chemicals was what led to the contamination of the site and for years there was controversy between the United States and Canada over the remediation (Government of Canada, 2010). The contaminants were various hydrocarbons along with PCB. The EDL MCD™ Reactor successfully remediated one of the sites.

In 2012, the EDL MCD™ Reactor was taken to Vietnam for a demonstration trial at the Bien Hoa airbase. The soil was heavily contaminated with “Rainbow” herbicides. Rainbow herbicides are a group of chemicals that were used by the United States military during the Vietnam War including 2,4-D (2,4-dichlorophenoxyacetic acid) also used during World War II. It was recognised as being toxic. Other compounds such as 2,4,5-T (2,4,5-trichlorophenoxyacetic acid), TCDD (2,3,7,8-Tetrachlorodibenzodioxin) were studied by the US military and it was found that 2,4,5-T had double the TCDD concentrations in Agent Pink and Agent Green. There are a range of compounds which adopt the name “Agent” and due to its toxicity. They were named “Rainbow” herbicides. The dioxins in the “Agent” classes are now classified as POP’s (Young, 2009).

150 tonnes of soil contaminated with dioxins were milled. The initial contamination concentration was approximately 30,000 parts per trillion (ppt). This was drastically reduced down to under 1,000 ppt, which is a decrease of nearly 98% of contaminants (Robertson, 2013).



Figure 23 – Four drum EDL MCD™ Reactor used at Bien Hoa (Robertson, 2013)

## 2.5 Alternative Applications to EDL MCD™ Reactor

There have been successful soil remediation projects which have used mechanochemistry to destroy the organic pollutants just like the EDL MCD™ Reactor.

In 2014, a site in Stockholm contained hexabromocyclododecane and a team of scientists used mechanochemistry to remediate the site. The absence of organic compounds after the mechanochemistry treatment was demonstrated by thermogravimetry and GC-MS analysis, indicating the complete degradation of hexabromocyclododecane and its conversion into inorganic compounds (Zhang, et al., 2014).

In 2016, a site in China containing polychlorinated biphenyls (PCBs) was remediated using a planetary ball mill. The grinding was assisted using  $\text{SiO}_2$  and  $\text{CaO}$ . Around 98% of the PCBs were destroyed which was analysed on a GC-LRMS. This study demonstrated that mechanochemical technology has a lot of potential for the remediation of PCB contaminated soil (Wang, et al., 2017).

Just like those two, there are many applications being carried out now using mechanochemistry to remediate soil polluted by organic compounds.

## 3.0 Methods

### 3.1 Equipment

The various equipment used during this project is outlined and detailed below. The method is relatively straightforward allowing rapid analysis of the samples with a quick summary of results.

#### 3.1.1 Planetary Ball Mill

A Retsch PM-100 planetary ball mill was used as the mechanochemical reactor for this research project. Retch states on their description of the ball mill that “the extremely high centrifugal forces of the planetary ball mills result in very high pulverisation energy”. Therefore, this ball mill was the ideal instrument to use as it provided the mechanical energy required to breakdown the organic compounds and destroy them.

The motion of the ball mill is with its name. The milling jar rotates on its own axis clockwise and the sun wheel rotates on its own axis anticlockwise. This causes grinding via friction and impact. The Retsch PM-100 can be operated at a range of speeds which is effectively the input energy to the reaction.



*Figure 24 – Retsch PM-100 Planetary Ball Mill (Retsch GmbH, 2016)*

### 3.1.2 Milling Balls

Three factors that contribute to the milling outcome are the number of balls being used, the size of the balls and the material that the balls are made up of. These three factors were observed in past research which was been done on ball milling.

There has been an indication that larger size and weight milling balls are able to transmit significantly more pulverisation energy to the silica sand matrix within the ball mill jar (Suryanarayana, 2001). In this experiment, 20 steel balls were used which had an average diameter of 20 mm. The figure below shows the balls in the jar combined with the standard matrix of 50 g of quartz to show the loading.



*Figure 25 – 20 Steel balls 20 mm in diameter in the milling jar with quartz.*

### 3.1.3 Milling Jar

The milling jar used was obtained when the ball mill was purchased from Retsch and had previously been used by other students. As the milling was carried out for long periods of time, and high temperatures were reached, the jar was able to easily carry out milling for hours. This jar proved to be effective as it was able to withstand high temperatures of over 350°C (Retsch GmbH, 2016).

The milling jar is made of a chrome steel alloy and therefore was able to be used numerous times without losing its effectiveness. Though, overtime milling did cause some damage the jar as the mass of the jar decrease, but not drastically.

In this experiment, a 500mL jar was used which allowed more than enough space for milling balls to move about internally.

### 3.1.4 Sonicator

A L&R Ultrasonics Quantrex 90H sonicator was used for the extraction of hydrocarbons from the milled quartz matrices.

## 3.2 Analytical Instruments

The analytical instruments used provided both qualitative and quantitative data of the milled samples.

### 3.2.1 Gas Chromatograph (GC)

A Shimadzu GC-2010 was used for this project. A ZB-5 column provided by Phenomenex was used: 5% Phenyl 95% dimethylpolysiloxane, 25.0 m x 0.32 mm, 0.50  $\mu$ m.

Standard GC conditions for hydrocarbon analysis is outlined in the table below:

*Table 2 – Gas Chromatograph conditions for analysis of hydrocarbons.*

<b>GC</b>	Shimadzu GC-2010
<b>Inlet</b>	250°C, split mode, 20:1 split ratio, flow 44.7 mL/min
<b>Injection</b>	1.0 $\mu$ L
<b>Carrier Gas</b>	Nitrogen gas
<b>Column</b>	ZB-5, 25.0 m x 0.32 mm, 0.50 $\mu$ m
<b>Temperature Program</b>	40°C – Hold for 1 minute. Temperature increased 30°C/min to 250°C – Hold for 15 minutes
<b>Detector</b>	Flame Ionization Detector (FID)

### 3.2.2 Fourier Transform Infrared Spectrometer (FT-IR)

The samples that were analysed were the ones that were synthesised in the laboratory. The instrument used was the Nicolet iS10 FT-IR spectrometer. Due to the convenience of an IR being able to analyse solid samples, reflectance mode was used to give the results, which in turn was presented in transmittance mode.

### 3.2.3 Nuclear Magnetic Resonance (NMR)

The samples were dissolved in deuterated chloroform ( $\text{CDCl}_3$ ) and analysed on a Bruker Ascend™ 400 NMR instrument. Each of the synthesised samples were analysed by adding approximately 0.5 g of sample dissolved in 1 mL of deuterated chloroform.

## 3.3 Materials and Compounds

### 3.3.1 Quartz Sand

The material chosen to mill the samples with was high-grade silica sand. This was chosen due the properties being ideal for the destruction of the compounds. The sand was purchased from Placemakers, a hardware store. The table below represents the typical composition of high-grade commercial silica sand.

*Table 3 – Chemical analysis of silica sand (Alnawafleh, Tarawneh, & Alrawashdeh, 2013)*

<b>Compound</b>	<b>Formula</b>	<b>Concentration (%)</b>
Silica	$\text{SiO}_2$	97.6
Aluminium Oxide	$\text{Al}_2\text{O}_3$	1.31
Ferric Oxide	$\text{Fe}_2\text{O}_3$	0.028
Titanium Oxide	$\text{TiO}_2$	0.18
Calcium Oxide	$\text{CaO}$	0.06
Magnesium Oxide	$\text{MgO}$	0.01
Potassium Oxide	$\text{K}_2\text{O}$	0.01
Sodium Oxide	$\text{Na}_2\text{O}$	0.01
Loss of Ignition (L.O.I)		0.61

### 3.3.2 Organic Compounds

The following compounds were purchased or were available from the School of Science.

<b>Compound</b>	<b>Source</b>	<b>CAS Number</b>	<b>Vendor Code</b>
Hexadecane	School of Science	544-76-3	-
Hexadecanoic Acid	School of Science	57-10-3	-
Hexadecylamine	Sigma Aldrich	143-27-1	H7408-100G
Hexadecan-7-one	Sigma Aldrich	45206-91-5	S544086- 250MG
Hexadecan-1-ol	Sigma Aldrich	36653-82-4	258741-5G
Hexadecanoyl chloride/Palmitoyl chloride 98%	Sigma Aldrich	112-67-4	P78-100ML
Hexadec-1-ene	Sigma Aldrich	629-73-2	H2131-100ML

### 3.3.3 Compounds Synthesised For This Study

#### 4.3.3.1 Methyl Hexadecanoate

Methyl hexadecanoate is an ester that was synthesised using Fischer Esterification (Robertson, Organic Chemistry Laboratory Manual, 2014). 10 grams of palmitic acid and 10 mL of methanol were combined with 2 mL sulfuric acid as a catalyst and was refluxed for approximately 8 hours. The sample was analysed on the NMR and FTIR. By GC, the product was >98% pure. The yield was 83%.

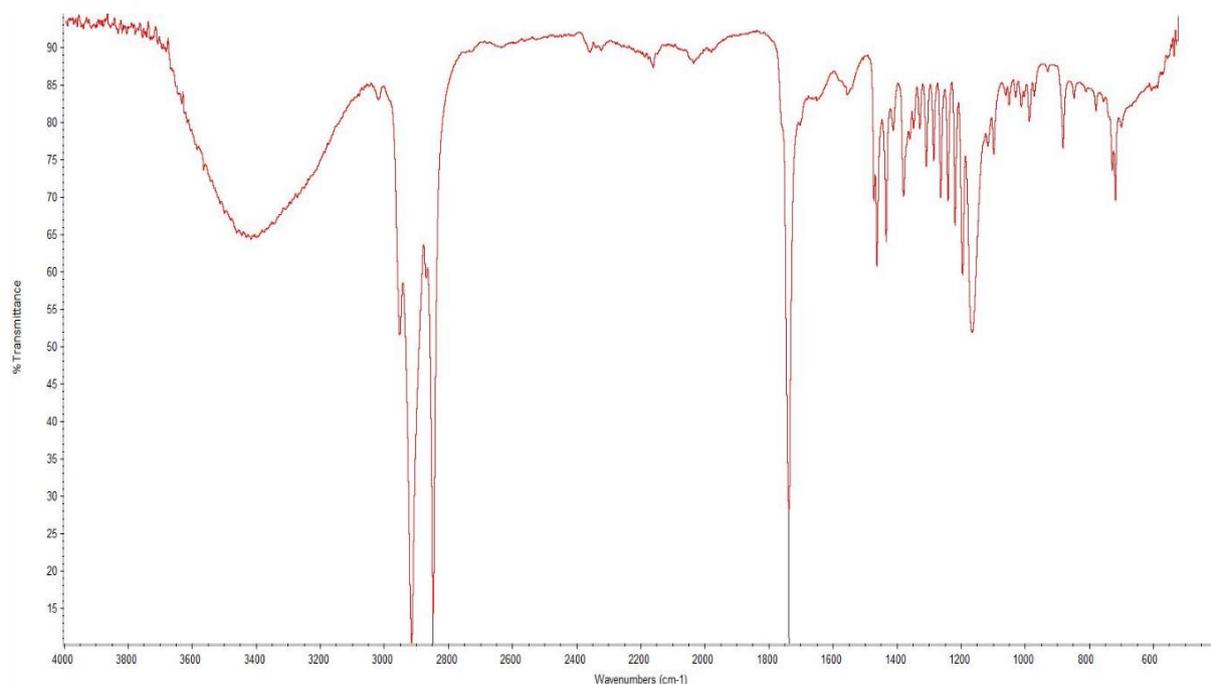
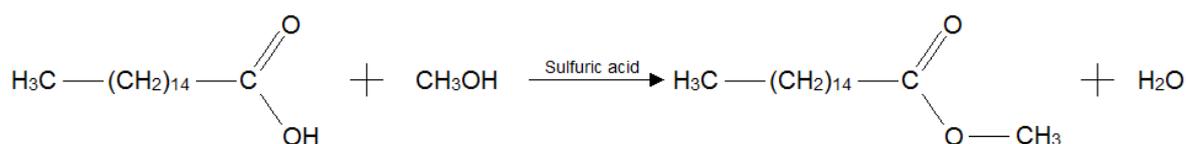


Figure 26 – IR spectrum of methyl hexadecanoate

A broad peak around 3500 to 3000 cm<sup>-1</sup> indicates the presence of hydroxyl which could be from the acid or methanol. It could also be from moisture in the product. A sharp peak at 1750 cm<sup>-1</sup> shows that a carbonyl group is present. The third peak to notice is the C-H bonds around 2850 cm<sup>-1</sup>. There is a lot of noise which can be seen in the spectra. Though the noise prevents the spectra from being clear, we can assume that there is a peak around 1300 cm<sup>-1</sup> which is the C-O. A library search gave 86% similarity to methyl hexadecanoate.

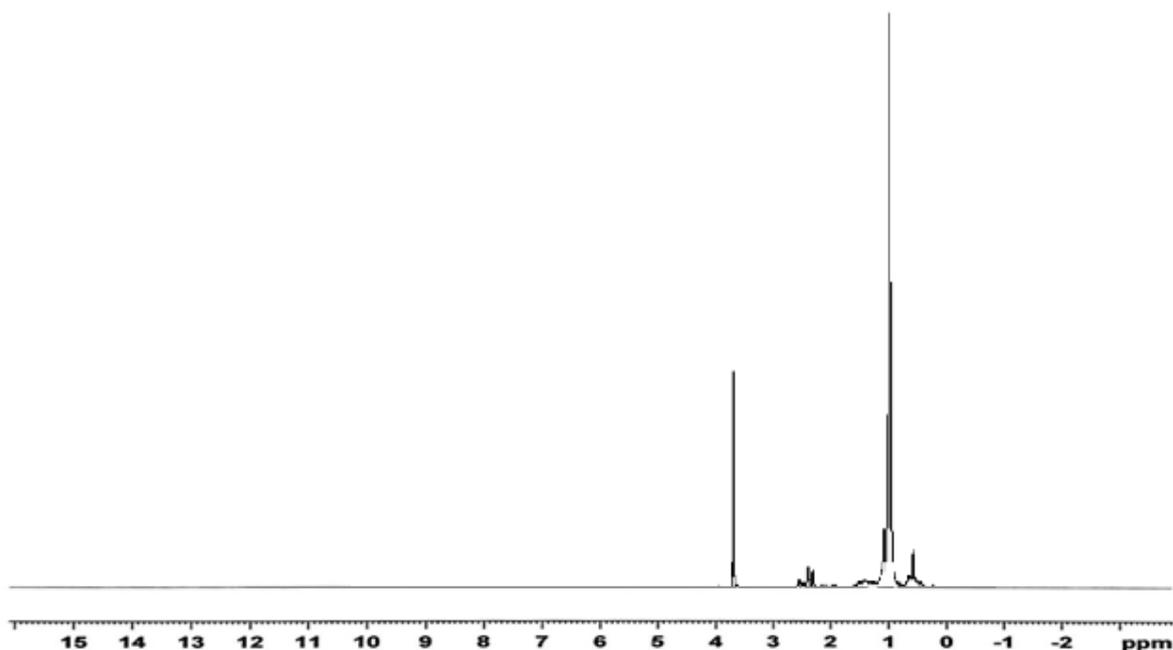


Figure 27 – Proton NMR spectra of methyl hexadecanoate

The most prominent peak is between 1 to 1.5 ppm which are all the CH<sub>2</sub> present in the ester. The peak around 3.8 ppm is the CH<sub>2</sub> next to the single bonded oxygen in the ester. Zooming into the spectra shows that this is a quartet due to being next to CH<sub>3</sub>. Around 2.5 ppm, the hydrogen neighbouring the carbonyl group is a triplet. A small peak around 0.6 ppm is the CH<sub>3</sub> present at the ends of the compound. No peaks around 13 ppm indicates that no carboxylic acid was detected therefore the product was pure and was indeed an ester.

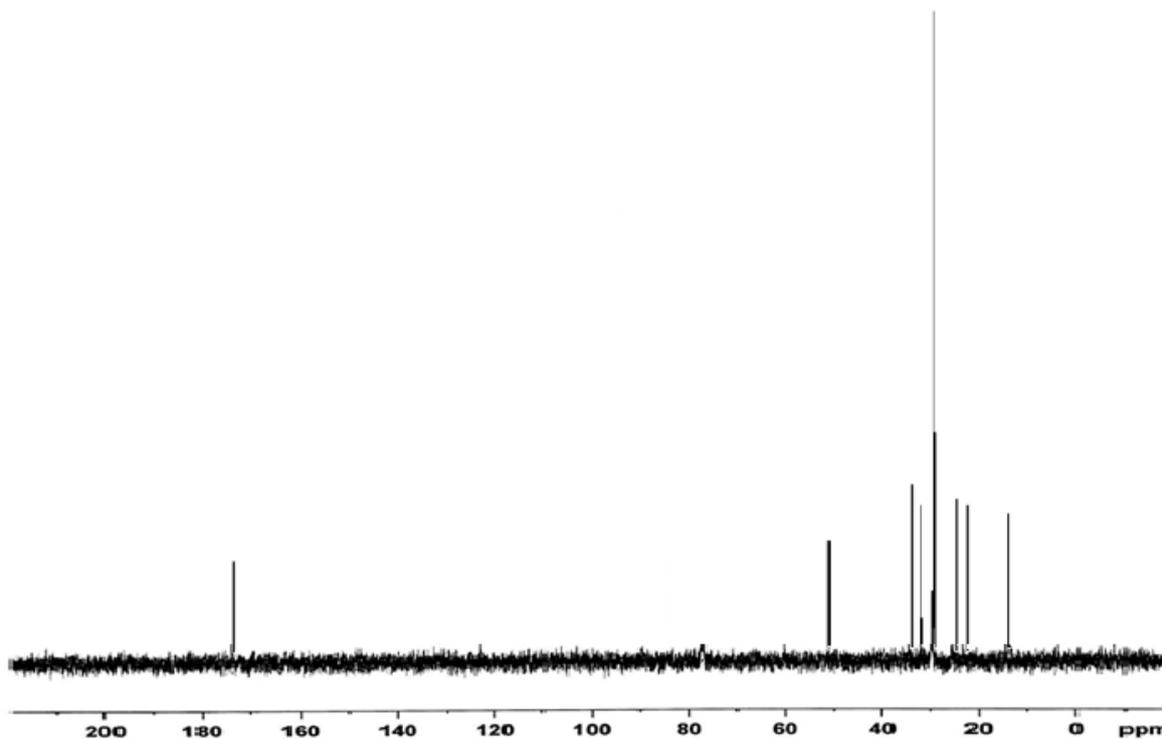


Figure 28 – Carbon NMR spectra of methyl hexadecanoate

The peak around 175 ppm identifies the carbonyl group in the ester. There is a peak around 50 ppm which is for the single bonded oxygen. The peak next to the carbonyl group is found around 35 ppm. A large peak around 30 ppm is all the CH<sub>2</sub> present in the ester. A peak around 15 ppm is for the CH<sub>3</sub> found in the ends of the compound. The spectrum gives a good indication that an ester was formed even if there is a lot of noise.

### 4.3.3.2 Ethyl Hexadecanoate

Ethyl hexadecanoate was synthesised using the same method as the methyl hexadecanoate, however, ethanol was used in place of methanol (Robertson, Organic Chemistry Laboratory Manual, 2014). The sample was analysed on the NMR and FTIR. By GC, the product was >98% pure. The results showed that there were very little traces of unreacted ethanol and palmitic acid in the product. The yield was approximately 80%.

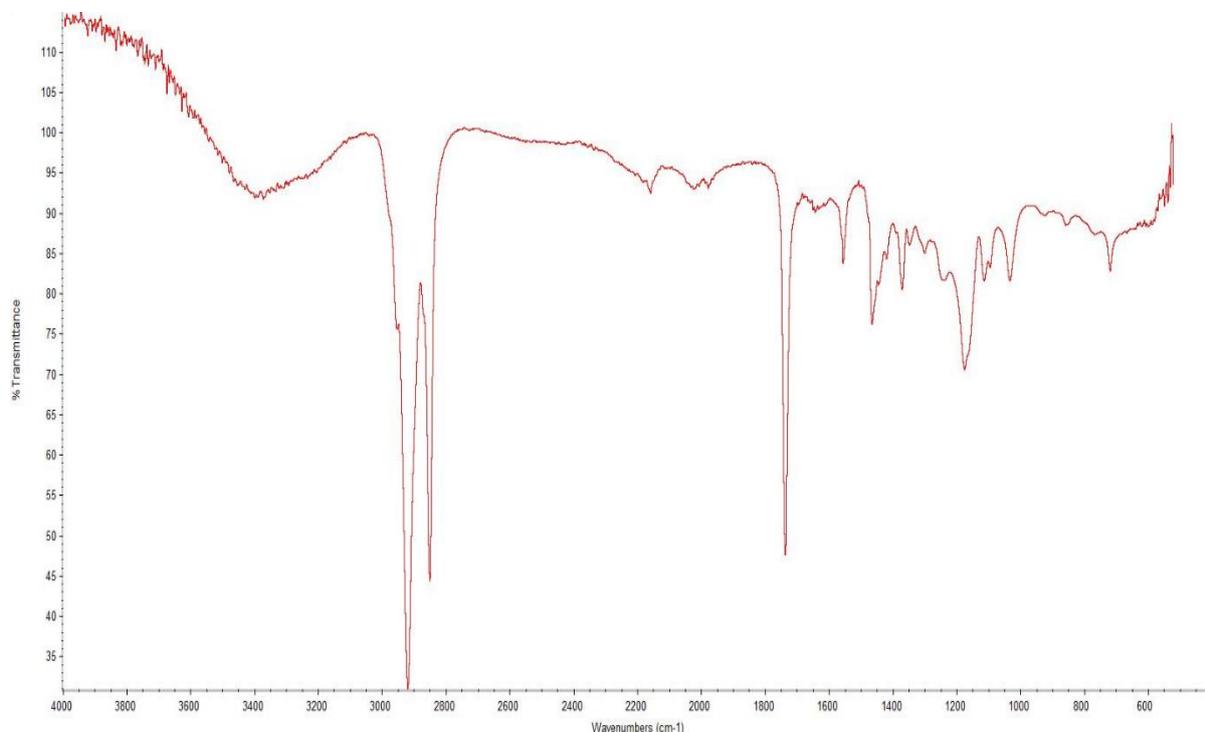
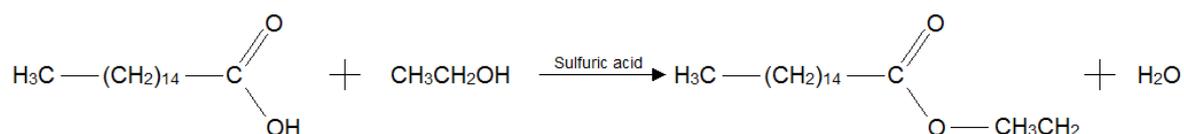


Figure 29 - IR spectrum of ethyl hexadecanoate

The IR spectrum gives 3 main peaks which indicate that an ester was synthesised. Firstly, the saturated aliphatic C-H stretch is identified at 3000-2850  $\text{cm}^{-1}$ . Secondly, the carbonyl functional group C=O is identified between 1750-1735  $\text{cm}^{-1}$ . Lastly, the C-O peak is found at 1320  $\text{cm}^{-1}$ . This peak shows that it is not as prominent as the other two meaning only small vibrations are caused by the C-O bond. The IR spectra does show that the synthesis was not 100% completed as OH can be visible between 3500-3000  $\text{cm}^{-1}$ . The presence of OH can be caused by two factors. Either the synthesis was not completed and the reflux was stopped too early, or there was

moisture in the product indicating H<sub>2</sub>O. A library search showed 89.7% similarity to ethyl palmitate.

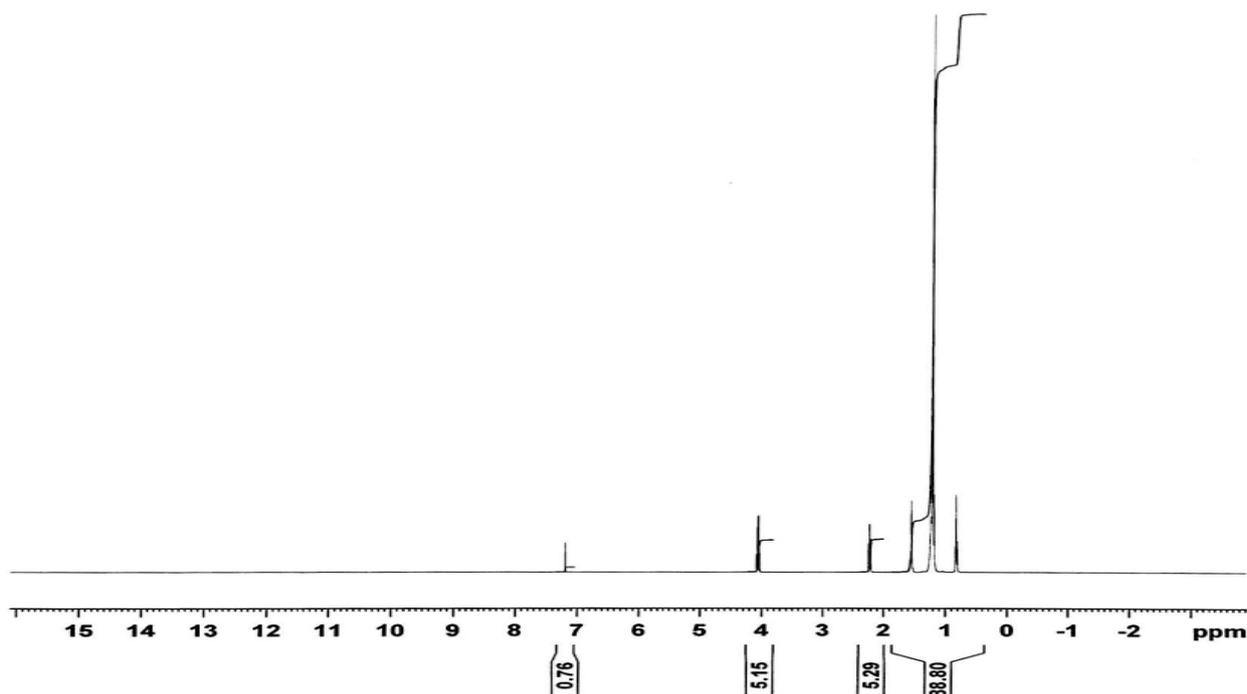


Figure 30 – Proton NMR of ethyl hexadecanoate

The proton spectrum gives a rough idea that the product synthesised is an ester. The peak around 4.1 ppm is the CH<sub>2</sub> next to the single bonded O found in an ester. A closer look at the peak shows a quartet due to the neighbouring CH<sub>3</sub> bond. The peak at around 2.2 ppm is the hydrogen neighbouring the carbonyl group and is a triplet due to the neighbouring carbon having 2 hydrogens. The proton shift between 1 to 1.5 ppm is for all the CH<sub>2</sub> groups present. The intensity of the peak indicates the ratio of hydrogens. The peak at 0.8 ppm is the CH<sub>3</sub> group at either end of the molecule. There is no peak around 13 to 14 ppm indicating majority of the carboxylic acid has been converted into an ester.

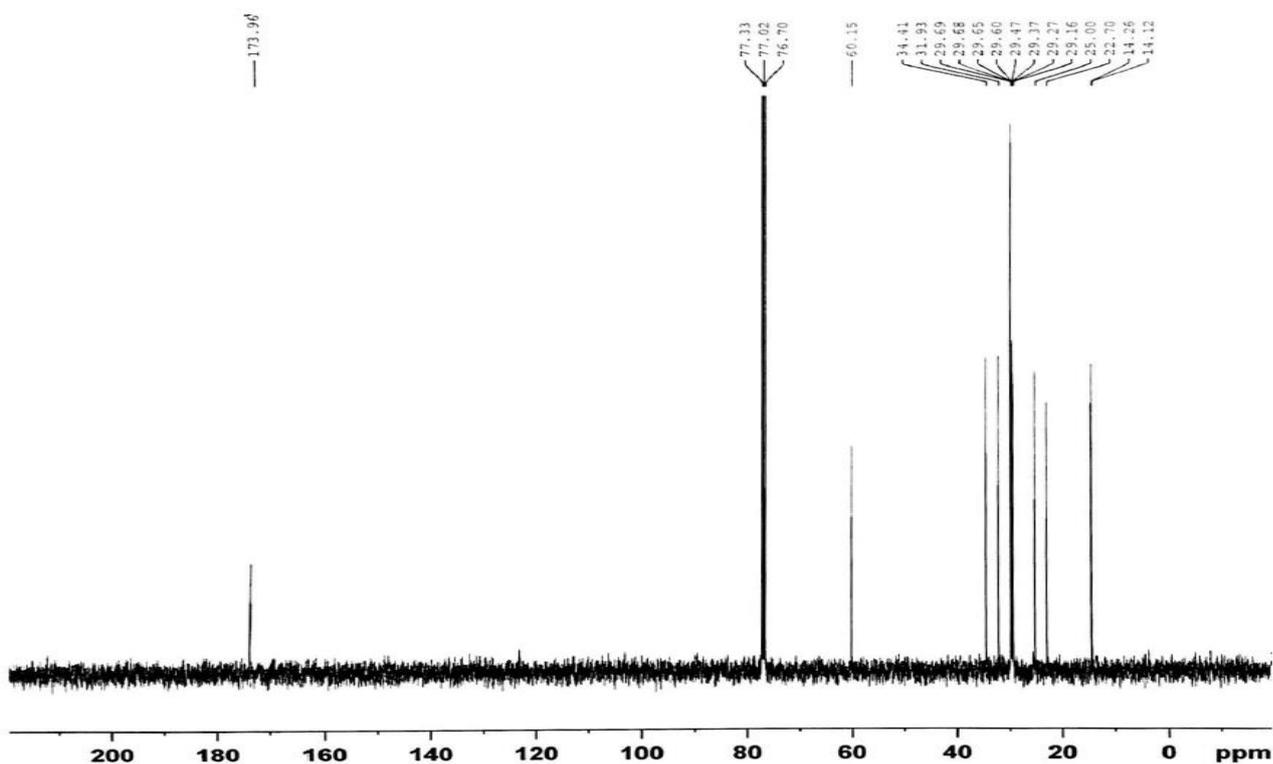


Figure 31 – Carbon NMR spectra of ethyl hexadecanoate

The peak at 173.96 ppm indicates the carbonyl group in the ester. The peak at 60.14 is the carbon adjacent to the single bonded oxygen. The peak next to the carbonyl group is found at 34.41 ppm. A very large peak around 29 ppm is for all the CH<sub>2</sub> groups and the peak at 14.12 ppm is for the CH<sub>3</sub> found on the end of the chain. There is a lot of noise in this spectrum however the NMR does give a good indication of the purity of ethyl hexadecanoate.

### 4.3.3.3 Propyl Hexadecanoate

Propyl hexadecanoate was synthesised using the same method as the methyl hexadecanoate, however, propanol was used in place of methanol (Robertson, Organic Chemistry Laboratory Manual, 2014). The sample was analysed on the NMR and FTIR. By GC, the product was >98% pure. The results showed that there was still unreacted traces of propanol and palmitic acid however the yield was high enough for it to be used in the milling stages. The yield was approximately 80%.

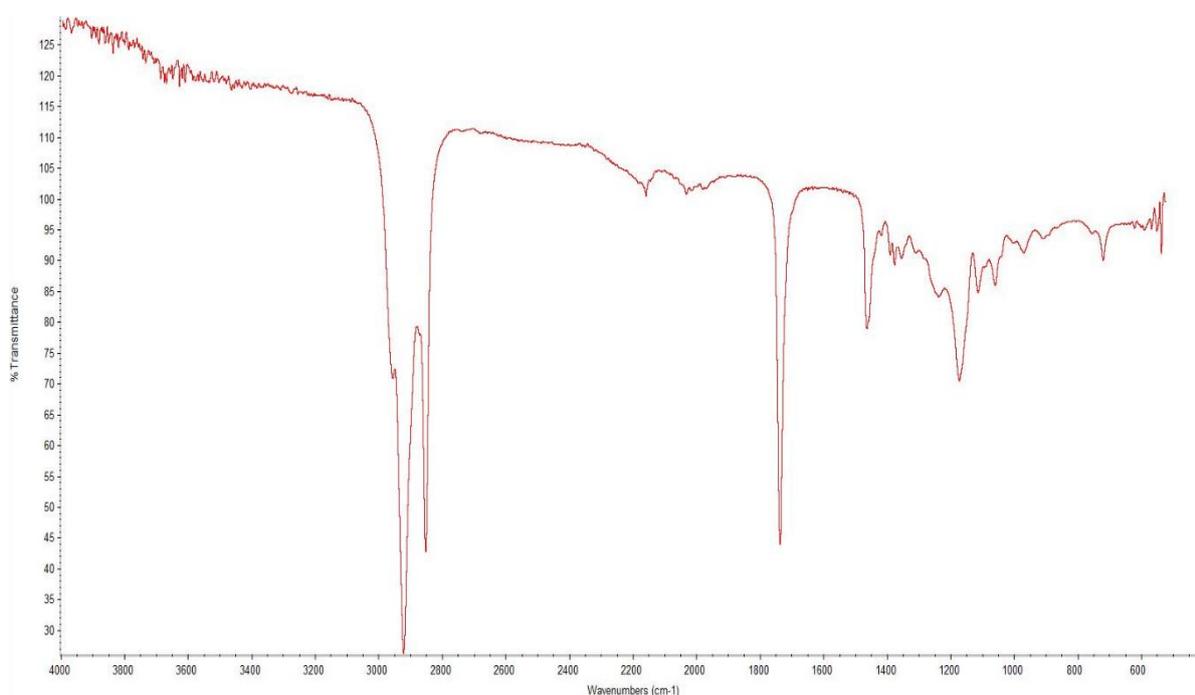
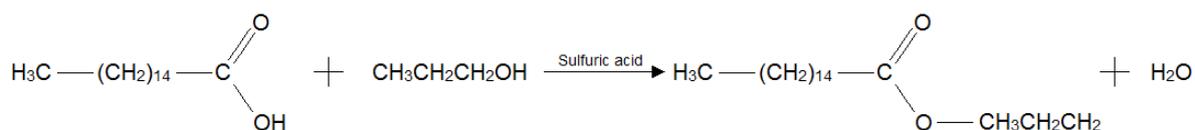


Figure 32 - IR spectrum of propyl hexadecanoate

The IR spectrum for propyl hexadecanoate has quite a bit of noise. A broad hydroxyl peak around 3000 to 3500  $\text{cm}^{-1}$  cannot be observed which indicates that all the carboxylic acid was reacted to form an ester. It also shows that no propanol is present. The peak just after 3000  $\text{cm}^{-1}$  indicated the C-H bonds present. A sharp peak around 1750  $\text{cm}^{-1}$  indicates that a carbonyl group is present. A small peak around 1300  $\text{cm}^{-1}$  indicates that a C-O bond is present.

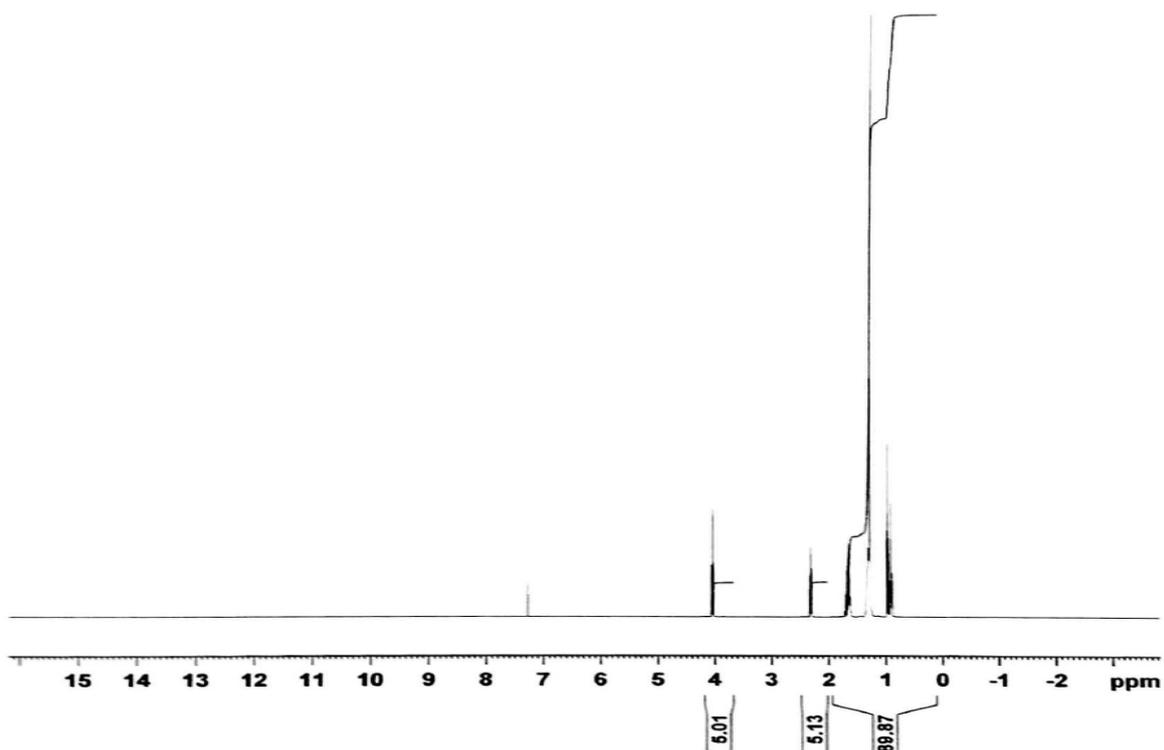


Figure 33 – Proton NMR of propyl hexadecanoate

The purity of propyl hexadecanoate is quite good though some impurities are present. The peak around 4.0 ppm is a triplet and is for the single bonded oxygen. The peak is a triplet as the adjacent carbon contains two hydrogens. The peak around 2.3 ppm is the CH<sub>2</sub> bond neighbouring the carbonyl group. The large peak around 1.0 to 1.5 ppm is all the CH<sub>2</sub> bonds present in the compound. A peak around 0.8 ppm can vaguely be seen which is the CH<sub>3</sub> present in the compound.

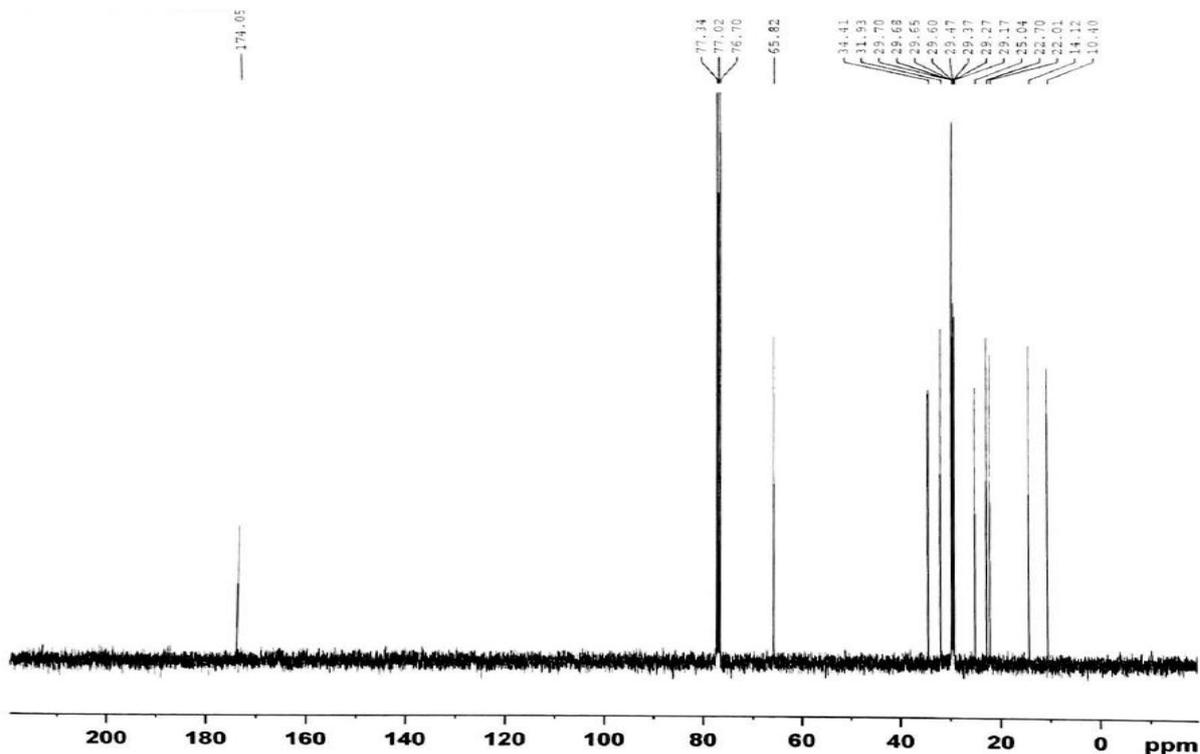


Figure 34 – Carbon NMR of propyl hexadecanoate

A peak around 175 ppm confirms that a carbonyl group is present. The peak around 65 ppm is for the carbon adjacent to the single bonded oxygen in the ester. The peak next to the carbonyl group can be found at 35 ppm. A large peak at 30 ppm are all the CH<sub>2</sub> groups in the compound. The peak around 15 ppm is the CH<sub>3</sub> found on the ends of the compound. The spectra give good an indication that the product is fairly pure and is an ester.

#### 4.3.3.4 Decyl Hexadecanoate

Decyl hexadecanoate was synthesised using esterification via thionyl chloride ( $\text{SOCl}_2$ ). The method was taken from an AUT advanced organic chemistry laboratory manual (AUT Faculty of Science, 2014). The first part involved the synthesis of hexadecanoyl chloride. 11 g of hexadecanoic acid was refluxed with 12 mL of thionyl chloride, which was added dropwise over 10 minutes and refluxing continued for a further 2 hours. The apparatus was rearranged for distillation and anything under 80 °C was disposed of. 12 mL of decanol was added to the flask and was gently refluxed for 2 hours and then cooled. The crude ester was firstly washed twice with 20 mL saturated sodium bicarbonate to remove any acidic material and then washed with 20 mL of water. Finally, it was dried using anhydrous sodium sulphate. The product remained very waxy. The final product was analysed on the FTIR. The yield obtained was approximately 74%.

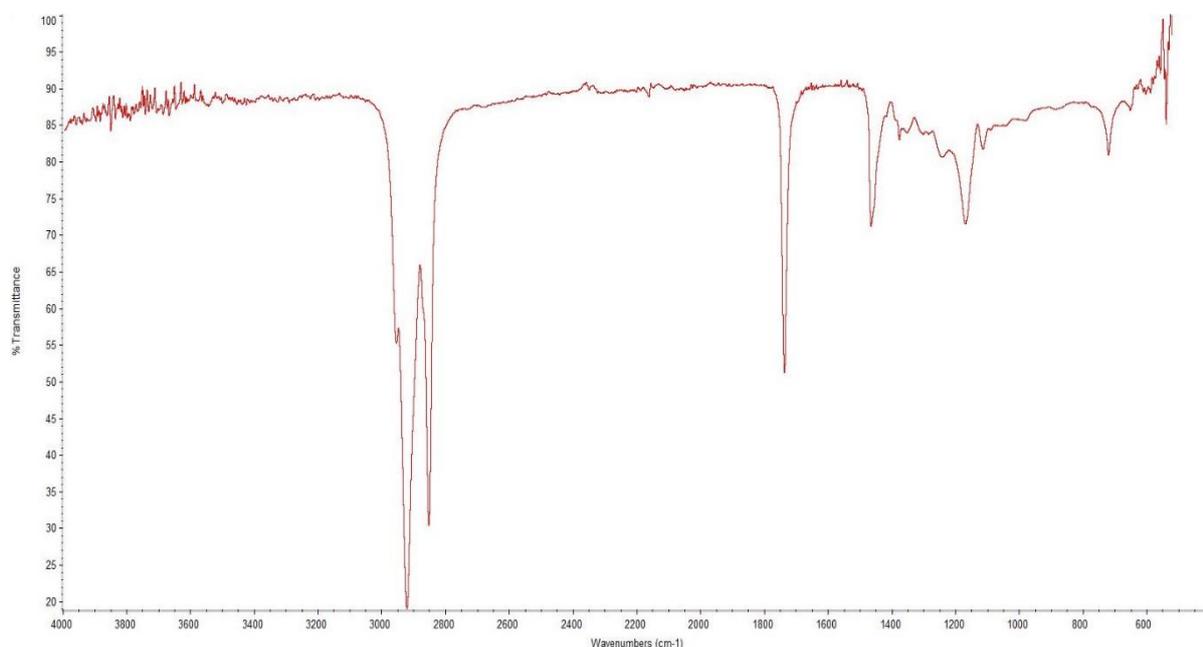
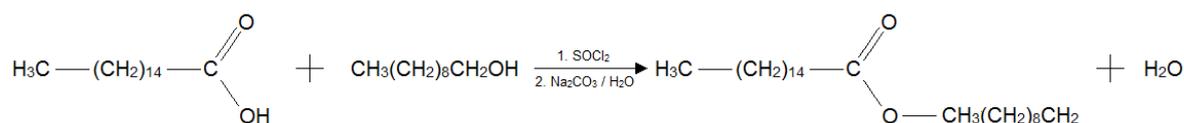


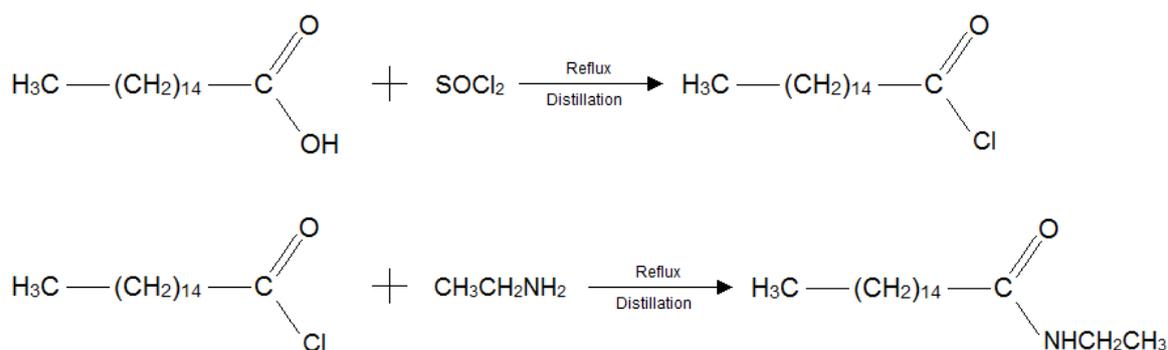
Figure 35 - IR spectrum of decyl hexadecanoate

The spectrum shows three main peaks that indicates the formation of decyl hexadecanoate. The sharp peak around 3000 to 2850  $\text{cm}^{-1}$  is the saturated aliphatic

C-H stretch. It appears to be very prominent due to the number of C-H carbons present. The peak at 1750 to 1735  $\text{cm}^{-1}$  is the carbonyl group. A small but sharp peak at 1320  $\text{cm}^{-1}$  is for the small vibrations caused by the C-O bond. No peak at 3500  $\text{cm}^{-1}$  indicates that there is no water in the sample or no decanol left.

### 4.3.3.5 N-ethylhexadecanamide

The N-ethylhexadecanamide was made by synthesising an acid chloride using thionyl chloride ( $\text{SOCl}_2$ ) then adding an amine to convert the acid chloride into an amide. Firstly, 10 g of hexadecanoic acid was refluxed with 10 mL  $\text{SOCl}_2$  added dropwise for 10 minutes, which was then refluxed for 2 hours. The apparatus was rearranged for distillation and all materials under  $80^\circ\text{C}$  was disposed of to get rid of the excess  $\text{SOCl}_2$ . The apparatus was rearranged for a reflux. To the acid chloride, 10 mL of concentrated ethylamine was added dropwise over 10 minutes and again refluxed for 2 hours. The crude product was washed twice with 20 mL saturated sodium bicarbonate to remove any acidic material. The crude product was attached to a rotary evaporator and the amide was obtained free of any unreacted acid chloride and ethylamine (Robertson, Organic Chemistry Laboratory Manual, 2014). The yield obtained was around 82%.



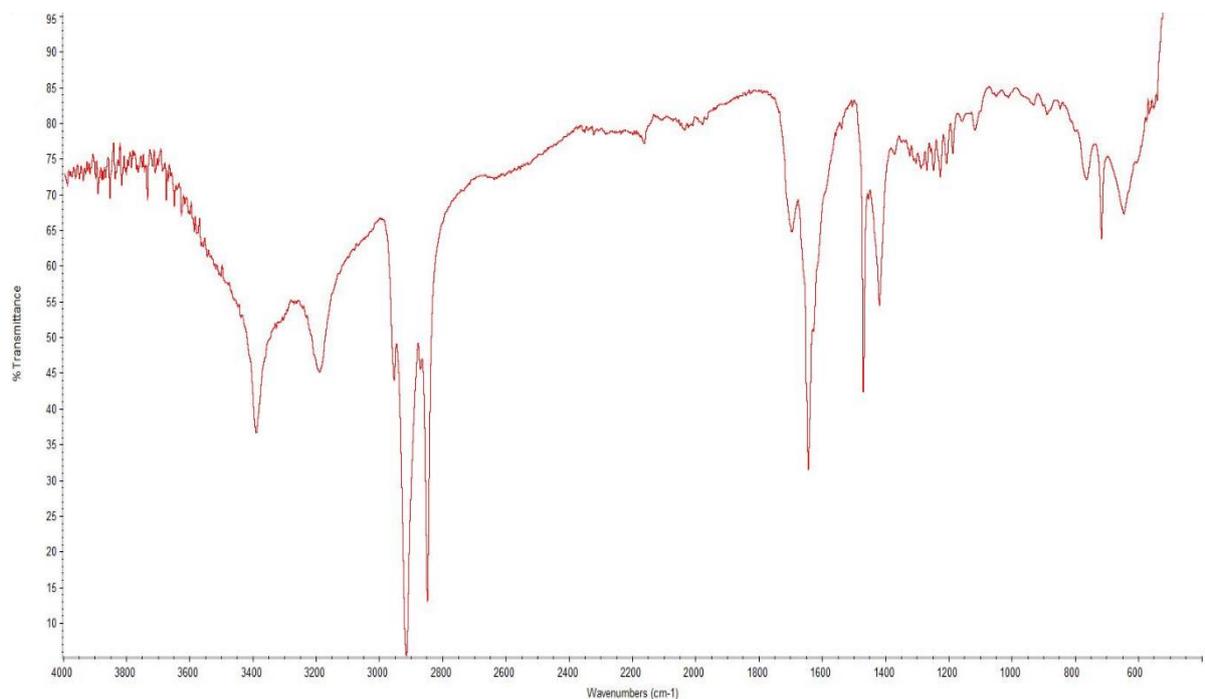


Figure 36 - IR spectrum of *n*-ethylhexadecanamide

There are many characteristics to identify when looking at an amide. The first indication is the long chain of hydrocarbons with a peak at 3000 to 2850 cm<sup>-1</sup> which shows the C-H. This peak is quite big therefore shows the number of carbons there is. The sharp peak at 3400 to 3250 cm<sup>-1</sup> indicates the N-H bond in the amide. Hydroxyl groups are found in this stretch too. A peak at 1750 cm<sup>-1</sup> shows the presence of C=O and distinguishes between an amine and amide.

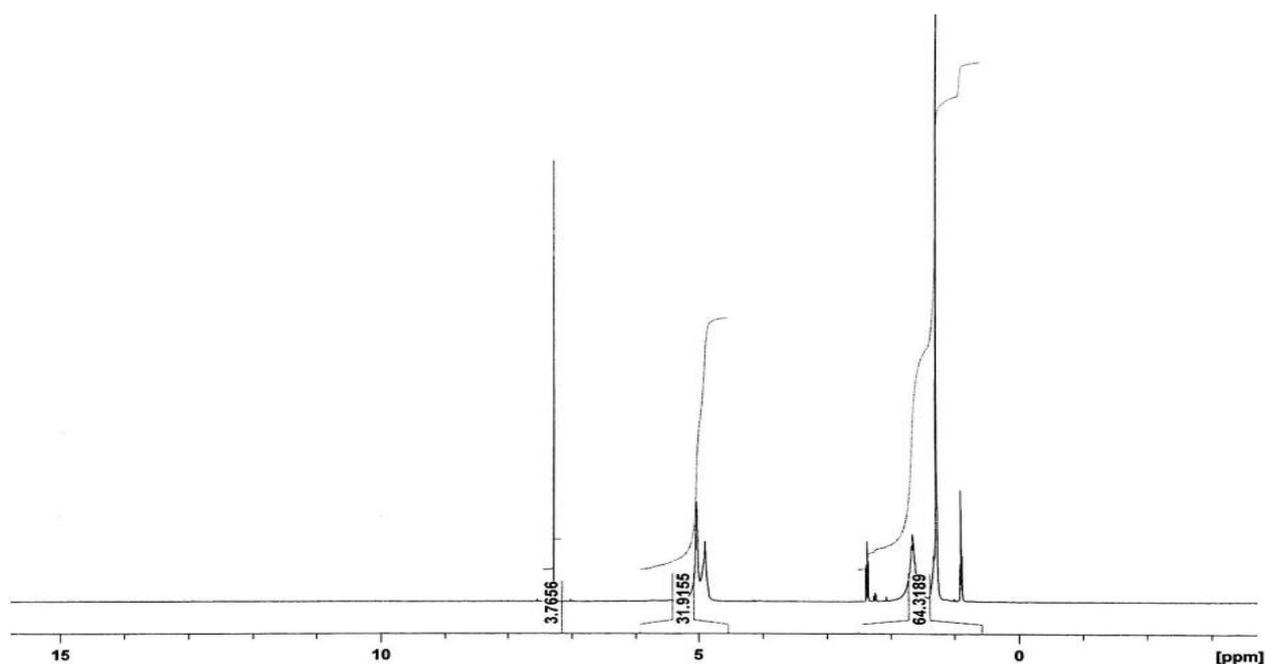


Figure 37 – Proton NMR of *n*-ethylhexadecanamide

The proton NMR gives a pretty fair idea on the purity of the amide. The peak around 2.30 ppm is the CH<sub>2</sub> group adjacent to the carbonyl group. The peak is a triplet which was expected. The peak around 1.6 ppm is for the CH<sub>2</sub> group that comes after the CH<sub>2</sub> mentioned before. This CH<sub>2</sub> has a slightly different chemical shift when compared to the other CH<sub>2</sub> groups which is found around 1.2 ppm. The peak around 0.8 ppm is for the CH<sub>3</sub> group at the ends of the molecule and is a triplet.

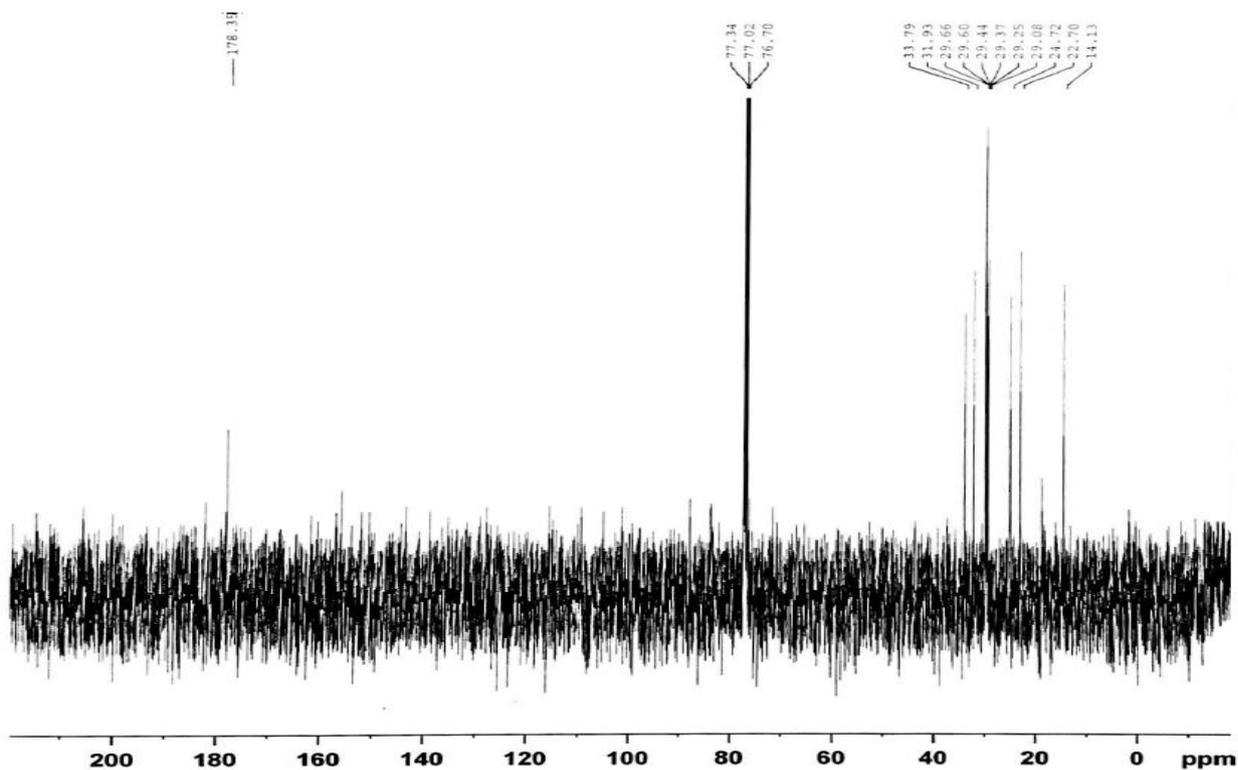


Figure 38 – Carbon NMR of *n*-ethylhexadecanamide

A peak observed at 176 ppm indicated is it the carbonyl group in the amide. The peaks between 20-40 ppm is for all the CH<sub>2</sub> groups throughout the compound. The peak around 17 ppm is the CH<sub>3</sub> group found at the end of the compound. The spectrum has a lot of noise and therefore some smaller peaks may be unnoticeable.

#### 4.3.4 Laboratory Reagents

Extraction solvents used in the experiment were:

- Analytical grade anhydrous Ethyl acetate (99.8%) (CAS 141-78-6) that was purchased from Sigma Aldrich. This was used as the primary solvent.
- The internal standard used was n-Eicosane (~99%) (CAS 112-95-8) which is C<sub>20</sub>H<sub>42</sub>. This was provided by the School of Science and was originally purchased from Sigma.

For organic synthesis:

- 95% Methanol (CAS 67-56-1), 95% Ethanol (CAS 64-17-5), 98% Propanol (CAS 71-23-8) and 99.5% Decanol (112-30-1) was provided by the School of Science.
- Thionyl chloride (98%) (CAS 7719-09-7) was purchased from Sigma Aldrich.
- Palmitic acid (CAS 57-10-3) was provided by the School of Science.
- Ethylamine (CAS 75-04-7) was provided by the School of Science.

### 4.4 Ball Milling Procedures

#### 3.4.1 Sample Preparation

Quartz sand was sieved which removed any particulate matter larger than 450 µm before drying it in an oven to remove all the moisture. As stated previously, moisture has been found to slow down the destruction efficiency, therefore removing all traces of water was important.

To a 500 mL milling jar, 20 steel balls (20 mm diameter) were added along with 50 g of contaminated quartz. About 0.5 g (w/w) of the organic compound was added to the quartz.

#### 3.4.2 Milling

Once the sample preparation was completed, the jar containing quartz and contaminants was put into the planetary ball mill and clamped securely according to the ball mill instructions.

The speed of the mill was set to 300 RPM and the time was set for 3 hours. The reason 300 RPM was used as it is a relatively slow speed and allows for the

temperatures to be low so that the samples do not evaporate away when the jar is opened.

During the 3 hours, a total of 9 samples were taken. First at 0 minutes of milling, then every 15 minutes for the first hour, then every 30 minutes for the last two hours. 0.5 g of spiked and milled quartz was taken and placed into 50 mL glass test tubes with screw caps.

### 3.4.3 Jar Cleaning

It was essential that this was done properly. It was important to ensure no residual hydrocarbon contaminants remained on the milling equipment. The milled quartz was disposed of in the rubbish bin and the jar, balls and jar lid was soaked in hot water with detergent for 10 minutes. They were then scrubbed and rinsed with clean water before being dried. Once dried, approximately 20 g of quartz was added to the jar with the steel balls and milled for 5 minutes at 500 RPM to remove any remaining material stuck in the jar and steel balls. The washing process was repeated once more.

The jar cleaning process was taken from (Gobindlal, 2013), who showed in his research that no traces of hydrocarbons remained after those steps (analysed on the FT-IR) were followed and therefore was adopted in this research.

### 3.4.4 Analysis via Gas Chromatography (GC)

The contaminants were analysed and monitored through GC analysis. To undergo this analysis, extraction of the contaminants was required.

The extraction method was taken from the United States Environmental Protection Agency (USEPA) Method 3550C which is ideal for extraction of organic compounds from soil (USEPA, 2007).

0.5 g of milled sample was weighed into 50 mL glass test tubes with screw caps and the weight was recorded. 5 mL of extraction solvent (ethyl acetate containing 50 ppm n-Eicosane) was pipetted into the test tubes. The test tubes were capped tightly and were vortexed for 2 minutes each. The test tubes were then placed in the ultrasonic bath for 30 minutes. After sonication, the test tubes were placed in the centrifuge and spun at 1500 RPM for 30 minutes to suspend any solid matter. It was very important that no solid particulate matter remained in the solution analysed on the GC as it

may have blocked the injector. The extract was then taken from the test tubes and placed into vials to be analysed on the GC in the conditions stated in section 3.2.1.

### 3.5 Milling at 400 RPM and 500 RPM

Even though the primary focus of this experiment was to see how the various functional groups behave in the ball mill, it was found that 300 RPM did not completely destroy some of the functional groups. The ones that stood out the most were hexadecanol, hexadecane and hexadecene. To show that these compounds do get destroyed if the speed is increased, these three samples were milled using the same method as used for 300 RPM, however the speeds were set to 400 RPM and 500 RPM. This will be looked at further in the results and discussion section.

### 3.6 Testing the Relative Extraction Efficiency of the Solvent

The extraction method used in this experiment was used in past research performed at AUT University and had proven to be effective. However, it was essential that it was tested on this projects samples as large organic compounds had not been used in the past.

To check the efficiency of the extraction method, approximately 10 g of quartz was weighed into a pre-weighed flask and the mass was recorded. To the quartz, 1 g of hexadecane and 50 mL of extraction solvent (ethyl acetate without the internal standard in it) was added. A magnetic stirrer bar was placed in to the flask and contents were mixed for 30 minutes at 35°C to imitate sonication.

Then the flask was put on the water bath at 100 °C to evaporate off all the solvent. Once majority of the solvent had evaporated, the flask with the quartz was placed in a hot air oven at 100°C for 30 minutes to evaporate off any excess ethyl acetate.

With the known masses, the efficiency of the extraction method was calculated by the use of the following:

*Mass of Flask + Quartz =*

*Initial mass of Compound =*

*(Mass of Flask + Quartz + Compound) – (Mass of Flask + Quartz)*

*Final Mass of Compound (after extraction) =*

*(Mass of Flask + Quartz + Compound) – (Mass of Flask + Quartz)*

$$\text{Extraction Efficiency} = 100 - \left( \frac{\text{Final mass of compound}}{\text{Initial mass of compound}} \times 100 \right)$$

To determine if the extraction efficiency differs for various functional groups, hexadecylamine and hexadecene were also analysed using the same method.

## 4.0 Results

### 4.1 Hexadecane

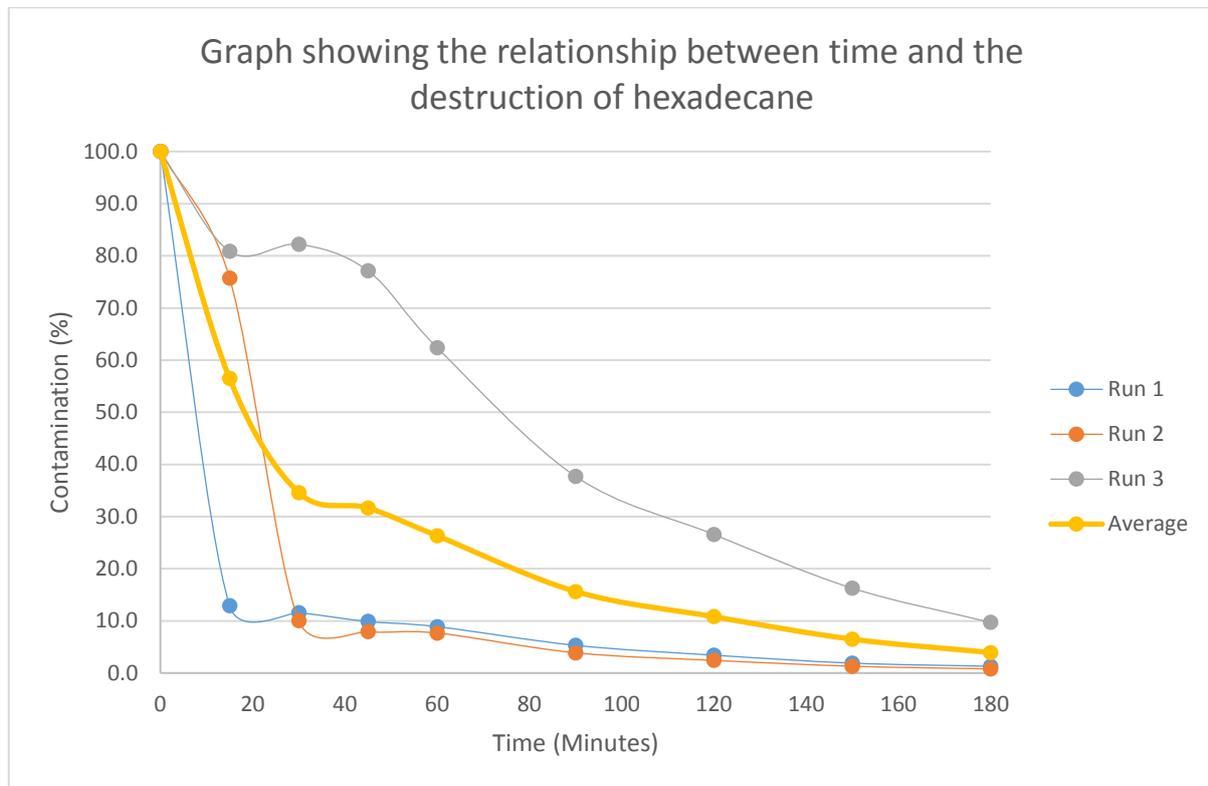


Figure 39 – Graph displaying time versus destruction of hexadecane at 300 RPM

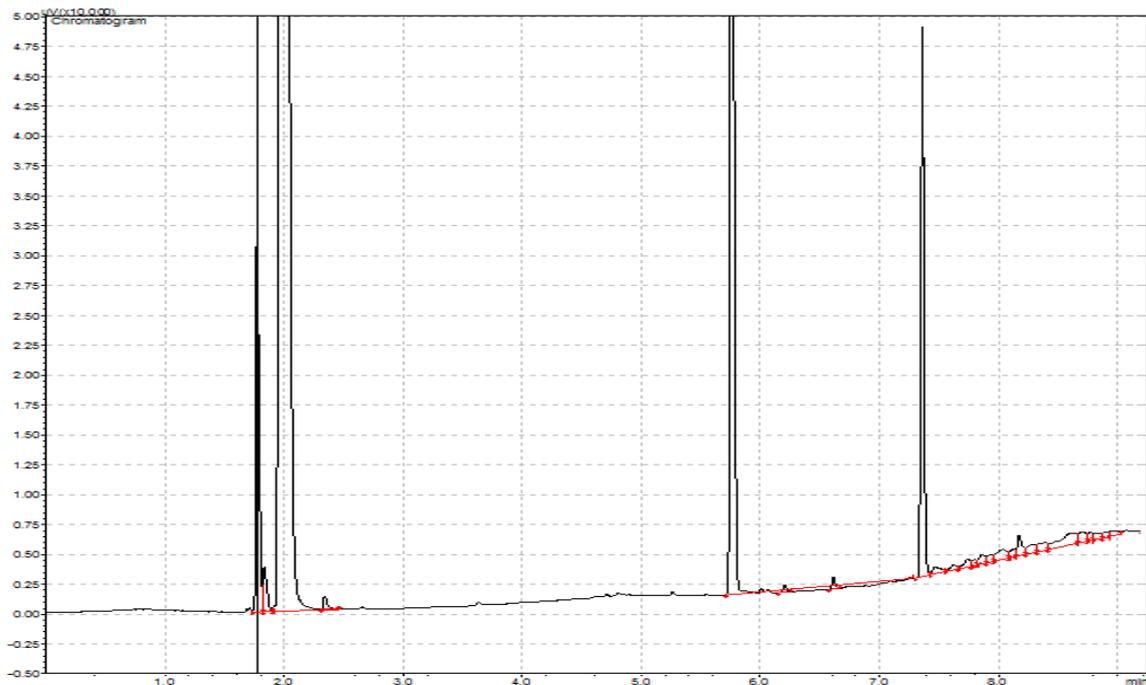


Figure 40 – GC chromatogram of Hexadecane. Retention times – 2.0 mins Ethyl Acetate, 5.8 mins Hexadecane and 7.3 mins n-Eicosane (Internal Standard)

## 4.2 Hexadecanoic Acid

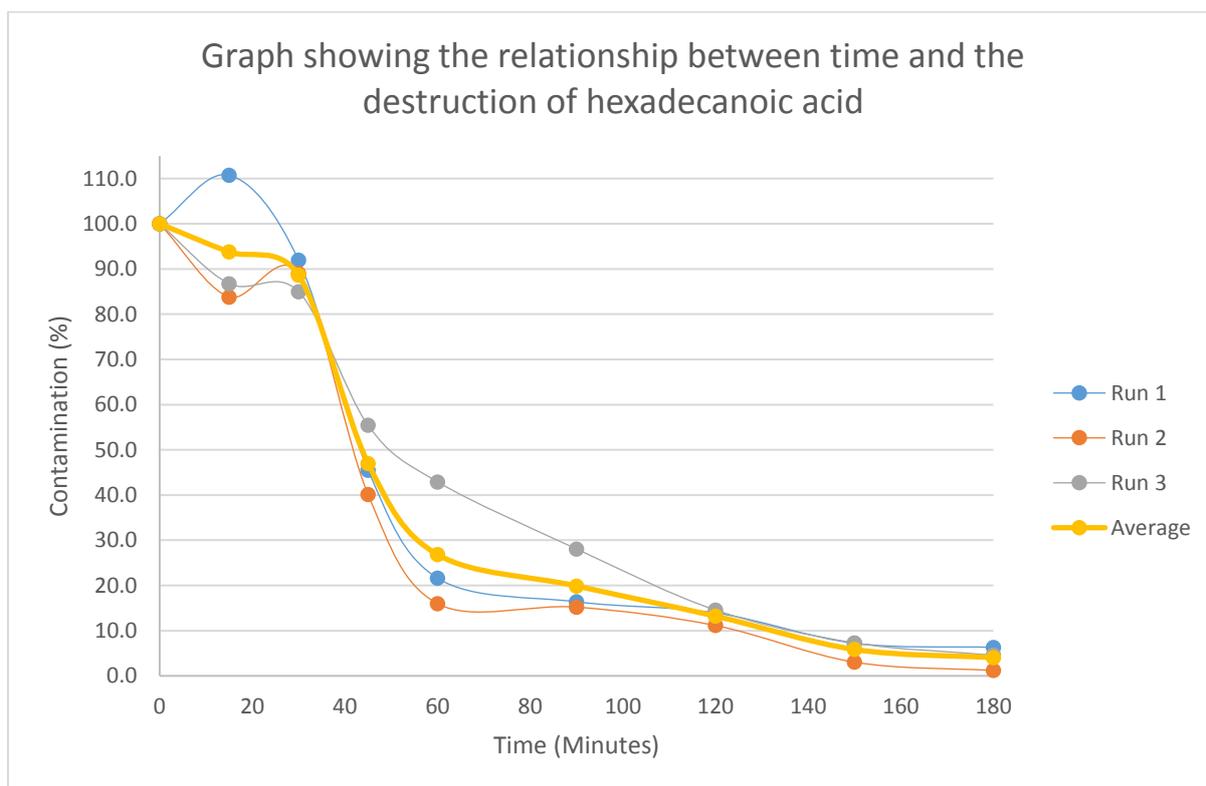


Figure 41 – Graph displaying time versus destruction of hexadecanoic acid at 300 RPM

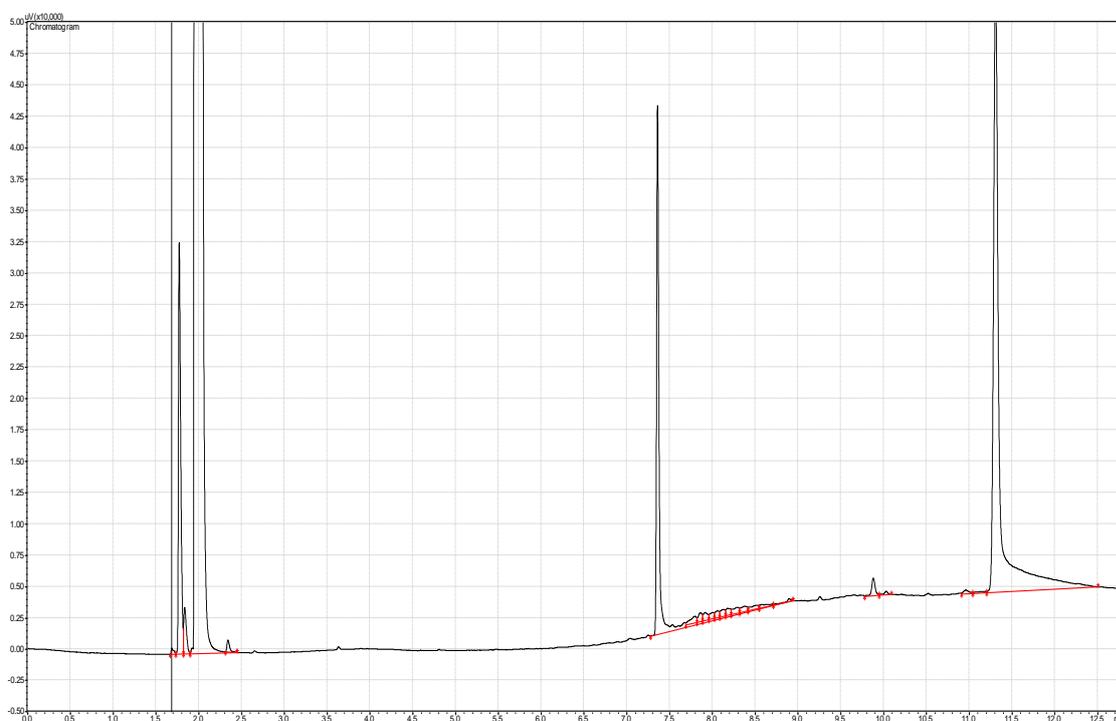


Figure 42 – GC chromatogram of Hexadecanoic Acid. Retention times – 2.0 mins Ethyl Acetate, 7.3 mins *n*-Eicosane (Internal Standard) and 11.4 mins Hexadecanoic Acid

### 4.3 Hexadecylamine

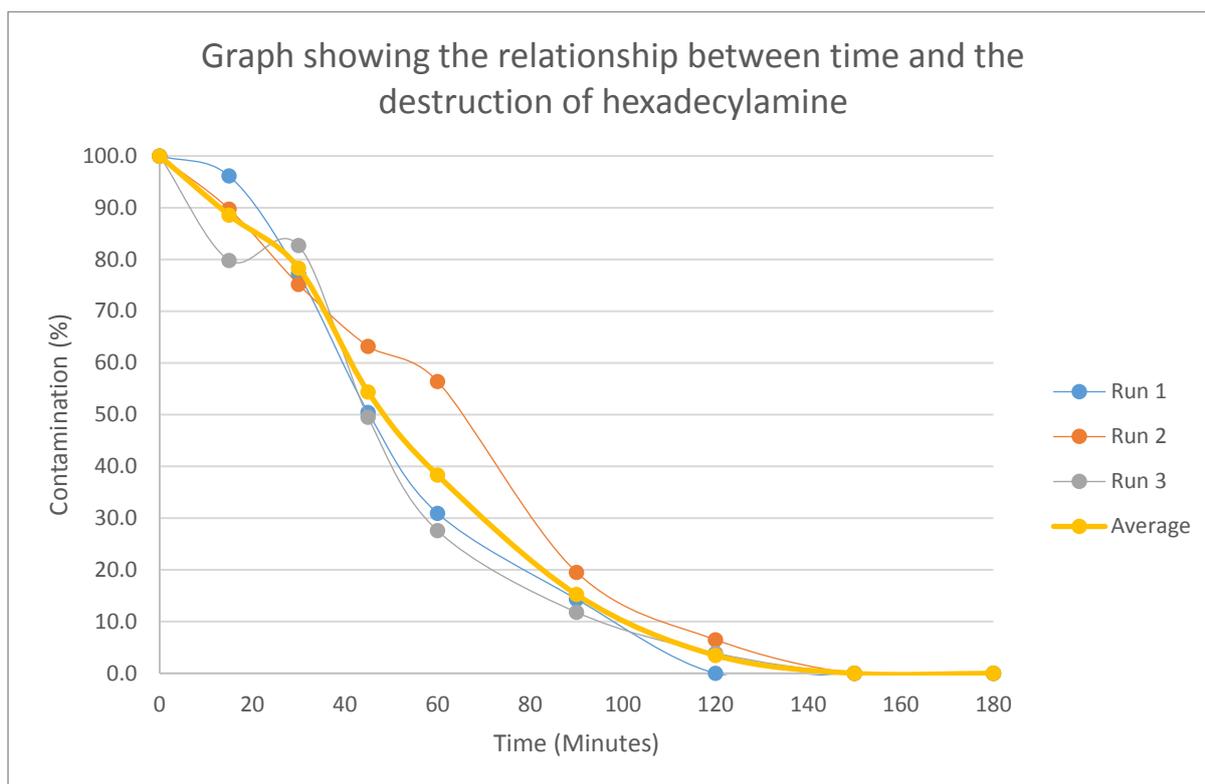


Figure 43 – Graph displaying time versus destruction of hexadecylamine at 300 RPM

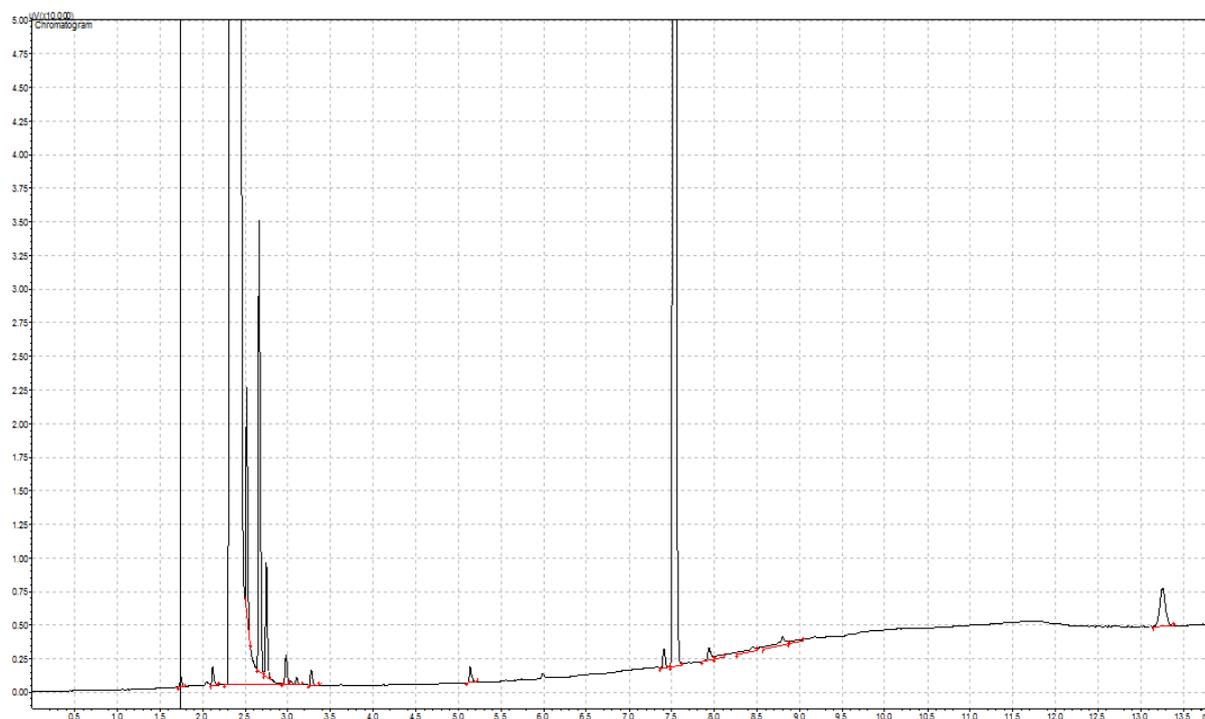


Figure 44 – GC chromatogram of Hexadecylamine. Retention times – 2.0 mins Ethyl Acetate, 7.55 mins n-Eicosane (Internal Standard) and 13.3 mins Hexadecylamine

#### 4.4 N-ethylhexadecanamide

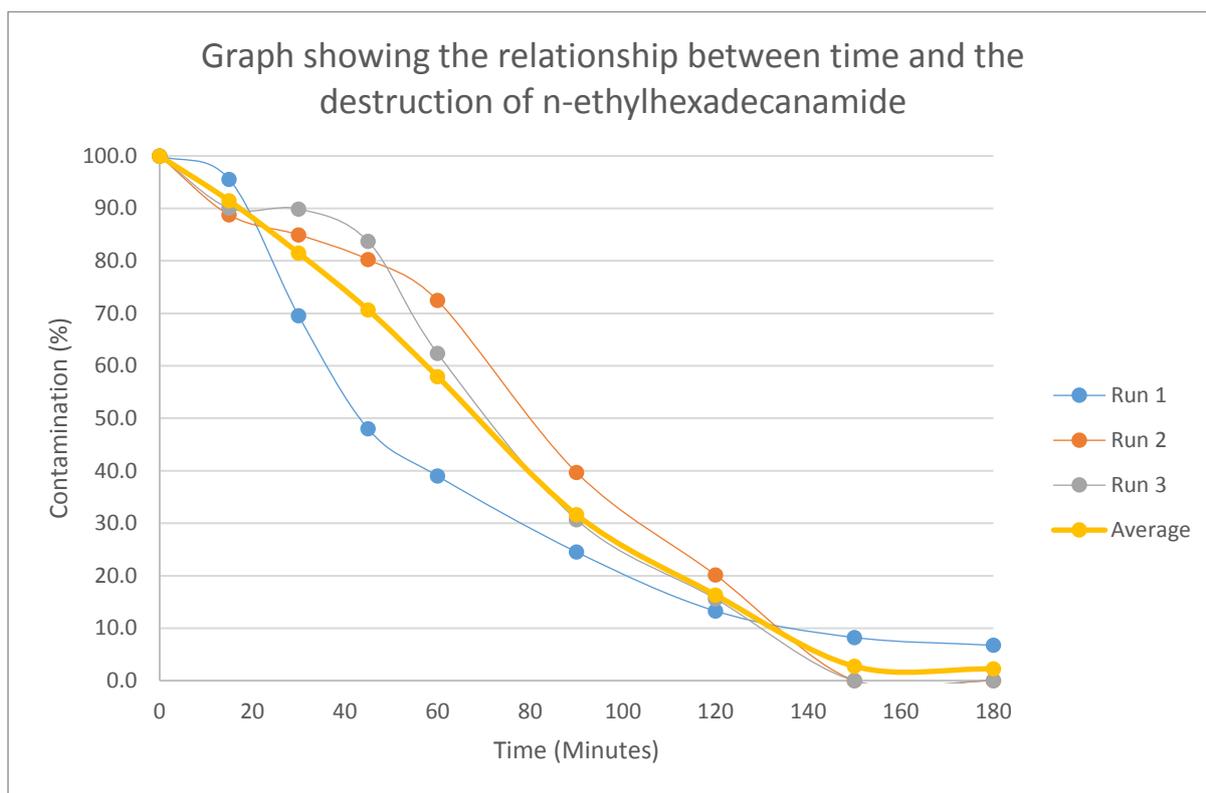


Figure 45 – Graph displaying time versus destruction of n-ethylhexadecanamide at 300 RPM

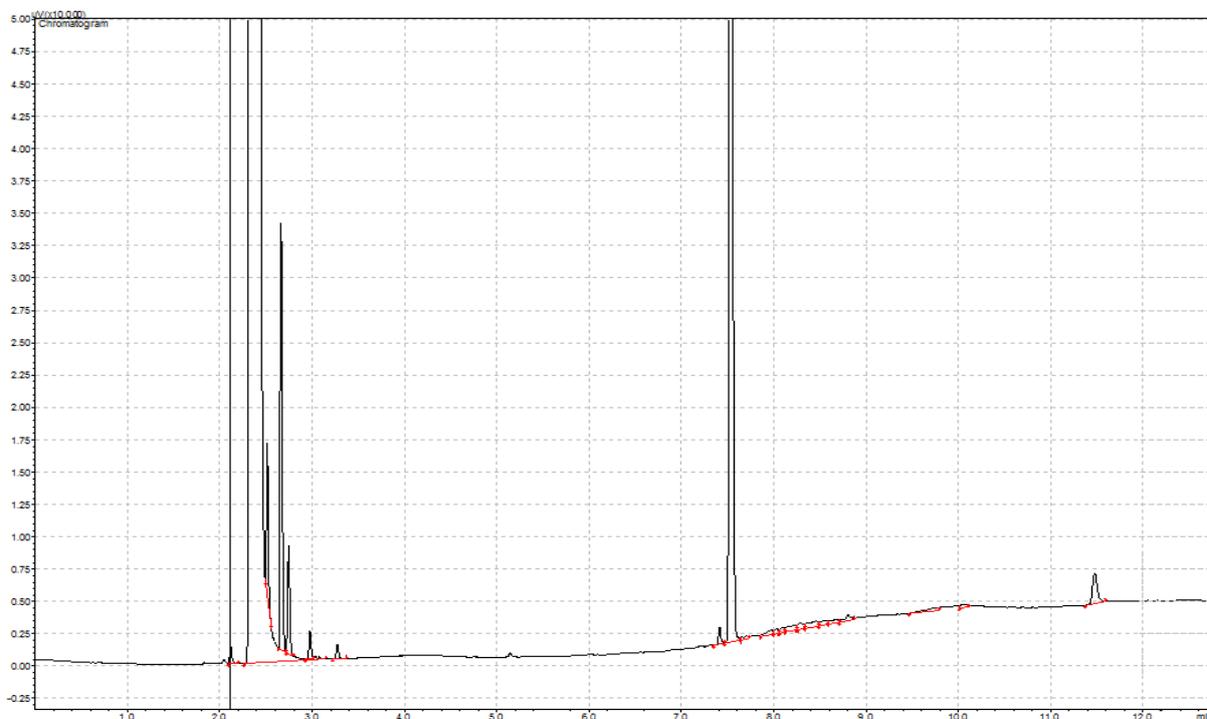


Figure 46 – GC chromatogram of N-ethylhexadecanamide. Retention times – 2.0 mins Ethyl Acetate, 7.55 mins n-Eicosane (Internal Standard) and 11.5 mins n-ethylhexadecanamide

## 4.5 Hexadecanol

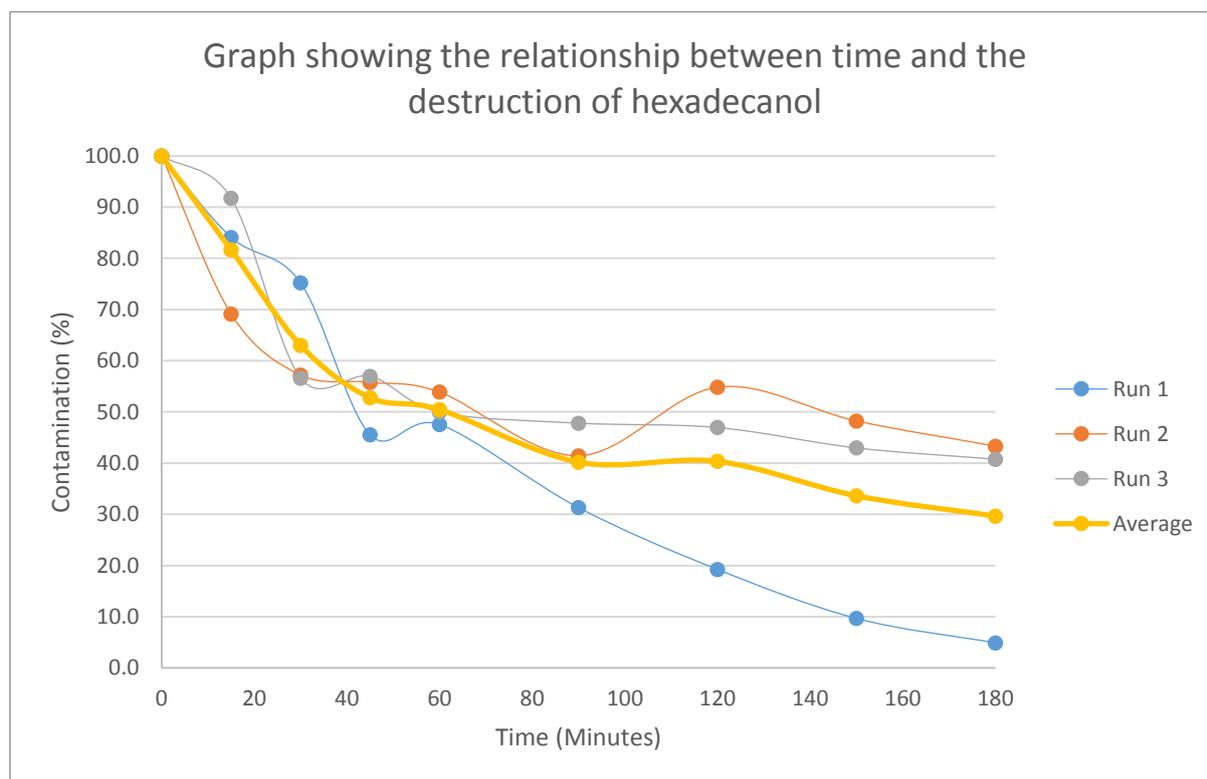


Figure 47 – Graph displaying time versus destruction of hexadecanol at 300 RPM

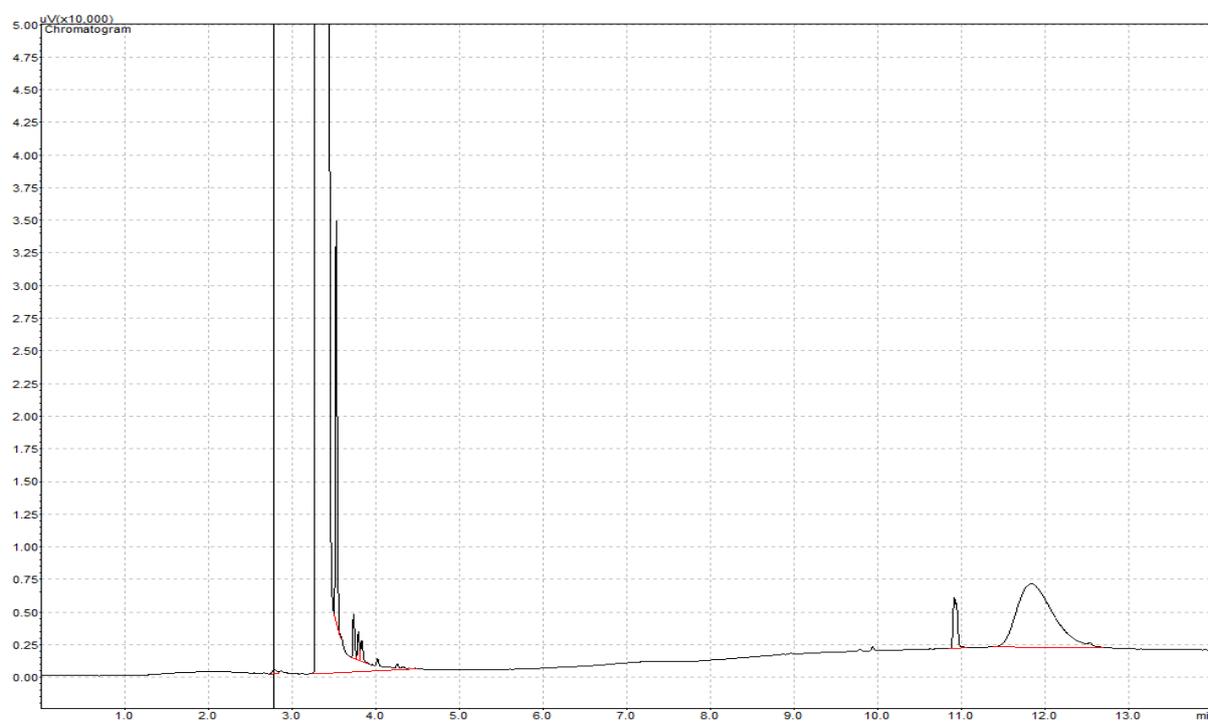


Figure 48 – GC chromatogram of N-ethylhexadecanamide. Retention times – 2.0 mins Ethyl Acetate, 10.9 mins n-Eicosane (Internal Standard) and 11.8 mins Hexadecan-1-ol

## 4.6 Hexadecanone

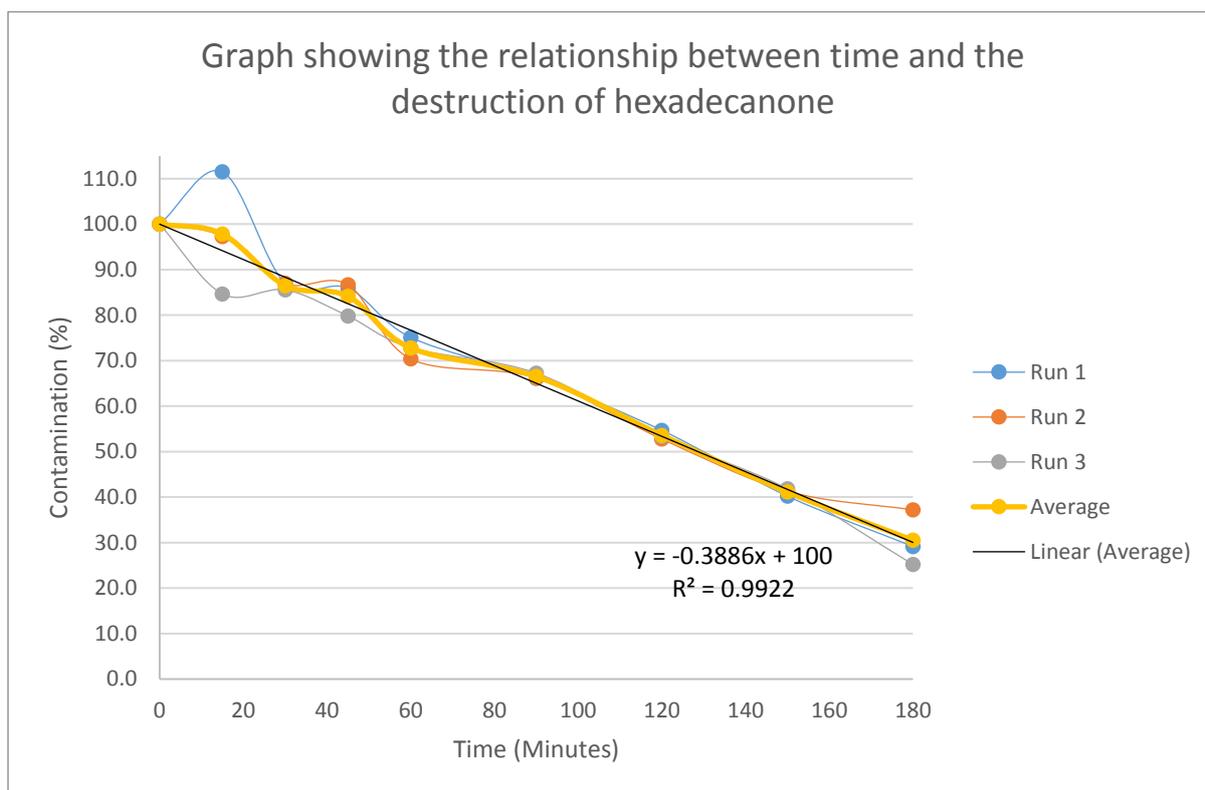


Figure 49 – Graph displaying time versus destruction of hexadecanone at 300 RPM

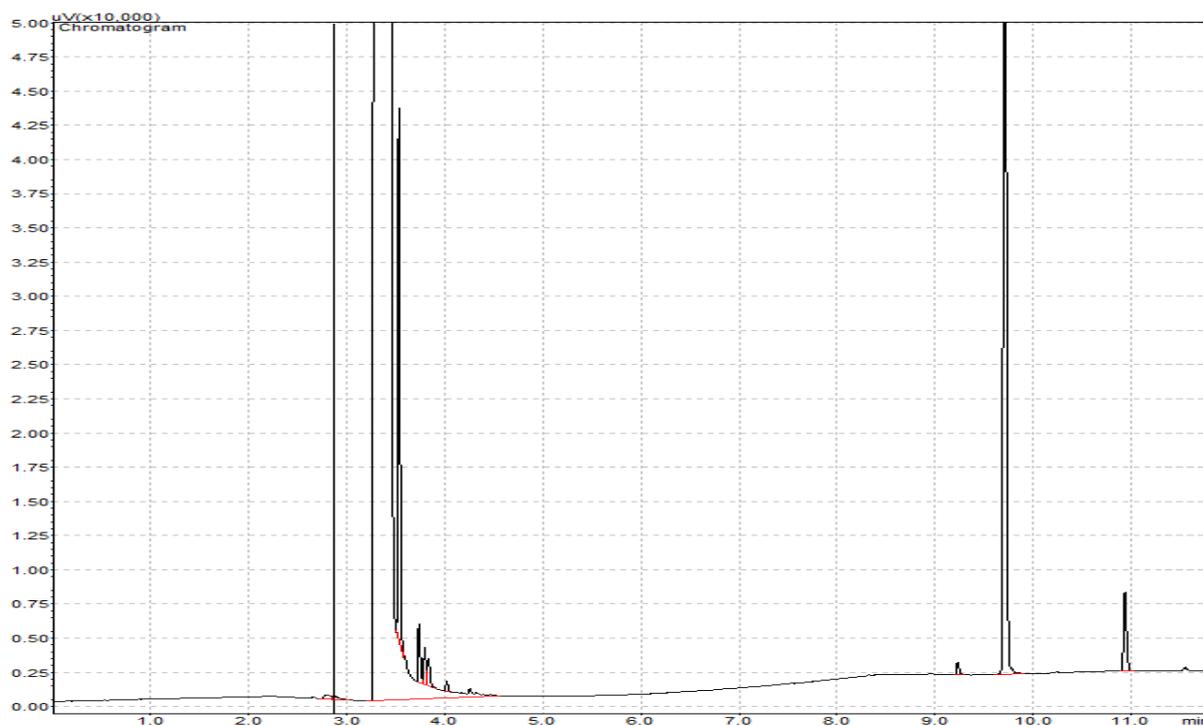


Figure 50 – GC chromatogram of Hexadecan-7-one. Retention times – 3.5 mins Ethyl Acetate, 9.6 mins Hexadecan-7-one and 10.8 mins *n*-Eicosane (Internal Standard)

## 4.7 Hexadecanoyl Chloride

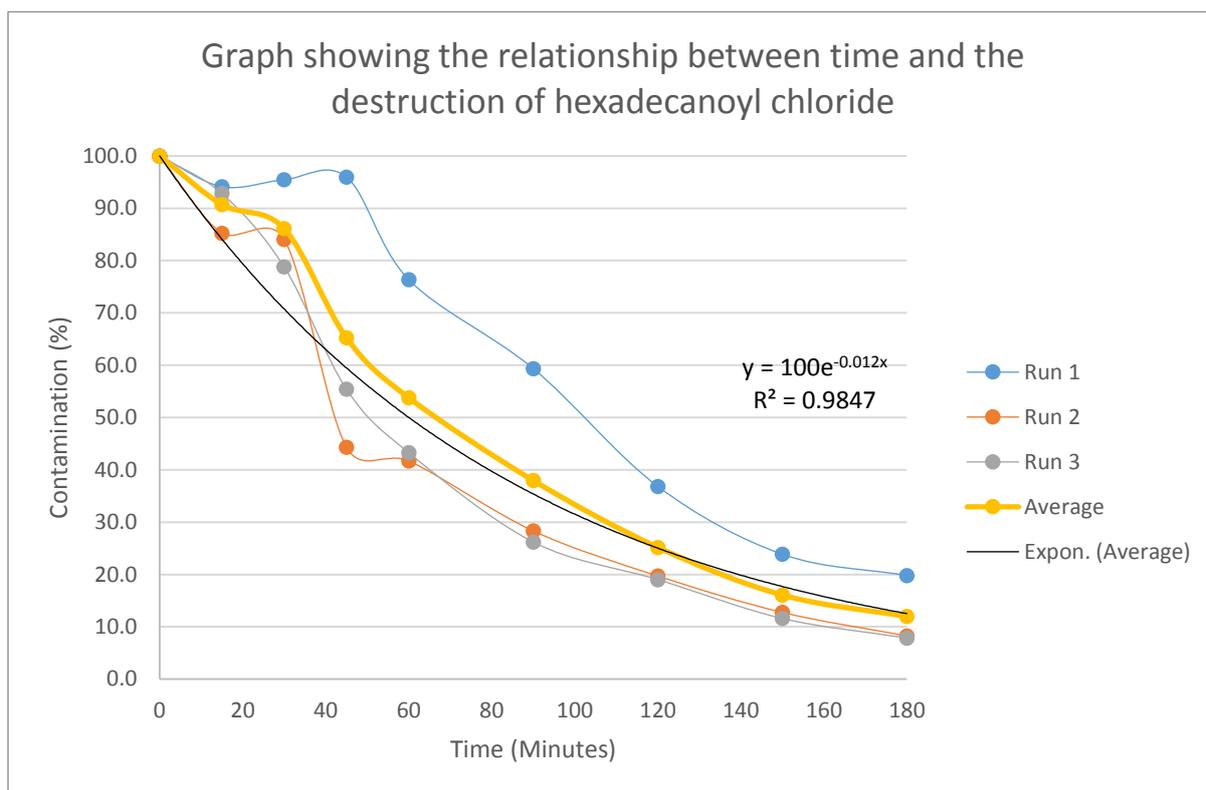


Figure 51 – Graph displaying time versus destruction of hexadecanoyl chloride at 300 RPM

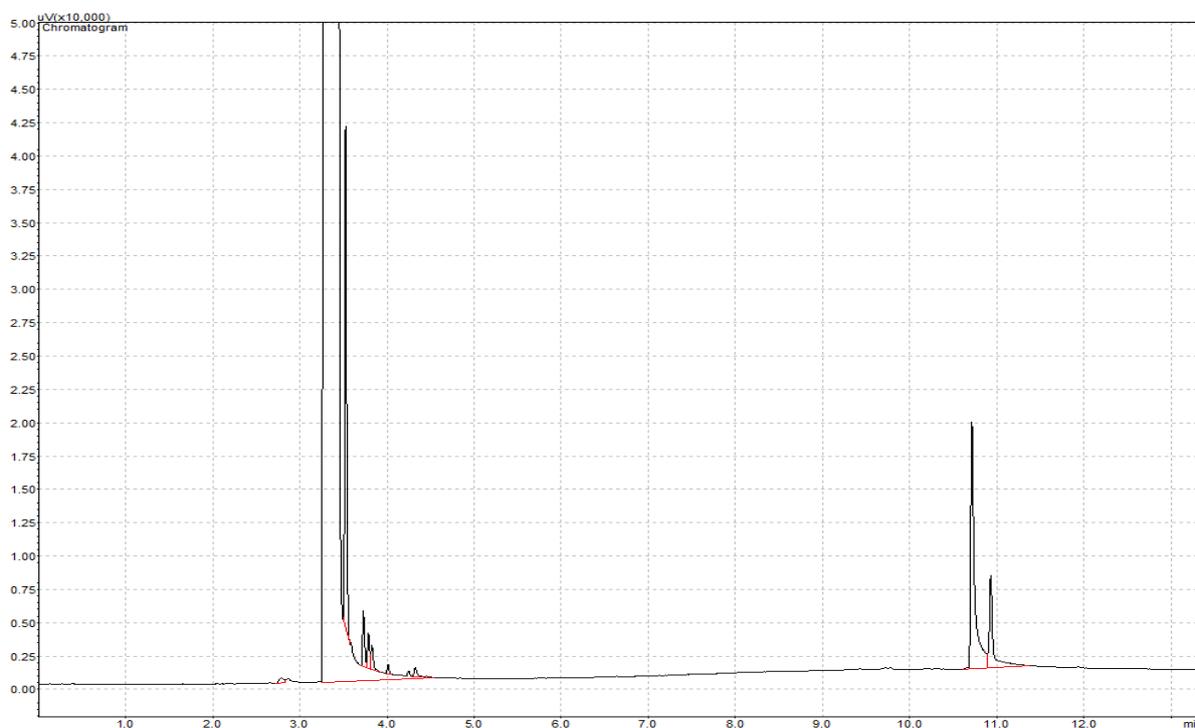


Figure 52 – GC chromatogram of Hexadecanoyl Chloride. Retention times – 3.5 mins Ethyl Acetate, 10.8 mins *n*-Eicosane (Internal Standard) and 10.9 mins Hexadecanoyl Chloride

## 4.8 Hexadecene

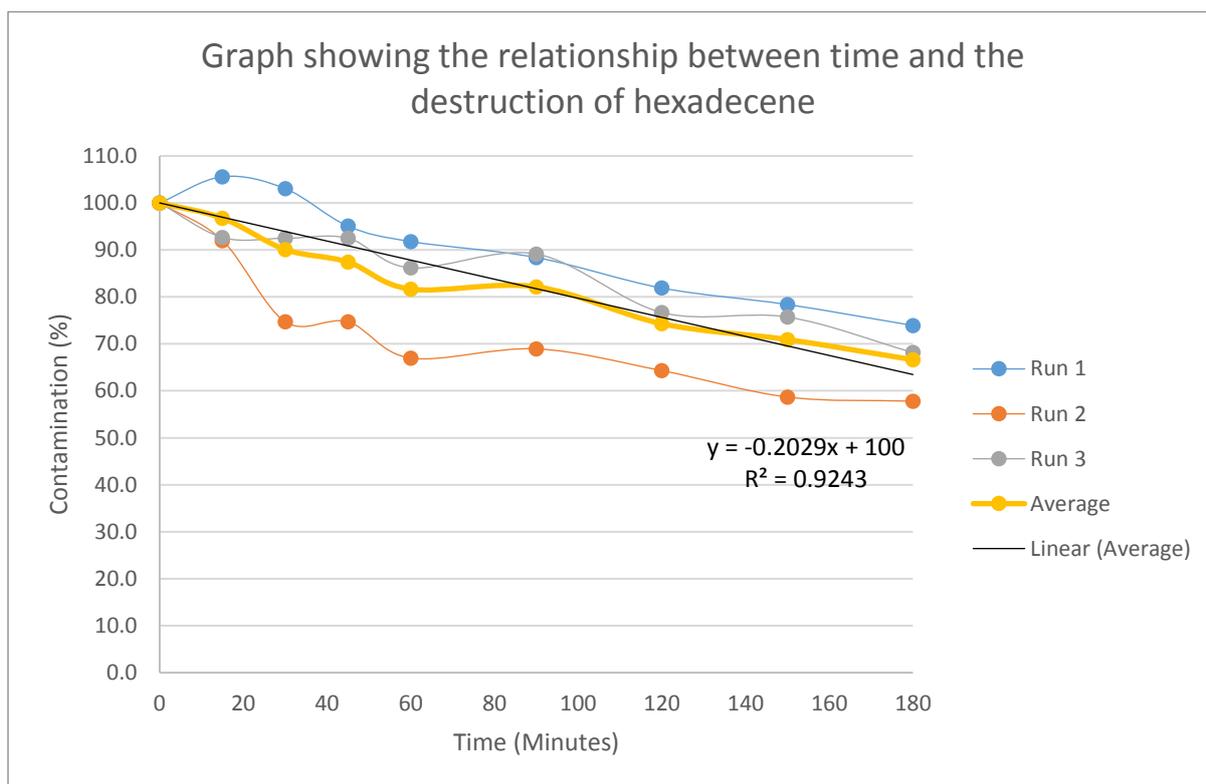


Figure 53 – Graph displaying time versus destruction of hexadecene at 300 RPM

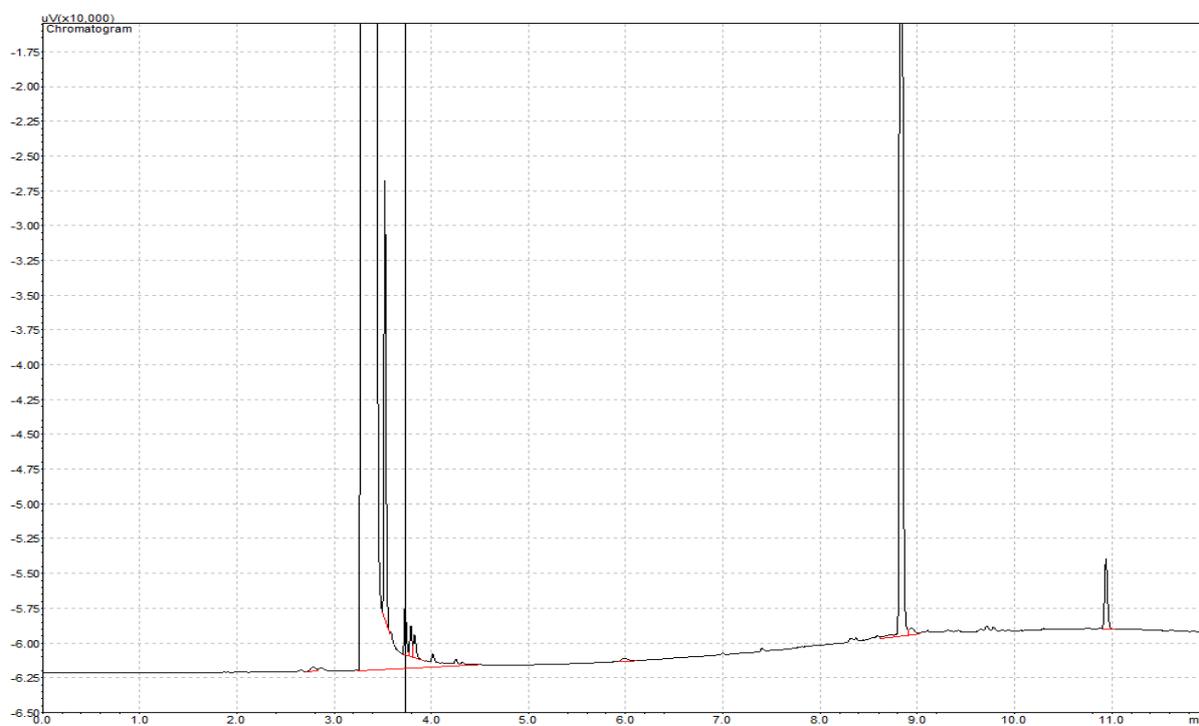


Figure 54 – GC chromatogram of Hexadec-1-ene. Retention times – 3.5 mins Ethyl Acetate, 8.8 mins Hexadec-1-ene and 10.8 mins n-Eicosane (Internal Standard)

## 4.9 Methyl Hexadecanoate

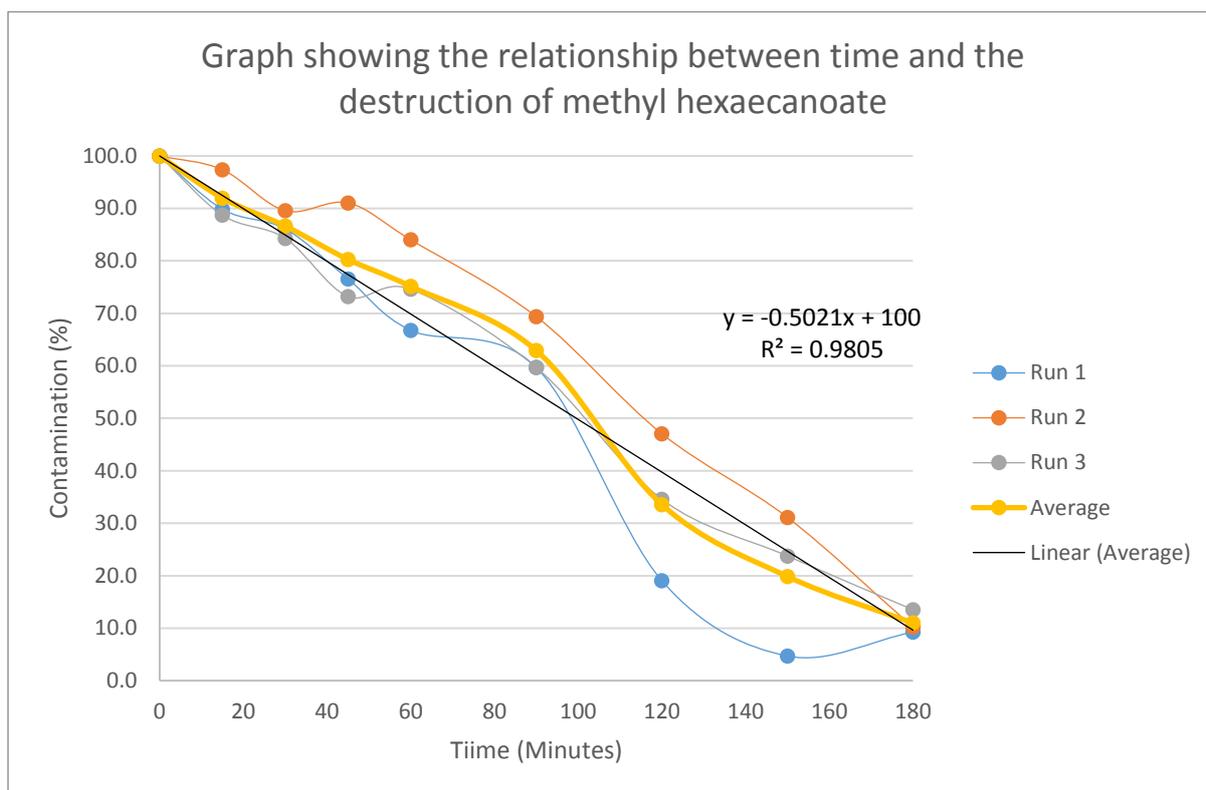


Figure 55 – Graph displaying time versus destruction of methyl hexadecanoate at 300 RPM

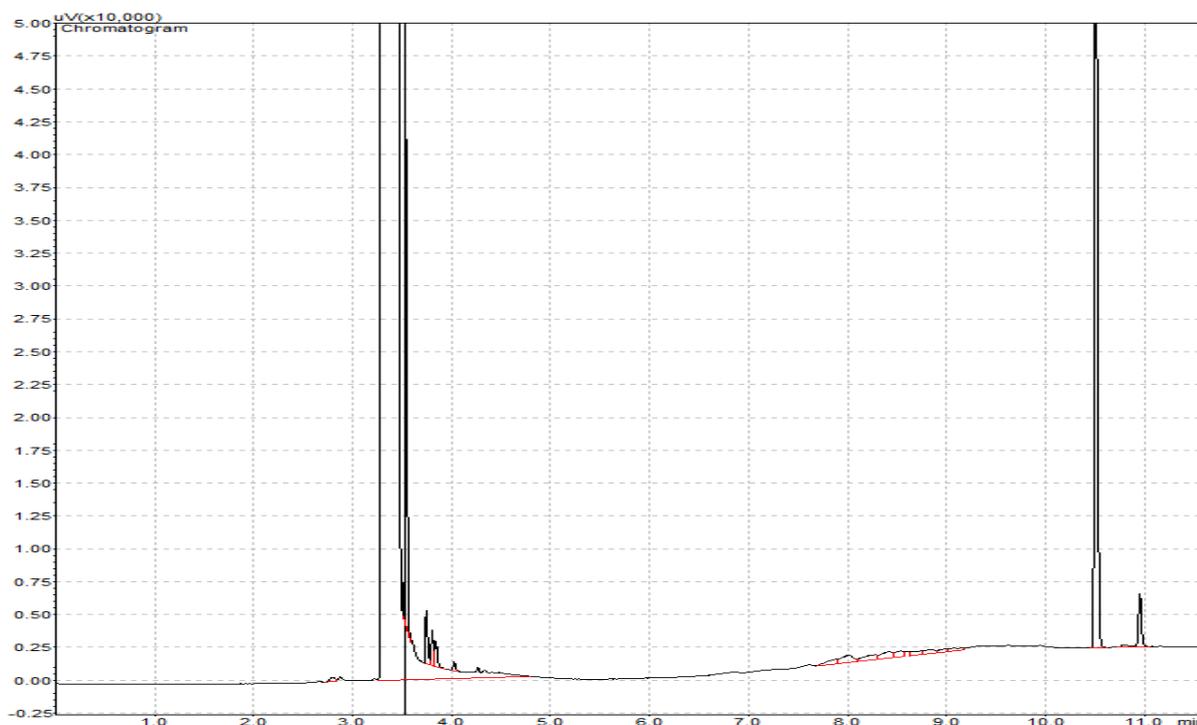


Figure 56 – GC chromatogram of Methyl Hexadecanoate. Retention times – 3.4 mins Ethyl Acetate, 10.6 mins Methyl Hexadecanoate and 10.8 mins n-Eicosane (Internal Standard)

## 4.10 Ethyl Hexadecanoate

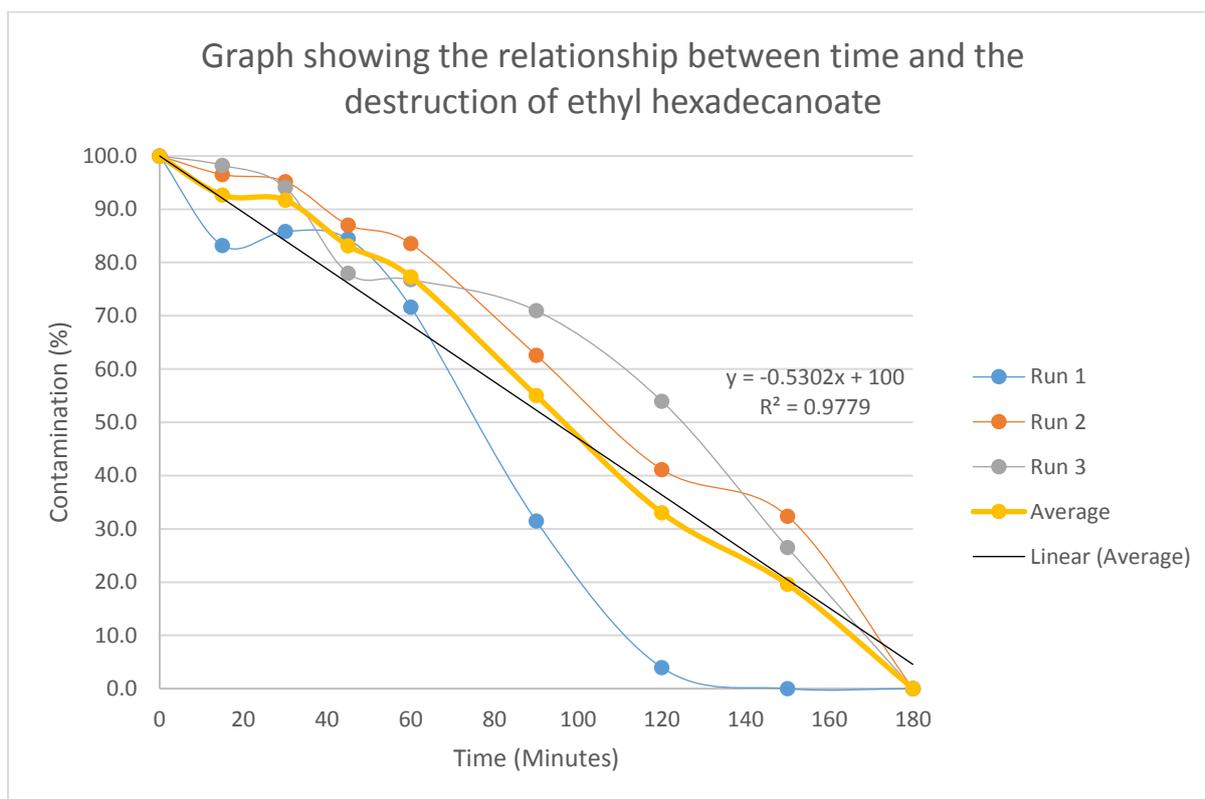


Figure 57 – Graph displaying time versus destruction of ethyl hexadecanoate at 300 RPM

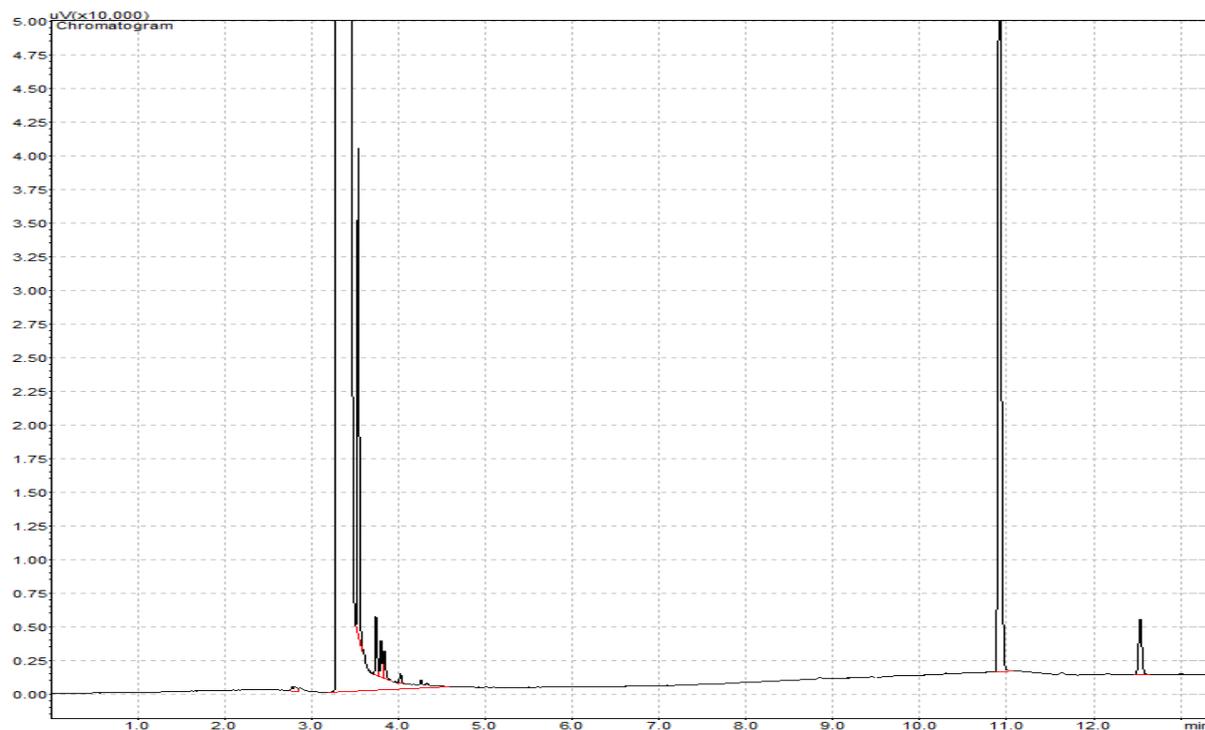


Figure 58 – GC chromatogram of Ethyl Hexadecanoate. Retention times – 3.4 mins Ethyl Acetate, 10.8 mins *n*-Eicosane (Internal Standard) and 12.5 mins Ethyl Hexadecanoate

## 4.11 Propyl Hexadecanoate

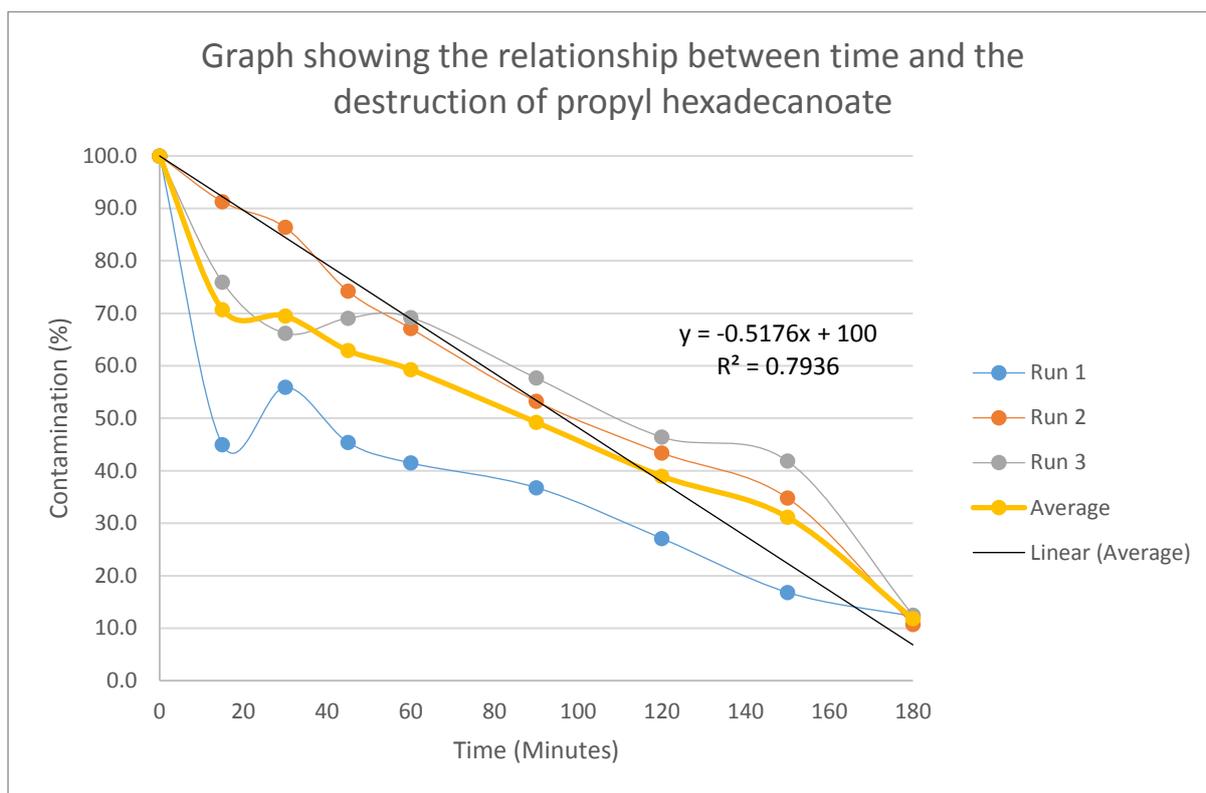


Figure 59 – Graph displaying time versus destruction of propyl hexadecanoate at 300 RPM

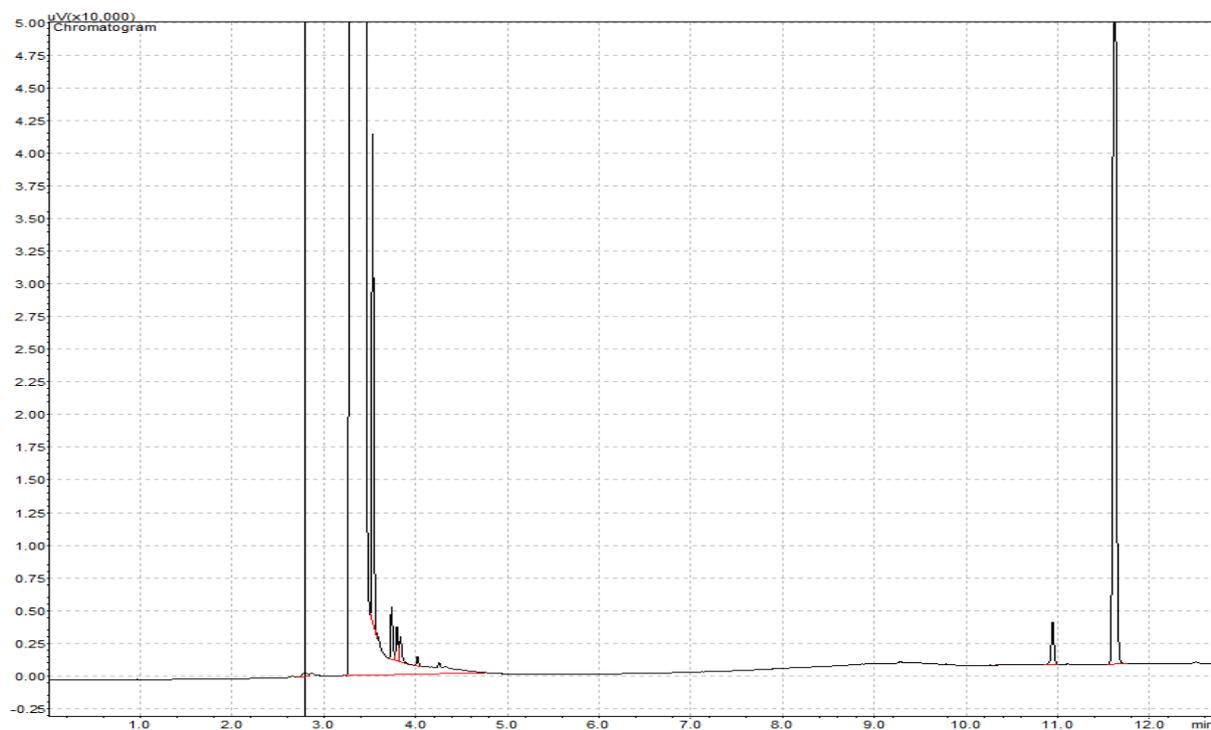


Figure 60 – GC chromatogram of Propyl Hexadecanoate. Retention times – 3.4 mins Ethyl Acetate, 10.8 mins *n*-Eicosane (Internal Standard) and 11.6 mins Propyl Hexadecanoate

## 4.12 Decyl Hexadecanoate

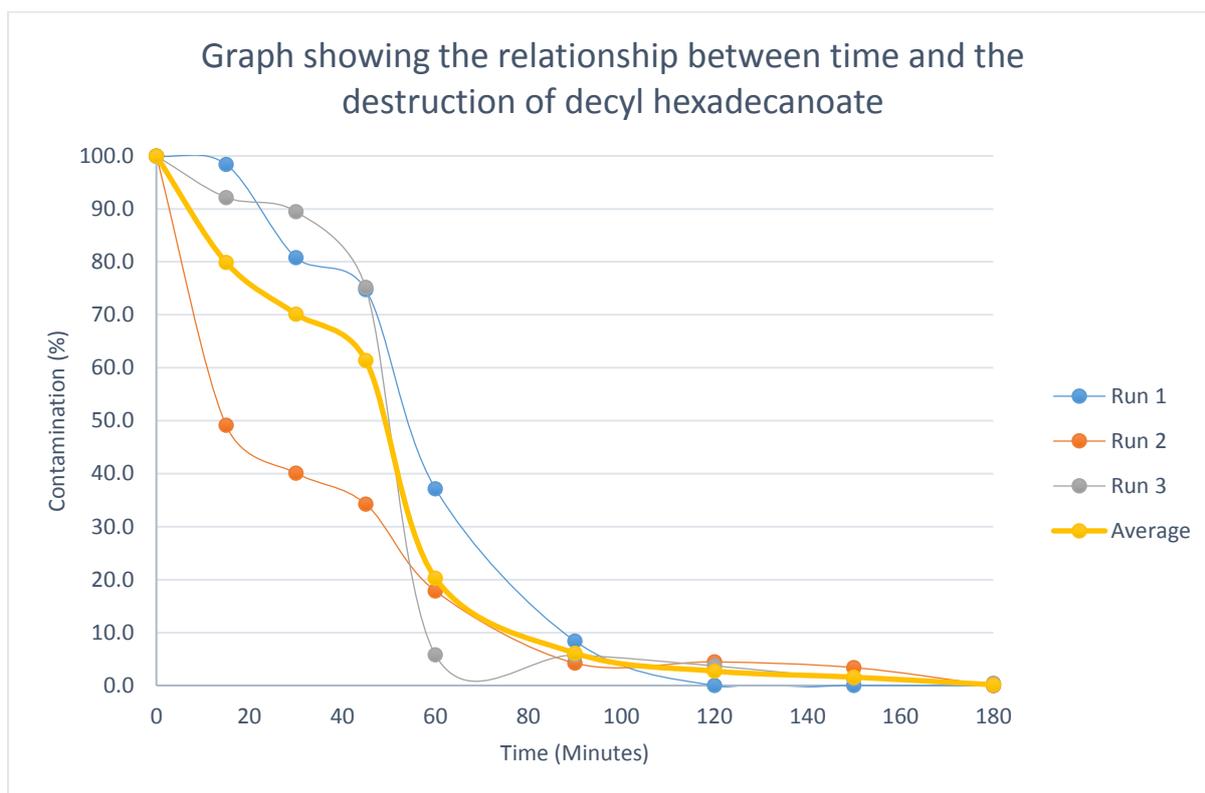


Figure 61 – Graph displaying time versus destruction of decyl hexadecanoate at 300 RPM

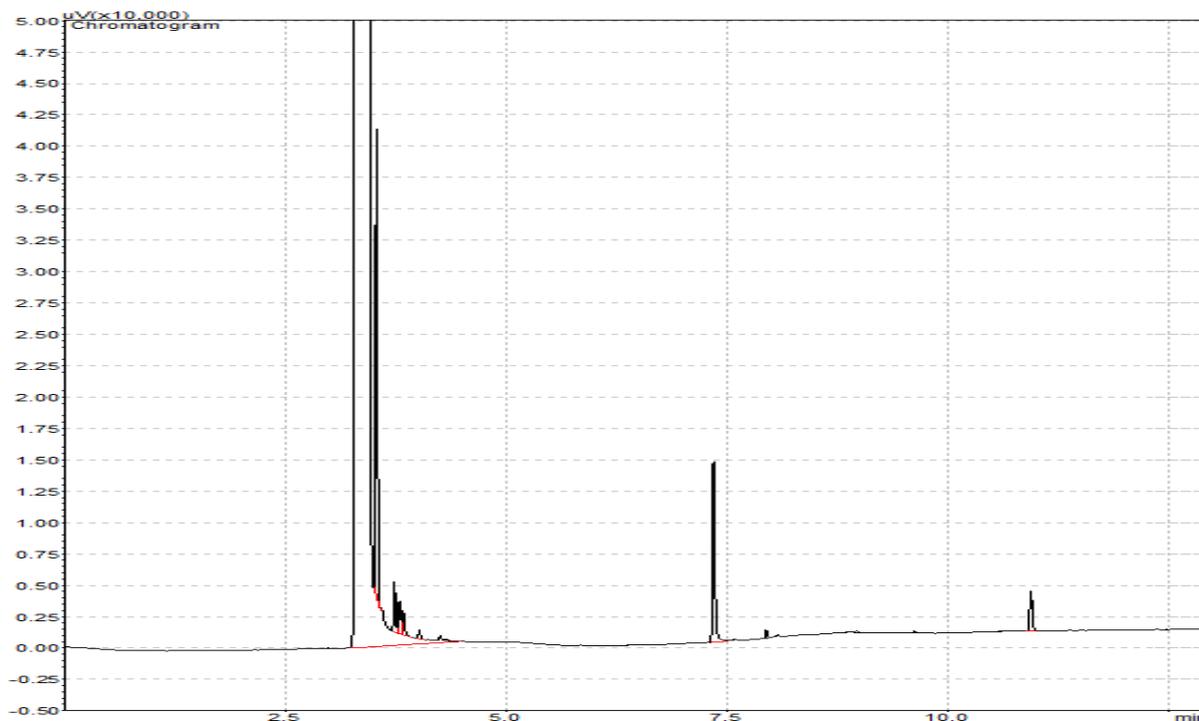


Figure 62 – GC chromatogram of Decyl Hexadecanoate. Retention times – 3.4 mins Ethyl Acetate, 6.8 mins Decyl Hexadecanoate and 10.8 mins n-Eicosane (Internal Standard)

## 4.13 400 RPM

### 4.13.1 Hexadecanol at 400 RPM

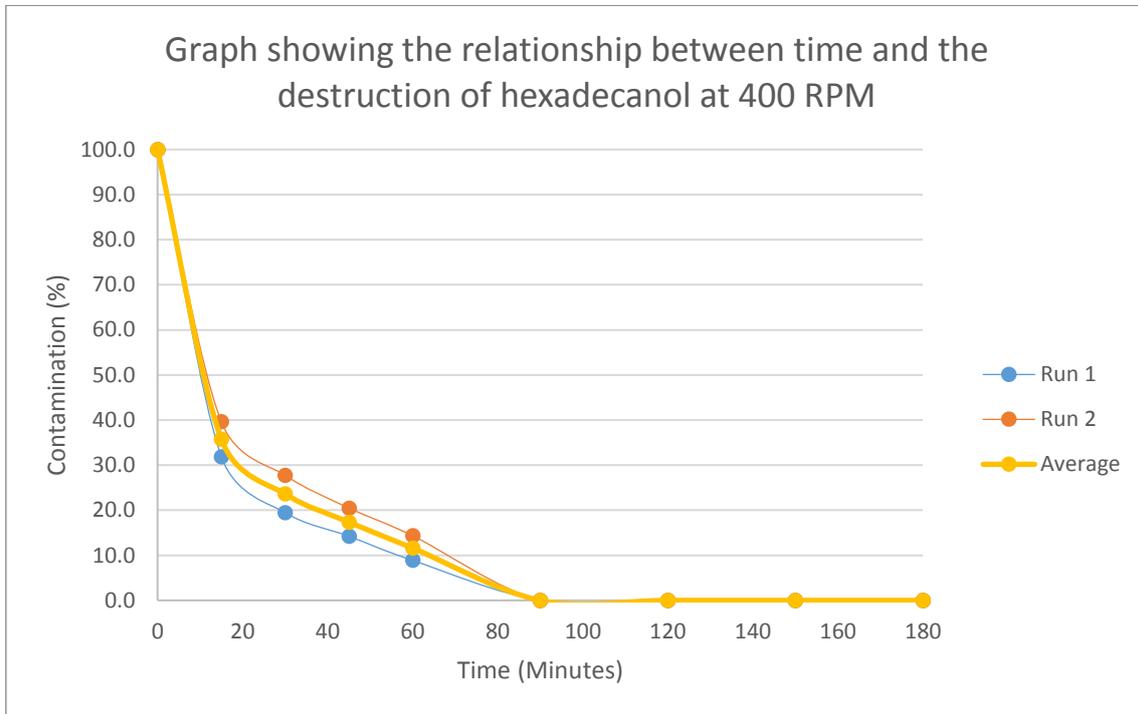


Figure 63 – Graph displaying time versus destruction of hexadecanol at 400 RPM

### 4.13.2 Hexadecanone at 400 RPM

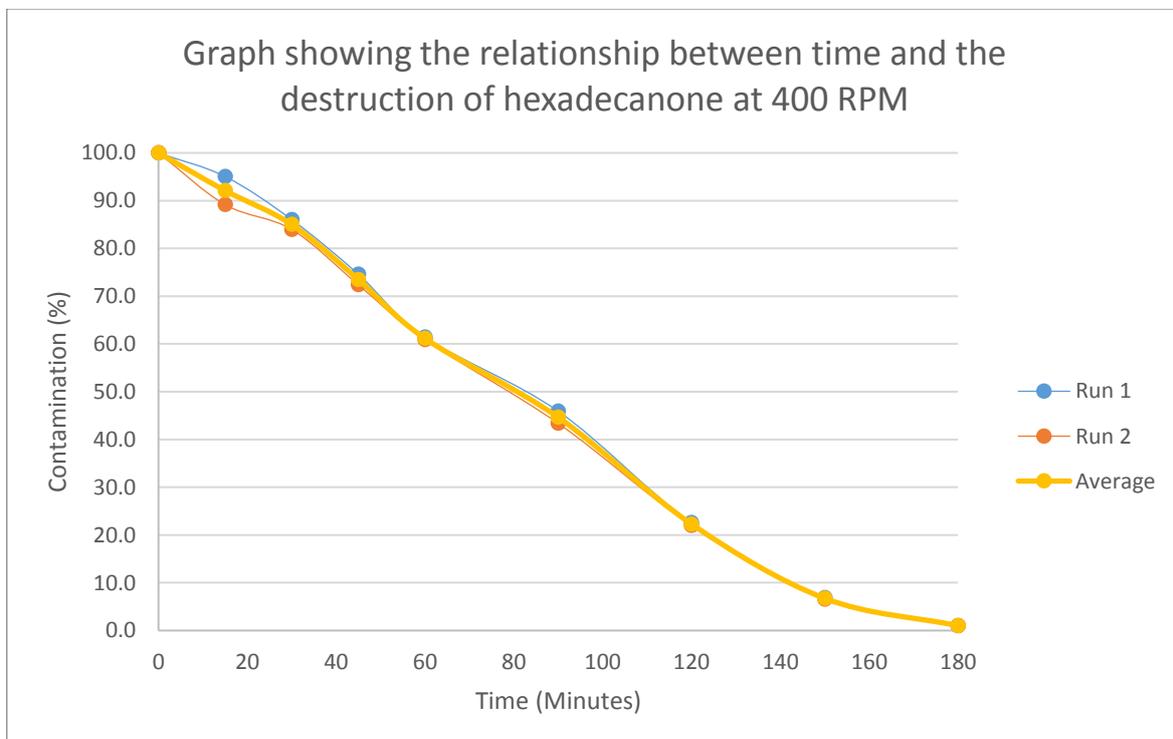


Figure 64 – Graph displaying time versus destruction of hexadecanone at 400 RPM

### 4.13.3 Hexadecene at 400 RPM

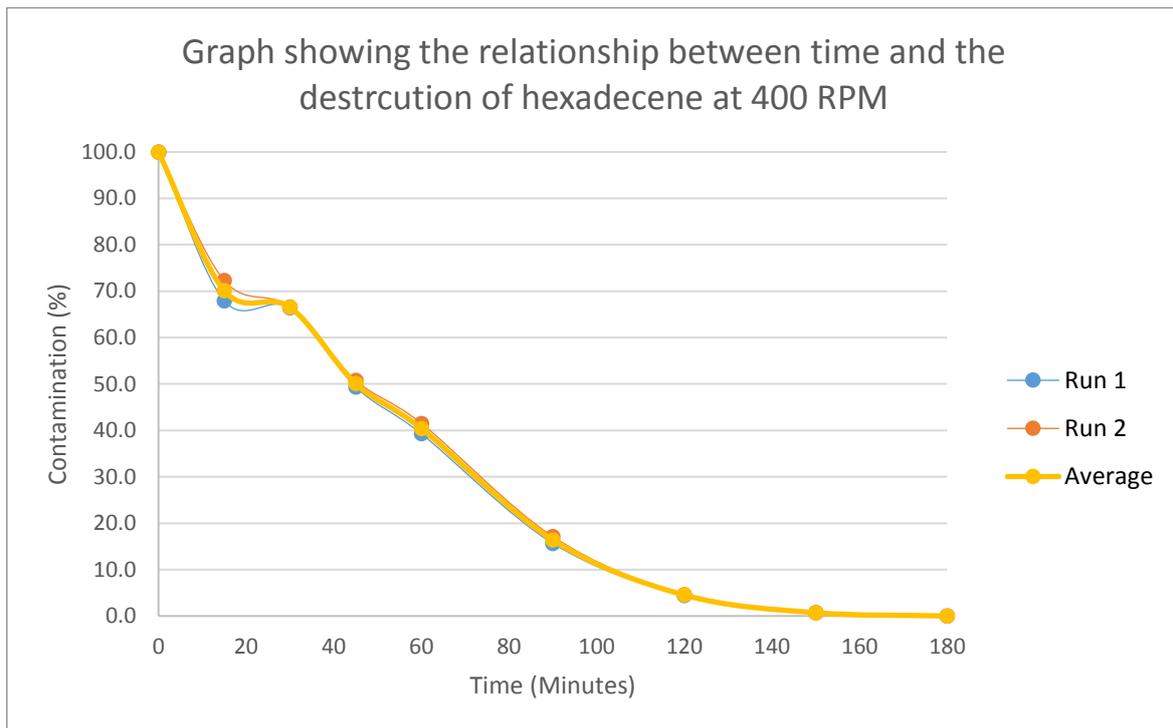


Figure 65 – Graph displaying time versus destruction of hexadecene at 400 RPM

### 4.14 500 RPM

#### 4.14.1 Hexadecanol at 500 RPM

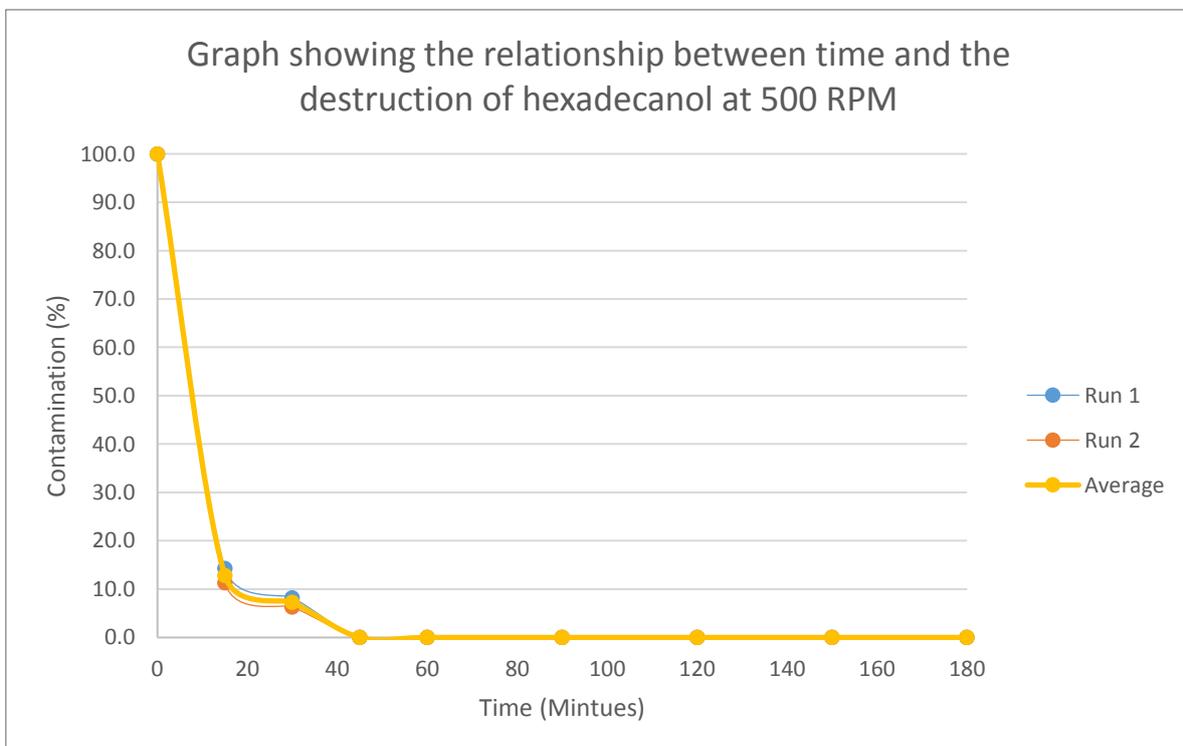


Figure 66 – Graph displaying time versus destruction of hexadecanol at 500 RPM

#### 4.14.2 Hexadecanone at 500 RPM

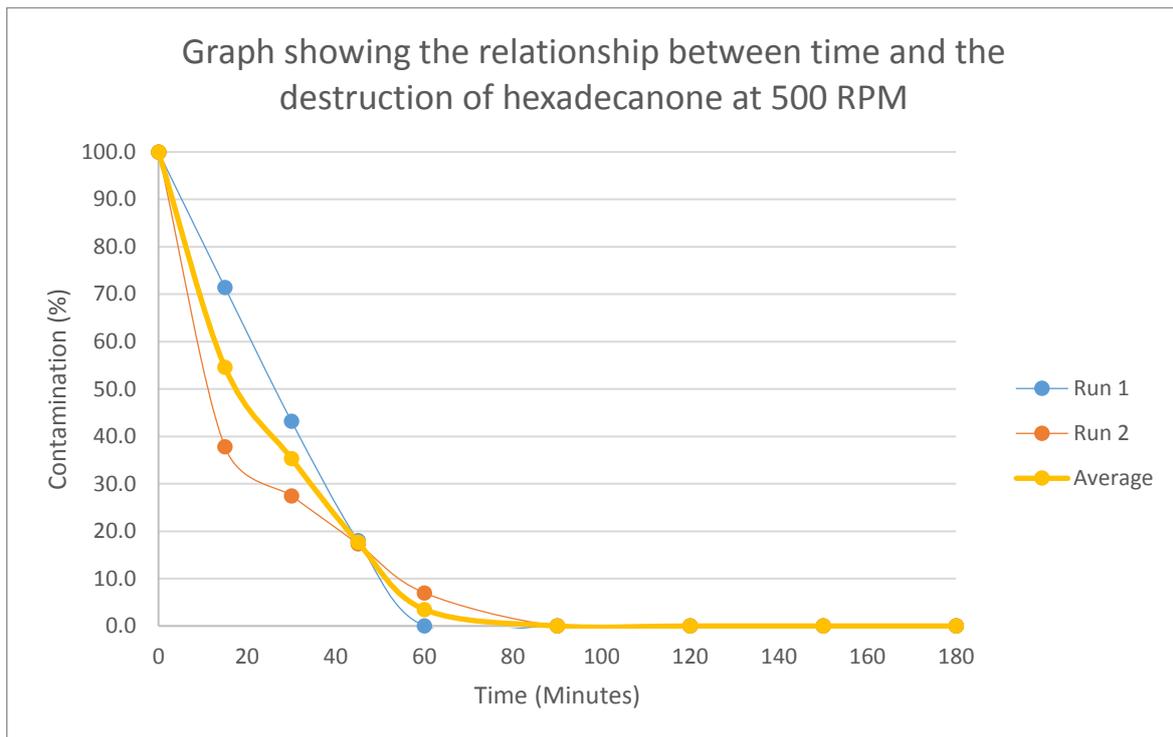


Figure 67 – Graph displaying time versus destruction of hexadecanone at 500 RPM

#### 4.14.3 Hexadecene at 500 RPM

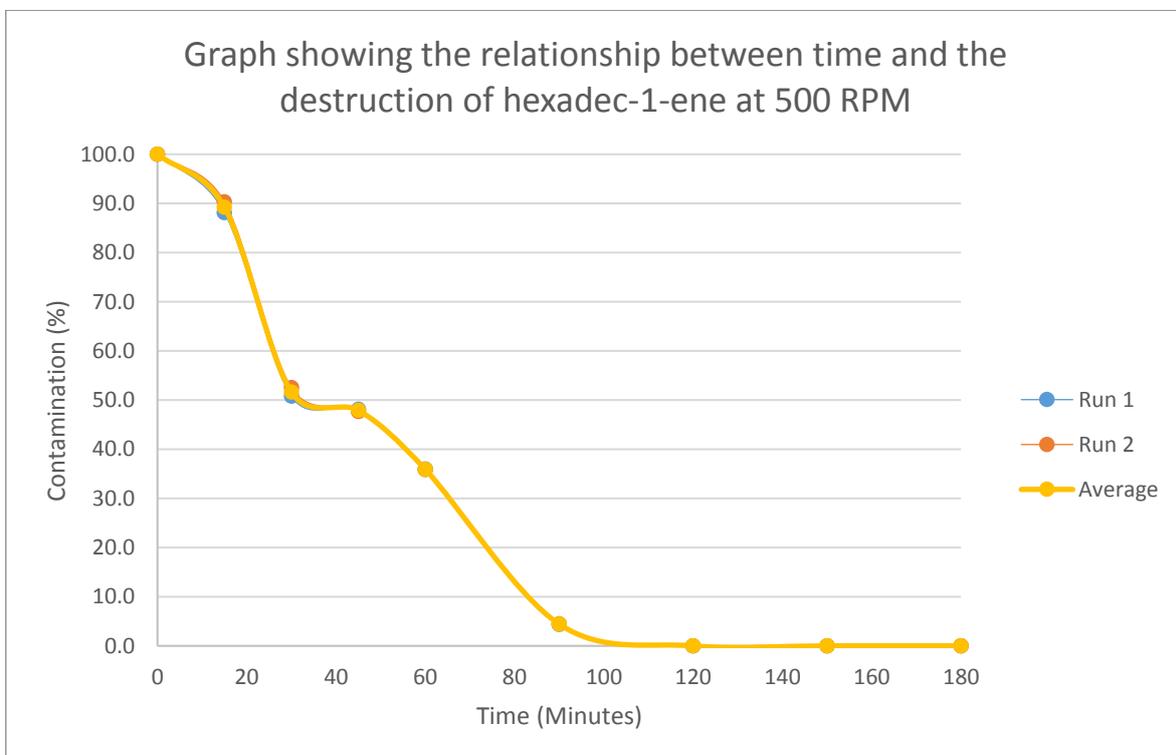


Figure 68 – Graph displaying time versus destruction of hexadecene at 500 RPM

## 4.15 Testing the Relative Extraction Efficiency of the Solvent

### 4.15.1 Hexadecane

Table 4 – Table showing the results obtained for the extraction efficiency of hexadecane

<b>Trial</b>	<b>Initial Mass (g)</b>	<b>Final Mass (g)</b>	<b>Extraction Efficiency (%)</b>	<b>Average Extraction Efficiency (%)</b>
<b>1</b>	1.002	0.096	90.42	90.11
<b>2</b>	1.093	0.099	90.94	
<b>3</b>	1.087	0.109	89.97	

### 4.15.2 Hexadecylamine

Table 5 – Table showing the results obtained for the extraction efficiency for hexadecylamine

<b>Trial</b>	<b>Initial Mass (g)</b>	<b>Final Mass (g)</b>	<b>Extraction Efficiency (%)</b>	<b>Average Extraction Efficiency (%)</b>
<b>1</b>	1.104	0.110	90.04	90.02
<b>2</b>	0.998	0.121	87.88	
<b>3</b>	1.043	0.082	92.14	

### 4.15.3 Hexadecene

Table 6 – Table showing the results obtained for the extraction efficiency for hexadecene

<b>Trial</b>	<b>Initial Mass (g)</b>	<b>Final Mass (g)</b>	<b>Extraction Efficiency (%)</b>	<b>Average Extraction Efficiency (%)</b>
<b>1</b>	1.016	0.096	90.55	90.09
<b>2</b>	1.077	0.105	90.25	
<b>3</b>	0.979	0.103	89.48	

## 4.16 Summary of Results

Table 7 - Table showing the approximate time to reach the half-life ( $t_{1/2}$  or 50%) and the 2 half-lives ( $t_{1/4}$  or 25%) from the average lines at 300 RPM.

<b>Compound</b>	<b><math>t_{1/2}</math> (Minutes)</b>	<b><math>t_{1/4}</math> (Minutes)</b>
Hexadecane	20	65
Hexadecanoic Acid	42	90
Hexadecylamine	50	81
N-ethylhexadecanamide	70	112
Hexadecanol	60	196
Hexadecanone	127	200
Hexadecanoyl chloride	70	120
Hexadecene	264	404
Methyl Hexadecanoate	105	135
Ethyl Hexadecanoate	100	130
Propyl Hexadecanoate	90	155
Decyl Hexadecanoate	50	60

The half-life and the 2 half-lives were calculated by reading time taken on the graph for 50% destruction then for 25% destruction. Interpreting the results like this allows for comparisons to be made easier. Due to the curves of the graph not being strictly first order, but assuming the destruction is a complex mixture of processes, the first and second half-life provide a way of comparing this complex process.

Table 8 – Table showing the estimated time needed for 100% destruction at 300 RPM.

<b>Compound</b>	<b>Time Taken for 100% Destruction (Minutes)</b>
Hexadecane	190
Hexadecanoic Acid	200
Hexadecylamine	145
N-ethylhexadecanamide	150
Hexadecanol	320
Hexadecanone	260
Hexadecanoyl chloride	240

Hexadecene	545
Methyl Hexadecanoate	220
Ethyl Hexadecanoate	180
Propyl Hexadecanoate	200
Decyl Hexadecanoate	170

Time taken for 100% destruction is very important. This provides the total time it took or would take in future under the same conditions. For the compounds that were not destroyed, the equation of the line was calculated and using the equation, the time it would take to reach 0% contamination could be worked out. It is important to note that it could have taken longer or less time than stated for those compounds as milling results are prone to randomisation.

*Table 9 – Table showing the estimated time needed for 100% destruction and half-life ( $t_{1/2}$  or 50%) at 400 RPM for selected compounds.*

<b>Compound</b>	<b>Time Taken for 100% Destruction (Minutes)</b>	<b><math>t_{1/2}</math> (minutes)</b>
Hexadecanol	90	15
Hexadecanone	180	80
Hexadecene	150	45

*Table 10 – Table showing the estimated time needed for 100% destruction and half-life ( $t_{1/2}$  or 50%) at 500 RPM for selected compounds.*

<b>Compound</b>	<b>Time Taken for 100% Destruction (Minutes)</b>	<b><math>t_{1/2}</math> (minutes)</b>
Hexadecanol	45	10
Hexadecanone	75	20
Hexadecene	100	35

The time taken for 100% destruction at 400 RPM and 500 RPM shows exactly how the time is nearly halved by increasing the speed of the mill. This is important as

increasing the speed adds a lot more energy inside the milling jar and therefore the rates at which the compounds breakdown increase significantly.

Below, are three graphs comparing the average destruction pattern at 300 RPM, 400 RPM and 500 RPM for hexadecanol, hexadecanone and hexadecene. By merging the three average lines at the three speeds, it allows us to have a better understanding of how much difference it can make.

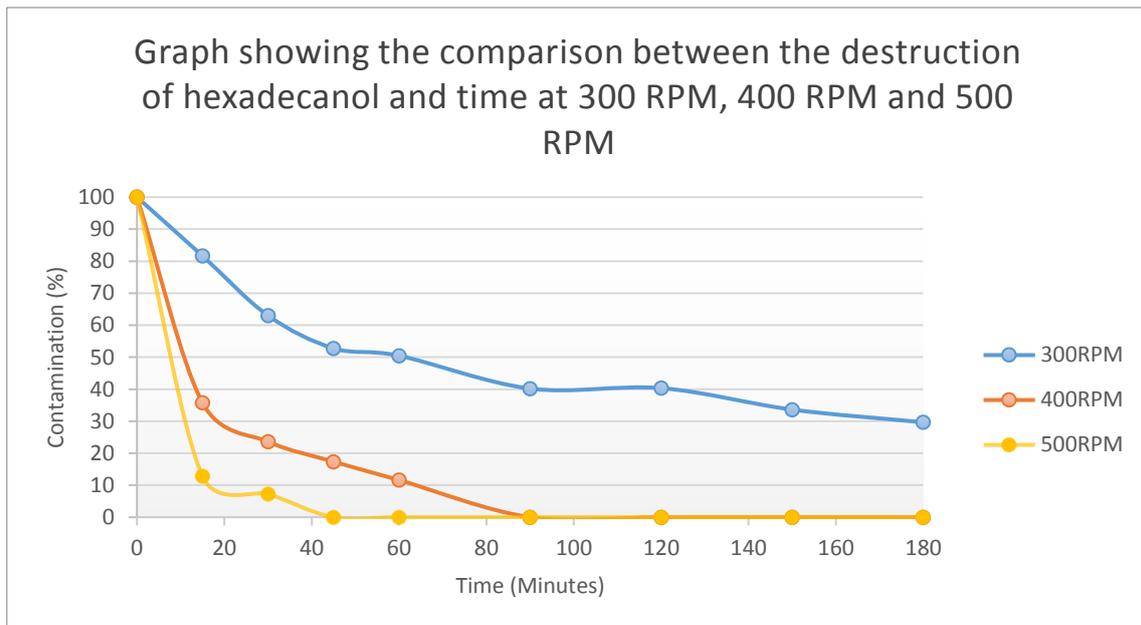


Figure 69 – Graph displaying time versus destruction of hexadecanol at 300 RPM, 400 RPM and 500 RPM

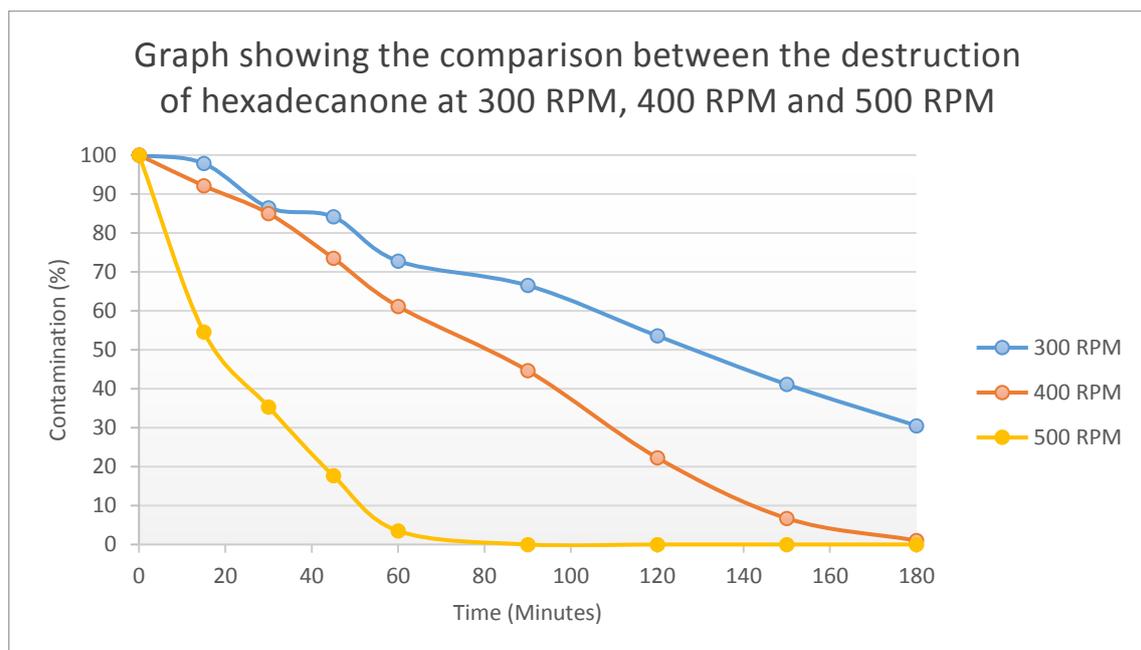


Figure 70 – Graph displaying time versus destruction of hexadecanone at 300 RPM, 400 RPM and 500 RPM

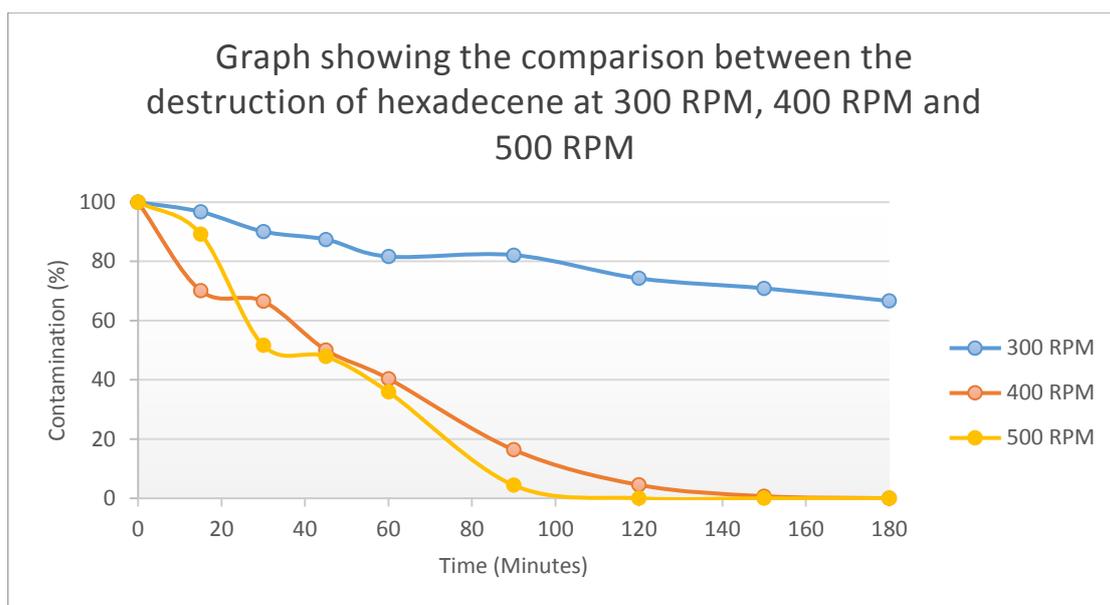


Figure 71 – Graph displaying time versus destruction of hexadecene at 300 RPM, 400 RPM and 500 RPM

Table 11 – Table showing the ionization potentials of 3-Carbon compounds with the half-life and the total time taken for 100% destruction at 300 RPM to occur of the compounds.

Compound	Ionization Potential of 3-Carbon Compounds (eV)	t <sub>1/2</sub> (Minutes)	Time Taken for 100% Destruction (Minutes)
Hexadecane	11.07	20	190
Hexadecanoic Acid	10.41	42	200
Methyl Hexadecanoate	9.86	105	220
Ethyl Hexadecanoate	10.00	100	180
Propyl Hexadecanoate	10.21	90	200
Hexadecanol	10.59	60	320
Hexadecanone	9.69	127	260
Hexadecylamine	9.50	70	150
N-ethylhexadecanamide	8.78	50	145
Hexadecene	10.73	264	545
Hexadecanoyl chloride	10.78	70	240

The table gives a broader look into the findings from this project. Due to not being able to find the ionization energies for 16 carbon compounds, instead of one of the

most established ionization energies available, 3 carbon compounds, was used. As one of the goals in this project is to determine whether there is a relationship between ionization and destruction rates, table 9 provides the information to determine that.

The two graphs next show whether there is a relationship between ionization energy and half-life, as well as, ionization energy and 100% destruction time.

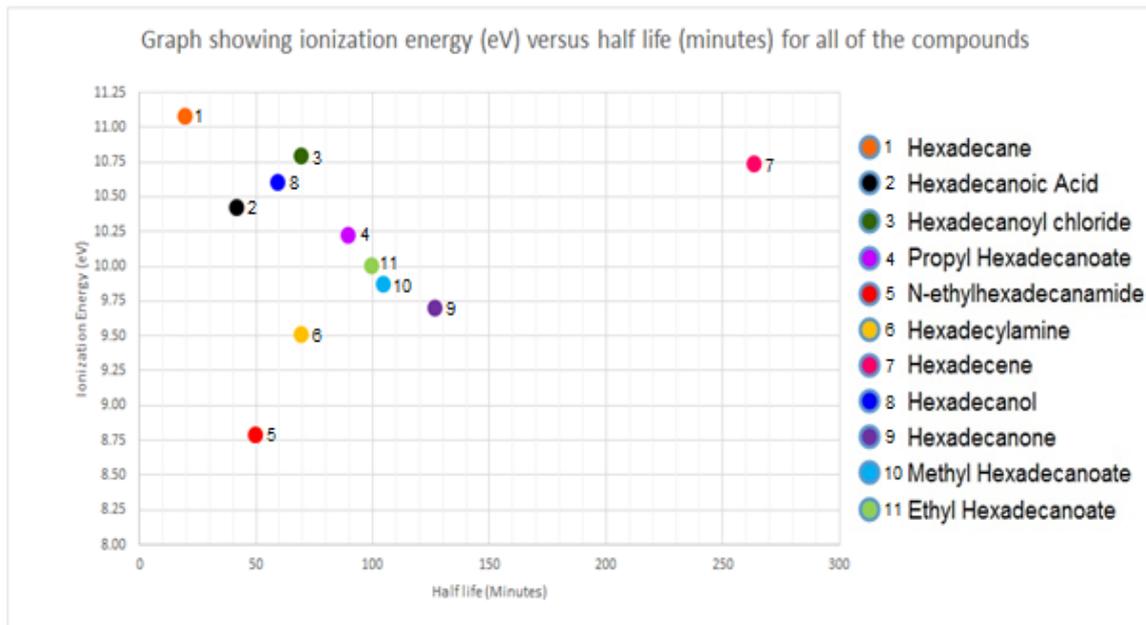


Figure 72 – Graph displaying ionization energy versus half-life for all compounds

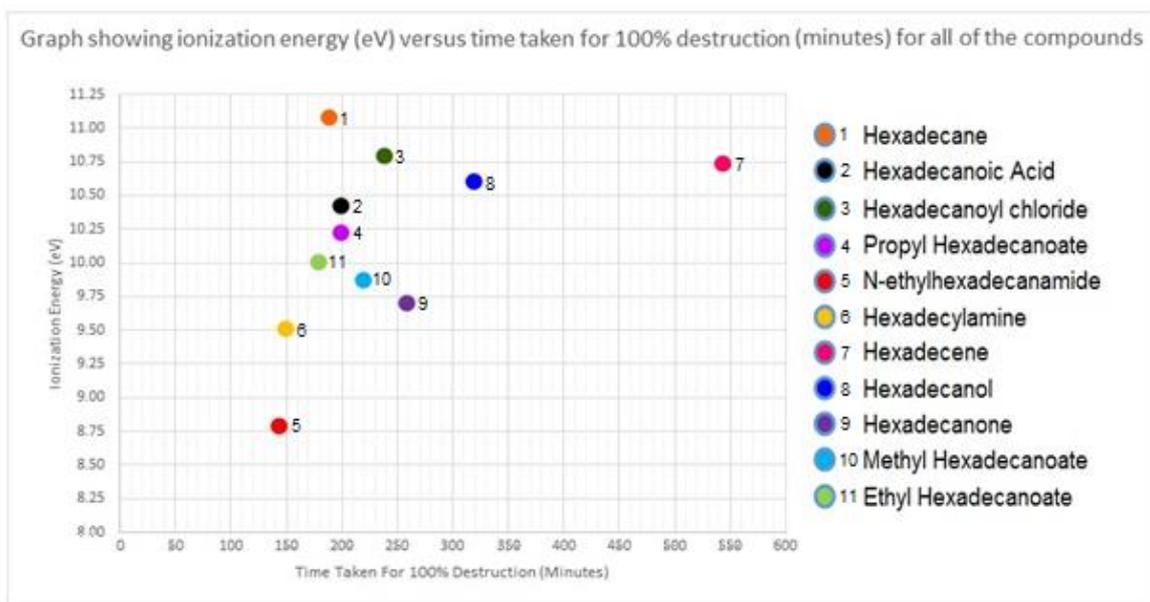


Figure 73 – Graph displaying ionization energy versus 100% destruction for all compounds

A comparison of the destruction times versus the milling speeds allows us to determine if there is a relationship between the two. Below, a table and graph shows the time taken for 100% destruction for all three speeds of the three compounds analysed. The same is shown for 50% destruction or the half-life of the three compounds.

Table 12 – Table showing the time taken for 100% destruction for the three speeds

Compound	Time Taken for 100% Destruction (Minutes)		
	300 RPM	400 RPM	500 RPM
Hexadecanol	320	90	45
Hexadecanone	260	180	75
Hexadecene	545	150	100

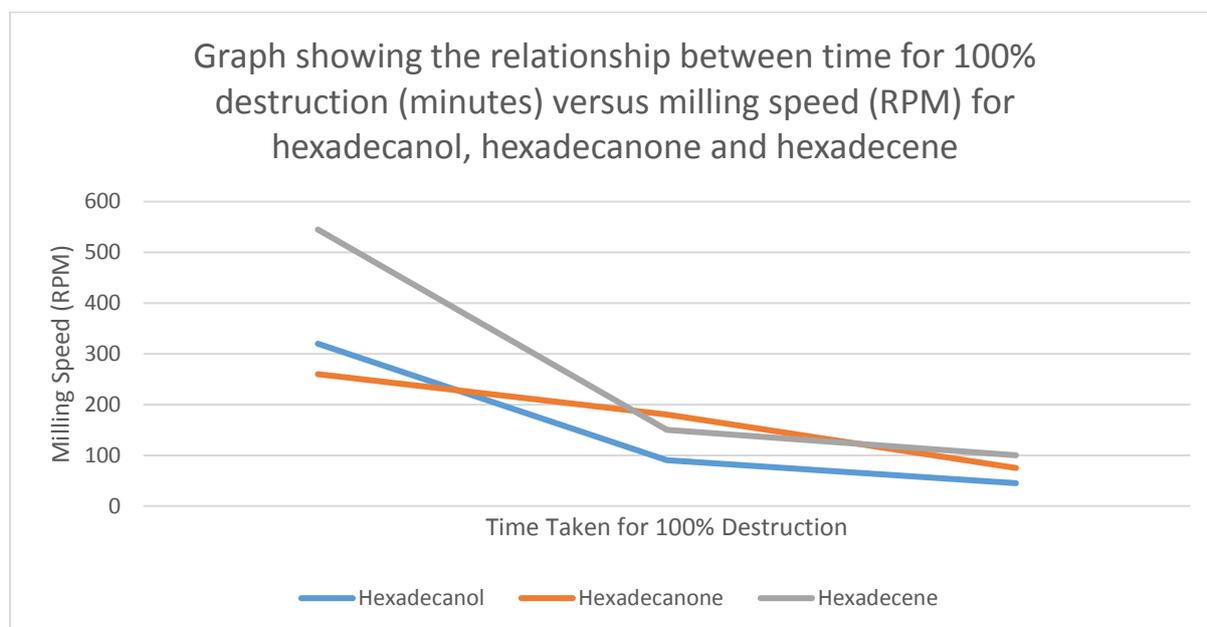


Figure 74 – Graph displaying time for 100% destruction versus milling speeds for selected compounds

Table 13 – Table showing the time taken for 50% destruction for the three speeds

Compound	Time Taken for 50% Destruction (Minutes)		
	300 RPM	400 RPM	500 RPM
Hexadecanol	60	15	10
Hexadecanone	127	80	20
Hexadecene	264	45	35

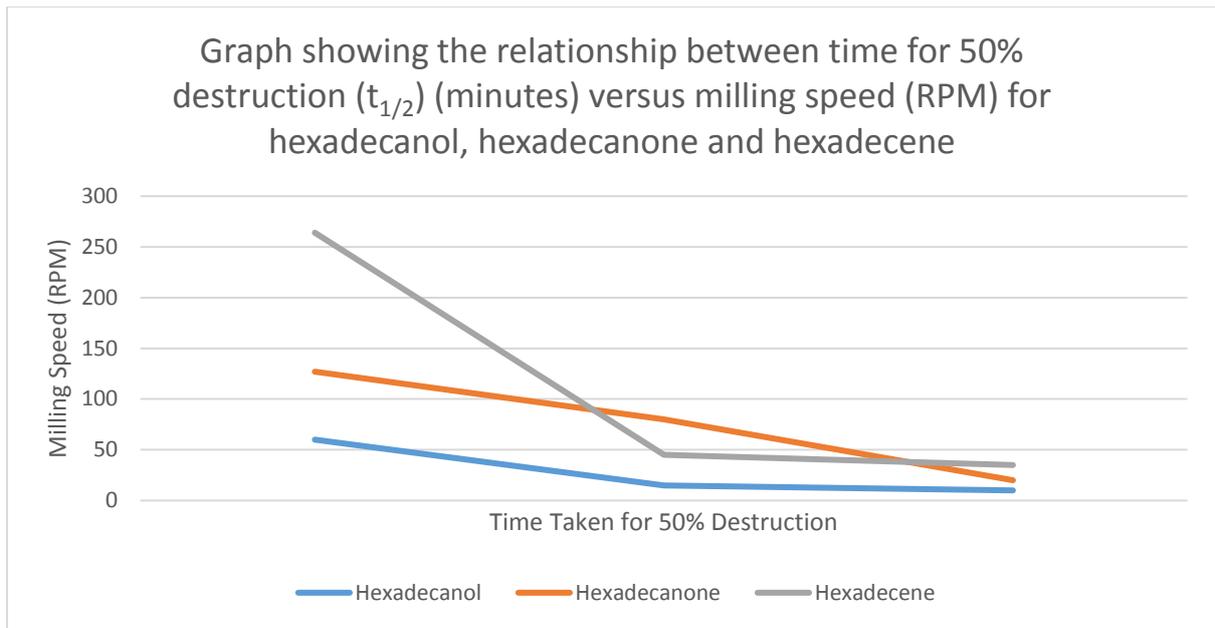


Figure 75 – Graph displaying time for 50% destruction versus milling speeds for selected compounds

## 5.0 Discussion

Having outlined the way various functionalised compounds behave in the same milling conditions above, it is now possible to discuss the aim and the achievement of this project. The aim of this project was to investigate if the destruction rate of organic compounds is dependent on the functional groups. Also, where ionization energy occurs on large organic compounds when using a ball mill.

The type of compound chosen was a long chain organic compound as past research tend to use small chain organic compounds. Therefore, 16 carbon containing compounds was selected with different functional groups. All experiments were conducted in the same conditions which were 300 RPM containing 20 balls with the same diameter.

It is known that during milling there is a high-energy impact between the surface of the balls, the balls and jar, as well as, between the ball and quartz surface. This results in areas of high energy. These high-energy areas initialize the breakdown of the molecule and is where ionization occurs.

While the milling process is taking place, there is deformation and fracturing of the particles of the reactants causing radicals to form. This increases the activated surfaces and continuously creates newer surfaces to allow further decomposition reactions and lead to the destruction of the chemical compounds. Ultimately, the whole organic compound is destroyed and all that is left is very fine fluid like minerals.

### 5.1 Discussion of Experimental Data

#### 5.1.1 Hexadecane

Hexadecane is an alkane containing 16 carbons and 34 hydrogens. This experiment used this compound as a reference as there are no additional functional groups attached to the alkane.

As seen above, the results for hexadecane was different in one of the three runs. The third run showed odd results because instead of destroying up to 90% in the first 30 minutes as in run one and two, run three followed a linear like destruction pattern.

Since two of the three runs were very similar, we can ignore run three therefore the average line should ideally be similar to run one and two.

Why run 3 behaved the way it did is inconclusive, although when looking at work done in the past, randomisation is common. It could also come down to an error in the preparation work before the milling was started, such as the quartz and compound not being mixed well enough or quartz being used could have contained moisture. Though there are theories as to why the third result was different, a valid answer is not concludable.

The bump observed in this graph near the start is quite common. Trapping competition is most likely the cause. This has been observed on most of the graphs in this research alongside many previous research projects.

Having 90% destruction in the first 30 minutes makes sense as past research has shown that the compounds are mainly broken down in bits like methane and ethane etc. Since hexadecane is simply made up of carbon and hydrogen, it can be assumed that hexadecane has followed that pathway of being broken down in mainly  $\text{CH}_4$  fragments which was proven by Tristan, Zhou and Kelvin.

If using that concept, then the destruction pattern can be described as 90% of the compound fragmented within the first 30 minutes. Then the compound continued to destroy slowly. The graph therefore shows a negative exponential pattern.

Implications with this experiment was that the hexadecane given from the School of Science was an old bottle kept in the storage for a long time. Whether this had effected the purity of the compound is still unknown. Alkanes that have been used in previous studies were short chain hydrocarbons as explained earlier. The pattern of destruction of those were similar in the sense that initially there was large amounts of destruction, then the destruction continued slowly.

Though over the past decade, a lot of research has been done on ball milling, the ability to completely replicate results were proven to be a very difficult task as mentioned before. Research shows that randomisation of the results is common in every mill. After thorough research of the methods used in the past and the implications involved, this research was designed to avoid those issues and aim to have similar results in the runs.

Hexadecane unfortunately was not able to do exactly that, but randomisation of results were always expected to be a possible outcome when milling even before the research was carried out.

### 5.1.2 Hexadecanoic Acid

The destruction of hexadecanoic acid was completely different to that of hexadecane. More energy was needed for the breakdown of acid compound to start and when it hit the 45-minute mark, there was large amounts of destruction, bringing the contamination down to 25%. At that stage, it slowed down to a gradual destruction rate.

It is evident that the carbonyl group on the carboxylic acid played a role in slowing down the initial destruction. This could be due to the presence of the oxygen in the carboxylic acid, which caused the compound to resist ionisation. Therefore, more energy was required for the initiation of the hexadecanoic acid destruction.

Again, a negative exponential pattern is observed with these results. One point to mention is in run 1 there is an increase in the contamination after 15 minutes. It could be due to the trapping competition. If just taking into consideration that the contamination increased, then that is not possible. Therefore, the quartz and hexadecanoic acid mixing may not done properly therefore, once milled for 15 minutes, there was more extraction of the hexadecanoic acid than initially.

As mentioned and proven before, randomisation of the results was expected however, the results obtained for this compound were very similar but run 3 was slightly different to the first two runs. This did not have much effect on the average though.

### 5.1.3 Hexadecylamine

Hexadecylamine appeared to destruct faster when compared to the other compounds. Complete destruction was obtained just after 2 hours of milling. This supports the results which were obtained in Creighton's research stating that the amine was easily destroyed.

It is evident that the nitrogen on the amine is the target at which ionization occurs on the compound. The results indicate that the nitrogen requires less energy to

breakdown and once the nitrogen is removed, the chain reaction of destruction becomes more rapid.

The graph follows the typical negative exponential pattern, however, does have a slight linear pattern. All of the runs for this compound behaved relatively the same. The average line is very similar to the runs therefore is a very good representation of how the amine behaved during the milling.

#### 5.1.4 N-ethylhexadecanamide

N-ethylhexadecanamide contains a double bonded oxygen with a nitrogen as the functional group. By looking at the results, it can be seen that the nitrogen is the location where ionization occurred as this compound was destroyed relatively fast, though its destruction was still slower than the amine.

With the data obtained, the oxygen seems to be what has shielded the compound from being destroyed as fast as the amine. Looking at the results from the carboxylic acid, the oxygen definitely played a role in making the compound harder to destroy, which in turn meant it required more energy to ionise.

The graph follows negative exponential shape, similar to the hexadecylamine, but has a slight linear shape to it. The negative exponential shape indicates that a large amount of destruction takes place initially. It then slows down but with the slight linear shape, which indicates that as time increases, so does the destruction. This indicates a directly proportional relationship between time and destruction of contaminants.

If the quartz used in the milling contains traces of water from moisture, then the amide, that is soluble in water, may have bonded to the water via hydrogen bonds during the liquid phase not the gas phase. With the energy created within the jar, it is a possibility that this could have slowed down the destruction.

#### 5.1.5 Hexadecanol

The results for hexadecanol were interesting as run 1 was completely different to run 2 and 3 in the way that the compound was destroyed. Run 1 showed approximately 95% destruction after 3 hours, but when using the average including run 2 and 3, then it was only destroyed around 70%.

As mentioned before this could be due to the randomisation of the milling results. If only the results for run 2 and 3 are looked at, then the destruction was at a mere 50% after the 3 hours. That means that there was not enough energy created in the jar to destroy the compound completely. A negative exponential curve is what best describes the destruction pattern.

What was obvious from the results is that the compound had not been completely destroyed after the 3 hours at 300 RPM. In fact, there was a lot of destruction in the first 30 minutes, after which it had slowed right down.

Hexadecan-1-ol was used specifically for this experiment and therefore contains an OH on the very first carbon. The pattern previously showed with hexadecanoic acid and hexadecylamide, that the oxygen on the hydroxyl group played a role in slowing down the destruction. Though, something that was questionable was the fact that the carboxylic acid didn't struggle to be destroyed, whereas the alcohol did.

Interestingly, the reason that the hydroxyl group slows down destruction that significantly, could be due to the strong bonds between the hydrogen and oxygen, requiring more energy to destroy.

Alkanes contain only intermolecular forces such as van der Waals dispersion forces. Alcohols on the other hand have hydrogen bonds which requires a lot more energy to break, though as mentioned earlier, these hydrogen bonds don't exist in the gas phase, there may be some hydrogen bonding to the quartz. Hydrogen bonding is not the only intermolecular forces in alcohols, there are also van der Waals dispersion forces and dipole-dipole interactions, as with hydrogen bonding it is uncertain how much of this will be involved in the actual milling process.

Though the hydrogen bonding and the dipole-dipole interactions will be similar for the alcohols of all sizes, as the number of carbons increase the dispersion forces increase. This is due to the molecules getting longer and having more electrons. Having to overcome this energy is the first challenge required for ionization to occur on the molecules. Only then, can destruction begin with reactive surfaces being created.

If the quartz used contained moisture, then the alcohol may have created new bonds between the water molecules and the hexadecanol molecules. Previous research

has shown that water has had the tendency to slow down the mill performance. This could be a factor to take into consideration.

### 5.1.6 Hexadecanone

Hexadecan-7-one was the exact compound used in this experiment. The compound contains a double bonded oxygen on the 7<sup>th</sup> carbon. This compound also showed low destruction. After 3 hours, there was only 70% destruction.

The results for this compound looks positive in the sense that all three runs were very similar and the results are uniform. There was very minimal randomisation. This shows that the data obtained is accurate at demonstrating how the ketone behaves during the milling process.

The shape of the graph took a linear shape rather than a negative exponential pattern which was seen in the other compounds. This means that for Hexadecanone, the destruction and time it takes for that destruction to occur is directly proportional. In other words, as time increases, the amount of destruction also increases. The linear pattern enables the rate of destruction to be calculated to approximately 0.4% per minute.

Even though there was only around 70% destruction after 3 hours, milling for a further 1 ½ hours would have resulted in complete destruction. This can be calculated from determining the equation of the line and using it to work out the time until contamination reached 0%.

Hexadecanone is a ketone that is a polar molecule due to the carbon and oxygen double bond. Alongside the dispersion forces, there are also attractions between the permanent dipoles on nearby molecules. This means that a lot of energy is required to breakdown the compound.

In general, the boiling points of alcohols are higher than that of ketones, therefore with the milling conditions being kept the same, the ketone should have more destruction than the alcohol. The results support this idea as it showed that hexadecan-1-ol was only 50% destroyed for run 1 and 2, whereas with hexadecan-7-one there was around 70% destruction.

### 5.1.7 Hexadecanoyl Chloride

The destruction for this acid chloride was not 100% after 3 hours however averaged around 90%. Run 1 was slightly different from runs 2 and 3, where only 80% destruction occurred. Runs 2 and 3 had just over 90% destruction. The pattern that this compound was following was a typical negative exponential shape. Very little randomisation occurred even though run 1 was different. The overall shape of the graph was similar.

Hexadecanoyl chloride is an acid chloride where a carboxylic acid has the hydroxyl group replaced with chlorine resulting in a 'COCl' at the end of the carbon chain. The bonds in the acid chloride are dipole-dipole attractions as well as van der Waals dispersion forces. Hydrogen bonds do not form therefore there is no requirement for large amounts of energy for destruction to occur, which was not the case for alcohol and ketone.

The oxygen present on the end of the molecule would have played a role in slowing down the destruction slightly as 100% destruction was never obtained. Taking into consideration the results from all the compounds analysed containing an oxygen, 100% destruction was never obtained.

Hexadecanoyl chloride is very water sensitive. There is a possibility that some may have reacted with water inside the milling jar to give hexadecanoic acid during the milling process. This reaction is extremely exothermic giving off the acidic gas, HCl. The mechanism is shown in the figure below.

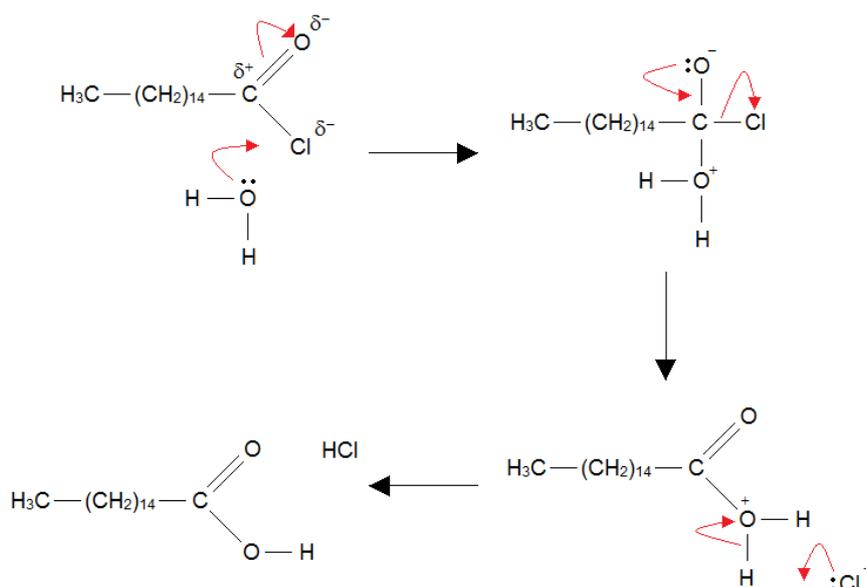


Figure 76 – Mechanism showing hexadecanoyl chloride reacting with water to form hexadecanoic acid

The results for this compound should be similar to the carboxylic acid. There were similarities, however, the acid chloride was slightly more resistant to destruction compared to the carboxylic acid.

### 5.1.8 Hexadecene

There was very little destruction when it came to this unsaturated compound. Hexadec-1-ene was used in this experiment. Runs 1 and 3 behaved similarly, where run 2 had slightly more destruction, although all three followed a very similar pattern. Looking at the average line of the graph, approximately 30% of the hexadecene was destroyed after the 3 hours. Hexadecene is by far the most resistant.

The effect of the double bond on the milling performance was not expected to be this significant. Bonding in alkenes consist of a double bond between two carbon atoms, which is two pairs of shared electrons. One of the pairs of electrons is between the two carbon nuclei ( $\sigma$  bond) and the other pair is in the molecular orbital around the molecule ( $\pi$  bond)

Due to the  $\pi$  electrons not being under the control of the carbon nuclei like they are in the  $\sigma$  bonds, the  $\pi$  electrons are more prone to being attacked. Even though the energy required to break the double bonds is higher than breaking the single bonds in the alkanes, the exposed electrons in the  $\pi$  region are easier to break. Once one bond is broken then a chain reaction follows with more bonds being broken.

Taking this into consideration, the alkene was expected to breakdown faster than the alkane, however, proved to be very different as it was the compound that showed the least amount of destruction. Future research is essential to figure out exactly why this was the case. With hexadecene being an anomaly, bonding to the silica being an important factor in the destruction can be ruled out as that would mean that hexadecane would have taken the longest to destroy.

The trend of the destruction is best described as linear where time and destruction is directly proportional, meaning as time increased, so did destruction. If milling time continued, then the destruction would have continued but at a very slow rate. The rate of destruction for this compound can be calculated to be around 0.2% per minute which is very low compared to the 0.4% per minute from the Hexadecanone. That is half the destruction in the same amount of time.

### 5.1.9 Esters

The esters that were milled were methyl hexadecanoate, ethyl hexadecanoate, propyl hexadecanoate and decyl hexadecanoate. The methyl, ethyl and propyl esters all behaved similarly in the ball mill, whereas the decyl hexadecanoate had a completely different profile.

Methyl hexadecanoate was 90% destroyed after the 3 hours where ethyl hexadecanoate had complete destruction after 3 hours. Propyl hexadecanoate also had around 90% destruction after the 3 hours. All three of these compounds behaved in a near linear destruction pattern, each with very similar equations. The propyl hexadecanoate did have a slight negative exponential curve to it.

The decyl hexadecanoate behaved completely different to the other three and had around 90% destruction in the first 90 minutes then slowed right down. This shows a very good exponential curve pattern.

Esters are polar molecules that have dipole-dipole interactions and also van der Waals dispersion forces. Hydrogen bonds are not present in esters however if reacted with water, the lone pair electron on the oxygen can bond with a water molecule forming a hydrogen bond when initial low energy was applied.

Therefore, the overall bonds on the esters are not significantly strong and destruction of the compounds can be obtained fairly easily. Methyl and propyl hexadecanoate

not being destroyed completely could come down to randomisation of data during runs or moisture in the quartz slowing down the mill efficiency. Though, there was not much interference in the results and therefore the results obtained is still a good representation of how the compounds behave while milling.

The target of ionization for the esters seems to be the oxygen which bonds the carboxylic acid and alcohol parts of the ester together. Further research would be required to see exactly how extending the number of carbons on the alcohol region of the ester would differ as 1 or 2 carbons behaved slightly different to 3 carbons and 10 carbons behaved completely different to the other three. If there is a trend to be observed from the results obtained, then as the number of carbons increased i.e. the alcohol group, then more destruction occurred during the initial part of the destruction. This results in an exponential curve pattern rather than a directly proportional linear pattern.

## 5.2 Milling at 400 RPM and 500 RPM

When milling at 300 RPM, not all the compounds had destroyed completely. The three major ones that stood out were hexadecanol, hexadecanone and hexadecene. Ultimately, this experiment is designed to back up the concept of using mechanochemistry like ball milling to remediate soils.

To prove that these three compounds can be destroyed, they were milled at 400 RPM and 500 RPM. When milling at 400 RPM, hexadecanol was completely destroyed at 90 minutes. Hexadecanone was 100% destroyed at 180 minutes and hexadecene took 150 minutes.

Compare these results to 300 RPM, which showed both hexadecanol and hexadecanone were only destroyed to 70% after 180 minutes and hexadecene to only 30% after the 180 minutes.

Then when the compounds were milled at 500 RPM, there was even more rapid destruction. Hexadecanol was 100% destroyed in 45 minutes, hexadecanol in 70 minutes and hexadecene in 100 minutes. That is nearly half the time needed only by increasing the RPM by 100.

By obtaining this data, it can be proved that increasing the RPM of the milling produces a lot more energy to breakdown the compounds and if used in the

commercial industry, 400 RPM would be the minimal speed recommended specifically for those compounds.

While carrying out the milling of these three compounds at 400 RPM and 500 RPM, when it came to taking samples during the intervals, the milling jar got a lot hotter when handling. This supports the fact that a lot more energy was being produced inside the jar which caused the compounds to get destroyed faster.

### 5.3 Testing the Relative Extraction Efficiency of the Solvent

This was carried out to see if the extraction method being used was valid and to test what percentage the recovery was. With approximately 90% extraction efficiency, the results obtained show good accuracy. The extraction efficiency issue may be the same sequestering process observed in past research for inorganic compounds.

Not being able to obtain 100% extraction means that there may have been a step in the method of extraction that was not done properly. This could be the sonication step where the tubes were sonicated for 30 minutes in a water bath. It could also be that 30 minutes was not long enough. Another possibility could be that using ethyl acetate was not the best solvent and other solvents could have worked better.

Regardless of it not being 100%, having obtained 90% efficiency just means that when it comes to milling commercially for a real project, milling times will just need to increase slightly or the speed at which the milling will be carried out will need to be increased.

### 5.4 Comparison of Destruction

The best way to compare the way the compounds were destroyed is by using half-life and two half-lives. This gives the ability for the compounds to be compared easily providing a clear indication to which compounds were the easiest to destroy. Table 5 has been reordered below to show the half-lives from the fastest destruction to the slowest destruction.

*Table 14 - Half-lives of the compounds in order from fastest destruction to slowest destruction at 300 RPM*

<b>Compound</b>	<b>t<sub>1/2</sub> (Minutes)</b>
Hexadecane	20

Hexadecanoic Acid	42
Hexadecylamine	50
Decyl Hexadecanoate	50
Hexadecanol	60
N-ethylhexadecanamide	70
Hexadecanoyl chloride	70
Propyl Hexadecanoate	90
Ethyl Hexadecanoate	100
Methyl Hexadecanoate	105
Hexadecanone	127
Hexadecene	264

As we can see, hexadecane was the fastest to reach 50% destruction, but when looking at the total time needed for 100% destruction, hexadecylamine was the fastest. One of the compounds that stood out the most was Hexadecene as shown in the results and explained above. Hexadecene is not just slightly different to the rest, but is completely different in the way it behaves in the ball mill.

The question which was asked and investigated was if the functional group has an effect on the destruction rates. The base structure of the compounds are very similar as they all contain 16 carbons. They all have different elements on the end of the compound with the exception of the ketone where the oxygen is on the seventh carbon.

If the destruction patterns and the destruction rates were similar then we could have concluded that regardless of the functional group, it is the main chain on the organic molecule which determines the rate of destruction.

However, this was not the case as the evidence shows that there is a range of destruction times. Mentioned earlier in the discussion of experimental data, specific elements played a role in the destruction rate. Nitrogen showed characteristics of allowing the compound to completely breakdown, very fast. Oxygen slowed down the breakdown of the compounds ranging from a little to a lot. A good example of it being slowed down a little is hexadecanoic acid where COOH is present on the end of the compound.

This carbonyl group contains two oxygens. The other example is the opposite, where the oxygen showed characteristics of slowing destruction down a lot and the results for hexadecanone show just that. With a double bonded oxygen on the seventh carbon. The position of the oxygen along with what is bonded to it and around it plays a huge factor in the destruction rates.

Looking at table 10 above, three esters and the ketone is positioned near the end of the half-lives in order of destruction. With the exception of the decyl hexadecanoate, having an oxygen bound in the middle of the compound makes it harder to destroy and in turn having a longer destruction rate.

The presence of a double bond, meaning an unsaturated compound, has proven to be very hard to breakdown. One could assume that an alkyne would have been harder to destroy, but that would need to be looked at in future studies. The alkene, which had a double bond on the first carbon, has behaved unexpectedly and the reason for this cannot be determined from these results. For this, future studies would need to investigate if other alkenes behave the same way and if alkynes are harder to destroy or not.

The results answer the investigating question very well and provide a very good background to show how some functional groups behave during the milling process. Other functional groups investigated in the future will add to the data collected in this research and provide users the knowledge to be able to remediate soil from organic contaminants accurately and efficiently.

Section 4.16 included a comparison of 100% and 50% destruction rates for hexadecanol, hexadecanone and hexadecene. It is evident that the destruction rates were milling speed/energy dependent, but there cannot be any simple relationships i.e. it was not in a linear form. The ball energy is at a basic level as the kinetic energy  $E = \frac{1}{2} m v^2$  so as a simplistic analysis, the relative energies at 300:400:500 RPM could be 9:16:25 or even simpler 1:1.8:2.8. What this means is that the rate of destruction at 400 RPM is 1.8 times faster than 300 RPM and rate of destruction at 500 RPM is 2.8 times faster than 300 RPM.

Since no dominant relationships were observed, this further emphasises that there seems to be a number of mechanisms and processes going on during milling.

Evidence to prove that there are no simplistic relationships can be shown in the following tables.

Table 15 – Table showing that there is no simple relationship between speed and destruction time for 100% destruction of the selected compounds

Compound	Original Destruction Times Divided By		
	2.8 300 RPM	1.8 400 RPM	1 500 RPM
Hexadecanol	114	50	45
Hexadecanone	93	100	75
Hexadecene	195	83	100

If there was to be a simple kinetic energy relationship between speed and destruction time, then the numbers would have been the same in the table. Research in the past was focused on whether speed has any relationships with destruction rates. Just like these results, there was no evidence towards it being as speed increases then destruction rates increase at a fixed rate. Instead, many complex things are going on in the mill which will need to be researched further.

Table 16 – Table comparing half-life versus 100% destruction at 300 RPM

Compound	t <sub>1/2</sub> (Minutes)	Time Taken for 100% Destruction (Minutes)
Hexadecane	20	190
Hexadecanoic Acid	42	200
Methyl Hexadecanoate	105	220
Ethyl Hexadecanoate	100	180
Propyl Hexadecanoate	90	200
Hexadecanol	60	320
Hexadecanone	127	260
Hexadecylamine	70	150
N-ethylhexadecanamide	50	145
Hexadecene	264	545
Hexadecanoyl chloride	70	240
Decyl Hexadecanoate	50	170

For some of the compounds, 50% destruction was reached before half the time of 100% destruction. Past research has always pointed towards a lot of destruction occurring initially then slowing down. This is the exponential relationship we have observed in the results from this project too. Again, why this has happened is a question that still cannot be answered. Whether it is the complex mechanisms that undergo during the milling or something else that is yet to be figured out, research in the future will need to look at other factors that cause this initial major destruction.

Methyl hexadecanoate, ethyl hexadecanoate and propyl hexadecanoate stand out in the results as they are all esters differing in one or two carbons on the alcohol region of the ester. They all took around half the time of 100% destruction to reach 50% destruction. There is not enough evidence to say that this is a property of esters and how they specifically behave during the milling process, but there may be some connection.

Other compounds which follow similarly is hexadecene, hexadecanone and hexadecylamine. They too showed that 50% destruction was reached at the half-life. Regardless of when half-life was reached, this all is related to the mechanisms and when radicals were formed in the early stages resulting in photoionization and other mechanisms in the later stages.

When comparing the results from this research to research completed in the past, there are no similarities. In fact, none of the results in the past have ever been the same. This comes down to the complex mechanisms going on inside the jar when milling. The only common trend that was noticed was that most of the recent research done in the last 5 years or so have all had situations where the concentration of the contaminant increases after the initial milling has begun. Now concentration cannot increase above 100% theoretically however, a possible explanation could be that the molecules are bound in the initial stages of milling then unbound when the size of the fragments are smaller.

Everyone in the past have tried to reduce the number of factors that could give rise to results being abnormal. This study tried to tackle the volatility issue by using long chain organic compounds so that the boiling points of those used in this study were higher than what was used in the past. Though being able to reduce that factor, the fact that similar behaviour is observed in all the studies where the data is

randomised means a lot more research is required in the future focussing on the mechanisms besides what have been looked at. It is possible that many mechanisms occur in the jar when milling and simultaneously work together to degrade the compounds.

## 5.5 Ionization

Though the major question being investigated was whether destruction is dependent on the main carbon chain of the compound or the functional group, another concept was being looked at too.

This concept was whether ionization is the major initiator in the breakdown of the compounds. Looking at the graphs in section 4.16, the summary of the results, there are two graphs which provide essential information regarding this. The graph displaying ionization energy versus half-life shows that there is no relationship between the two. The plots are not in any order and to see if there was a relationship between the two, there would need to be some sort of regression between the ionization energy and half-life whether it be a positive regression or a negative regression.

However, the graph displaying ionization energy versus total time needed for 100% destruction shows a slight relationship. The results indicate that as the ionization energy increases, the total time required for 100% destruction increases too. The relationship is not strong between the two but by drawing a line of best fit, it shows a weak positive regression. The graph below has the line of best fit drawn on to display this regression.

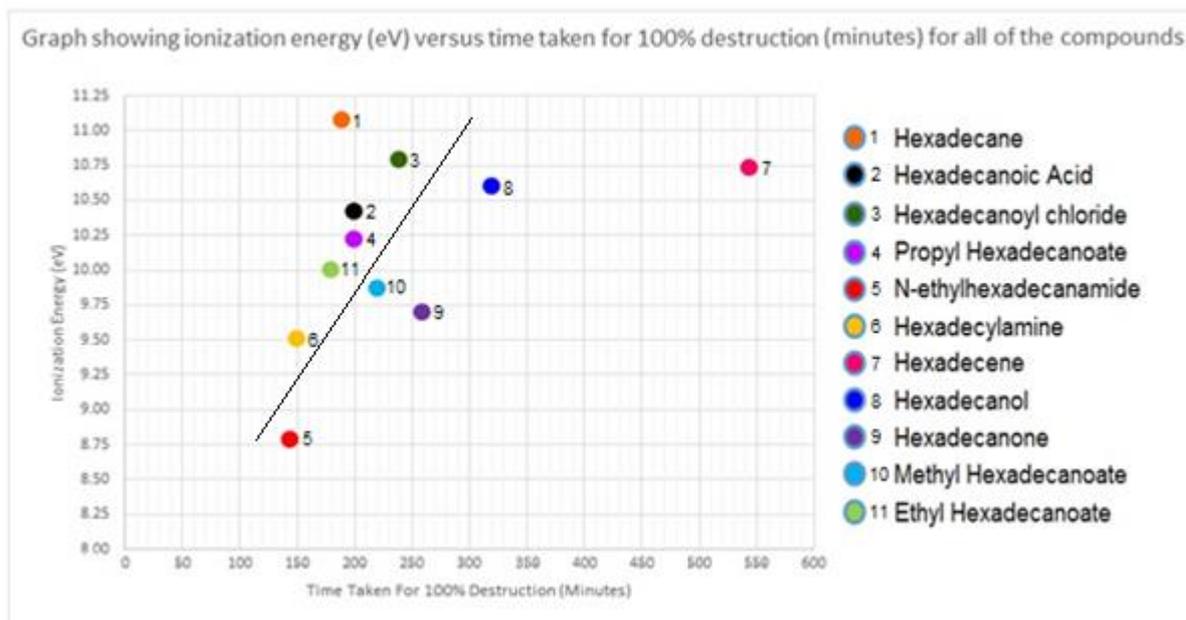


Figure 77 – Graph displaying the line of best fit on figure 60

Hexadecene stands out quite a bit compared to the other compounds. Looking at each compound individually, it could be that hexadecene has a far more complex process going on than the other compounds. It could be that all of them have ionization as the major initiator but have other processes, which are yet to be investigated, going on during the milling process.

Whether ionization is the sole initiator of the breakdown process or part of the initiation, working in conjunction with other mechanisms, the question which was investigated, whether ionization is the major initiator in the breakdown of the compounds, cannot be answered completely and therefore is inconclusive.

## 6.0 Conclusion

The aim of this project was to determine if the destruction rates of organic compounds in a ball mill is dependent on the main carbon chain itself, or the functional group. This was achieved by obtaining from commercial or in-house sources and synthesising large organic compounds containing 16 carbons which vary in functional groups. These compounds were milled under the same conditions to obtain the data to provide the answers to this question.

Results show that the functional group does affect the destruction rates during ball milling. It is evident that functional groups do have a major effect as destruction rates both during the reaction and the time it takes for the contamination to reach 0%.

A mill speed of 300 RPM was chosen for most of the work because it was slow enough that several sub-samples could be taken over a reasonable time. At this speed the two fastest compounds to be destroyed were hexadecylamine and N-ethylhexadecanamide, both of which contain an  $sp^3$  nitrogen atom. This is consistent with Creighton's results and somewhat consistent with these functional groups having low ionisation energies.

Next came the carbonyl containing molecules ethyl and decyl hexadecanoate with very similar results, followed closely by propyl hexadecanoate and hexadecanoic acid. Hexadecane is in this group and whether that is unexpected is unclear. Methyl hexadecanoate was next which was slightly different to the other esters.

Hexadecanoyl chloride and hexadecanone were very close for 100% destruction, then came hexadecanol and finally followed by hexadecene which took the longest.

Some compounds were not able to be fully destroyed at 300 RPM. Those were hexadecanol, hexadecanone and hexadecene. To show that they can be destroyed with the addition of energy, they were milled at 400 RPM and 500 RPM. Results showed that by increasing the speed of the milling, but by keeping the duration the same, the compounds were easily destroyed especially at 500 RPM. Therefore, we can conclude that increasing the speed on the mill will increase the rate of destruction.

The results point towards compounds containing a nitrogen atom being destroyed faster. This is followed by compounds such as saturated hydrocarbons and then

compounds containing oxygen atoms, which showed that they were hard to destroy and requires a lot of energy. Unsaturated hydrocarbons are the hardest to destroy and required the most energy.

Ionization is thought to be the major initiator in the breakdown of the compounds. Past researchers have hypothesized that once ionization occurs on the molecule, a radical is formed which is very unstable. With other reactive surfaces being exposed, a chain reaction begins and the breakdown of the compound occurs with the energy inside the mill.

This project also looked at whether ionization is the major initiator in the breakdown of the compounds and if the ionization energies have a relationship with the rate of destruction.

The results are inconclusive and do not provide enough evidence to state that ionization is the sole mechanism behind the breakdown process. Instead, it can be concluded that ionization is only part of a complex mixture of mechanisms including thermal excitation, photo ionization, phonon transfer yet to be investigated.

Future work should be concentrated on other functional groups and investigating how they behave. In particular, looking at other alkenes and comparing it to how hexadec-1-ene behaved and seeing if alkynes are harder to destroy than the alkenes. Work to do with ionization and other mechanisms need to be done to determine what the exact initiator of the breakdown of the compounds is.

## 7.0 References

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