

The rates of formation of carbon and gases from high energy ball milling of organic compounds.

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Abstract

Mechanochemical reactions induced by high energy ball milling have been known as a method of compound destruction but the mechanics behind the destruction has not been well understood. This study focuses on reactions induced by air, resulting in end product formation of principally carbon dioxide, methane and elemental carbon.

The use of ball milling to destroy pollutants in soils has several advantages. Including the use of a sealed container reducing direct human exposure to compounds and intermediates, low maintenance coupled with low level of technological sophistication and the ability to break compounds -down into harmless carbon, water and gases, principally methane, carbon dioxide and hydrogen. This makes ball milling a very attractive mitigation technology for organic pollutants. This research has found that at 0.1% concentration (typical for seriously polluted soils), most of the organic compounds were destroyed under a standard set of conditions and proved very effective against a wide variety of chemical structures ranging from polynuclear aromatics (PAHs) to linear hydrocarbons.

Initial work to quantitatively isolate the elemental carbon from reactions was only partially successful. Pure samples of carbon were obtained, analysed by Raman spectroscopy and shown to be partially graphitic but it was not possible to get quantitative results. Methane formation from a variety of organic compounds was investigated in detail. It was found that gases such as nitrogen and oxygen can significantly alter the rates methane production, suggesting that a number of mechanisms are competing. By changing the atmospheres in the jar it possible to change the rates and types of gas formation, from this it was postulated that organic compounds degrade into intermediates which further degrade to the observed gases.

It was also found that carbon dioxide was able to form methane from available hydrogen sources, either organic or water. When milling organic compounds in air or oxygen, the formation of carbon dioxide initially predominates over methane but as the reaction progresses this is reversed.

This research has shown that ball milling is a more complex series of equilibria than previously thought and has also found an unexpected pathway where carbon dioxide is converted to methane.

Table of Contents

Acknowledgement	ii
Abstract	iii
List of Tables	vii
List of Equations	vii
List of Figures	vii
Statement of Originality	viii
Chapter 1. Introduction	1
1.1 Background	2
1.1.1 When does pollution become a problem?	3
1.1.2 Sources of pollution	5
1.1.3 Sources for pollution into soil	6
1.1.4 Hydrocarbon contamination	7
1.2 Persistent organic pollutants (POP)	9
1.3 Pesticides	11
1.3.1 Dichlorodiphenyltrichloroethane (DDT)	13
1.3.2 Aldrin, Dieldrin, Chlordane, Endrin, Heptachlor	15
1.3.3 Hexachlorobenzene and Mirex	16
1.4 Polychlorinated biphenyls (PCB)	17
1.5 Polychlorinated dibenzo-p-dioxins (dioxin) and polychlorinated dibenzofurans (furans)	19
1.6 Phthalates	20
1.7 Toxaphene	20
1.8 Mitigation methods of pollutants	21
1.8.1 Recycling	21
1.8.2 Incineration	22
1.8.3 Landfills & Storage	23
1.8.4 Photodegradation	24
1.8.5 Chemical remediation	25
1.8.6 Convention & Regulation	26
1.8.8 Mechanochemical Reaction	27
1.9 Ball Milling	28
1.9.1 History of ball milling	29
1.9.2 Types of ball mills	32

1.9.3 Soils.....	34
1.9.4 Interaction of soils subjected to intense planetary ball milling	37
1.10 Possible mechanisms for formation of carbon and gaseous products	38
Chapter 2. Materials and Methodology.....	40
2.1 Materials	41
2.1.1 Quartz Sand.....	41
Chapter 3. Method	41
3.1 Gas formation from milled samples.....	41
3.1.1 Methane standardisation for GC.	43
3.1.2 Standardisation of carbon dioxide, ammonia methane and nitrous oxide for FTIR	44
3.2 Intermediate analysis from milled samples.....	44
3.3 Milled matrix composition.....	45
3.3.1 Quartz absorption analysis	46
Chapter 4. Results	46
4.1 Methane formation from milled samples	46
4.1.1 Phthalic acid esters (comparisons of ester chain size)	47
4.1.2 Low molecular weight esters comparison with high molecular weight esters.....	48
4.1.3 Comparison of an aromatic ester, ketone and ether.	49
4.1.4 Phenol comparison.....	50
4.1.5 Aromatic esters	51
4.1.6 Phenyl ketones	52
4.1.7 Comparison of a simple aromatic amide and aromatic ketone	53
4.1.8 Comparison of an aromatic ketone to a similar aromatic ester	54
4.1.9 Comparison of 3 chlorinated aromatics	55
4.1.10 Aromatic amines and an aromatic ether.....	56
4.1.11 Comparisons of long chain linear hydrocarbons with or without a functionalised end .	57
4.1.12 Comparison of an aromatic amine, chlorinated amine, ether, amide and imidazole. ...	58
4.1.13 Comparison of 1-Naphthylamine, 1-Naphthol, 2-Naphthol and Coumarin.....	59
4.1.14 Comparison of polyaromatic hydrocarbons	60
4.2 Effects of various atmospheres on methane production	60
4.2.1 Naphthalene	61
4.2.2 Oleic Acid	62
4.2.3 Air exposure at sampling intervals.....	63

4.2.4 Quartz milled in modified headspace gas	65
4.3 Gas formation analysed by FTIR	67
4.4 Intermediate analysis from milled samples.....	71
4.5 Milled matrix composition.....	73
4.5.1 Quartz moisture absorption analysis	75
4.6 Mass “estimative analysis”	75
4.7 Standards for quantification of methane and carbon dioxide.....	75
4.8 Mass “estimative analysis” for naphthalene	77
Chapter 5. Discussion	78
5.1 Methane, carbon dioxide and carbon yields.....	79
5.2 Benzene derivatives	84
5.3 Esters, phthalates and carboxylic acid	85
5.4 Linear aliphatic hydrocarbons.....	86
5.5 Composition analysis	88
Chapter 6. Conclusion.....	89
Chapter 7. Recommendation.....	91
References.....	92

List of Tables

Table 1 shows the differences between types of ball milling and key properties which distinguish them from one another. (Tristan, 2005)	31
Table 2, Chemical analysis of quartz sand used in analysis.	41

List of Equations

Equation 1 shows cyanidation also called Elsner's equation. (Gönen, Kabasakal, & Özdil, 2004)	6
Equation 2 shows the possible free radicals that can be formed during milling of water	37
Equation 3 shows the formation of methane from atomic carbon through chemical reactions of hydrogen gas and ionised H_3^+ (Herbst, 1995).	39
Equation 4 shows some of the possible ion reactions methane can undergo during ionisation in the mass spectra (Gates, 2005).	39
Equation 5 shows the decomposition of SiO_2 by HF to SiF_4 and H_2SiF_6	45
Equation 6 Some decomposition pathways to give carbon, methane hydrogen and water	47
Equation 7 Demonstrates the degradation of dibutyl phthalate into monoethyl phthalate.	86

List of Figures

Figure 1, illustrates groups of interest (R1) during natural mitigation of benzyl benzene derivatives.	14
Figure 2, Illustrates the groups symbolised by R2 which can either be Cl, Br or H groups.	18
Figure 3, shows a SPEX SamplePrep 8000M Mixer/Mill	32
Figure 4, shows the rotation of the jar and movement of balls a planetary type ball mill (Suryanarayana, 2004).	33
Figure 5, shows the possible types of free radicals which could form during ball milling arrange from a to d, a being most likely. R1 represents the degree of bonding that Si could have to the tetrahedral quartz most importantly bonds which are not attached to oxygen radicals.	37

Statement of Originality

‘I hereby declare that this submission is my own work and that, to the best of my knowledge and belief, it contains no material previously published or written by another person (except where explicitly defined in the acknowledgements), nor material which to a substantial extent has been submitted for the award of any other degree or diploma of a university or other institution of higher learning.’

Signed

Date

Chapter 1. Introduction

The environment has become a pressing issue for the 21st century as people become aware that their decisions can have direct and indirect consequences on the environment. Modern society has been extensively exposed to man-made chemicals at most times unknowingly; It has been found that “every person on earth has absorbed at least 250 synthetic chemicals into their body”(Gaag, 2000). This comes about from the constant exposure to elevated levels of manmade contaminants found in our land, air and water supplies these contaminants eventually enters the food chain. Obviously in order to mitigate these hazardous substances there is a price and time factor involved. Substances like polystyrene are made with ease but take more than 500 years to biodegrade (Bandyopadhyay & Basak, 2007).

There are many ways to reduce or eliminate pollution. This thesis examines some aspects of a relatively new process which uses high energy ball milling to destroy organic contaminants in polluted soil. Specifically, using a laboratory scale planetary ball mill, it focuses on some aspects of the process that need to be better understood, both to refine our understanding of the chemistry of the process but also some of the products of the reaction. By furthering our understanding we will be better able to predict end products at given milling times and improve the efficiency of the process. The specificity of a planetary ball mill is due to availability of other machines which are described under the heading of 1.9.1 History of ball milling.

Previous work (Magoha, 2004; Tristan, 2005) has focused on the destruction of actual pollutants however along with these, polluted soil contains a range of other less hazardous materials that will compete with the pollutants and reduce the overall efficiency of the process. Rather than working with environmentally hazardous materials, the compounds chosen were in general less hazardous structural or functional analogues of selected hazardous pollutants or simply examples of functional groups or structures that can be

expected to be present during decontamination. The analogues were broadly aromatic esters, linear/fatty acids and aromatic derivatives.

Earlier work (Magoha, 2004; Tristan, 2005; Zhou, 2009) had also established that the final products of a milling reaction were carbon dioxide, methane, water, hydrogen and carbon. There had been some considerable uncertainty about both the pathways that lead to the formation of these gases and the yields. These were investigated for various compounds under various conditions.

1.1 Background

Pollution occurs when contaminants enter ecosystems and results in negative impacts, these negative impacts are defined by humans. Pollution can be categorised into four scenarios of effect: noise, land, water and air. The sources of pollution come about indirectly or directly these are termed as nonpoint sourced and point sourced. Often several pollution types may occur when contaminants are identified.

Initially nonpoint source pollution was exclusively related to sources effecting water pollution with much focus placed on runoffs and storm water. Modern society has expanded their understanding of non-point source pollution and has included other forms of diffuse pollutants (Loague & Corwin, 2005). Non-point source pollution has been defined as “contaminants of surface and subsurface soil and water resources that are diffused in nature and cannot be traced to a point location” (Corwin & Wagenet, 1996).

Point source pollution, are sources which can be directly identified and the emission defined. Some examples are:

- Noise pollution from construction sites
- Water pollution from an abattoir
- Radio emissions from electrical devices classed as an interference producing.
- Land pollution from large scale commercial feeding of livestock

We have to keep in mind that at times some pollutants such as fertilizers when used at the right concentration are necessary for soil to be fertile, and help resist soil degradation.

These pollutants are classified when a desired effect has been found to interfere with other biological cycles significantly.

Soil pollutants can be classified into two groups being organic or inorganic. Examples of organics include hydrocarbons from fuel, polynuclear aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), chlorinated aromatic compounds, detergents and pesticides. Inorganics encompass salts include phosphates, nitrates, sulphates and heavy metals such as mercury, arsenic, cadmium, lead and radionuclides.

Pollutants can be found as solids, liquids or gases. The states in which we find pollutants are very important they can predetermine several things such as what vectors would most likely carry them, likely-hood of dispersion in what medium and concentration of pollutant dependant on and not limited to time, temperature and vector rate.

The majority of funding for the removal of contaminants originates from tax payer dollars with exceptions to legislation which holds the polluter accountable; this is provided they can afford to mitigate their pollution after an event, in some cases companies may be forced into insolvency. In fact it has been found that companies would knowingly bury their pollutants concealing the pollutants they have produced because the cost of mitigation or disposal was unaffordable. Such a case was the “Valley of the Drums” in Kentucky which sparked the initiation of the Environmental Protection Agency (EPA) Superfund to help address these issues. At times these companies may have closed and their disappearance taken the location of such sites with them. To address the cost and potential parties responsible for such incidents the EPA has setup the superfund process. In the US, potential sites are assessed and placed on the national priorities list after which they establish a mitigation program which has the community involved (EPA Superfund, 2010).

1.1.1 When does pollution become a problem?

Until recently, pollution issues tended to be based on events that had already occurred, only recently have many governments enacted legislation which has been directed at pollution which may affect ecosystems of the future and yet this is still limited to the research available, it is a noble step with many hurdles to overcome due to the vast number of variables involved. It is difficult to predict the future, models are only as good as the data collected. At times poor standards may occur due to poor understanding of future implications and even ambiguous terminology used in legislation. Environmental

conventions, protocol and modern legislation will be discussed further below under the subheading convention and regulations.

Unfortunately most pollution which captures public attention is restricted to those things which are obvious or of direct use to society, unseen or long term effects are still usually ignored. Such as sources of raw water which is destined to be potable water, agricultural land, agricultural water supplies, air and land used for development of commercial or residential properties. Even the use of a tray to hold leaking fluids from a container is easy and cost effective but it is commonly only used when a problem has already occurred.

Pollution can be addressed when international peer pressure is applied. Prior to the 2008 Olympic Games in Beijing, air pollution was of major concern. In order for Beijing to comply for hosting the Olympics, the pollution found in Beijing had to be of a level acceptable to the International Olympic Committee. This resulted in several plans for reducing pollution starting with the relocation of steel manufacturing. This could be viewed as spreading pollution rather than fixing the problem, but at the time of relocation it was pledged that the manufacturing company would adhere to strict international environmental standards at the new location. To further reduce the haze in Beijing, driving curfews were enforced, forcing the local community to use green methods of transports such as bicycles, walking or public transport. Controversy has come about from the figures released by the Chinese government in regards to particle sizes found and statistical manipulation. (Spencer, 2008) However the fact remains that there have been initiatives to curb pollution, whether the initiatives remain after the Olympics are finished is uncertain.

Developing and third world countries struggle the most with pollution. Tradition approaches to managing resources are often at odds with high population densities, modern chemicals and machinery. Their first focus would be to establish a drinkable and usable source of water, like most civilisations the dependency on water is paramount; other types of environmental mitigation is treated as a government expense which does not take precedence. These areas lack the required technology, expertise as well as funding to carry out pollution mitigation techniques which will save lives as well as money.

Bangladesh, West Bengal and India are experiencing this problem, in an attempt to alleviate problems with polluted surface water, wells were dug but with large quantities of arsenic found in the groundwater surpassing the World Health Organisation's permissible

limit of 50 µg/L. It was found in an environmental study that 93% of the Bangladeshis sampled had concentrations of arsenic above the 50 µg/L maximum limit. The extent of arsenic poisoning is severe enough for some living in Bangladesh and West Bengal to have arsenicosis identifiable from skin lesions, keratosis, ulcers and a variety of other skin diseases. (Chowdhury et al., 2000)

Arsenic is distributed in the earth's crust, it becomes concerning when water acts as a vector due to the dissolution of arsenic salts from minerals and ores (World Health Organisation, 2001). Arsenic contamination of water can be found around the world. It is difficult to remove inorganics like arsenic from water and current technologies available are expensive or unreliable. Arsenic cannot be mitigated by ball milling this is due to arsenic already being in its simplest stable form defined as an element. It cannot be broken down any further by chemical or physical means; this restricts treatment to concentrating and storing the metal in another vessel.

Due to the ever increasing population cities are ever expanding, as per capita densities increase so does the demand for land and water. Society's appetite for resources creates pollution and ironically it is during progress when pollution matters.

1.1.2 Sources of pollution

Humans have had a poor conception of waste disposal and the impact it may have in the future, presumably as a mobile hunter/gatherer waste was simply abandoned and was of no further concern. This is demonstrated by previous civilizations and their attitude towards the disposal of waste. Mayan Indians of Central America had waste dumps which would at time explode due to poor management of waste (Barbalace, 2003). This does not mean previous generations did not recycle. Prior to the industrial revolution, the costs involved in making many materials were labour intensive and therefore expensive. During the industrial age processes were optimised and large portion of day to day items which ultimately resulted in mass manufacturing reducing the cost of these items. The methods of manufacturing often use materials or processes that have negative impacts on the environment or are considered pollutants. It is still cheaper to throw consumables away as opposed to recycling them, ignoring the environmental costs involved.

Nature can of course cause pollution, this occurs predominately during natural disasters. Severe storms, earthquakes, tsunamis and volcanic eruptions can all disrupt land forms and

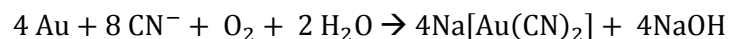
release hazardous materials into the environment. Volcanoes in particular can release large amounts of toxic material into the air and onto the Earth's surface. Polluting water supplies and changing the weather including other things in the environment. A recent example in Europe due to the Icelandic volcano Eyjafjallajökull erupted, shooting plumes of ash 6 km high causing much of Europe's airspace to be closed. If this had occurred over a large land mass it would not have just been disrupted flights but could have caused serious pollution by dust and toxic elements (Valdimarsson, 2010).

1.1.3 Sources for pollution into soil

Anthropogenic pollutants can be the result of a flagrant disregard for the environment but most are introduced into an environment due to absence of or poor containment. Plastic containers can degrade or micro leak. Deteriorating liners and poorly maintained containers housing obsolete pesticides are a major issue in some places; this can result in leaching of pollutants into the ground which result in secondary water sources like water tables to be contaminated.

Many variables can affect the rate and concentration of pollutants leaching into soils. They can include: pH, soil matrix composition, water retention capacity, geological contours, quality of water and water flow. Vectors play a key role in dispersion of pollutants; water can complement the leaching of liquids solids and gases, pollutants do not necessarily need to be soluble to be dispersed. A scenario which has been well researched is the environmental problems faced during silver and gold mining. This mining involves the use of sodium cyanide, which forms soluble silver or gold cyanide complexes.

This mining involves the use of sodium cyanide, which forms silver or gold cyanide complexes referred as cyanidation refer to equation 1 below.



Equation 1 shows cyanidation also called Elsner's equation. (Gönen, Kabasakal, & Özdil, 2004)

Cyanide complexes form with a variety of other elements which maybe present such as other heavy metals, potassium, sodium and calcium. These salts are very soluble depending on conditions and are thus mobile in the environment. Not only can this transport ions considerable distances if the complexes decompose they not only liberate the metal but also

free cyanide (CN and HCN) which can be very toxic. Due to free cyanide and cyanide complexes dissolving in water they can be easily leached into soils when not contained or treated appropriately. A brief overview of the impact cyanide has on the environment can be found at the following reference (International Cyanide Management Code For the Manufacture Transport and Use of Cyanide In the Production of Gold, 2006).

The wide spread adoption of many persistent organic pollutants (collectively known as POP's) occurred after World War II, in part due to the elevated synthesis of chemicals due to breakthroughs in synthetic methods. Thus was born the intentional synthesis of pesticides, which were extremely effective in mitigating pests, weeds and disease. Tragically it was unforeseen the future implications on mankind and the environment some pesticides have due to their long half lives. Just as concerning is the formation of dioxins and furans, come about from incineration of wastes, open burning of trash and industrial processes. These compounds are known carcinogens and some quite toxic both to humans and the environment.

An example of one of the most toxic is the dioxin 2,3,7,8-tetrachlorodibenzenedioxin (TCDD), the material data safety sheet (MSDS) notes TCDD having oral rat LD₅₀ of 20 µg/kg and lowest published lethal dose via skin absorption of 80 µg/kg. This means that exposure to 0.004g of TCDD onto the skin could be enough to kill a 50kg human. With such high toxicity TCDD has also been part of a controversial failed assassination attempt on Viktor Yushchenko (Sorg et al., 2009).

Underlying all manmade soil pollution is either ignorance or negligence which can come about from a variety of factors but predominately it is an issue of viable solutions which are cost effective, legislation and enforcement.

1.1.4 Hydrocarbon contamination

Hydrocarbons are a broad range of organic compounds. The majority of manmade hydrocarbons come from crude oil. While most have relatively low toxicity, some are extremely toxic and carcinogenic and because of the wide use of hydrocarbons in the modern world, they are one of the most common pollutants.

Crude oil spills are particularly damaging. Because hydrocarbons have a wide range of structures and densities, we would expect to find bands of hydrocarbons in a water system

due to varying densities. Compounds which could be found in the water-band are those which are polar enough for water to dissolve such as short chained alcohols, esters and carbonyl groups. We will also find inorganics such as nitrates, phosphates and sulphates dissolved in water at varying concentrations depending on pH of the aquatic system. Compared to land oil spills, water oil spills tend to have a larger area of impact affecting more ecosystems due to the seas current moving crude oil over vast distances.

Crude oil spills can cause chaos, drastically changing ecosystem and killing organisms. Fish have a low tolerance to these oils with their acute toxicity set around 4000 ppm.(Prasad & Kumari, 1987) Apex predators which may feed of these fish may die from acute toxicity since crude oil being a mixture of fat soluble organic compounds can be bio-amplified to toxic levels. Sea birds can become covered in oils from diving into waters polluted with oils when hunting for fish, the oil causes their feathers to mat and separate inhibiting flight. In the event they are able to take flight their wings are a lot heavier and therefore put more stress on the bird. The majority of these birds without human intervention will die either from the inability to take flight making them easy prey, inability to regulate body temperature due to oil matting feathers and even acute crude oil poisoning from cleaning their feathers.

When crude oil is introduced onto land, a key difference between aquatic and soil environments is the affinity soil matrixes can have for crude oil. Similar scenarios can occur with aromatic organics as well like PAHs. The crude oil is described to have a “smearing” affect in porous soil, as they pass these porous soils they leave behind hydrocarbons in the pores.(Taylor, 2007) In the event of high water flow through the soil matrix occurs due to rain or groundwater fluctuations, these pores can be a source of continued contamination.

When the polluted soil matrix settles, they can act as chemical interfaces allowing an array of biodegradation reactions (bioremediation) to occur on the trapped crude oil. These reactions are governed by environmental conditions including the presence of different compounds. They are not purely chemical reactions they can also be assisted via natural decomposition by increasing the interaction surface area of the crude oil. Some bioremediation methods include phytoremediation, photodegradation and bacterial remediation.

Phytoremediation involves the use of plants to remove pollutants this could be from storage and decomposition for consumption, this was demonstrated with great efficiency in removing PCBs and PAHs (Huesemann, Hausmann, Fortman, Thom, & Cullinan, 2009). Photodegradation happens constantly provided the medium has been exposed to the sun for periods of time long enough for photons to cause chemical changes, an obvious limitation of photodegradation comes about from periods of exposure to the sun and only surface reactions occurring; these types of reactions are competition reactions with the volatility of the compound. Bacterial remediation as the title implies involves bacteria being used to breakdown pollutants in this instance crude oil, the use of bacteria for potential crude oil remediation can be dated to 1975 where bacterium was cultured on crude oil (Horowitz, Gutnick, & Rosenberg, 1975). Limitations of bacterial remediation are the environmental restricted, such as elevated salinity levels. Bacterium maybe culture at optimum conditions in the lab prior to replication but when exposed to elevated salinity lyses can occur due to osmosis. This was demonstrated when bacterial remediation was used during the explosion of *Mega Borg* well, resulting in roughly 100,000 barrels of crude oil being split into the gulf of Mexico; tests done on the results achieved were inconclusive(Dimond, 2010).

Land based oil spills can cause contamination of raw water and saturate soil with crude oil. This reduces the water retention of soil this at times can make soil unfertile hindering growth of plants. When left untreated, these soils can release volatiles into the air which can be carcinogenic, toxic and undergo photolysis. In the event of rain, saturated soils will leach oils into surrounding rivers and streams. Soil matrixes with more porous nature like sand tend to transport the oil down into the ground eventually reaching water tables, this is accelerated with rain.

1.2 Persistent organic pollutants (POP)

Persistent organic pollutants are organic compounds that have a strong resistance against biological, chemical and physical decomposition. Making them persist in the environment. At times the amounts initially ingested by organisms are not harmful but due to the resistant nature of POP's they have a biomagnifications effect.

The halogenations of carbon bonds with chlorine often produces toxic compounds and thus has been widely exploited for use in pesticide development such as DDT, Mirex and PCBs. Carbon-chlorine bonds are extremely stable this in part is due to the size of chlorine being

larger than carbon atoms, when several chlorines surround a carbon based molecule the activation energy required to break these bonds to form a very unstable transition state increases, therefore stability is increased (McMurry, 2004).

With certain exceptions, chlorinated compounds are usually foreign to our biochemical pathways, and when introduced to living systems can be toxic or can take a long time to break down in the environment. An interesting exception is sucralose a non-nutritive sweetener used in foods

Persistent organic pollutants on the other hand are for the most part potent pesticides. While they may have relatively low acute mammalian toxicity they are obviously very harmful to plants or insects and because they are stable molecules and because few organisms are able to metabolise them easily, they persist in the environment. These characteristics and excessive use eventually caused them to be classed as persistent organic pollutants (POP) (Global Programme of Action for the Protection of the Marine Environment from Land-based Activities, 2000b). The introduction of these substances into ecosystems causing changes in biodiversity. Even small quantities can increase pressure on already endangered species of animals and plants, as either their food sources are reduced or accumulative effects of compounds can be toxic therefore resulting in death. This may eventuate into extinction; with 1.5 – 1.8 million species identified and an estimated 30 – 50 millions species unidentified. The large pool of unidentified organisms could be remedies for diseases or maybe key organisms in evolution; even before their identification they could be extinct (Marjorie L. Reaka-Kudla, 1996).

POP's which have been listed as of concern by the environmental protection agency (EPA) dubbed the "dirty dozen" are Aldrin, Chlordane, dichlorodiphenyl trichloroethane (DDT), Dieldrin, Endrin, Heptachlor, hexachlorobenzene, Mirex, Toxaphene, polychlorinated biphenyls (PCB), polychlorinated dibenzo-p-dioxins (dioxin) and polychlorinated dibenzofurans (furans). These POP's are of concern due to the quantities which have been produced and/or have potential for future production or because in the case of the dioxins (some of which are powerful toxins and carcinogens) have potential for long term harm and are very stable. The US EPA has also distinguished 2 categories based on manufacture of POP's as being intentional and non-intentionally produced.

Some research has drawn links to the DDT (inclusive of DDT metabolites) and PCBs mimicking estrogen production causing sex of Red-Eared slider turtles to predominately be female. They have been termed as endocrine-disrupting compounds (EDC). As some of these POP's mimic steroid or other hormones they have been proposed to interfere with developing embryos. DDT for example binds to the estrogen production receptor site; this causes the turtles to produce elevated levels of natural estrogen which is the governing hormone for the sex of the turtles.

Disruption is not limited to EDCs binding directly with hormone sites. They may mimic hormones or may interfere with stages of steroid production from regulation to activity. EDCs can disrupt the endocrine system, for example, estradiol is a key hormone in many biochemical pathways and EDCs can manipulate the biochemical pathways estradiol takes. This may elevate or depress levels of hormones and/or proteins such as enzymes potentially altering other biochemistries, this indicates that the effects EDCs can have is almost endless (Anonymous, 2002; Hammond, NA).

More recently organophosphate pesticides were found to increase the risk of young children getting attention deficit hyperactivity disorder (ADHD) when prenatal mothers were exposed. The biochemical pathway involves the formation of paraoxonase which was linked to interfere with enzyme activity and enzyme production (Eskenazi et al., 2010). Other studies have linked organophosphates to the development of several severe brain diseases such as Parkinson's disease and brain tumours (Paragh et al., 2002).

With an ever increasing population, society's demand for food increase. Food production is a multi trillion dollar industry, with this in mind it is foreseeable that there will always be a demand for chemicals to control pests and improve productivity. While we know more about what may be hazardous, there will always exist a possibility that harmful chemicals of these types will be created and get into the environment.

1.3 Pesticides

The Food and Agriculture Organization of the United Nations defines pesticides as:

“Pesticide means any substance or mixture of substances intended for preventing, destroying or controlling any pest, including vectors of human or animal disease, unwanted species of plants or animals causing harm during or otherwise interfering with the

production, processing, storage, transport or marketing of food, agricultural commodities, wood and wood products or animal feedstuffs, or substances which may be administered to animals for the control of insects, arachnids or other pests in or on their bodies. The term includes substances intended for use as a plant growth regulator, defoliant, desiccant or agent for thinning fruit or preventing the premature fall of fruit, and substances applied to crops either before or after harvest to protect the commodity from deterioration during storage and transport.”(Food and Agriculture Organization of the United Nations, 2009)

The use of pesticides has existed before the commercial cultivation of crops; these pesticides in question were elemental derived such as sulphur, mercury, arsenic and lead. Being elements they are in their simplest state, disposal would therefore be limited to storage or dispersion technologies. It was not until the 1940s did the manufacture of synthetic pesticides and their use become predominant (Daly, Doyen, & Purcell, 1998).

Pesticides when used, allow plants to be cultivated in ideal conditions free from fungi, vermin, weeds, insects and many others. This translates into higher yields per hectare, optimising production and exhausting nutrients from the soil. In fact modern agriculture produces more food than the world’s population can consume, world hunger should be absent but the naivety of that statement does not consider logistic, storage and pricing challenges which till this day hinder humanity efforts in third world countries.

Pesticides expenditure globally totalled to USD\$32 billion for the year of 2001. Herbicides accounted for the largest portion followed by, insecticides, fungicides and other pesticides. The amount of synthesised DDT approximately amounts to 400,000 tonnes in China alone, before they were banned. A figure on the total amounts of phthalates produced in the world could not be found, but several articles mention it to be in the several million of tonnes a year. (Gómez-Hens & Aguilar-Caballo, 2003; Huang & Islandar, 2000; Waliszewski & Szymczyski, 1990) Globally the use of pesticides exceeded 2.3 million tonnes for the year 2001. In the United States of America 53% of the pesticides were hypochlorites or chlorinated (Timothy Kiely, 2004).

These vast amounts of produced compounds have not just found to be dispersed into the environment of the areas of use, be it from the manufacturing facilities off runs or from rain as a vector (Hüskes & Levsen, 1997). The compounds dichlorodiphenyltrichloroethane (DDT) and di(2-ethylhexyl) phthalate (DOP) have been found at Antarctica, these samples

were taken 3 metres below the snow and in the air; it should be noted that other compounds such as organochlorides, n-alkanes, aldehydes, alcohols and benzenes have also been found at Antarctica (Bidleman, Walla, Roura, Carr, & Schmidt, 1993; Desideri et al., 1998; Hüskes & Levsen, 1997). The presence of these compounds at one of the least inhabited parts of the earth indicates the wide spread of such chemicals.

1.3.1 Dichlorodiphenyltrichloroethane (DDT)

DDT was first synthesised in 1874 by an Austrian chemist Othmar Zeidler and would later be the first chlorinated compound to be used as a pesticide. The application of DDT as a pesticide was discovered 66 years later when a Swiss chemist Paul Hermann Müller was researching the “high efficiency of DDT as a contact poison against several arthropods” in which he later won The Nobel Prize in Physiology or Medicine 1948. (Global Programme of Action for the Protection of the Marine Environment from Land-based Activities, 2000a)

DDT has been used extensively; this is partially due to the effectiveness of DDT which has a half life of 22 days to 30 year in soil depending on pH levels of the environment. After Paul Hermanns Müller discovery, the US started producing large quantities of DDT to combat insect borne diseases faced abroad like typhus and malaria. The excessive use of DDT in the US can be attributed to the eradication of malaria, the amount of DDT used was enough to increase insect resistance to DDT; to this day DDT is still produced as one of the few viable ways to combat malaria.

The persistence of DDT was initially recognised as having a significant advantage over other pesticides available at that time, this has made DDT a highly effective pesticide. With such persistence it was only a matter of time until it was recognised as an environmental pollutant resulting in tougher laws requiring registration and regulation for the use of DDT and DDT containing substances. (U.S. Environmental Protection Agency, 1975)

DDT is consumed through inhalation and ingestion; ingestion is the more common route of human exposure to DDT. Consumption of high concentrations of DDT comes about from sources of animal fats or vegetable oil; low concentrations of DDT can be consumed through foods which contain DDT residues. When DDT is exposed to the skin, uptake is slow; it is thought this is due to high amounts of water found in the skin which limits transport of the lipophilic DDT. (Sato, Yanai, Hirao, & Denda, 2000)

DDT is highly chlorinated. Not many naturally occurring biochemical pathways are able to easily deactivate chlorinated compounds which makes it slow to biodegrade. Its lipophilicity causes extreme persistence in fats. Even after several decades of pesticides like DDT and PCBs being banned from use, these compounds can still be detected in human adipose tissue.

Photolysis of DDT for about one hour yields dichlorodiphenyldichloroethene (DDE) and dichlorodiphenyldiichloroethane (DDD) (Zepp, Wolfe, Azarraga, Cox, & Pape, 1977). DDD resists any further photolysis. What is of interest is the similarities in DDE derived products organisms can metabolise; it is evident that the substructure benzyl benzene when halogenated with fluoride or chlorine forming 1-chloro-4-[(4-chlorophenyl) methyl] benzene is a key feature to the compounds being persistent compounds. Natural mitigation of benzyl benzene derivatives tends to focus on the carbon joining both the benzenes this is illustrated by “R1” in figure 1.

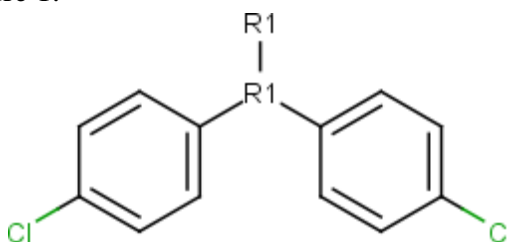


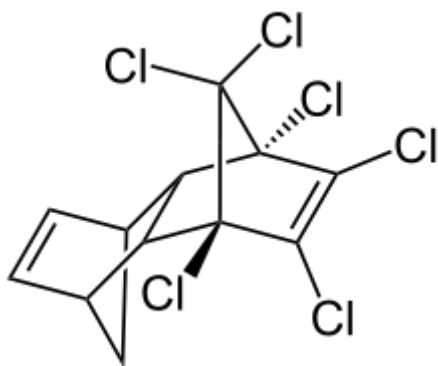
Figure 1, illustrates groups of interest (R1) during natural mitigation of benzyl benzene derivatives.

Research done on the metabolism of DDT in organisms such as insects and pigeons has found varying end products of different concentrations including water soluble compounds. In mammals two metabolites occur, the formation of DDE via dehalogenation (this occurs easily and is a common contaminant in DDT) and a stepwise degradation to 1,1-dichloro-2,2-bis [p-chlorophenyl] ethane (DDA) from DDD. (World Health Organisation, 1979)

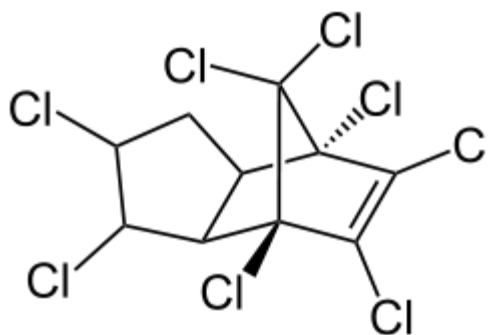
DDT is banned in most developed countries due in part to the Stockholm convention and a general awareness of the possible implications compounds can have on our environment. DDT has exempted from the ban for its controlled use to combat malaria, there is still a problem with disposal of DDT contaminated soils and DDT surplus stocks. (Stockholm Convention, 2008) but controversy remains. The debate of DDTs benefits outweighing the proposed detrimental affects it can have on society and the environment. The debate is due to DDTs extreme efficacy in killing the mosquito vector and the toxic effects on humans as well as affected ecosystems.

1.3.2 Aldrin, Dieldrin, Chlordane, Endrin, Heptachlor

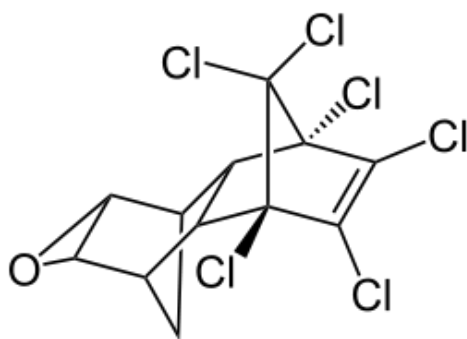
The reasons for grouping the following chlorinated POP's is because they have a similar modified bornane structures. The synthesis is a Diels-Alder reaction with hexachlorocyclopentadiene and varying cyclic compounds. For example the formation of Aldrin from hexachlorocyclopentadiene and norbornadiene.



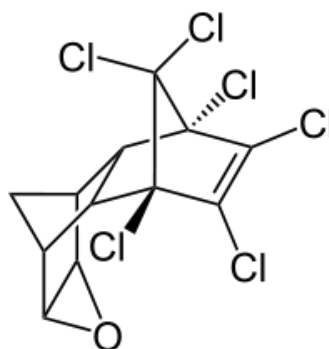
Aldrin



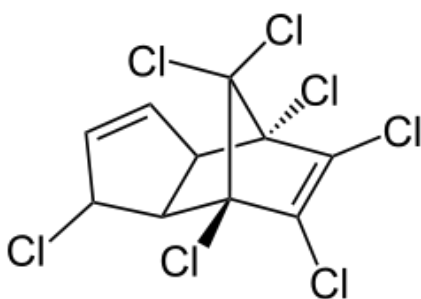
Chlordane



Dieldrin



Endrin



Heptachlor

Dieldrin comes from the epoxidation of Aldrin, oxidising the ring at the double bond.

Aldrin originates from the family of similar Diels-Alder reactions and was used extensively as a pesticide to treat soils until the 1970s before it was banned. Similar to other polychlorinated pesticides they are extremely hydrophobic making them highly lipophilic.

The use of Aldrin is banned in United States in the 1970s and the European Union. Research done in 1992 on adipose tissues on American citizens with an range of 6 months to 74 years found that of the 111 sampled 95% contained detectable levels of Aldrin ranging from 1 to 500 ppb, it was also found that concentrations increased with age. The increasing concentration of Aldrin with age comes about from the persistent nature and lipophilic characteristic of Aldrin. (Jorgenson, 2001) Similar findings have been found with other POP's with lipophilic characteristics.

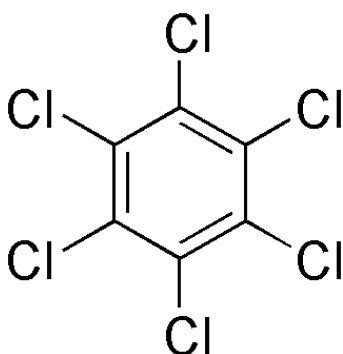
The fat solubility of POP's has a bioaccumulation effect, when individuals start to store fat it is due to reasons of energy storage due to the abundance of food (Murphy, 1983). The presence of fat indicates a well-nourished body with sufficient amount of food, but this also means more sites of storage for lipophilic compounds such as DDT. During consumption of meats we inevitably consume fats which could therefore contain lipophilic compounds. When concentrations reach a critical point sickness will occur, due to these compounds interfering with biochemical pathways which in the first place these compounds were designed to do. When constant consumption of these compounds occur possibly due to a contaminated food supply, death may occur.

The amounts found in the liver are not reliable for determining exposure to Aldrin and related lipophilic pesticides, due to it being the site of metabolism. A key difference between DDT and Aldrins are the concentrations found in the bone marrow which are 19 times higher than those found in pesticides with chlorinated benzyl structures (Scheele, 1998).

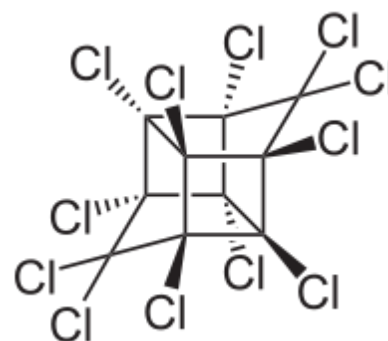
Research has also found that mammals vary in both their ability to store and metabolise chlorinated organic pesticides (Shellenberger & Fullerton, 1978). This poses some problems when toxicology studies are performed in different species.

1.3.3 Hexachlorobenzene and Mirex

Hexachlorobenzene (HCB) and Mirex do not have any similarities in terms of structure, but are related when based on degree of possible substitution and synthesis. Both these compounds have all their sites of substitution fully substituted with chlorine, making them foreign to natural biological systems. Due to the degree of substitution they are highly lipophilic, and therefore have characteristics which include biodegradation resistance and bioamplification in the environment.



Hexachlorobenzene



Mirex

Research on the mammalian metabolites of hexachlorobenzene have been limited to the dehalogenation of a single chlorine from the benzene ring resulting in the formation of pentachlorophenol, tetrachlorohydroquinone and pentachlorothiophenol, with lesser amounts of tetrachlorobenzene, pentachlorobenzene, 2,4,5- and 2,4,6- trichlorophenols and 2,3,4,6- and 2,3,5,6-tetrachlorophenols (Food and Agriculture Organization of the United Nations, 1991). The formation of these metabolites indicate the inefficiency mammals have to degrading hexachlorobenzene, again this demonstrates that most highly substituted compounds with chlorine like DDT are not well metabolised by mammals.

Mirex was first synthesised in 1946 and used in a combination with other pesticides to control fire ants. Mirex's metabolites are considered carcinogens and like most heavily chlorinated compound this chlorination causes bioamplification. Mirex does not share similar metabolism characteristics as seen in mammals with most chlorinated pesticides as it appears to almost completely resist mammalian degradation in mice, rats, rabbits and monkeys (Waters, Huff, & Gerstner, 1977). In soil it degrades by dehalogenation followed by oxidation (Carlson, Konyha, Wheeler, Marshall, & Zaylskie, 1976).

1.4 Polychlorinated biphenyls (PCB)

Polychlorinated biphenyls are another class of heavily chlorinated aromatics. Assuming random chlorination, 209 possible congeners can be formed but in during actual industrial manufacture, only 130 types of PCBs are likely to occur. (Neumeier, 1998)

The United Nations Environmental Programme defines PCBs as:

“polychlorinated biphenyls or PCBs are a subset of the synthetic organic chemicals known as chlorinated hydrocarbons. The chemical formula for PCBs is $C_{12}H_{(10-n)}Cl_n$, where n is a number of chlorine atoms ranging 1 – 10. The class includes all compounds with biphenyl

structure (i.e., two benzene rings linked together) that have been chlorinated to varying degrees.” (UNEP Chemicals, 1999) The number of n’s are represent by R2 in figure 2, R2 can be H or Cl when conforming to the UNEPs definition of PCBs.

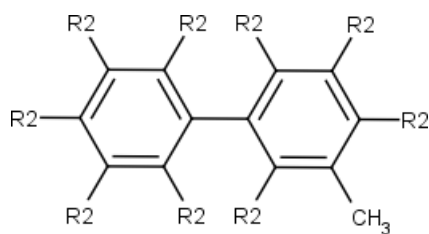


Figure 2, Illustrates the groups symbolised by R2 which can either be Cl, Br or H groups.

When Br is substituted in the R2 regions, we have the formations of polybrominated biphenyls (PBBs), they have similar properties and effects like PCBs. Two major incidences involving accidental ingestions of PCBs has been reported involving PCBs contaminating cooking oil originating from industrial oils. These incidences occurred in Japan 1968 and Taiwan 1979. A large study sampling Americans adipose tissue, breast milk and blood concludes that most individual have been exposed to PCBs and PBBs in the United States a with minimum amounts of 0.5 ppm found in adipose or breast milk fat extract.(Dillon, Martin, & O'Brien, 1981; Safe & Hutzinger, 1984) Possible health effects PCBs may have on humans include liver damage, ocular lesions, lowered immune response and a variety of skin conditions. In children it was reported to cause poor cognitive development (Aoki, 2001).

PCBs used to be used in many everyday consumables and are classified into availability of the PCBs when put in context to their application. PCBs are classified as the following open, partially closed and closed applications. Some examples of PCBs uses are in inks, dyes, hydraulic fluids, florescent tubes and electromagnets, thus their extent of exposure is very high due to the former dependency of these compounds.

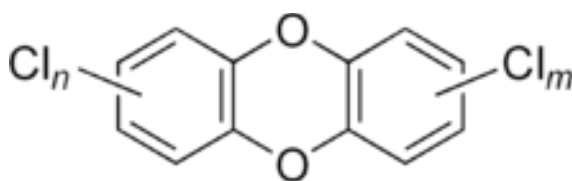
PCBs have strong chemical stability, which of course was one of the reasons they were manufactured in the first place. They resist breakdown via acids, bases, heat, radiation and redox agents. These properties are similar to those noted for other heavily chlorinated compounds and this contributes to the persistence of PCBs in the environment. When left alone in soil, PCBs undergo slow hydrolysis and oxidation. During photochemical

degradation groups are substituted at the ortho position they are dehalogenated more readily as opposed to para and meta positions. (Safe & Hutzinger, 1984)

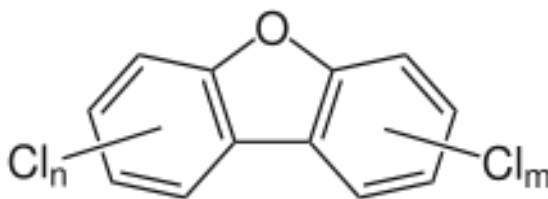
1.5 Polychlorinated dibenzo-p-dioxins (dioxin) and polychlorinated dibenzofurans (furans)

It was thought in the 1950s the main sources of dioxins and furans came about from industrial synthesis of chlorinated organic compounds. Later it was found that they can come from a variety of sources which involve combustion of chlorinated compounds this can include human refuse and high chloride peat (Meharg & Killham, 2003).

Some key differences between dioxins and furans are the number of carbons and oxygen found in the compound. Both dioxins and furans would prefer to maintain their aromaticity due to oxygen containing a lone pair of electrons which is delocalised into the ring; the importance of aromaticity is their unusual stability which enables these compounds to persist in the environment.



Polychlorinated dibenzodioxins

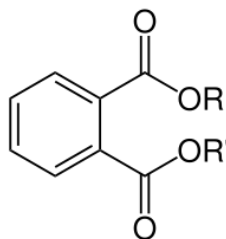


Polychlorinated dibenzofurans

The majority of the dioxins and furans produced are from combustion of chlorinated organic compounds for several intensions varying from refuse disposal from recycling of copper wires. This comes about from the extensive use of polyvinyl chlorides as wire insulation; a common method of insulation disposal from these wires is by incineration which produces dioxins and furans. We would also expect areas which have high salinity be it from the sea or natural deposits to be possible sites of dioxin and furan pollutants during burning material from these areas.

Exposure to these compounds have been linked to cancer; it has been theorised dioxins accelerate the formation of tumours and adversely have negative effects on tumour inhibition mechanisms without directly causing cancer (Minnesota Department of Health, 2006).

1.6 Phthalates



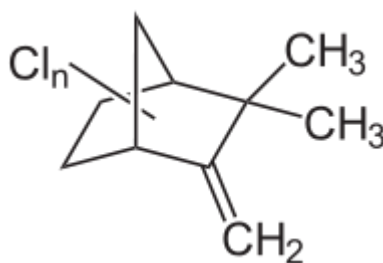
Phthalate esters

The synthetic compound polyvinyl chloride (PVC) which is used to make many consumer products ranging from pipes to clothing, the versatile application of PVC has created a dependency on this plastic. PVC is initially brittle and difficult to handle before the addition of plasticisers such as di-n-octyl phthalate (DOP) which is also known as di(2-ethylhexyl) phthalate (DEHP). The PVC absorbs the phthalate resulting in a flexible and more manageable material. DOP was used as a plasticizer for blood bags before it was found to leech into blood which could have adverse effects on those whom are already vulnerable. It was also found when excessive amounts of DOP are leached the PVC may turn brittle which may pose to be another hazard when large quantities of blood are involved in in vivo applications. (Szycher, 1991)

Exposure humans to phthalates has not been research extensively, most literature is based on animal exposure with inconclusive results; these results range from reproductive damage, hepatocellular carcinoma to respiratory inflammation and dermatitis. Shanna H. Swan attributes the difficulties in interpreting human related results due to the extensive exposure to different plasticizers in their environment. Sources of exposure include dust, household products, cosmetic products, breast milk formulas and food. (Latini, 2005; Swan, 2008)

1.7 Toxaphene

Toxaphene is synthesised by the partial halogenation of camphene with chlorine, this results in over 200 possible chlorinated products. The majority of these chlorinated compounds are chlorobornane, chlorochamphenes and chlorinated bicyclic compounds.



Toxaphene

Having a high degree of chlorinated substitution, toxaphene and metabolites are bioamplified in the environment (Buser, Haglund, Müller, Poiger, & Rappe, 2000). Rats have been found to dehalogenate up to 50% of the chlorine from Mirex and 7 other sub fractions which results in varying composition and toxicity (Casida et al., 1974). The difficulty faced by researchers is the complex composition of Mirex, so products found from analysis by high performance liquid chromatography or gas chromatograph mass spectra due to degradation have to be accounted for as a product found in Mirex.

Toxaphene has been found to degrade by microbial action in both anaerobic and aerobic conditions; these degradation products are at times more persistent than the original toxaphene compound. In aerobic conditions the breakdown of toxaphene is slow with half-lives of up to 14 years. Anaerobic conditions degrade toxaphene more rapidly with half-lives of one to several months. It was also found that nonachloro compounds degrade the fastest, followed by shorter chained octa and hepta chlorinated compounds (Buser et al., 2000; Fingerling, Hertkorn, & Parlar, 1996). When inhaled toxaphene has been shown to be a carcinogen damaging lungs, the nervous system and can eventually result in death.

1.8 Mitigation methods of pollutants

Our ability to mitigate various types of pollution varies enormously depending on the type of pollution and the associated cost. Numerous technologies and methods been devised, they can be categorised into pollutant source mitigation, pollutant disposal and pollutant removal/disposal from the environment.

1.8.1 Recycling

The term recycling includes reusing. Society has always been looking for ways to reduce cost and improve productivity. Historically recycling came about mostly for economic reasons. For example, during the roman era, stone slabs from unwanted buildings were recycled; this made good since it was easier and cheaper to reuse stone slabs than to mine

and transport them from the quarry. Today, depending on demand, it is often very cost effective to recycle metals.

To encourage recycling in domestic situations, governments have taken an education approach. Investment in education and advertising of recycling campaigns such as “reduce, reuse and recycle” as well as information on how to identify plastics from their recycling symbols allows them to be recycled efficiently.

Unfortunately, a large problem slowing the uptake of recycled plastics is the inconsistent supply and purity of recycled plastics. This hinders manufacturers from using recycled plastics which are usually more expensive than virgin plastics made from crude oil. Due to government intervention such as the US EPA in the recycling of polyethylene terephthalate (PET), the supplies of recycled PET plastic pellets are cost effective enough for manufactures to start adopting their use. This does not mean that recycled plastics are cheaper than virgin plastic; it is still up to the consumer and manufacturer to decide what they want and drive the demand of recycled plastic.

Some difficulties faced by recycling companies are the unknown and subtle effects of additives in plastics such as colours, fillers, and plasticisers. The importance of knowing these additives as given as an example by the MIT engineer Jennifer Sutton during a question and answer is that during PET recycling even small amounts of PVC can significantly degrade PET. The sorting of unknown plastics is labour intensive and therefore expensive as opposed to purchasing crude materials for plastic production, primarily coming from oil sources. (Sutton, 2010)

Chemicals such as solvents are to some extent recycled and products such as glass containers have in the past been extensively re-used but unfortunately it is still often cheaper to make new objects rather than re-use them.

1.8.2 Incineration

The combustion of waste is a popular technology used in several countries such as Japan, Denmark and Sweden. Incineration is the burning of unwanted materials at high temperatures this process generates ash, flue gas, particles and heat. The generation of heat can be used to generate power by steam-driven turbines. All modern incineration facilities are required to filter flue gases these gases can contain a variety of carcinogens include

furans and dioxins. This requirement came about from older facilities having been centres of attention for allegedly polluting communities due to the oversight of not filtering flue gases generated from incineration. Even now, incineration is still strongly debated amongst experts and communities.

Combustion of waste is very effective at saving space it can reduce mass of unwanted materials of up to 85% and up to 96% in volume, depending on the composition of the waste being incinerated (Ramboll, 2006). This can be important when countries such as Japan currently have limited space for landfills.

1.8.3 Landfills & Storage

Natural degradation occurs in landfills predominately by microorganisms and at times from intentionally added chemicals. Landfills could be considered as another method of storage for pollutants, these pollutants could be of various qualities include partial and/or full degradation with possible modifications from secondary mitigation processes.

Because of the low costs and simplicity involved, simple storage is one of the preferred methods for compounds which have been banned or are considered too hazardous to be buried in landfills which may have human contact. Unfortunately it is a short term solution as most of these unwanted compounds resist degradation when kept in containers. Such compounds include radioactive material and banned pesticides. Problems also arise when the containment materials degrade from a variety of process resulting in structural failure and eventual leaking. Storage sites are usually areas which have low human exposure such as disused mines.

When pollutants are stored in landfills they can degrade to varying degrees by various means including biodegradation and photodegradation. Biological degradation is the primary mode of degradation in landfills, in fact landfills traditionally were a large hole with garbage compacted on top. Some problems faced by traditional methods of land filling include leaching of liquids into surrounding soils or water tables and flammable methane gas pockets.

Leaching of liquids into soils can be extremely frustrating to mitigate due to the compositions and concentrations of waste liquids. The compositions come about from a large variety of sources from organic substances to consumer goods this means we can

expect to find naturally occurring and manmade compounds. Due to the variety of substances which can be found, remediation of these fluids involving several series of methods and technologies is common.

Methane pockets can be extremely dangerous as the build up of methane gets concentrated over time. If allowed to ignite, a catastrophic explosion can occur. Methane production comes about from anaerobic conditions due to poor aeration of trash. Due to the amounts of methane produced, some landfills harvest such gases and convert it into energy by combustion. A method used to harvest methane involves a pipe grid with many methane intake pipes the methane is pumped to a combustion engine which generates power.

More modern landfills take into account these problems by using a lining commonly made from layers of clay and polyethylene laid down prior to use. This temporarily inhibits liquids from permeating through. The use of polyethylene linings is controversial as they can degrade over time; this implies landfills could eventually leach hundreds of years of waste liquid into the soil which may eventually contaminate water systems with dire consequences.

To reduce the build up of methane, waste is aerated. This can be achieved by a variety of techniques such as injecting probes which push pressurised air into the compacted waste. Aeration also accelerates the bio-decomposition of materials eventually reducing the mass and volume of the landfill site(Rich, Gronow, & Voulvoulis, 2008).

1.8.4 Photodegradation

Exposure to the ultra-violet (UV) radiation predominately comes from the sun. Therefore only materials exposed to light can be affected, this would limit effectiveness on thin layers of soils or clean water. UV radiation excites molecules; in fact it can excite molecules till chemical changes can occur, this occurs due to interactions of photons. A possible mechanism involves the emitted photons creating reactive oxygen species which are a source of free radicals causing a variety of chemical reactions to occur such as polymerisation, substitutions and dehalogenation.(Usanmaz, Onal, & Bostan, 1989)

Free radical reactions can occur in DDT and PCBs resulting in degraded products which have been dehalogenated of varying degrees, usually 1 or 2 chlorines are removed or substituted with hydroxides due to free radical oxygen refer to figure 2.

1.8.5 Chemical remediation

The use of reactive compounds to remedy situations is effective under laboratory conditions; problems occur when these compounds are introduced into environmental contexts and when applied to real life scenarios at much higher amounts. It is very difficult to model and therefore simulate the environmental impact an introduced compound could have. Most chemical remediation techniques used for organic compound compliment the biodegradation processes and thus are reliant on nature. A good example is a large scale oil spill.

Following a recent oil well blow-out, the owner of the oil rig added a surfactant which disperses the crude oil this in turn increase the rate of biodegradation of the oil with the assistance from wave action. Mechanical movement is required to assist in dispersing the oil in the context of an oil spill wave action does this resulting in small droplets. This does not directly break down the oils, but can be considered as an additive to help accelerate degradation of oil by increasing surface area for bioremediation to occur thus speeding up the breakdown of oil.

Currently over one million litres of the surfactant has been used causing concern on the possible interactions this surfactant could have on marine organisms in large quantities. These concerns are valid as some forms of marine life rely on a slime protection barrier, this barrier could be fragmented by surfactants making them vulnerable. Our poor understanding of the ocean comes about from difficulties in exploration of the deep sea as quoted from Gene Feldman “it's easier to put a person into space than it is to send a person down to the bottom of the ocean”.(Stillman, 2009)

Sadly sludge has reached inshore, coating a wide variety of birds and defacing the beach. Beach areas which have sludge washed ashore can be hazardous due to the volatilisation of organic compounds from the sun and photodegradation. Due to the nature of crude oil, volatilisation of such organic material can yield carcinogenic organics which can penetrate through the skin, eyes and inhalation (Backe, Cousins, & Larsson, 2004).

Chemical remediation is most commonly used for removal of heavy metals from soil samples, using a wide variety of compounds which help assist the uptake of heavy metals in water this includes compounds like ethylenediaminetetraacetic acid (EDTA), calcium nitrate and dilute hydrochloric acid. Heavy metals as noted earlier are ions or metal

complexes which can dissolve in water, especially in acidic conditions. These deliberately contaminated water samples could be concentrated then stored or dispersed over a larger area.

1.8.6 Convention & Regulation

All civilisations have governing laws setting boundaries for society to follow so regulation is inevitable. The majority of legislation comes about hopefully from extensive research and modelling initiated by the responsible authorities and local bodies; resulting in a complied set of regulations and mandates. Thus convention and protocol are born; countries sign themselves abroad and are provided with a sufficient amount of information to help them achieve goals agreed upon by both the convention and signees. It has to be noted there is a startling differences between a convention and a protocol. These 2 terms describe the level of commitment, in a convention countries are encouraged whilst in a protocol countries are committed to achieve their agreed upon targets.

We could say regulation is one of the fundamental controls for pollutant mitigation; the requirement for industry to dispose of their waste in an environmentally acceptable manner at their own costs will help drive the development of more cost effective disposal systems. Regulations and laws also ensure costs involved in environmental protection are shared by respective manufacturing industries, allowing the corresponding industry to remain competitive amongst each other.

There are dozens of conventions and protocols which address critical topics of the environmental management they include atmospheric, freshwater, hazardous, marine environment global, marine environment regional, marine living resources, nature conservations and nuclear safety (Wikipedia, 2010a). Since reactive milling is only possible in solids like soils. The focus of this thesis leans towards land based pollutants, and several of the associated conventions and protocols will be briefly overviewed. They are the Rotterdam convention, Stockholm convention, Geneva Convention and Kyoto protocol.

The Rotterdam convention is one of the newer conventions established in 2004, it creates legal obligations requiring the implementation of the Prior Informed Consent process. These obligations encompass a variety of pesticides and deemed hazardous chemicals totalling to 40 chemicals as of 2010. The convention emphasises the exchange of

information between parties, allowing monitoring and accountability for the 40 imported chemicals. (Rotterdam Convention, 2010)

The Stockholm convention was established on the 22nd May 2001 and targets specifically POP's, as one can guess the main focus of this convention is to reduce the use of POP's and introduce safe management of POP's when they are used thereby limiting the release of POP's. This convention also indicates a party's acknowledgement that POP's are a health risk and appropriate actions are planned for the mitigation of the use of POP's. (Stockholm Convention, 2010)

1.8.8 Mechanochemical Reaction

Mechanochemistry is commonly understood to be a chemical change due to the intentional interaction of a mechanical action inducing chemical breakage. A clear example dictating this process as given by (Wikipedia, 2010b) where two pieces of wood are rubbed against each other causing friction, once the temperature rises enough for the ignition of dry wood is reached fire is produced.

Similar to rubbing, grinding processes could be considered as mechanochemical interaction. Where a substance is ground to finer powder, as we see a size reduction we will be cleaving bonds. Such an example is when a mortar and pestle grinds pepper. As one could imagine the main principals behind mechanochemistry could be considered crude thus the mechanics behind modern mechanochemistry are simple, but possible interactions with other compounds can cause complexity. In summary two or more surfaces have to contact each other in proximity significant enough for interaction; a mechanical action introduces movement therefore friction causing fragmentation.

A common approach to grinding where fine sizes are required is through the use of ball mills, this is extensively used in the cosmetics, paint and food beverage industry to improve dispersion or facilitate the dissolving process.. Less known is the use of ball milling as a means of chemical reaction or compound destruction; it has also been referred to in the literature mechanochemical treatment.

1.9 Ball Milling

Depending on the type of mill, ball milling involves a mixture of fracturing, crushing and grinding motions to reduce in particle size. When higher energies are used, the high velocity of the balls can cause a variety of chemical reactions depending on materials present both polymerisation and total compound destruction have been observed. This high energy ball milling, is widely used for mechanical alloying, mechanical milling and to a much lesser extend compound destruction.

In terms of chemical processes during ball milling there are two typical conditions, wet and dry. The wet process is usually used to give a finer product. The milling can be continuous or batch. The key variables which effect ball milling are ball size, ball velocity and base materials.

There are several types of high energy ball mills which can vary from rotation directions, capacity, temperature controls and milling efficiency based on their use. These types of mills include the Spex shaker, planetary ball, attritor, jet, bead and rod mills (Takacs & Šepelák, 2004). Efficiency will depend on what the user wants to achieve, therefore models developed for determination of optimum ball size to reduce material size may not apply to a user who is more interested in total destruction of organic compounds. In the enclosed jar of a ball mill, ball velocities can vary significantly at different rotations per minute, these ball velocities are fundamental in estimating the force and number of successful impacts on a compound or material.

A ball mill consists of balls, a cylindrical jar and lid. The components can be made from various materials such as bronzes, steels and ceramics, this broadens the types of materials which can be milled including explosive mixtures like black powder. As one could imagine there are numerous ways a jar can be rotated for grinding.

High energy ball milling is in essence the same as the more traditional ball milling but high ball velocities are used to generate high energy ball impacts. The impact energy does more than simply shear or fracture the material being milled. It induces chemical reactions to take place.

1.9.1 History of ball milling

The use of grinding can be traced back centuries where herbs were ground down into fine powders with a mortar and pestle, to improve the aromatic penetration of the herbs into foods. There are many types of milling technologies of varying complexities which achieve the desired particle size reduction.

High energy milling was first used for mechanical alloying and dates back to 1966 when mechanical alloying was invented by INCO's Paul D. Merica Research Laboratory. Mechanical alloying overcomes the hurdles of alloying mixtures of high and low melting temperature of elements (Lü & Lai, 1997).

Some modern mill designs actually have a long history; in the 2nd century AD the Chinese used an edge mill to grind cinnabar and cereal grains. A very common type of mill by both eastern and western cultures for milling of grains is the stone mill, where two pieces of stone circulate one another. One stone is stationary while the other circulates around; grooves are cut into from the centre out until the outer edges of the stone this results in a centre chamber in which grain is feed into the stone. When the stone grinds the grain the finer powders are extruded out along the grooves (Lynch & Rowland, 2005).

It is very difficult to trace the origins of the development of the ball mill, which has been speculated to have been developed during the industrial era where the invention of the steam engine would be a key contributor to the ball mills modernisation. The steam engine allows much larger weights to be rotated in a drum through a series of cogs and chains. Traditional ball milling which increases particle surface area by reducing particle size has been previously researched in 1996 as a complimenting technique to biodegrading of cellulose contaminated with plutonium with a 90% efficacy (Ogden, Ogden, Hanners, & Unkefer, 1996). After which extensive research has been done on the use of ball milling as a pre-treatment for sludge with mixed results (Baier & Schmidheiny, 1997; Wett, Phothilangka, & Eladawy, 2010). The use of ball milling solely as methods of destruction of compounds is relatively new but has been found to be particularly effective in the destruction of halogenated and aromatic compounds.

More importantly is the actual destruction of these compounds, usually these compounds were either stored or destroyed a high temperature furnace creating carbon dioxide, furans and dioxins (Kilgroe, 1996). Ball milling is attractive as an organic compound destruction

method because it can be applied to a variety of organics including POP and hazardous highly chlorinated pesticides without the production of furans and dioxins. During certain conditions a composition of predominately methane, ethane and propane which could be used as fuel thereby reducing the cost of destroying these compounds with prolonged milling, organics are destroyed and converted to carbon (Tanaka, Zhang, & Saito, 2003; Tristan, 2005). The differences amongst several types of ball mills are summarised in the table below:

	Mill Type				
	SPEX	Simoloyer	Planetary	Attritor	Tumbling
Relative Impact Energy	1	0.8	0.5	0.4	0.1
Relative collision frequency	1	1	0.5	1	0.5
Maximum ball velocity	12	14	5	5	<5
Mode of action	Impact	Impact	Impact	Friction & shear	Friction & shear
Scale up	No	Yes	Yes	Yes	Yes

Table 1 shows the differences between types of ball milling and key properties which distinguish them from one another. (Tristan, 2005)

When compared to incineration of pollutant destruction, planetary ball milling involves lower temperatures which reduce the combustion, volatilization hazards. . Most importantly dehalogenation of halogenated compounds such as PCBs and several other highly chlorinated compounds similar to DDT has been observed by several articles which note the dehalogenation and conversion of organic chlorine to inorganic chloride in fact the rate of destruction of these compounds is almost 100%. (Tanaka et al., 2003; Tristan, 2005)

Planetary ball milling has also been found to be effective against petroleum residues mixed with quartz sand. Petroleum residues can be made into shorter chained higher value hydrocarbons, as milling time increases we would expect to find high concentrations of natural methane after which the final products of amorphous carbon and graphite will be formed. These observations are limited to the most ideal conditions as mentioned before; variables can significantly alter the mechanochemistry observed. This was observed during mitigation of DDT of Mapua soil in New Zealand, wet soils thus wet milling has been found to be not as efficient in the destruction of DDT in an environmental site as opposed to drier samples (Tristan, 2005).

1.9.2 Types of ball mills

1.9.2.1 SPEX mill

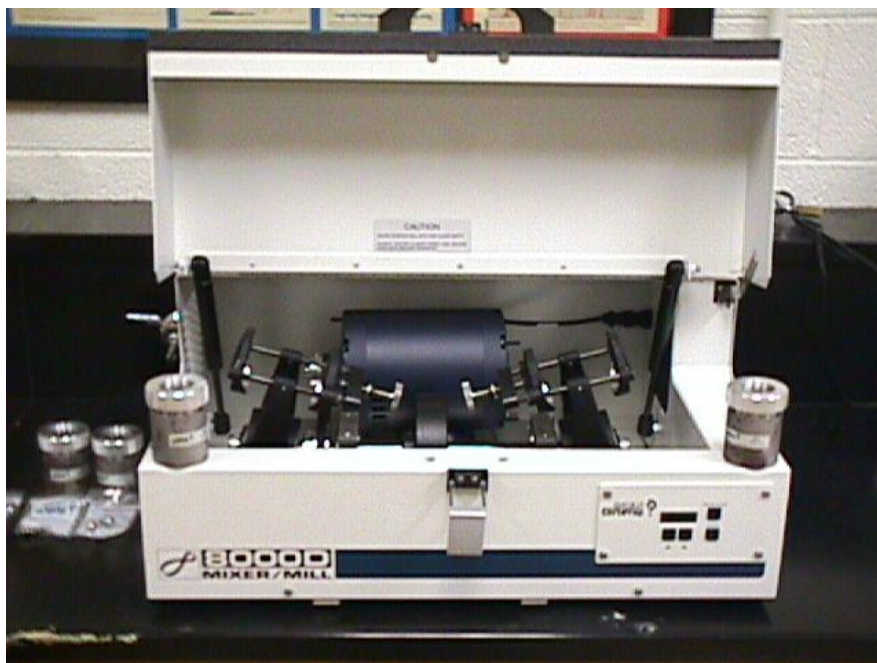


Figure 3, shows a SPEX SamplePrep 8000M Mixer/Mill

Spex mills are a type of shaker mill, which consist of a horizontal cylinder termed as a vial in which solid materials and balls are added inside. When activated the vial is shaken several thousand times in a side to side motion and induced lateral movements at the end of the cylinders results in a 8 shape causing the balls to reach up to velocities of 5 m/s (cylinder length: 5cm RPM: 1200). Due to the types of research done on ball milling, SPEX ball mills can be made from various materials such as stainless steel, ceramics, plastic, tungsten carbide and even more exotic Teflon coated vials. Limitations of SPEX ball mills are the low amounts they are designed to grind ranging from 10 -20g of powder and are therefore found in laboratory settings as opposed to commercial applications. Another limitation of SPEX ball mills comes about from the design of the vials which solids maybe trapped at edges and within the ellipse centres. More modern types of SPEX ball mills in cooperates an additions vial thereby increasing the amounts process able (SPEX Sample Prep, 2010; Suryanarayana, 2004).

1.9.2.2 Planetary ball mill

One of the most popular ball mills used is the planetary ball mill, it has components which are very typical of ball milling where consists of an enclosed vessel and balls. A planetary

ball mill consists of three fundamental components being a jar, balls and a jar lid. Due to the planetary like motion in which the jar is spun on a free rotation supporting disc platform, a clamp is required to secure the jar and the jar lid onto the rotation platform.

The spinning of balls in the jar creates centrifugal forces causing the balls to slide around in the jar and at times assisted by the grooving found in the jar. This sliding motion causes the balls slide back down the jar causing friction, the intense spinning can also cause balls to colloid in numerous directions at the inner chamber of the jar this causes powders to be ground down and assists in the destruction of organic compounds (Suryanarayana, 2004); refer to figure 4 for illustration of the aforementioned movements.

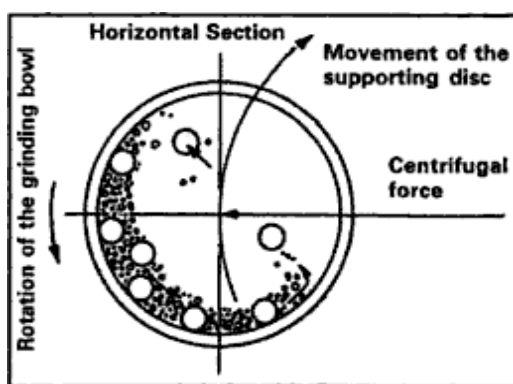


Figure 4, shows the rotation of the jar and movement of balls a planetary type ball mill (Suryanarayana, 2004).

The impact energies experienced in a typical planetary ball mill can be almost 20 gravities and therefore are more vigorous than gravity type of mills where the balls simply fall under the force of gravity. Impact energies are controlled by the rotational speed) of the mill, as lower speeds are used the impact energies are reduced; they can be reduced until a point where grinding no longer occurs and mixing predominates. As with more ball mills they the jar and balls can be made from various materials agate, tungsten steel and plastic polyamide to name a few. (Suryanarayana, 2004)

1.9.2.3 Attritor ball mill

The key principal behind attritor type mills is a cylindrical container filled with balls and equipped with a paddle type stirrer. As the balls are stirred they grind material, there is no rotation and/or vibration of the vial/jar. Dry grinding of material is achieved through kinematic porosity; this results in tumbling, direct impact and shear. These interactions of

dry material allow them to be reduced to micron sized particles as well as obtaining more spherical shapes when compared to other types of milling.

Due to the nature of attritor ball milling there is a criteria for the media to be used to achieve reduced particle sizes, in general in order to obtain a reduced particle size the media should be larger. A more obvious property is the hardness of the media, the harder the media the more efficient the grinding. Similar to most kinds of ball milling the components can be made from a variety of materials such as stainless steel, polyurethane and rubber.

A development of the attritor mill is used by Environmental Decontamination Ltd. as a commercial mechanochemical destructor. (Environmental Decontamination Ltd. (2006) Unlike the more gentle milling action commonly used, these attritor mills have very heavy alloy paddles and turn at very high speeds providing ball velocities considerably greater than those available from a planetary mill.

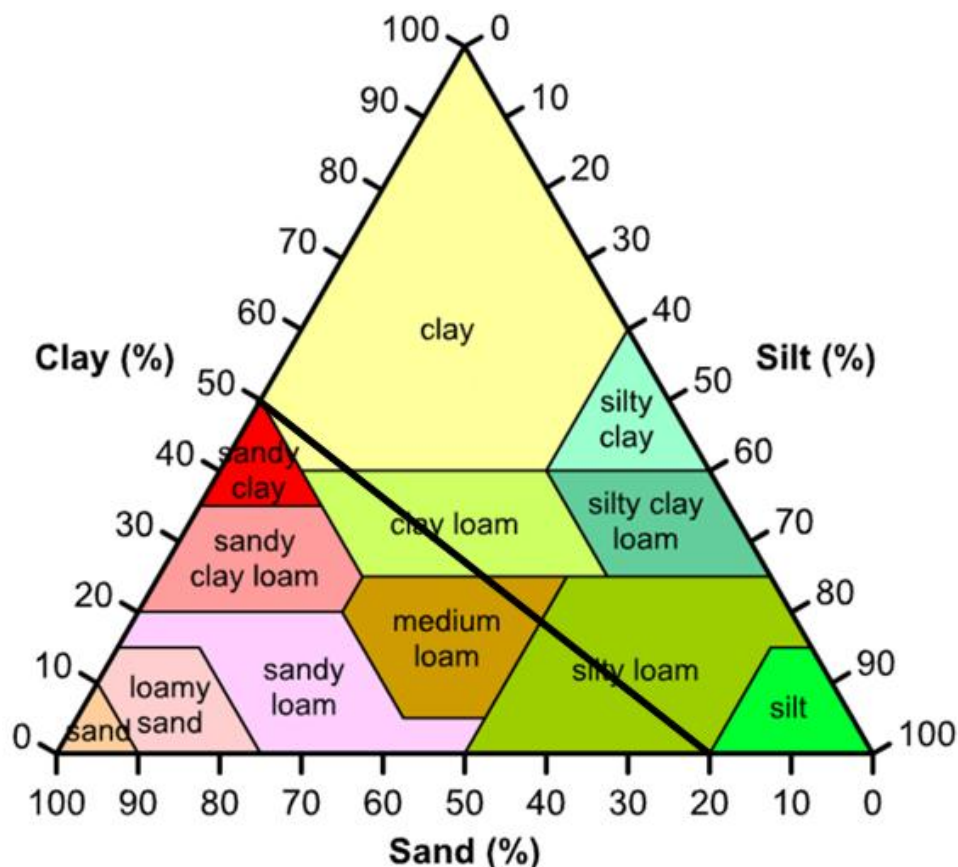
1.9.3 Soils

The Food and Agriculture Organization of the United Nations has realised the wide varieties of soil and have established the World Reference Base for Soil Reference (WRB) refer to table 2. They have categorized soil into key features and/or properties which can interact with the soil, meaning one type of soil may lie in several categories.

Organic pollution which occurs on land penetrate a variety of soils depending on factors such as climate, rainfall and foliage. Typical substances which can be found in soil include various silicates alumina-silicates such as clays, organic material and humus due to the vast compositions soils can have there are an almost indefinite composition of soil. In order to produce commercially viable solutions to pollution mitigation via high energy ball milling, it is important to distinguish between wet and dry types of samples and thus the chemistry. One more overlooked variable are the chemical properties and composition of the predominate substances found in soil.

The diagram below shows the types of soils and their compositions. The black line below starts at 50% clay and ends at 20% sand is the border line drawn which are an estimative indication of soils on the left which are more likely to respond easily to being cleaned with ball milling whilst on the right side shows soils which are less left susceptible to intense

ball milling. This could be due to firstly high amounts of water content and soil matrix structure which has resulted in high malleability.



Malleability of a soil can play a large role in the efficiency a soil substrate can have on compounds, soils which can be moulded into various shapes and hold their shape can resist high intensity impacts from the balls during high intensity planetary ball milling.

Malleability can come about from soils containing high amounts of clay and/or water.

Highly malleable types of soils such as kaolinite which can hold their shape are difficult to mill in a planetary ball due to the mineral being a layered silicate tetrahedral sheet linked via an oxygen atom to an octahedral sheet of alumina. This chemical structure causes sheering to be reduced while high energy impacts from the balls in the jar are damped as the malleable material has a matt like effect on the balls and the jar reducing distance the balls travel; malleability could increase when a soil has a certain degree of water retention and surface hydrophobicity. The final result is reduced efficiency in the ball milling system resulting in lower destruction of organics and increase particle size when grinding material; these effects were observed in clay, limestone trials and noted in a study on wet soil milling by Bellingham (Tristan, 2005).

Almost 60% of the earth's crust is made of feldspars, which are silicate salts of sodium, potassium, barium and calcium. They come about from crystallization of magma and can also be found in several types of metamorphic rock (Dutch, 2004). There are numerous uses of feldspars ranging from fillers to the manufacture of ceramics and glass; this comes about from feldspar acting as a flux reagent reducing the melting temperature of quartz in glass and helping quartz to mix with clays in ceramics (Schlesinger, 1997). Weathering of feldspars can come about from acid rain resulting in soluble silicates which can assist in the breakdown of organic compounds when subjected to ball milling.

Quartz structurally has silicates oxidise in a tetrahedral matrix and are found as SiO_4 . The structural formula for quartz is SiO_2 due to the sharing of oxygen in the tetrahedral matrix between two tetrahedral. The tetrahedral conformation makes quartz extremely resistant to chemical reactions and is considered the most stable when exposed to weathering (Essington, 2003). The free radicals from quartz has been shown to cause silicosis which can impair and scar lungs (V Vallyathan et al., 1995). Free radicals in quartz are in part are formed from breaking the strong covalent bonds in the mineral, (Gasgnier, Szwarc, & Ronez, 2000). The formation of these free radicals is not a new observation, it has been documented as a possible active site of reactions with organic liquids in 1958 (Benson & Castle, 1958). This research focuses on a soil substrate of quartz mixed with organic compounds which were subjected to high intensity planetary ball milling resulting in the formation of intermediates and gases.

Quartz is an ideal candidate for several of the following reasons. It is cheap, easily available in high purity and it is the second more abundant mineral on earth. That coupled with feldspars and kaolinites makes the presence of silicates in environmental samples almost inevitable. Therefore the interactions of silicates and compounds when subjected to intense planetary ball milling are one of precedence and require a thorough understanding prior to investigations to other mineral interactions.

If planetary ball milling were to be used to remove pollutants from a site, the medium is contaminated would the soil itself or possibly the soil with added minerals such as quartz. Soils themselves are very complex matrices with varying sizes which could be a composition of various organics and inorganics. When placed in an intense context

constituting of sheering and high energy ball, soils can have drastic effects on the pollutant being treated.

1.9.4 Interaction of soils subjected to intense planetary ball milling

The most ideal conditions currently known for effective destruction of organic compounds and similar analogy of POP's are in dry conditions with high amounts of quartz in the soil. The proposed role quartz has in assisting the destruction of organic compounds is the formation of free radicals (Tristan, 2005).

The occurrence of free radicals depends on which bonds are broken during the ball milling process, based on the structure of α -quartz there are several possible free radicals which could be formed during this process figure 5.

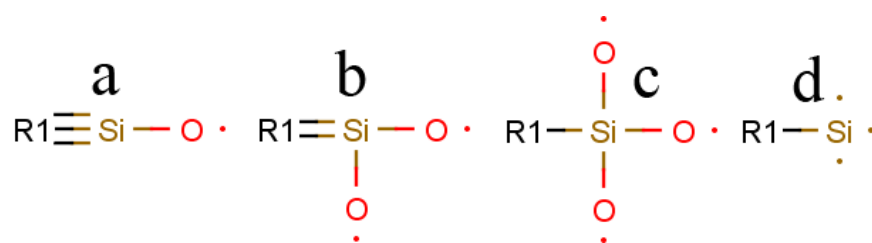
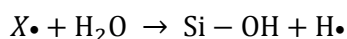
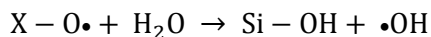


Figure 5, shows the possible types of free radicals which could form during ball milling arrange from a to d, a being most likely. R1 represents the degree of bonding that Si could have to the tetrahedral quartz most importantly bonds which are not attached to oxygen radicals.

During wet ball milling the formation of hydrogen and hydroxide radicals has been proposed by several publications (Benson & Castle, 1958; Tristan, 2005; V. Vallyathan, Shi, Dalal, Irr, & Castranova, 1988) shown by equation 2. These free radicals could progress on to assist in the dehalogenation of halogens and perhaps even destruction of organic compounds, it has to be noted that current research has found wet samples are not as efficient in destroying DDT as opposed to dry samples. Water can facilitate sliding of particles, therefore reducing friction and surface to surface interactions.



Equation 2 shows the possible free radicals that can be formed during milling of water

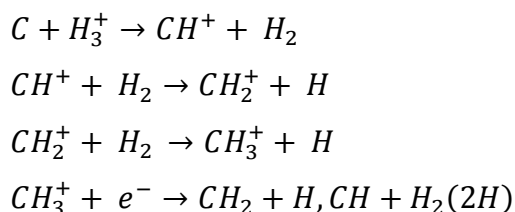
Pulse mechanochemical radical formation research has found oxidised aromatics at the ortho and meta positions are more susceptible to oxygen radicals found on the surface of

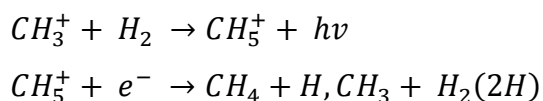
quartz after ball milling. Research also suggests that other types of oxides such as AlO_3 , ZrO_3 and TiO_3 may have similar free radical characteristics to quartz (Aleksandrov, Aleksandrov, Prokofev, & Bubnov, 1999).

1.10 Possible mechanisms for formation of carbon and gaseous products

The mechanisms behind the formation of methane, carbon and gaseous products have still not been completely understood. The first theory I propose is the formation of methane to be similar to the origin of methane on planets which comes about from a chaotic processes involving high velocity impacts of clouds of material in the solar nebula. The solar nebula in some aspects have similar conditions found in the ball mill, where clouds of material are mixed together in an orbital direction as differential rates of rotations are experienced this causes dissipation yielding different levels of interaction between material (Lunine, 1997). It should be noted that the formation of compounds could be a combination of these proposed mechanisms. The first would be the most obvious the formation of methane from atomic carbon and hydrogen. Carbon may come from the steel, organics and air in the form of carbon dioxide or carbon monoxide. The origins of hydrogen has been well established as being in the form of hydrogen radicals, more information on the formation of hydrogen radicals from water can be found in the section titled “Interaction of soils subjected to planetary ball milling”. The involvement of carbon dioxide has been justified from the milling of carbon dioxide atmospheres in standard milling conditions without the presence of organic compounds, which yielded the volatiles including methane, ethane and propane. This is indicative of several forms of hypothesised carbon interactions starting with the electrophilic addition of a carbene to a carbocation, carbon-carbon radical bonding, carbocation with methane (Herbst, 1995) and methyl radical with methane (Rodgers & Charnley, 2002).

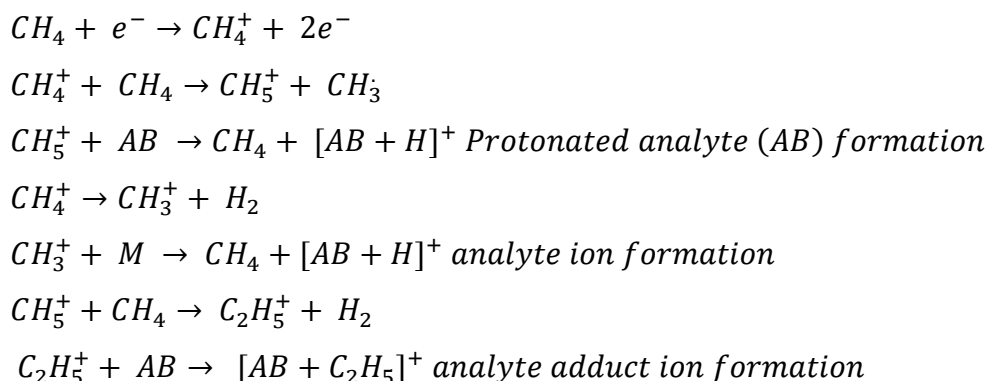
Interstellar chemical pathways involving atomic carbon (C) with protonated hydrogen H_2^+ which comes about from the ionization of H_2 , further reactions of H_2^+ with H_2 forms H_3^+ and H by a ion molecule reactions equation 3 summarises these reactions.





Equation 3 shows the formation of methane from atomic carbon through chemical reactions of hydrogen gas and ionised H_3^+ (Herbst, 1995).

A feature of equation 3 is the formation of CH_5^+ , this species can react several ways and not necessarily be as described in the equation. Some other pathways include CH_4 and H^+ being generated from CH_5^+ from dissociation. When taking into consideration chemical ionisation which occurs in the mass spectrometer the formation of CH_5^+ and CH_4 have similar pathways, one may argue that ionisation takes place on CH_4 and not on atomic carbon which is valid and places chemical ionisation type of reactions as those possibly experienced either after the formation of CH_3^+ or CH_4 . Equation 5 shows possible ionisation of methane; when compared against equation 4 we can see similar compounds being formed through different pathways. The importance of both these equations shows that there is no definite one way path methane can be formed, it also acknowledges that methane can be formed several ways and can even be involved in side reactions themselves creating longer hydrocarbons. Further interactions of carbocations with methane, such as $C_2H_5^+$ could propagate with methane increasing its length.



Equation 4 shows some of the possible ion reactions methane can undergo during ionisation in the mass spectra (Gates, 2005).

The reactions of CH_5^+ are not just limited to organic volatiles research has also found their reaction with molecular oxygen yielding O_2^* and O^* radical species. These could in fact accelerate the degradation of organic compounds due to the increase in free radical species which may inject themselves onto organics (Stahl et al., 1985).

The second theory involves grain surface chemistry where alkali metal oxides such as nickel, magnesium and iron act as catalysts. Most diatomic alkali metal oxides are ionic crystals with defects which can come about during the original formation or by irradiation of gamma-rays, UV and neutrons. These defects give rise to electrons, cations and anion vacancies making them reactive sites. It is more likely for OH[•] to be formed on these surfaces since oxygen was already partially bound to the surface and would be surrounded by a sea of hydrogen radicals. But in fact the role of these catalytic reactions have also been theorised to also be involved in reactions with molecular oxygen and atomic carbon forming methane by the alkali metals in incorporating these molecules into their lattice (Duley, Millar, & Williams, 1978). A summary of possible surface reactions at defect sites on oxide grains can be found in the reference Duley, 1978. The increased number of hydroxide radicals being produced could potentially drive the thermodynamic reaction of hydroxide and hydrogen radicals from water towards the right therefore producing more hydrogen radicals in the system.

The origins of C₂-C₃ volatiles appear to be initiated from reactions of methane which would be indicative of their formation only after methane is produced refer to equation 4. This may be validated by results obtained via GC analysis of gas samples when organic compounds were milled. Ethane and propane were only present after a methane was formed, which always exceeded the concentration of ethane and propane. Based on the above 2 equations free radical carbon-carbon formation is unlikely, due to the environment having large amounts of hydrogen radicals to react with free radical carbon in the system.

Chapter 2. Materials and Methodology

All experiments were conducted at the applied science laboratory in the WS applied science and engineering building at the Auckland University of Technology, Wellesley campus, Auckland, New Zealand.

The term standard milling conditions refers to planetary ball milling at 500 rpm at a predefined time interval.

2.1 Materials

2.1.1 Quartz Sand

Quartz sand was purchased from Fletcher Distribution Ltd at New Lynn Auckland, New Zealand.

The chemical analysis of the sand as provided is given in table 2 (Tristan, 2005).

Compound	Formula	Percent
Silica	SiO ₂	99.32%
Aluminium Oxide	Al ₂ O ₃	0.16%
Ferric Oxide	Fe ₂ O ₃	0.07%
Calcium Oxide	CaO	0.10%
Magnesium Oxide	MgO	0.02%
Sodium Oxide	Na ₂ O	0.02%
Potassium Oxide	K ₂ O	0.01%
Titanium Oxide	TiO ₂	0.10%
Loss on ignition		0.18%

Table 2, Chemical analysis of quartz sand used in analysis.

Chapter 3. Method

3.1 Gas formation from milled samples

As noted before, there is a gap in our understanding of gas formation and interactions associated with different atmospheric conditions.

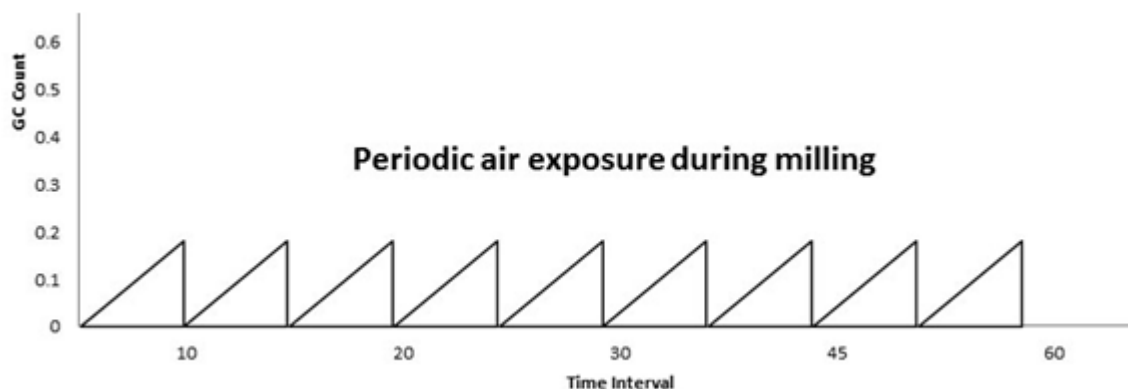
Organic compounds were standardised at a concentration of 0.1% w/w which were added to 50g of quartz with 20 steel balls minimum diameter of 15 mm . The majority of samples were liquids and at slightly lower concentrations when compared to solid samples due to

density variations. Samples were milled in a Retsch PM 100 planetary ball mill at 500 rpm at the predefined set time.

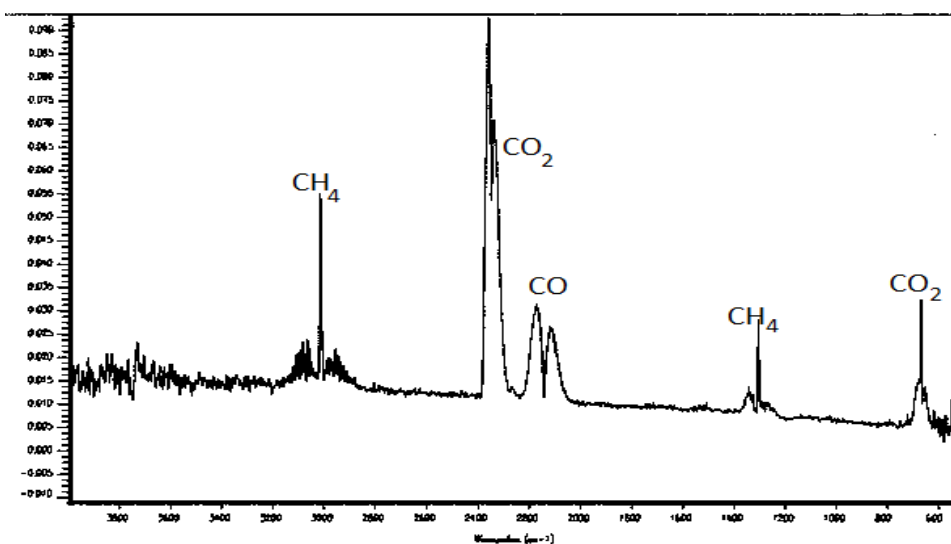
The custom gas sampling port incorporated the use of Swagelok pipe reducer coupled with a Swagelok cap sandwiching a gas chromatograph (GC) rubber septa. Samples were taken at 10, 20, 30, 45 and 60 minute intervals using 22G needles which were then injected directly into the GC (Shimadzu GC2010) using a GasPro column. The heating program used was 10 minutes isothermal at 40°C.

There are 2 sets of samples, the first sample does not involve the removal of the ball milling lid. The second sample has the lid removed at 10, 20, 30, 45 and 60 minute intervals exposing the milled sample to air. By removing the lid at the set time intervals it would be safe to assume that most volatiles have been flashed out due to the intense heat of the milling equipment as determined by internal measurements temperature ranged from 77°C to 140°C. Temperatures increase in direct relationship to increased milling time.

The reasons behind this analysis was firstly, to reduce pressures, secondly to see the total methane production as well as rates achievable from the reaction and lastly to mimic conditions seen during milling in a continuous ball mill where fresh sample is continuously injected into the system along with considerable amounts of air. (personal communication with Dr John Robertson). In summary about methane calculation samples where the lid was kept intact without removal would have total levels recorded at the apex over the 60 minute duration whilst samples which involved lid removal would have all the methane GC counts added together refer to graph below. It is acknowledged that this is an “estimative analysis” as methane has been known to be absorbed by the soil matrix and therefore may not be fully flushed out when the milling lid was removed.



Peaks were identified using standards of methane, ethane, butane, propane and hexane with



corresponding retention times of 1.119, 1.717, 4.831 and 17.655 minutes. These peak intensities were compared against gas composition data obtained from Vector gas.

Initially the focus of the research was on methane measured with the use of a gas chromatograph equipped with a flame ionization detector. Fourier transform infrared spectroscopy (FTIR) was used later because I was unable to obtain legible results for CO₂ and NO₂ using the GC due to the

absence of a suitable column. So FTIR was used, this would also account for the small amount of data obtained as opposed to methane. FTIR machine used was a Shimadzu IR-Prestige 21.

10 mL gas samples from Xanthine and Napthalene were also analysed at time intervals 10,20,30,45 and 60 minutes and analysed using FTIR. Characteristic peaks as determined by internal standard and referenced literature seen by both samples were illustrated in the FTIR graph below.

3.1.1 Methane standardisation for GC.

Natural gas was used for the standardisation of methane which was analysed by GC FID. The composition of gas was provided by Vector Gas for the periods of October 2009 to November 2009. Vector gas has sampled their gas daily, with consistent methane content recorded over the two months provided in the data set. Therefore we are able to take the mean of 60 samples without statistical adjustment resulting in the composition of methane

being 81.64%. Natural gas standards were prepared by injecting 0.5 mL increments of natural gas was injected by syringe into a 1L bottle of air lined with Parafilm, the volume had been predetermined by measuring the volume of water it contained. The mixture was stirred with the aid of a string bar for 5 minutes and 1 mL of the mixed gas was removed by GC syringe and injected into the GC FID with GasPro column, the same column as used above. The peak area was then determined by GCSolution and recorded as GC counts versus amount of natural gas sampled. Based on the percentage of methane in the natural gas, the concentration of methane was then determined.

3.1.2 Standardisation of carbon dioxide, ammonia methane and nitrous oxide for FTIR

Carbon dioxide, ammonia, methane and nitrous oxide were injected in 1 mL increments until 5 mL into the closed gas chamber which has been flushed with air for 5 minutes prior. Nitrous oxide was synthesised from a decomposition of ammonium nitrate, the gas was immediately injected after synthesis. 15mL of ammonia with a concentration of 3 mol L^{-1} was placed into a 1L container and covered, it was then heated and 5 mL gas sample was injected into the gas cell. Other gases were obtained from gas cylinders.

FTIR spectrum were saved and then overlaid with experimental data obtained to valid the presence of gases in milled material samples.

3.2 Intermediate analysis from milled samples

The analysis of intermediates will further our understanding of compound degradation during milling as well as investigate the hypothesis of intermediate formation being similar to that seen during compound ionisation in the GCMS.

Samples were prepared exactly the same as the analysis of gas formation from milled samples at intervals of 5, 10, 15, 45 and 60 minutes a sample of 1.5 to 3 g was taken and placed in 10 mL glass vials with foiled caps. Glass vials were pre-weighted before and after addition of sample to determine amount of sample obtained for the specific time interval.

1.5 mL of phosphoric acid was added with 10 mL of a 50:50 hexane and acetone mixture in a ratio of approximately 2 g of sample as determined from weight difference. Samples were allowed to rest for 24 hours allowing fine particles to settle.

Sample standardisation was achieved using to 0.1% concentration. Which was added to 10 mL the solvent mixture of 50:50 hexane:acetone. Elution of compound was optimised for a

minimum of 5 minutes when possible. For GC-MS sample analysis 1uL of sample was taken from the solvent layer and injected into the GC-MS with ZB-WAX column.

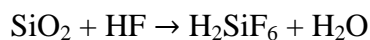
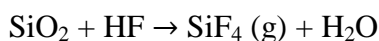
3.3 Milled matrix composition

The investigation of matrix composition allows us to further our investigation of degradation pathways and establish the amount of compound that is degraded to carbon and their allotropes.

A sample of 2% naphthalene was prepared by mixing 2 g of naphthalene in 100g of 99.9% pure quartz sand. The ball milling jar was rinsed with acetone and placed in a 100°C oven for 5 minutes, the naphthalene and quartz was then added to the jar. The sample was milled for 60minutes at 500rpm, resulting in a dark grey fine powder.

3 sets of 2.5 g of milled samples were transferred into a 1L glass boiling tubes. 5 mL of acetone was then added and mixed thoroughly with the sample. 30mL of aqua regia was added the boiling tubes and left at room temperature for 24 hours. The sample was then washed using excess deionised water until litmus paper turns green indicating the majority of acid was removed. The excess water was decanted followed by the addition of 15mL of acetone. Upon addition boiling tubes were transferred to the digester and samples were heated up to 90°C for 24 hours.

The now solid pellet is now transferred to 50 mL polypropylene tubes which were weighted previously. Assuming all the silicon dioxide will be transformed into fluorosilicic acid; some silicon dioxide goes to silicon tetrafluoride refer to equation 5. 20mL of 50% Hydrofluoric acid was then added in excess and allowed to digest in the fume hood for 24 hours.



Equation 5 shows the decomposition of SiO_2 by HF to SiF_4 and H_2SiF_6

Deionised water is then added, centrifuged for 30 minutes at 3000 rpm and the top layer decanted. Process is repeated until litmus turns green. Excess water was then decanted and 15 mL of acetone was added. The samples were then heat to 100°C for 24 hours. The now dried sample is weighted. The dried sample is now added back to the 1L glass boiling tube

which was pre-weighted. Residues in the polypropylene tube were removed using 10g of sodium chloride which was shaken vigorously using an agitator. Deionised water was added to the sodium chloride which was poured into the 1 L boiling tubes.

The sodium chloride was washed repeatedly until sodium in the decanted water samples were undetectable by flame atomic absorption spectrometry. Samples were re-digested with 30mL of aqua regia overnight and then washed with excess deionised water. The sample is then dried using 20mL of acetone and weighted.

3.3.1 Quartz absorption analysis

A quantitative analysis based on weight was carried out twice on 50g of quartz. Quartz was initially heated to 100°C and allowed to sit in a container for several weeks. These quartz samples were then subjected to 100°C in an oven for 30 minutes, allowed to cool in silica gel equipped desiccators for 15 minutes and their weights taken. Immediately after weighting samples were placed in a furnace and heated to 300°C for 30 minutes, after which the same cooling procedure as used before was carried out. Weight differences were then calculated.

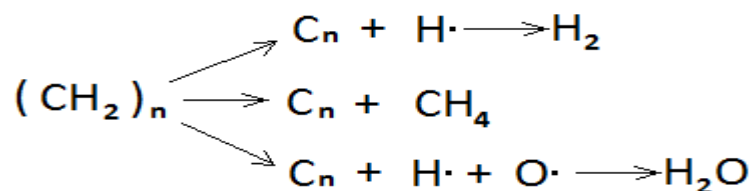
Chapter 4. Results

4.1 Methane formation from milled samples

From our current understanding of mechanochemical destruction, organic compounds are broken down into intermediates after which they are broken down into gases or carbon when these gases are milled extensively they are broken down into amorphous carbon and graphite. We can therefore assume a gradual increase in gas production to the maximum of methane production indicates the maximum amount of methane produced during the destruction of intermediates. All research done so far on mechanochemical destruction of organic compounds suggests this reaction is non reversible.

High and rapid production of methane could be indicative of the intermediate's readiness to form methane; low production of methane could be explained by three possible mechanisms. Firstly may intermediates may resist the break down to give methane, giving higher yields of carbon and hydrogen if this is true we expect to see slow production with

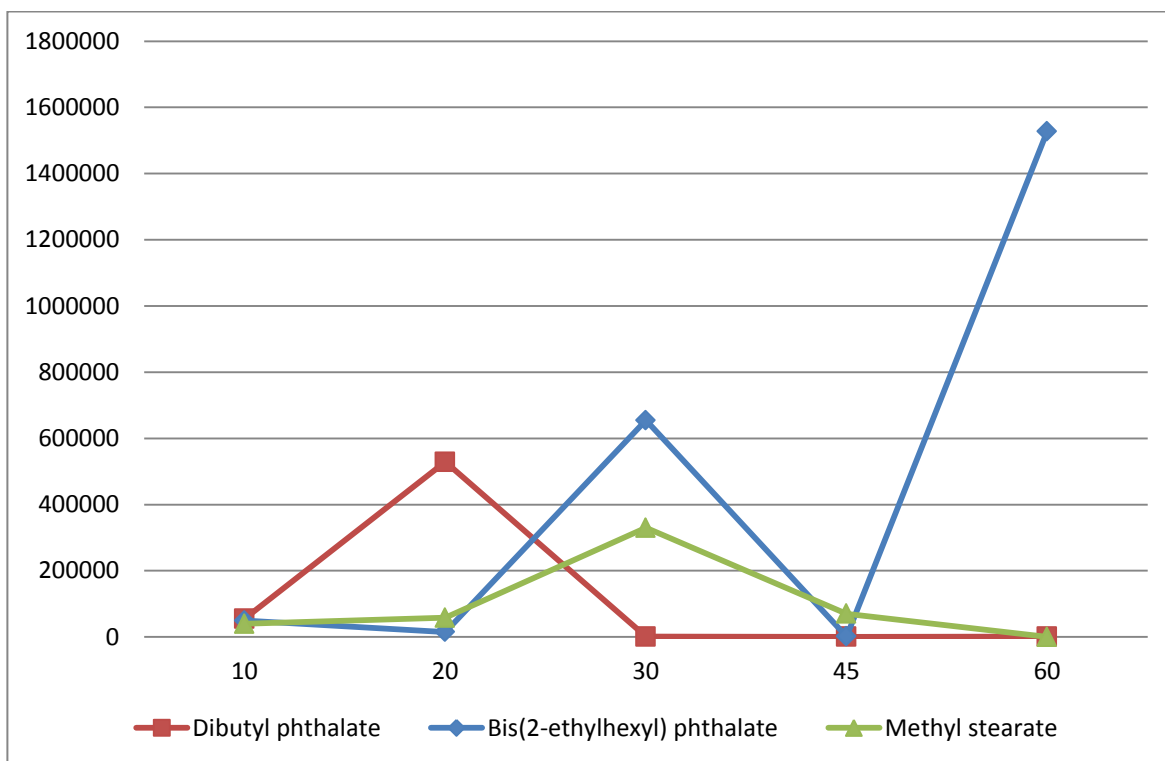
the maximum of methane production at later time intervals. The second possible mechanism is based on intermediates preferring to form elemental carbon instead of



methane and thus giving low methane production but not by destruction of intermediates. The third possible mechanism is based on the atmospheric conditions in the milling jar experiences, due to standard milling conditions where the jar lid is not removed volatile organic gases such as methane can be broken down further to elemental carbon and releasing hydrogen (radicals or H_2) or water. This is illustrated in equation 6.

Equation 6 Some decomposition pathways to give carbon, methane hydrogen and water

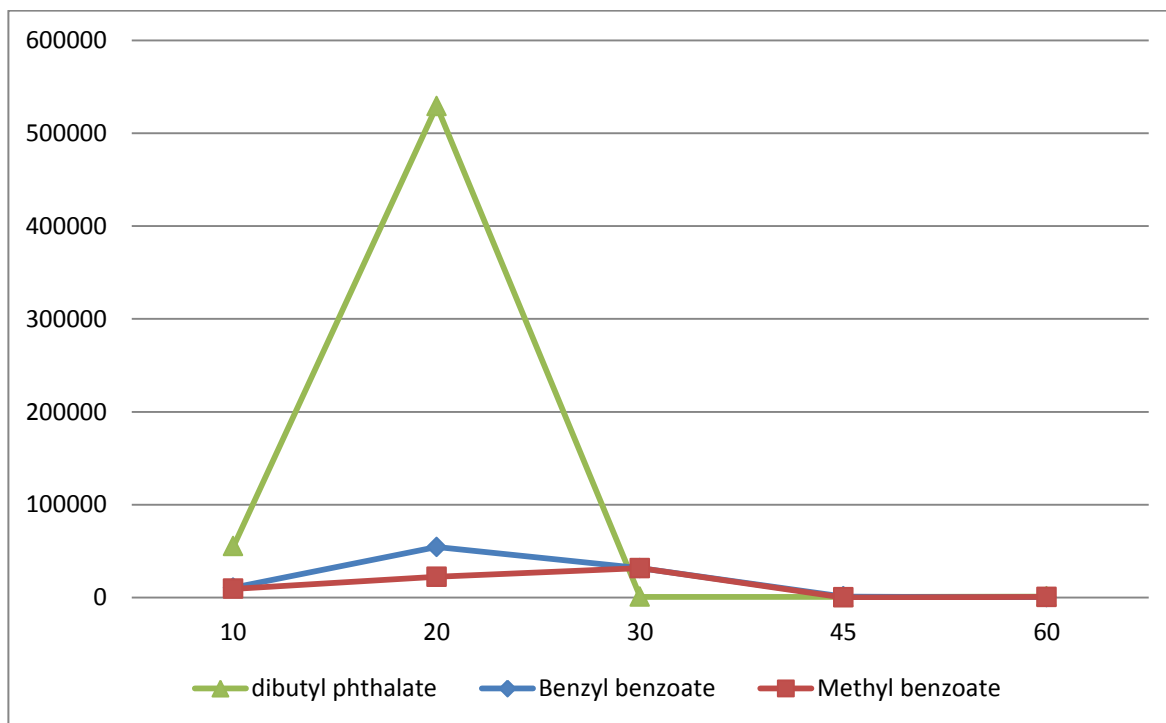
4.1.1 Phthalic acid esters (comparisons of ester chain size)



The presence of 2 ester groups in the phthalates may be the cause of increased amounts of methane produced when compared amongst the esters at the 60 minute, this comes about from a previous research which has found ball milling at 500rpm would yield 100%

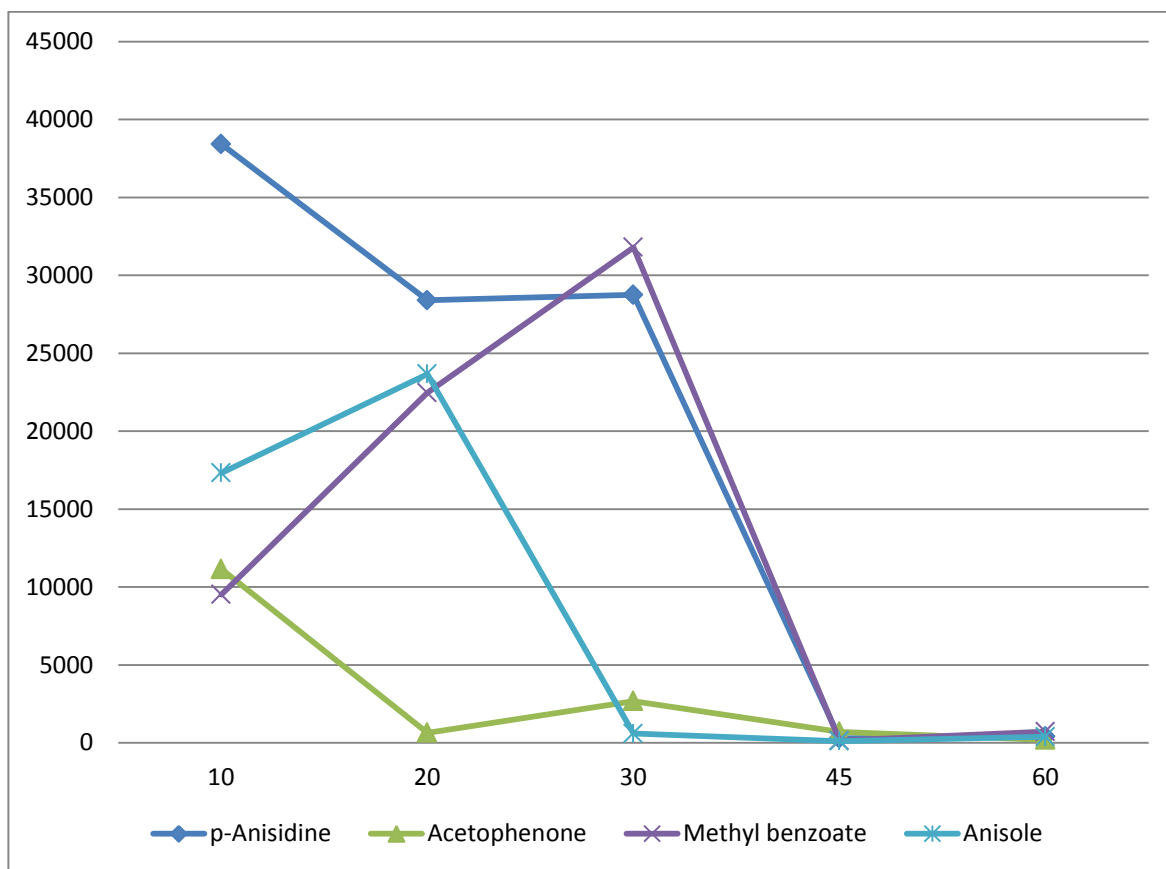
destruction of compounds with prolonged time conversion of natural methane into amorphous carbon.(Magotha, 2004; Tanaka et al., 2003; Tristan, 2005) A possibility for the steep increase in gas produced by DOP could be the method of cleavage experienced during milling. Possibly the linear aliphatic hydrophobic chains of DOP were cleaved off during the process converting the esterified benzene into methane, followed by the linear aliphatic hydrocarbons.

4.1.2 Low molecular weight esters comparison with high molecular weight esters



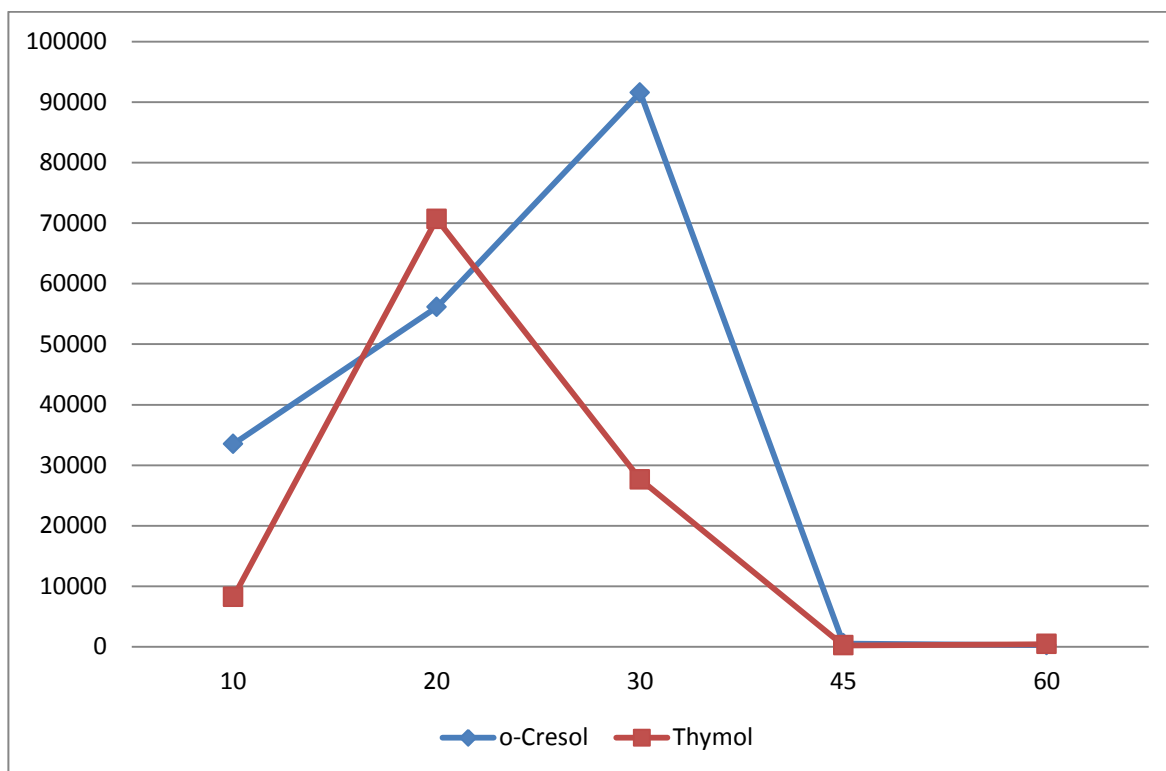
When comparing more complex esters, such as dibutyl phthalate against benzoates there appears to be a critical point of gas formation at the 20th or 30th minute regardless of molecular weight or size. This could further validate a hypothesis where mechanical ball milling tended to cleave short hydrocarbon as opposed to chains of > C6 as shown by GCMS and therefore able to form methane more almost immediately when subjected to standard milling conditions.

4.1.3 Comparison of an aromatic ester, ketone and ether.



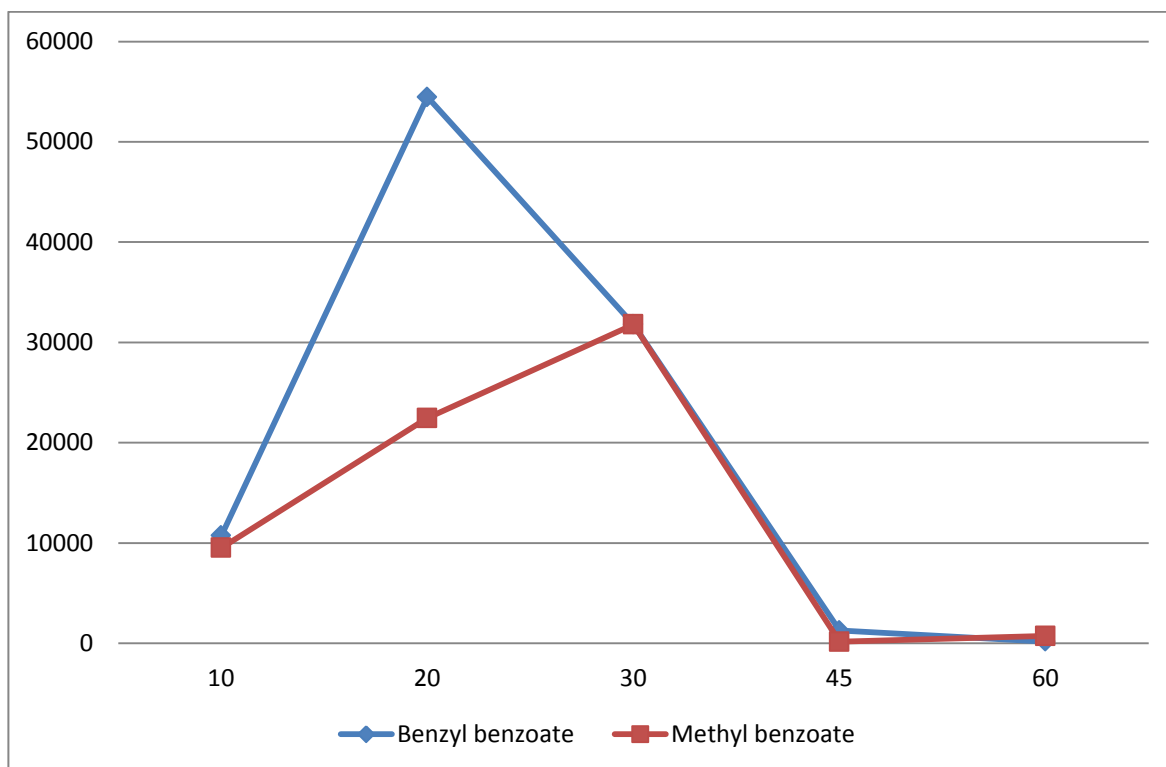
The comparison of acetophenone against anisole and methyl benzoate further confirms that the presence of an extra oxygen group OCH_3 or COCH_3 could help facilitate the production of methane during the destruction process. It appears ketone carbonyls yielded a higher maximum than the methoxy group. Solely comparing p-anisidine and anisole, we can clearly see the amine group on the para position of p-anisidine greatly increased the total amount of methane produced. It can also be observed that all methane production ceased at the 45th minute onwards.

4.1.4 Phenol comparison



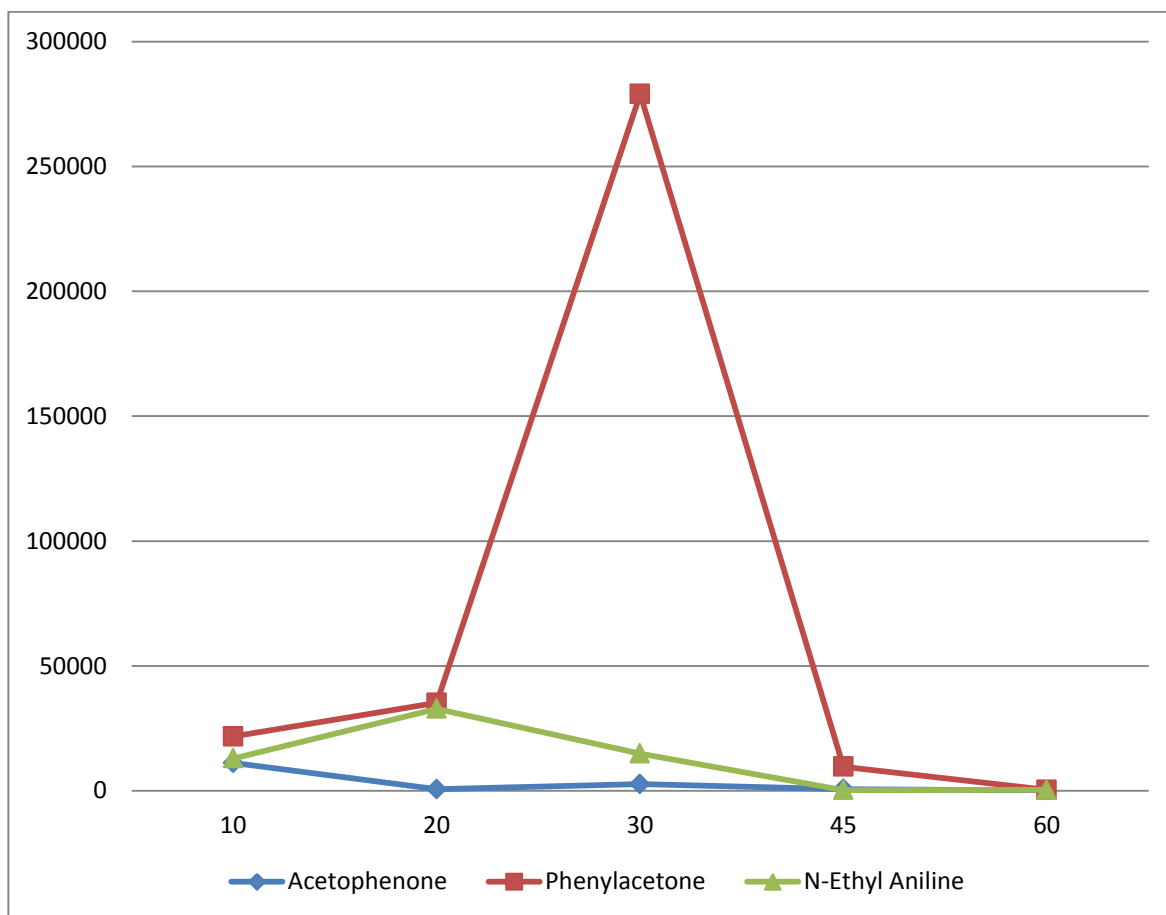
The alkylated phenol, thymol overall produced less amounts of methane over a period of 60 minutes, as opposed to o-Cresol which was producing methane at 10, 20 and peaking at the 30th minute. This could be explained from the high amount of chlorination found in on the benzene ring of thymol which could carry free radicals to facilitate breakdown, and therefore facilitate the formation of amorphous and analogous of carbon.

4.1.5 Aromatic esters



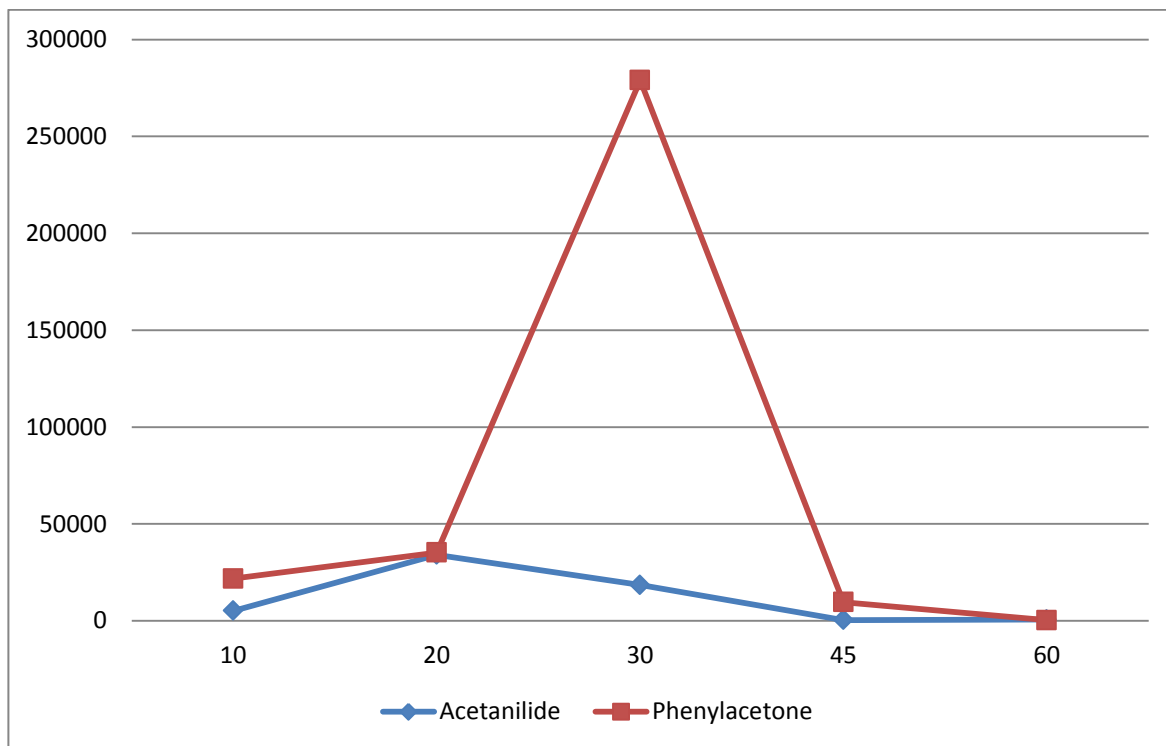
The similarities between benzyl benzoate and methyl benzoate in terms of methane production suggests a more ordered type of reaction, it is observed the conversion of intermediates to methane gas occurs more readily in the more aromatic benzyl benzoate.

4.1.6 Phenyl ketones



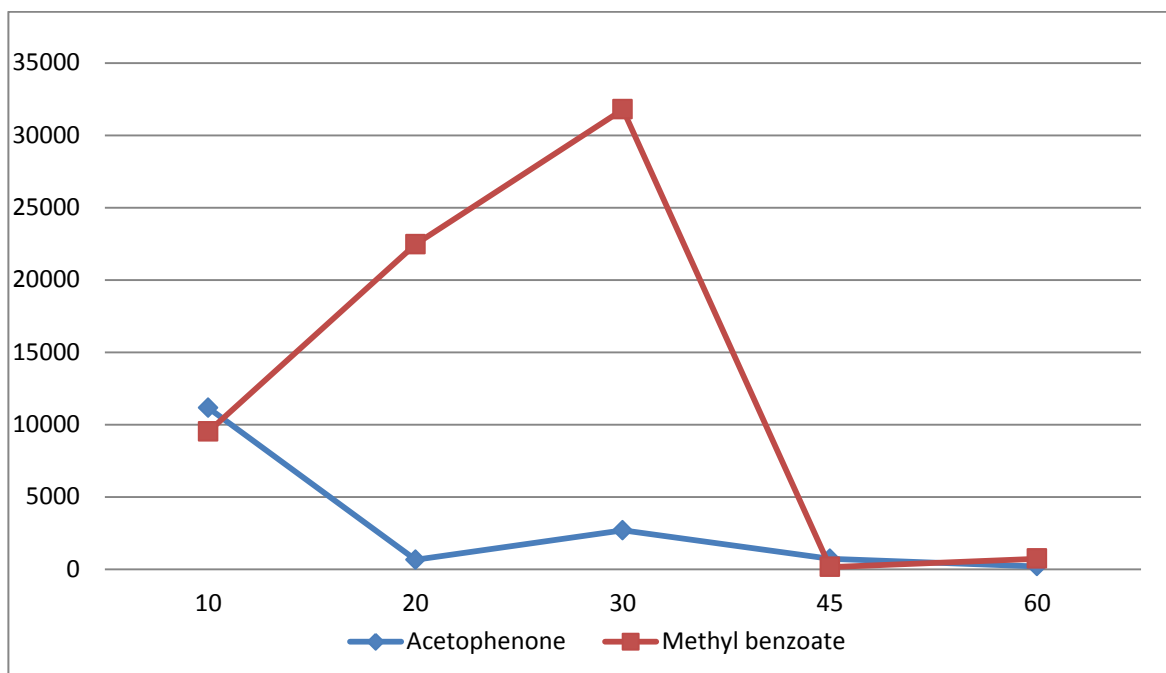
An interesting comparison is acetophenone and phenylacetone. The difference between both these compounds is that phenylacetone has an extra carbon group on the carbonyl chain. When the oxygen is 2 carbons away from the aromatic benzene, it appears to delay the formation of methane significantly as observed by phenylacetone during the 30th and 45th time interval. Clearly phenylacetone produces more methane later than acetophenone, this suggests that the presence of oxygen substituted groups closer to aromatic compounds can facilitate formation of methane sooner. In fact when phenylacetone is compared to n-ethyl aniline we can clearly see that the presence of the extra carbon group affixing the carbonyl group has a profound effect on the rate of destruction for intermediates to amorphous carbon and graphite. Contrary to initial observations seen by anisole, n-ethyl aniline decreased the production of methane but suggests a more rapid rate of destruction of organic to carbon and graphite.

4.1.7 Comparison of a simple aromatic amide and aromatic ketone



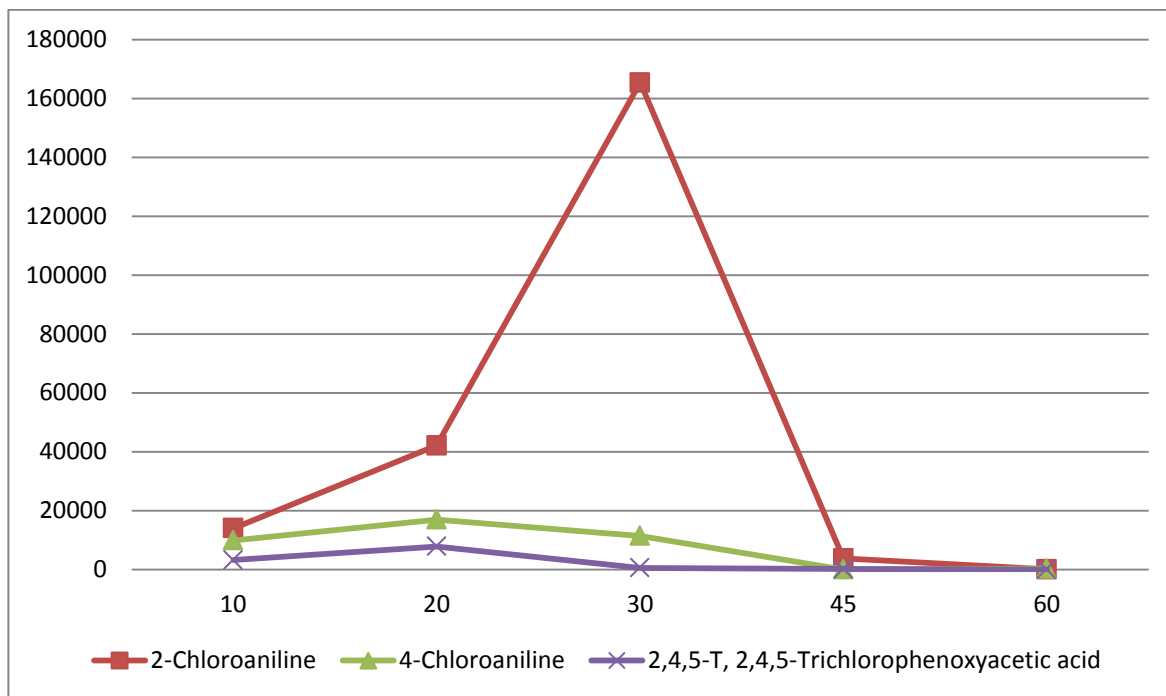
Comparing acetanilide and phenylacetone, further validates the observations that carbon alkyl substituted benzenes yielded higher amounts of methane as opposed to their amine and chlorine substituted counter parts.

4.1.8 Comparison of an aromatic ketone to a similar aromatic ester



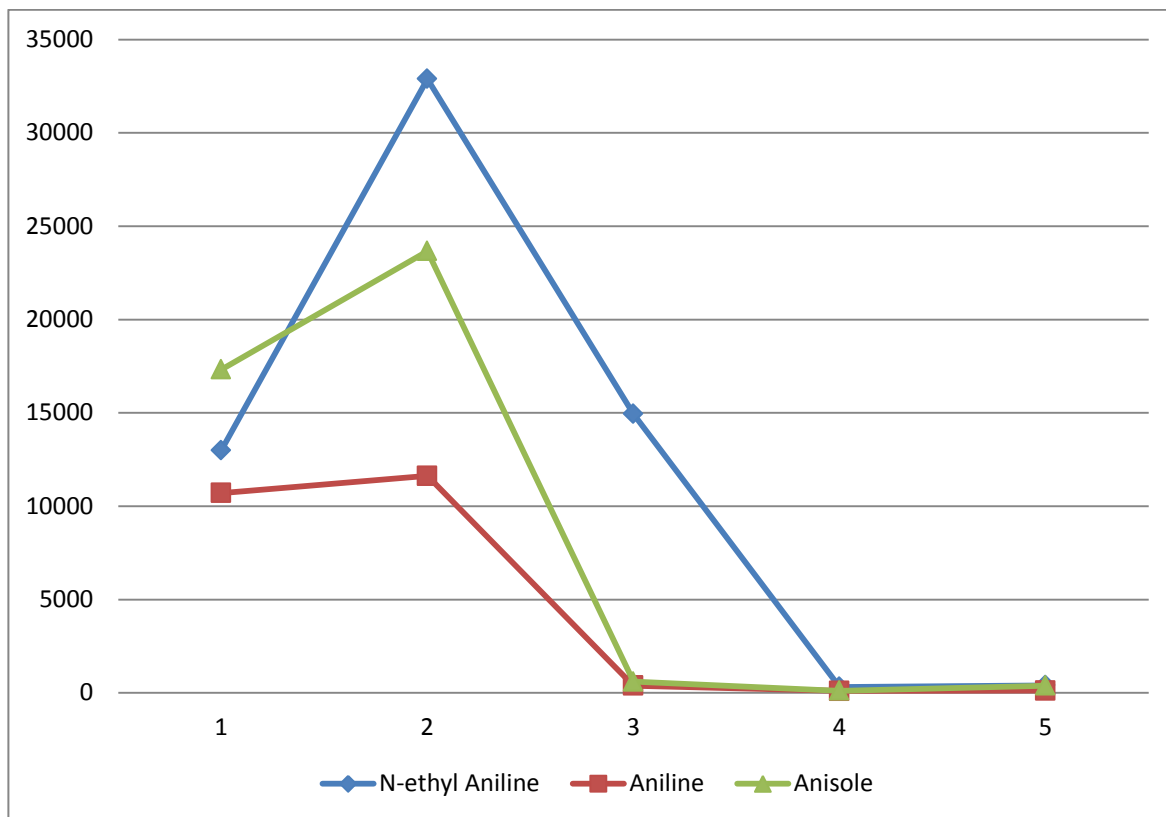
The presence of an extra oxygen group connected to the carbonyl carbon has a dramatic effect on the decomposition of intermediates to methane, it is clearly seen that acetophenone's intermediates peak methane formation before 10 minutes in the standardised milling process. The extra oxygen could increase stability of electron shifting reactions by drawing electrons towards it, delaying breakdown of intermediates to methane this is supported by research done earlier which has mentioned sodium benzoates as non enzymatic free radical scavengers (Pihan, Regillo, & Szabo, 1987).

4.1.9 Comparison of 3 chlorinated aromatics



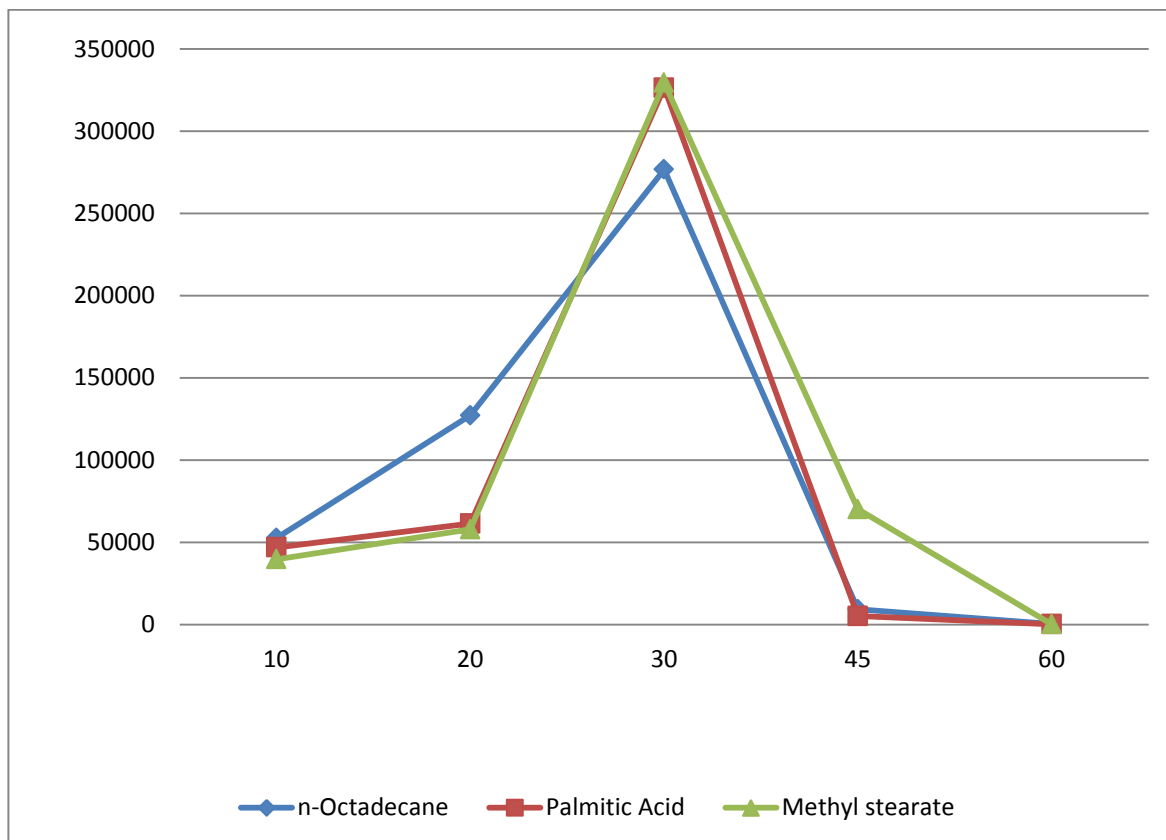
When comparing positions of chlorine as demonstrated by 2-chloroaniline and 4-chloroaniline, these results have demonstrated that substituted groups on the ortho positions tended to produce higher amounts of methane as opposed to para and meta. What was also seen, was that 2-chloroaniline an ortho substituted chlorine containing compound produced a higher amounts of other gases such as ethane and propane as opposed to 4-chloroaniline. These observations from these results only apply for singly substituted chlorine groups; when additional groups are substituted such as the three chlorine substituted groups in 2,4,5-trichlorophenoxyacetic acid it was found to have a startling effect on the intermediates to produce methane.

4.1.10 Aromatic amines and an aromatic ether



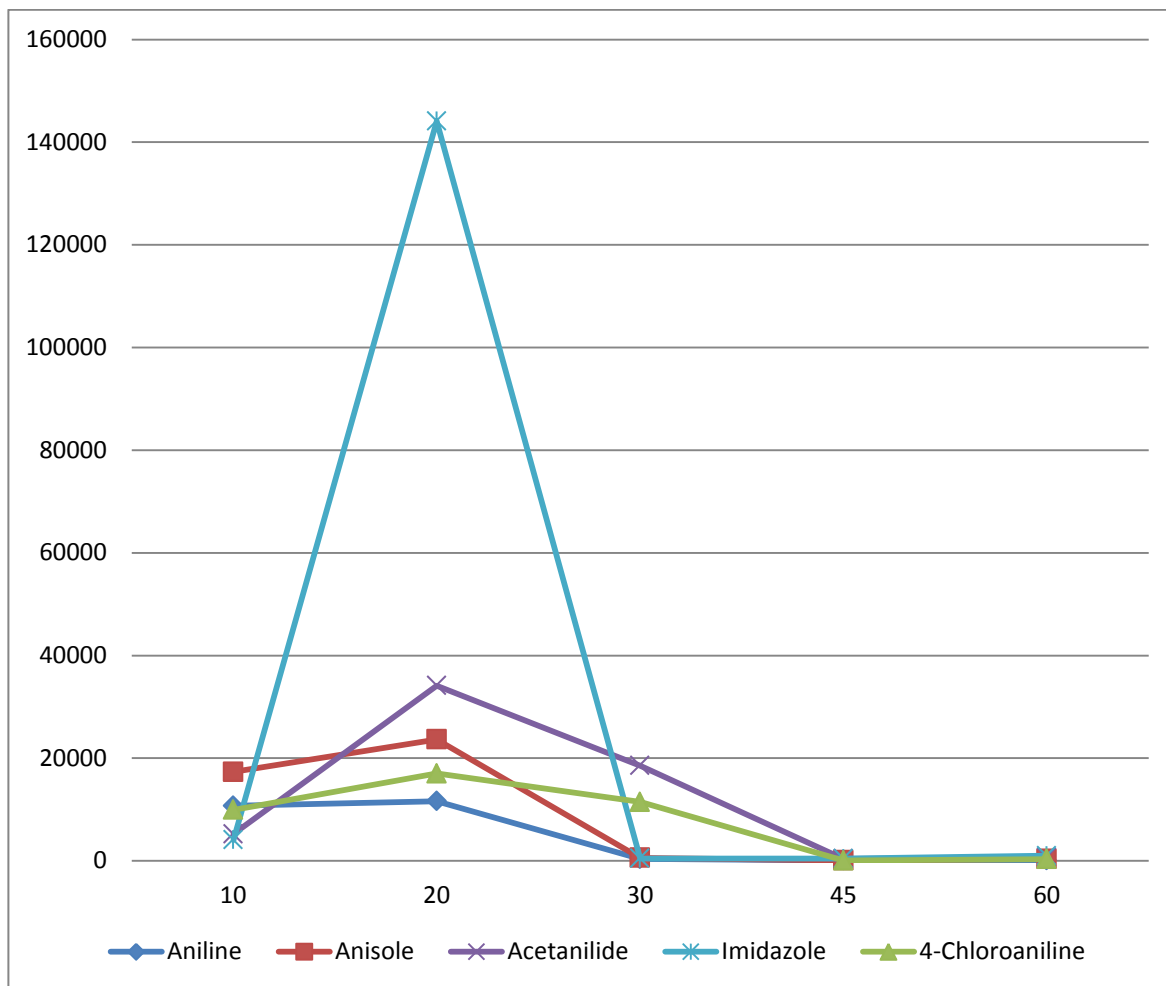
When comparing the significance of a substituted group on a benzene ring, it was found that the alkyl amine substituted group in N-ethyl Aniline produced the most amount of methane at the predefined milling conditions. Rates of methane gas formation between 10 minute intervals depict differences in the destruction of intermediates to methane. It can be seen that the intermediates formed from N-ethyl aniline were more readily broken down into methane than anisole. Aniline showed resistance to the production of methane over time, spreading the amounts of produced methane equally between the periods of 10 and 20 minutes. This was an unusual result as one would expect Aniline to yield higher amounts of methane initially due to the sole amine group which could alpha cleave yielding a site for reaction.

4.1.11 Comparisons of long chain linear hydrocarbons with or without a functionalised end



The results are very similar with the exception of the 45th minutes which suggests, the presence of the methyl group would have an impact on the formation of methane from intermediates. This could be from different intermediates being formed or more delayed composition to intermediates due to an extra carbon group for free radicals to transfer across from quartz (V Vallyathan et al., 1995).

4.1.12 Comparison of an aromatic amine, chlorinated amine, ether, amide and imidazole.

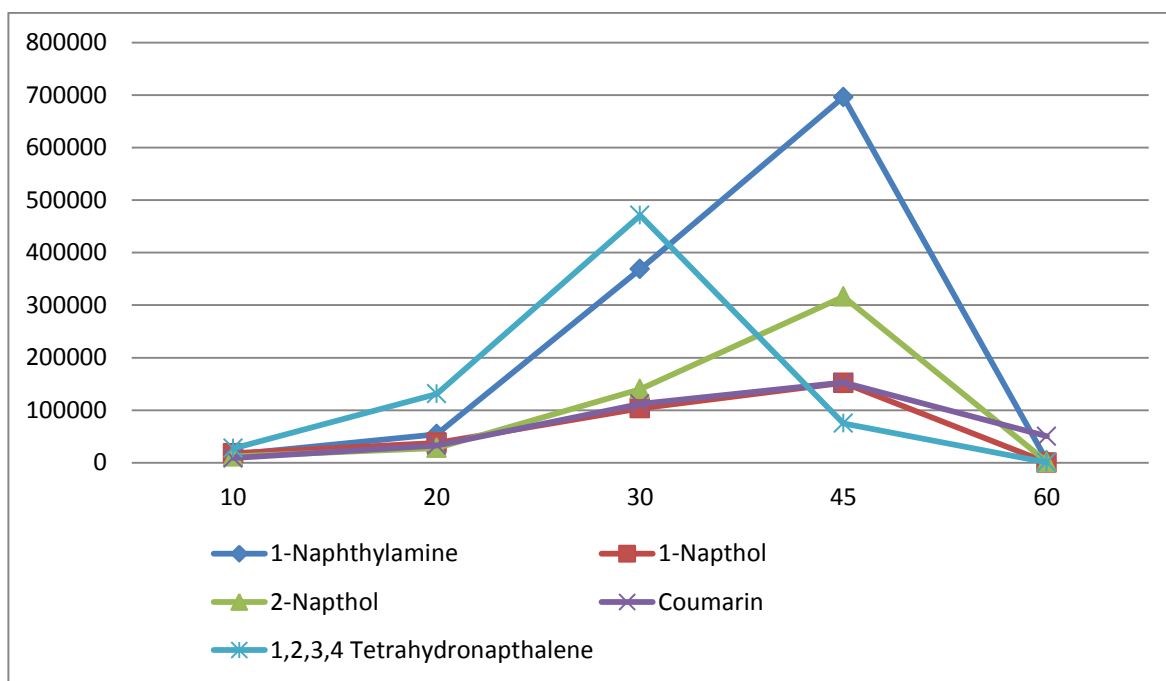


The presence of nitrogen groups in an aromatic heterocyclic context would produce the greatest amounts of methane when comparing maxima of similar compounds. This in part could be due to the formation of nitrogen as an intermediate from breakdown of imidazole, it has been observed that nitrogen conditions accelerated the production of gases from intermediates. A possible reason for increased amounts of methane produced at a sole time interval is a reduction in the competition for free radical sites by oxygen, as nitrogen is relatively inert as opposed to oxygen.

The comparison of amines, show us that oxygenation of the amine group resulting in a carbonyl yielding a higher maximum of methane in acetanilide. Followed by the para substitution of chlorine of benzene in 4-chloroaniline. This is summarised in the following associations in terms of methane production based on methane maximum: nitrogen containing rings > amine ketones > methoxy substitution > substituted chlorine amines > sole amine substitution. The sole amine substituted benzene aniline has a constant methane

GC value between the 10th and 20th minute interval and produced the lowest maximum out of the nitrogen containing compounds sampled.

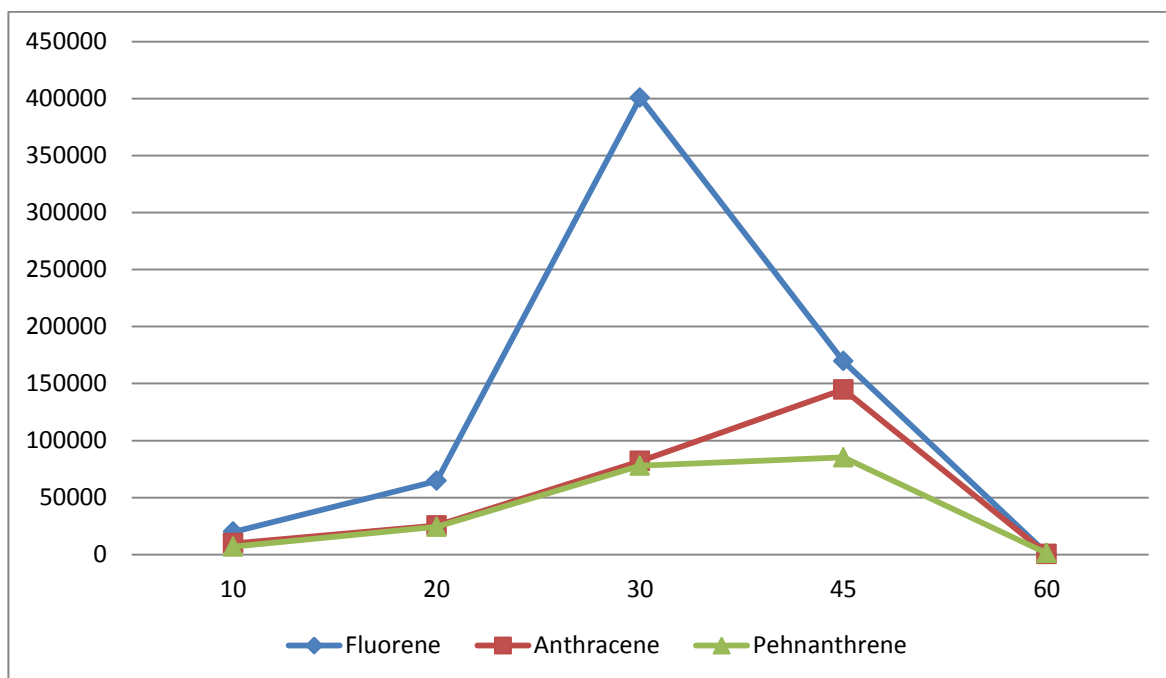
4.1.13 Comparison of 1-Naphthylamine, 1-Naphthol, 2-Naphthol and Coumarin



Comparing these double aromatic structures with the exception of 1,2,3,4 Tetrahydronaphthalene, we can see that intermediates would most likely be formed at the 10th and 20th minute interval as represented by a gradual increase in methane production. When comparing substituted groups of an amine and an alcohol, it is clear that an amine substitution in 1-Naphthylamine encourages production of methane from intermediates as opposed to 1-Naphthol. The less aromatic 1,2,3,4 Tetrahydronaphthalene yielded higher amounts of methane during the 10th, 20th and 30th minute of milling this can be attributed to the saturated ring which could breakdown more readily as opposed to an aromatic benzene ring.

Coumarin has a carbonyl and oxygen group found on one of the two aromatic rings, the methane production was spread suggesting the intermediates formed to be less prone to formation of methane and perhaps favour a direction formation of amorphous carbon or graphite.

4.1.14 Comparison of polyaromatic hydrocarbons

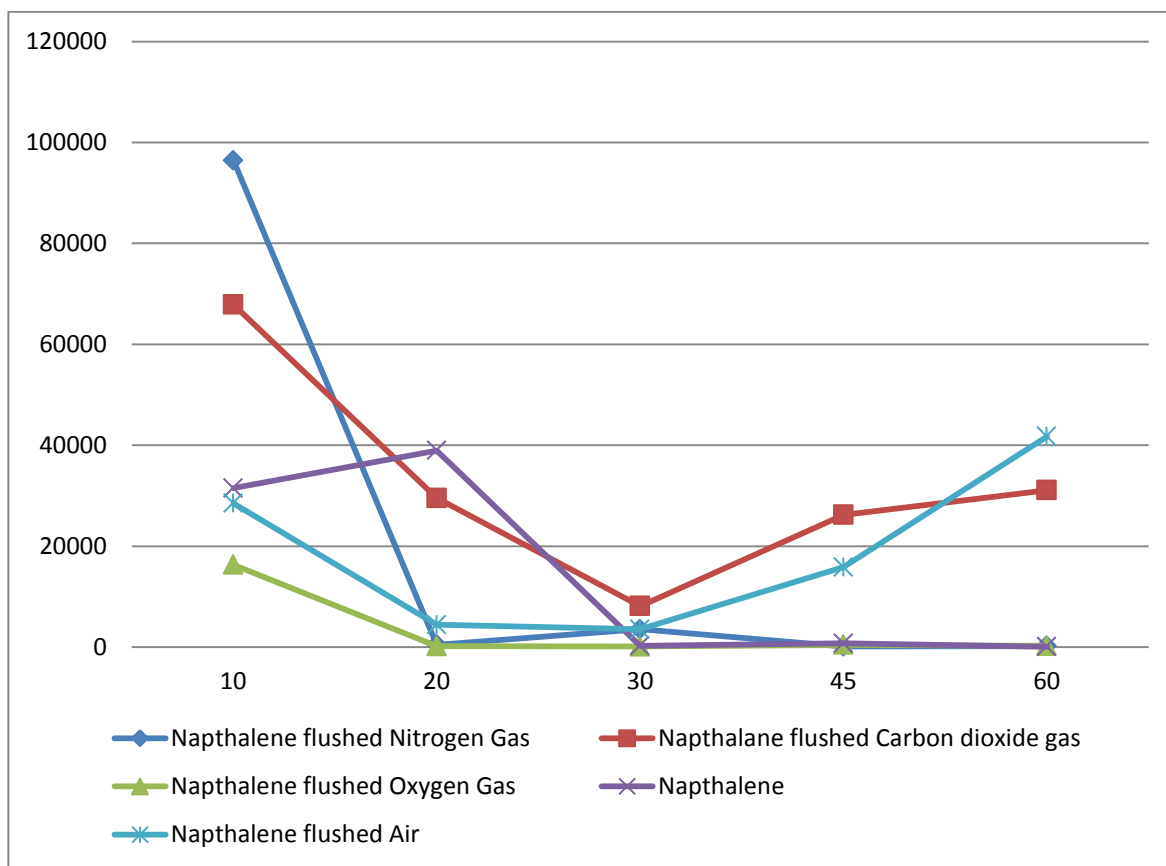


When comparing compounds with three rings, we can see once again the compound fluorene with the least amount of aromaticity yielding the highest amounts methane, similar to what was observed with 1,2,3,4 Tetrahydronaphthalene and naphthalene derivatives. Solely comparing rings the two compounds which have three aromatic rings we do not see much difference in terms of methane elution, except at the 45th interval where Anthracene produces more methane than Phenanthracene.

4.2 Effects of various atmospheres on methane production

The compounds naphthalene and oleic acid were selected as representative aromatic and aliphatic compounds. Naphthalene has been extensively studied oleic acid was chosen because it produced the highest maximum of methane during the gas formation study.

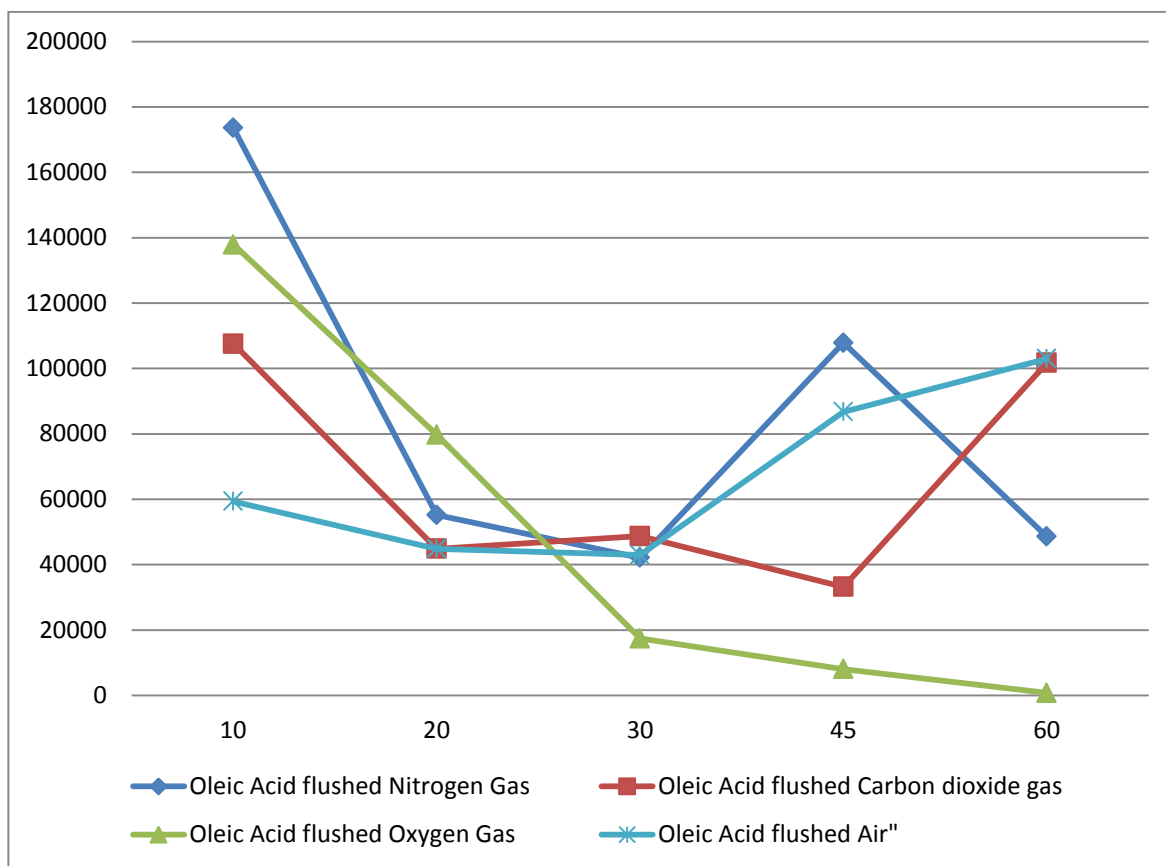
4.2.1 Napthalene



The gases found in the headspace illustrate influences atmospheric gases have on intermediates to form methane, during mechanochemical reactions. Nitrogen conditions produced the highest apex and amounts of methane when compared to other head space conditions. When comparing the rate at the 10th minute interval of nitrogen against air, the apex was found to be 3 times greater. Bellingham had obtained similar results based on DDX destruction claiming the presence of elevated nitrogen gas yielded destruction rates 2.5 times faster when compared to atmospheric air (Tristan, 2005).

Other trends can be seen between samples flushed with carbon dioxide and air. Taking on a second degree polynomial curve fit, where the counts of methane measureable at the 10th and 60th minute exceed the amounts found the 30th minute interval. The production of ethane was more prevalent when elevated levels of carbon dioxide were used.

4.2.2 Oleic Acid



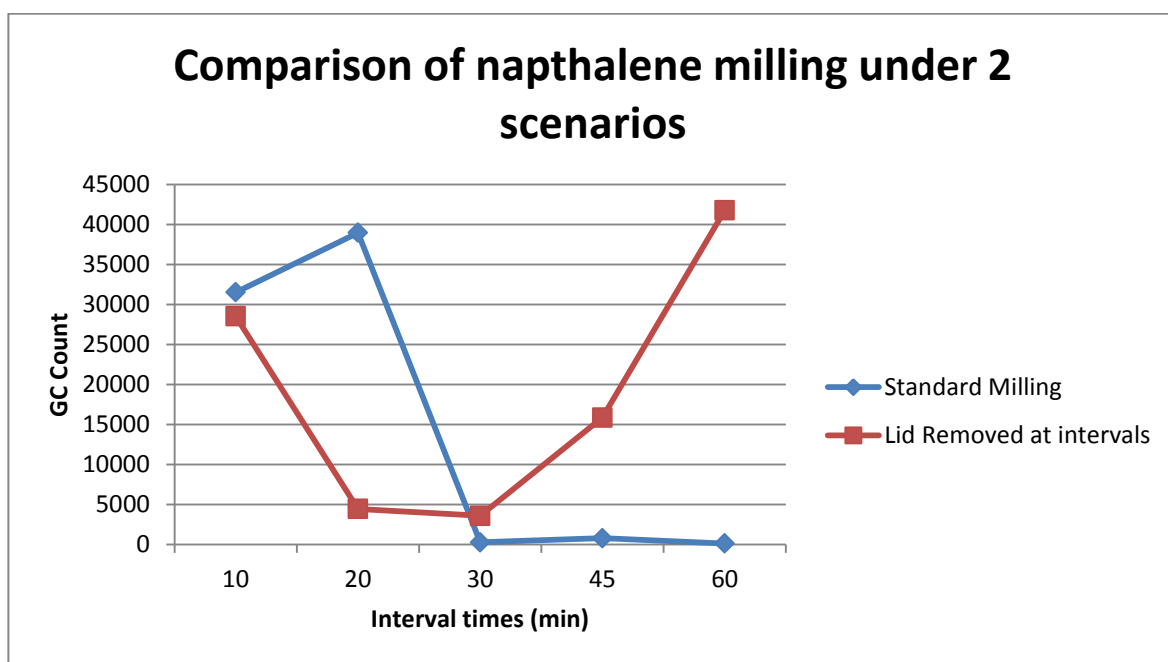
Altered headspace conditions have a significant effect on the formation of methane from intermediates for oleic acid. Some possible reasons to the susceptibility of oleic acid when compared against naphthalene are the absence of aromatic rings, where naphthalene is therefore stabilised by resonance. Other possible reasons which describe the susceptibility of oleic acid to free radical attack include the length of the linear aliphatic hydrocarbon, the presence of a double bond which and presence of the carboxylic acid group at the tail of the molecule.

Similarities in terms of methane production between naphthalene and oleic acid include the two degree polynomial relationship between time and methane counts, for carbon dioxide and air samples. Differences observed, are the higher recorded methane counts at all intervals under nitrogen and oxygen conditions. This would suggest as expected different pathways of intermediate formation to that of naphthalene.

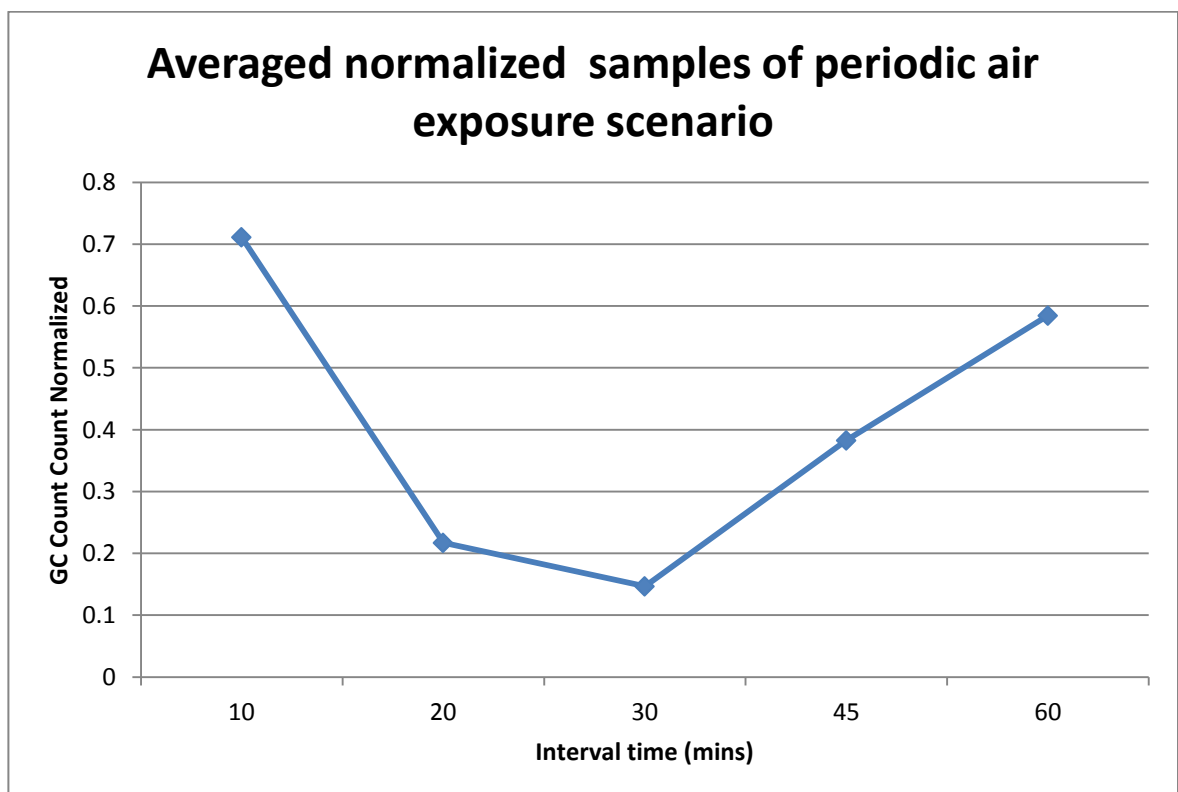
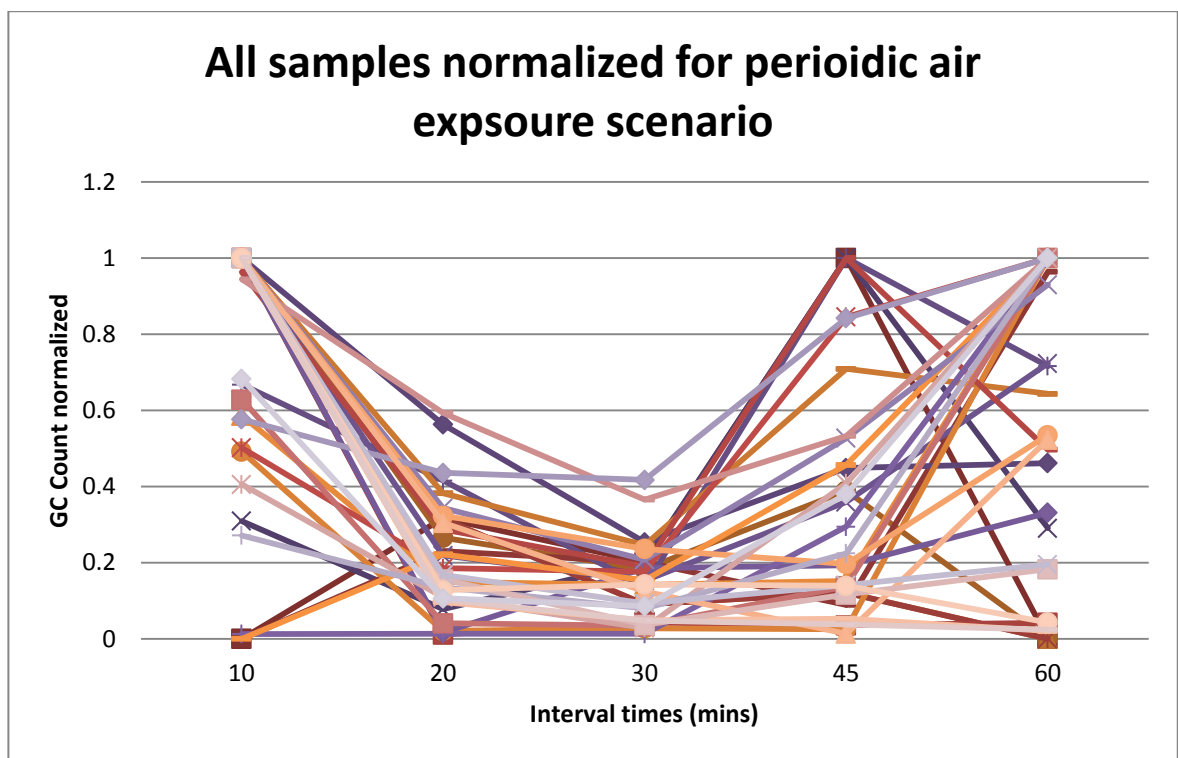
4.2.3 Air exposure at sampling intervals

An attempt to address rates of methane production and total methane production possible was carried out at standard milling conditions. Refer to the methods section gas formation from milling sample on the exact details how methane was analysed.

What was observed for most of the samples analysed was the initial and final amounts of methane produced usually exceed that of the amounts produced at 20, 30 and 45 minutes resulting in a curve like that seen in the two graphs below. This was seen at varying rates; a pattern based on compound structure involving rates of methane formation could not be established conclusively.



The graph below omits the sample legend as the graph was included to depict the curve formed when samples were periodically exposed to air.



From the observation of methane production having 2 apexes at the 10 min and 45 or 60 minute interval, it can be proposed that there would most likely be 2 possible mechanisms in competition involved in production of methane. The key variable which was changed

was the introduction of air at each interval and the reduction of methane due to the milling jar lid being opened.

The actual amounts of methane produced at both scenarios was calculated and compared. In general total amounts of methane produced during interval air exposure to sample were lower than that seen during standard milling conditions.

This experiment demonstrated that continuous systems of milling can cause shifts in methane production in most instances reducing the total amount of methane produced. A continuous system feeds sample into the mill continuously which in turn introduces more air into the mill, the change in atmospheric gas concentration will change the concentration of volatiles as well as total methane produced at each interval as discovered by experiment.

4.2.4 Quartz milled in modified headspace gas

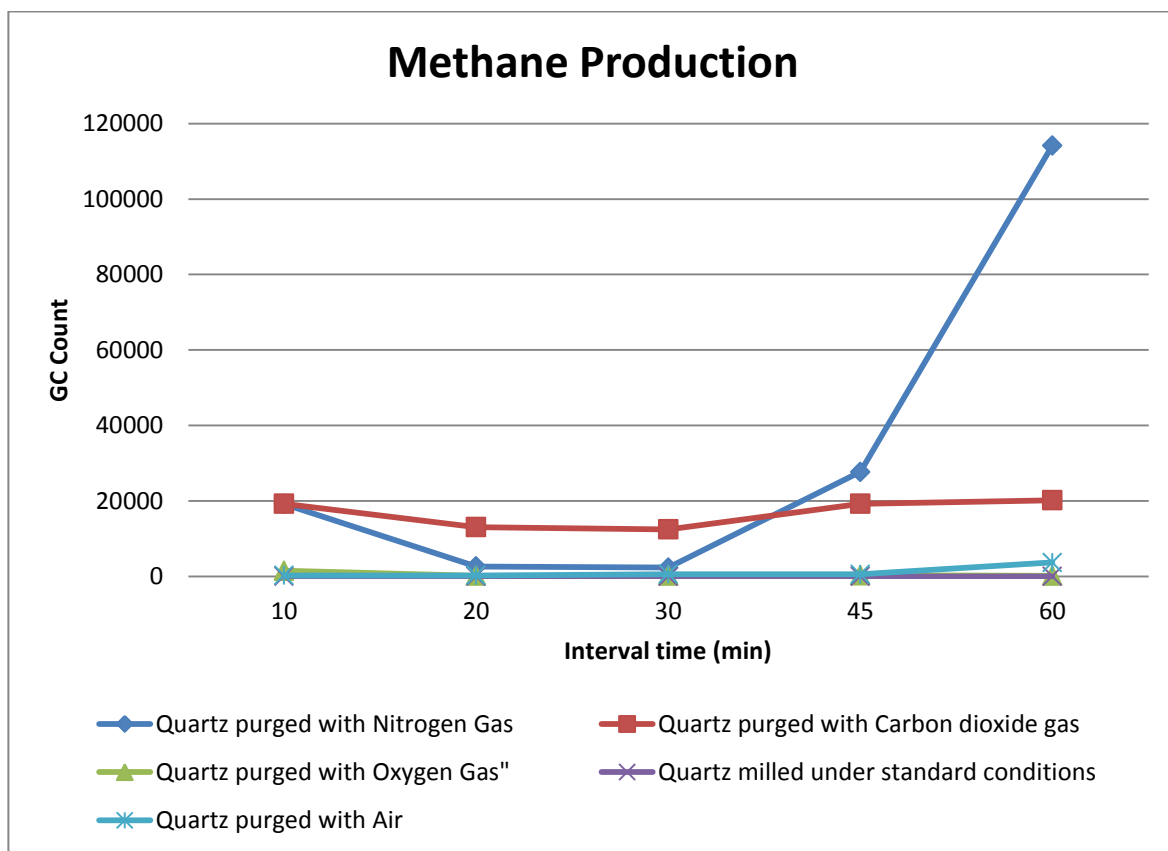
Quartz milled in nitrogen conditions yielded higher amounts of time methane counts as milling time increased with the exception of the 10th minute interval. The sole formation of methane itself suggests other sources of carbon and hydrogen in the milling system originating from either the quartz, steel balls or milling jar.

When the headspace was purged with oxygen methane was still formed at all intervals with a maximum at the 10th minute but at gradual reduced level as milling time increased. This yet against confirms the presence of another carbon and hydrogen source, but at much lower concentrations as indicated by the small methane count. Before making the assumption that lower concentration of methane was seen we have to consider the methane count decreasing steadily from the 10th minute it is therefore possible that the methane count as the apex of methane production maybe before the 10th minute.

When carbon dioxide was purged into the headspace, the amount of methane produced was <2000 methane unit counts which is 0.71mg of methane. With a slight increase in methane unit counts as milling time increased with the exception of the 10th minute, a similar pattern was observed with oxygen.

Most interestingly, when milling was performed in standard conditions that is milling continuously without introducing air periodically the amounts of produced methane greatly exceed those of nitrogen. A key difference between milled samples in standard conditions versus those with modified atmosphere headspace is the actual amount of methane

produced; standard milling conditions when higher than the previous interval can include the previously produced methane, when vice versa this clearly shows the destruction of methane into amorphous carbon and possibly hydrogen or even water.



Air as most people know is a composition mostly of nitrogen, oxygen and carbon dioxide (David R Lide, 1997). These compositions are not fixed and vary depending on location.

The compounds compared were those with similar readings obtained during the 10th minute interval. The comparison comes about from atmospheric conditions in the milling jar head space; where the headspace air was maintained in one sample and in the other was allowed to be filled with environmental air for 2 minutes. As both samples when milled at 10 minutes should have similar atmospheric conditions these values were used as a consistency guideline for comparison.

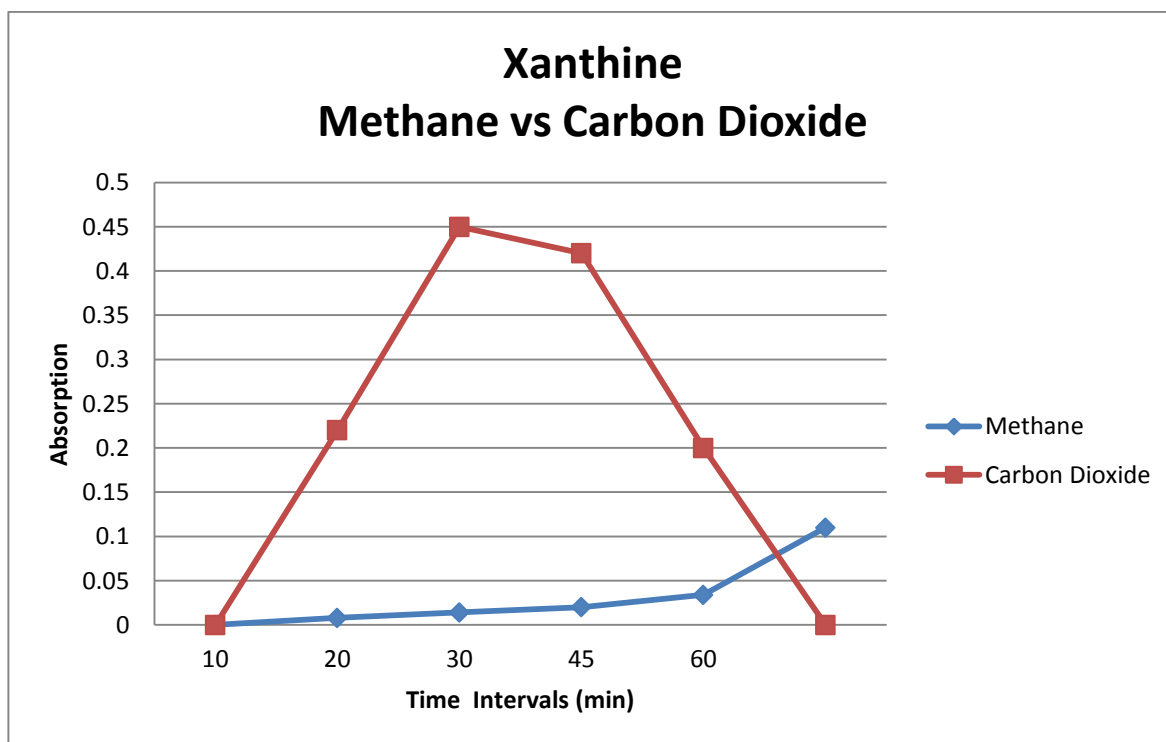
The periodic removal of the milling jar lid produced a wide variety of results and will be termed as intermittent opening. Where in some instances methane formation was drastically increased as opposed to standard milling conditions seen in acetophenone and to a lesser extent anisole. What was observed was that the introduction of atmospheric air in all the 32

compounds sampled would produce higher amounts of methane at the 60th minutes which usually were at low counts during standard milling conditions with the exception of imidazole.

4.3 Gas formation analysed by FTIR

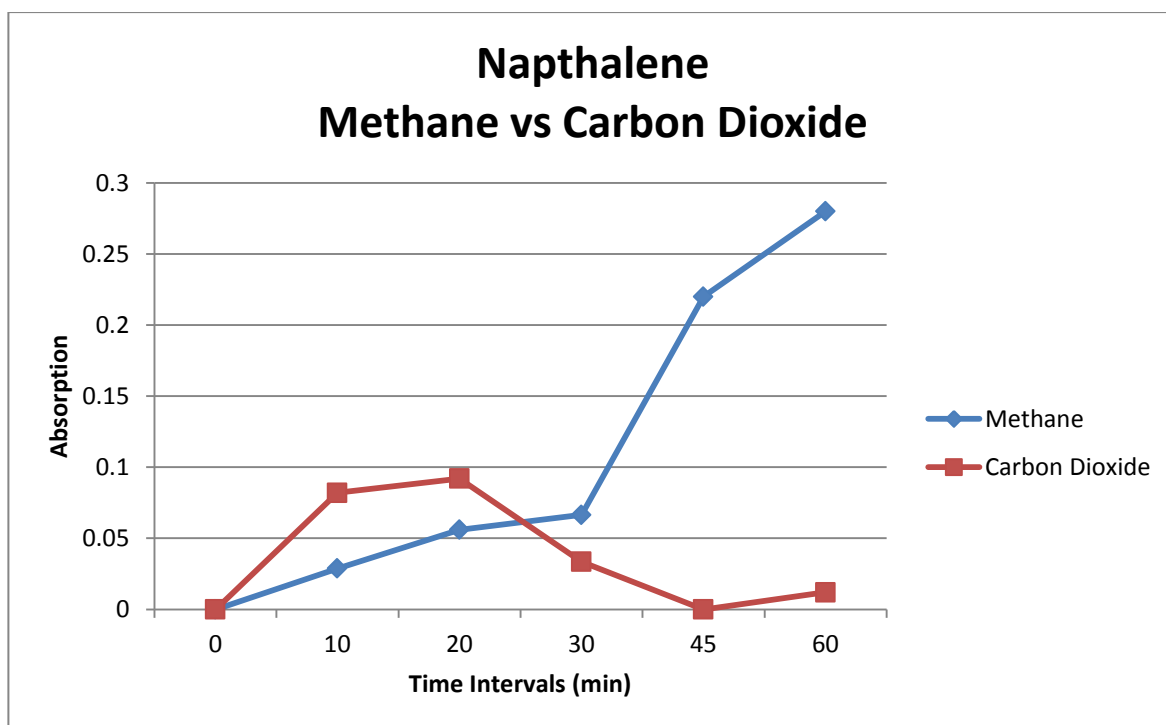
Xanthine

Time (min)	CH ₄ (absorption)	CO ₂ (absorption)	CO (absorption)
10	0.008	0.22	0.044
20	0.014	0.45	0.05
30	0.02	0.42	0.052
45	0.034	0.20	0.012
60	0.110	0	0



Naphthalene

Time (min)	CH ₄ (absorption)	CO ₂ (absorption)	CO (absorption)
10	0.0288	0.082	0.021
20	0.056	0.092	0.031
30	0.0665	0.0335	0.0194
45	0.22	0	0
60	0.28	0.012	0



Methane, carbon dioxide and carbon monoxide were identified at wavelengths 3000 cm^{-1} , 2360 cm^{-1} and 2180 cm^{-1} (M. B. Esler, D. W. T. Griffith, S. R. Wilson, & P. L. Steele, 1999; Su Kanabus-Kaminska, 2002). From the table and graph we can clearly see an indirect relationship between the amounts of carbon dioxide produces versus that of methane. It is obvious that carbon dioxide is produced in much larger amounts than methane initially, as milling time increases the amount of carbon dioxide reaches 0 while methane amounts continuously increases which h was demonstrated between naphthalene and xanthine samples.

What was seen in the graphs was the xanthenes seemed to produce less methane over the duration of 60 minutes, which suggested that the increase of nitrogen groups may affect the

carbon dioxide conversion to methane. A similar compound imidazole was compared in terms of methane produced yielded similar trends of methane produced over the same milling conditions and times refer to graph below. This would future validate our assumptions nitrogen substituted substances help resist the formation of methane from carbon dioxide. Naphthalene as illustrated by the graphs that the conversion of carbon dioxide to methane was more readily achieved when compared to xanthine.

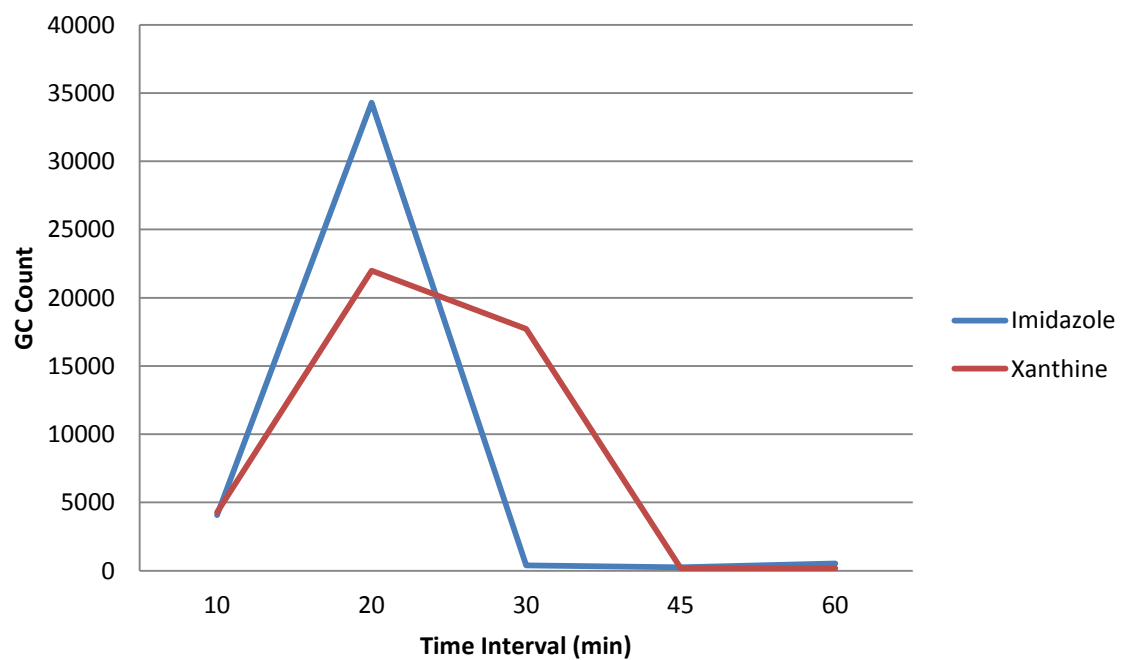
Contradictory to results obtained when head space was flushed with nitrogen gas periodically. In the presence of nitrogen gas during milling high amounts of methane were produced over a short period of time as opposed to the control sample steadily increase when milling time was increased. Nitrogen containing compounds indicate like imidazole and xanthine were more resistance to the formation of methane from carbon dioxide.

Another hypothesis was the possibility for the formation of NH type of compounds such as ammonia following a similar chemical pathway as with the formation of methane as proposed in equation 3 and 4, but was found to be absent due to the absence of spectra at wavelength 960 cm^{-1} as determined by internal standard. A closer inspection of the FTIR graphs indicates the absence of a HCN types of bonds no doubt substances like xanthine are a nitrogen containing compound this was represented by the absence of wavelengths (HCN) 718 cm^{-1} , (NH) $3500\text{--}3300\text{ cm}^{-1}$ and (CN) $1180\text{--}1360\text{ cm}^{-1}$ (Chemistry and Biochemistry Department University of Colorado, 2010; Kanabus-Kaminska, Kanabus-kaminska, Su, & Kanabus-kaminska, 2002). Also FTIR demonstrated based on the samples milled that nitrogen dioxide and nitrogen peroxide was not produced over the periods of times milled demonstrated by the absence of peak spectra at wavelengths 1625 cm^{-1} and 1750 cm^{-1} (Exova Service, 2010).

Most interestingly trace amounts of nitrous oxide was detected this could not be further confirmed by an internal standard due to the concentration of nitrous oxide but the distinct position between carbon dioxide and carbon monoxide of the nitrous oxide peak was seen at wavelength 2255 cm^{-1} . Other characteristic peaks were not seen which could be due to the small concentrations detected. (Esler, Griffith, Wilson, & Steele, 1999)

The approximate lowest level of detection as calculated is 0.0022 absorption, meaning that any substances detected at 0.0022 absorption would be considered as noise and therefore not seen as a distinct peak.

Methane comparision of Imidazole vs Xanthine



4.4 Intermediate analysis from milled samples

	Presence of compound up to** (minutes)	Intermediate Compound	Methane (mg)
Diisooctyl phthalate	<10		40
Dibutyl phthalate	<10	Monomethyl ester CAS(2306-33-4)	*
Imidazole	<10		3
Aniline	<10		1
Anisole	<10		2
N-ethyl aniline	30		3
O-toluidine	10	n-heptane	
Acetanilide	<10		3
M-anisidine	<10		3
Acetophenone	<10		1
Methyl benzoate	<10		3
Phenylacetone	<10		26
Benzylbenzoate	10		5

* Samples data was not recorded due to software compatibility issues

** The presence of the original compound up to but not including the 10 minutes was not analysed and was determined by the absence of the original compound at the 10th minute interval.

2-chloroaniline	<10		16
Trans-cinnamic acid	<10		1
O-cresol	<10		7
4-chloroaniline	<10		2
2,4,5-T,2,4,5-	<10		1
Xanthine	<10		2
Octadecane	10	4-Decene Trans-3-dodecene n-Octadecanol 8-Octadecanone	26
Palmitic acid	45		25
Methyl stearate	20	Heptadecanoic acid,	25
Tetrahydronaphthalene	10		36
Fluorene	10	Fluorene-9-one	31
1-Naphthylamine	30	Ethylbenzene	65
Coumarin	30		

1-Napthol	<10	Ethylbenzene	
2-Napthol	<10		24
Athracene	<10	Anthraquinone, 2-hydroxy Anthraquinone	11
Phenanthrene	30	1-Dodecene Cyclotetradecan e Hexadecen-1-ol 1-Octadecanol	7
Naphthalene	30		4

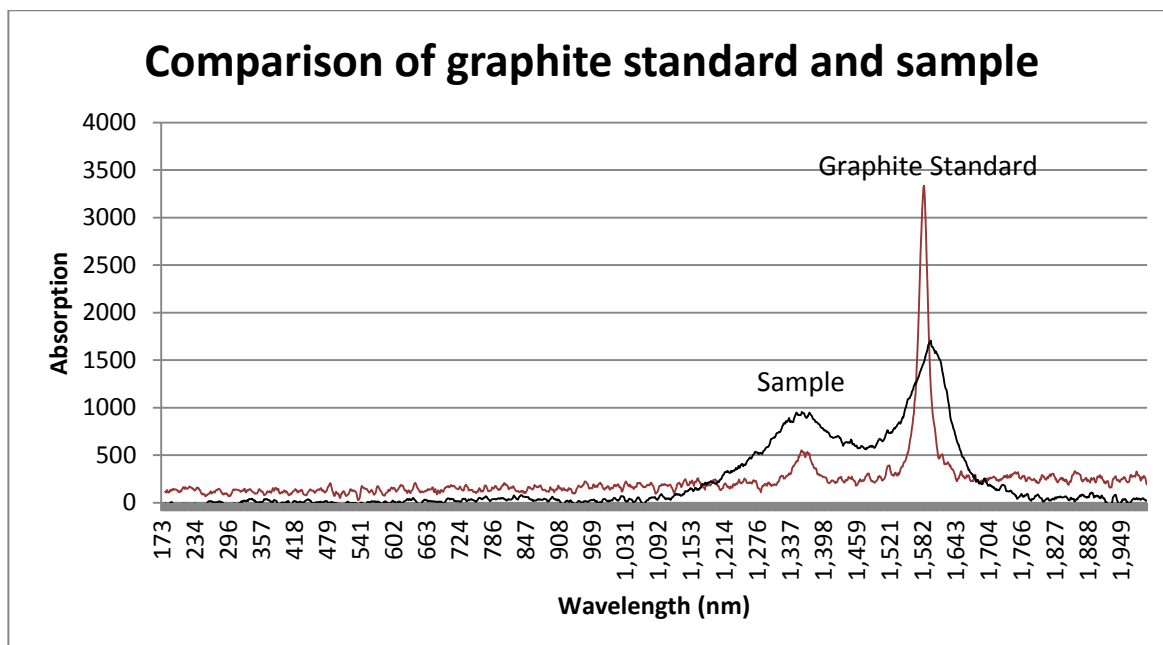
4.5 Milled matrix composition

Sample	A	B	C
Weight of milled sample	2.5633	2.5090	2.5162
g of inorganic metals	0.5773	0.5471	0.5261
g of SiO ₂	1.9457	1.9099	1.9301
g of Carbon	0.0172	0.0303	0.0463
g of Others	0.0231	0.0217	0.0137

Naphthalene has a molecular weight of 128.17 g/mol the milled sample with 94% of naphthalene's mass contributed from carbon. Naphthalene has a molecular weight of 128.17 g/mol the milled sample was carried out at a 1% concentration. This will have a theoretical weight of 0.47g of carbon available.

The indicative amount of SiO₂ loss, may not be a true reflection due to HF ability to formed SiF₄ which is gaseous, refer to equation 5. Therefore losing Si product to the air, which would be sucked up in the fume hood readily; even under a fume hood etching and deposition of silicate complexes on surrounding apparatus including glassware was seen.

The efficiency of the method developed for silicate removal was proven to be satisfactory as determined by the absence of silicate oxide peaks in the Raman spectra.



Another observation was that the matrix being composed of inorganics and silicates were relatively constant in terms of structure digestible. But the amounts of carbon were found at varying amounts indicates that standard ball milling conditions does not result in a homogenous dispersion of carbon in the matrix.

The composition analysis also shows an inversely proportional relationship to the percentages of inorganic material:quartz sand. Suggesting lower levels of inorganic metals in the matrix tended to increase the amounts of amorphous carbon found in the milled matrix.

4.5.1 Quartz moisture absorption analysis

% Weight loss after 100°C	0.12%
% Weight loss after 300°C	0.07%
% Weight gained after 48 hours	0.07%

The measured average weight loss represents substances that have been removed at the corresponding temperatures; these increased temperatures facilitate the release of substances from the quartz matrix by thermal expansion. Based from the weight gained after 48 hours, we can assume most of the weight absorbed is water the significance of this is the possibilities for peroxide radicals and therefore providing a source of hydrogen for the formation of volatile gases like methane. Refer to section 1.10 for an introduction on methane formation from hydrogen radicals.

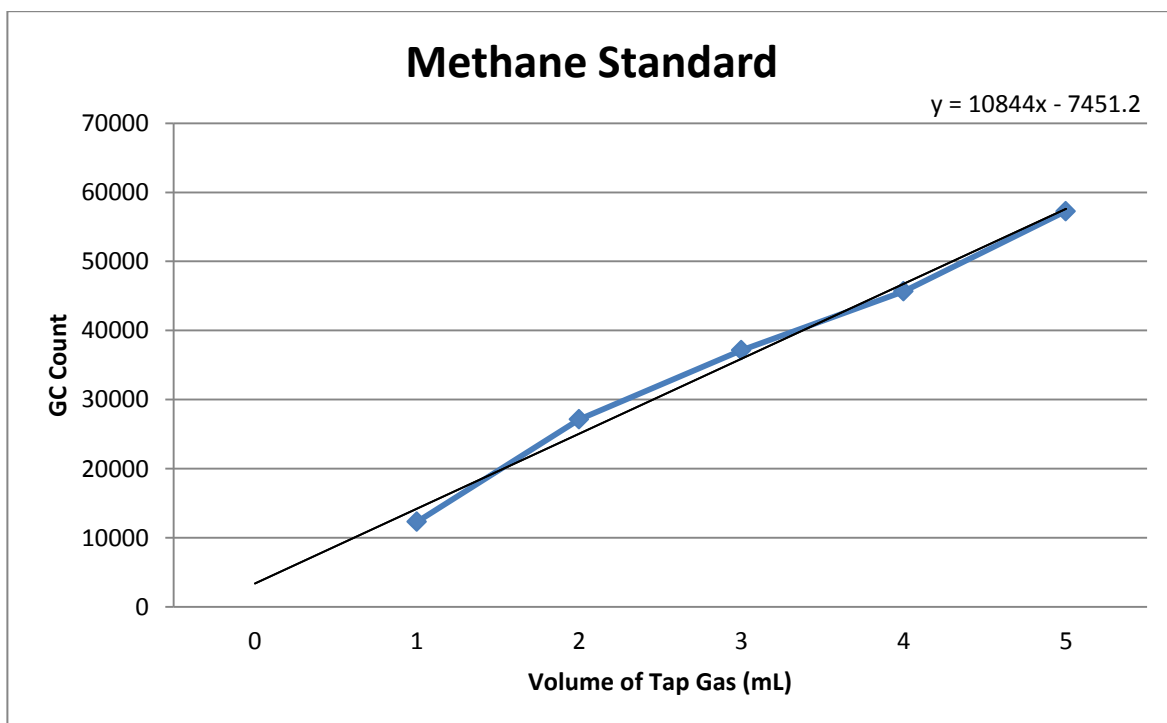
No doubt the most ideal conditions would involve quartz free from absorbed compounds, these conditions would not be realistic in terms of achievability (refer to section on ball milling) or attainability in a commercial context due to costs and environmental samples obtained. A more detailed account

4.6 Mass “estimative analysis”

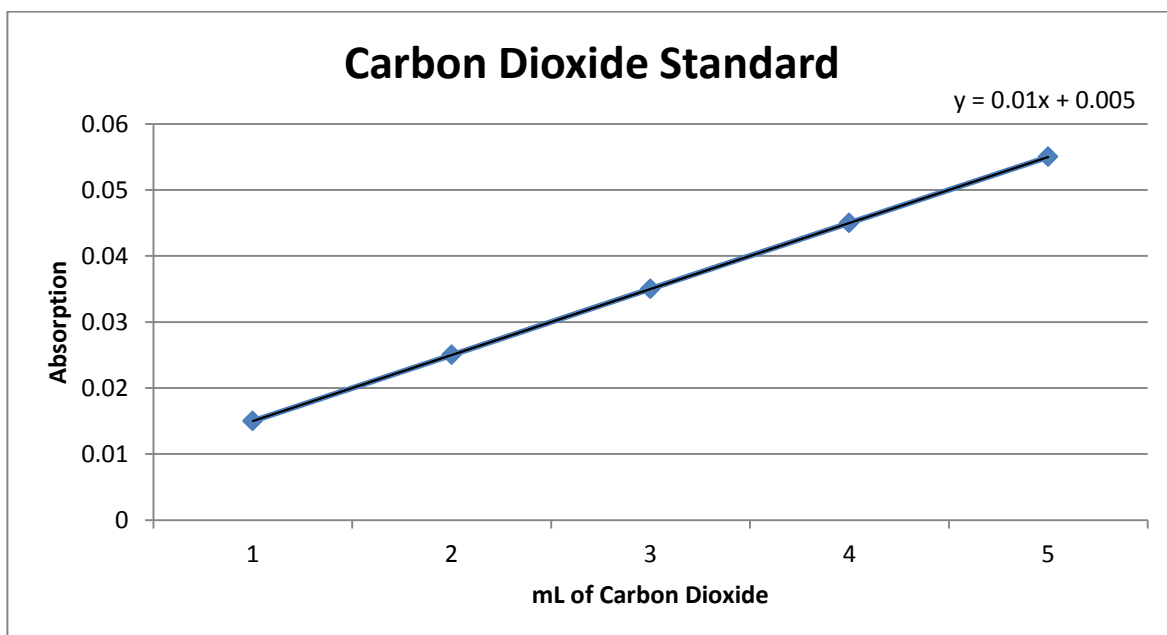
Based on the data obtained an estimation on the amount of carbon accountable is calculated. It was hoped to have total accountability for the destruction of naphthalene, proving that almost all substances of significance were analysed.

4.7 Standards for quantification of methane and carbon dioxide

From the graph we can see a linear relationship between peak area (expressed as counts) and volume of tap gas used, with the exception of 3 and 3.5mL of tap gas. This could be due to septa leaking or sample lost through the connecting port of syringe to needle. The determination for the amount of methane per unit area which was later expressed as g/L was done through the following steps:



1mL of the air mix was injected for analysed with a split ratio of 50, the amount of air sampled is therefore 20 μ L. Due to the percentage composition of methane being 81.64% of 20 μ L the volume of methane analysed is 16.328 μ L. The density of methane at 20°C is 1.919 kg/m³ therefore the mass of methane produced for 1 GC count area unit measured is 0.560 mg of methane



Standards for carbon dioxide analysed by FTIR, indicate a clear linear relationship. Carbon dioxide has a density of 1.830 g/L at 20°C as calculated from the equation:

$$density = \frac{molar\ mass \times p}{RT}$$

1 absorption count will yield 99.5 mL of CO₂ and therefore result in 0.182g of CO₂.

4.8 Mass “estimative analysis” for naphthalene

Mass of carbon will be determined based on 0.1% concentration milling of naphthalene in 50g of quartz, theoretically yielding 0.0468g of carbon.

FTIR was used as opposed to GC as initially mentioned was due to the absence of proper column.

Mass of carbon as determined from milled matrix composition: 0.00463 g

Methane 0.007g of methane being a 1:1 reaction will yield 0.4375 m mol of carbon which is: 0.00525 g

Carbon dioxide as determined by FTIR had absorption of 0.092 (determined by CO₂ standard) yielding: 0.0159 g of CO₂

Amount of carbon present in CO₂: 0.00434 g

Carbon monoxide as determined by FTIR has an absorption of 0.031 yielding: 0.00325 g

Amount of carbon present in CO: 0.00140 g

Total carbon accountable: 0.01099g

Results obtained was not satisfactory, and warrants the further development of an efficient carbon accountability method. One of the key difficulties was the complete sealing of the milling jar; several o rings were tested and pressure test trailed.

Chapter 5. Discussion

The intermediate results obtained by GCMS, confirmed the effectiveness of the planetary ball mill at mechanochemically destroying compounds. Most compounds with <9 carbons, were broken down into intermediates, methane or carbon analogues. Every compound with the exception of oleic acid analysed, when subjected to 60 minutes milling at 500 RPM were no longer detectable by GCMS. Possible reasons for this are discussed in the linear aliphatic hydrocarbon subsection. A key difference between oleic acids and all the other compounds studied is the presence of a double bond mid way between the alkyl chains, which could explain the high amounts of methane produced. The formation of methane would also indicate a lower tendency to form amorphous carbon at that given point in time.

Based on results obtained from the milling of quartz under modified head space conditions and quartz absorption analysis we can be certain methane is produced in trace amounts in the background of ball milling. When nitrogen was milled with quartz methane was produced indicative that the sources of carbon and hydrogen could be attributed to the steel of the milling jar and even the quartz sand itself. The steel used on the jar had a 2.20% carbon content and based on the quartz absorption analysis done previously there was < 0.2% of volatiles as potential sources of hydrogen determined by analytical weight difference of quartz (Retsch, 2010). The majority of these volatiles were assumed to be water due to re-absorption work done on quartz for 48 hours refer to section on quartz absorption analysis. When naphthalene was purged with carbon dioxide methane formation yielded an increased by 325%. Coupled with results obtained from quartz being purged with carbon dioxide, there is a clear carbon contribution from carbon dioxide gas to the formation of methane.

Water has been found to fragment into hydrogen and peroxide radicals, these radicals could be assisted by the multiple oxidations states iron undergoes (Castranova, 1994). It is theorised they come about from an interaction between the surface active Si^* , SiO^* , SiOO^* and SiOOH^* during the fracturing of quartz crystals during milling. Other possibilities excluding quartz include activated O_2^* , N_2^* and O_3^* (Williamson, Pastiroff, & Cressey, 2001). The significance of this are the potential sources of hydrogen radicals required for formation of methane from carbon dioxide.

5.1 Methane, carbon dioxide and carbon yields

The importance of methane analysis can help answer several questions firstly involving the build up of pressure due to gases formed during milling which could cause material failure. Secondly since methane is a greenhouse gas it would be important to know the amounts of methane which is required to be mitigated. Lastly since methane is a volatile gas which can be used to generate electricity it would be of commercial value to understand the amounts of methane produced during the mitigation of organics and therefore assist in the evaluation of methane production being used as a means for energy production. The formation of methane during milling has been acknowledged in numerous publications (Mago, 2004; Tristan, 2005; Zhou, 2009) but the quantification, formation and use of it as a comparative tool has yet to be explored and thus will be included as part of this thesis. The actual formation of methane remains purely speculative no doubt it is measureable in a closed system it is extremely difficult to analyse methane intermediates.

The precedence of methane versus of carbon dioxide was initially thought to be insignificant. In fact FTIR results demonstrated the formation of carbon dioxide initially predominates over methane; this means that during milling of organic compounds carbon dioxide is the preferred pathway after which it is then converted to methane.

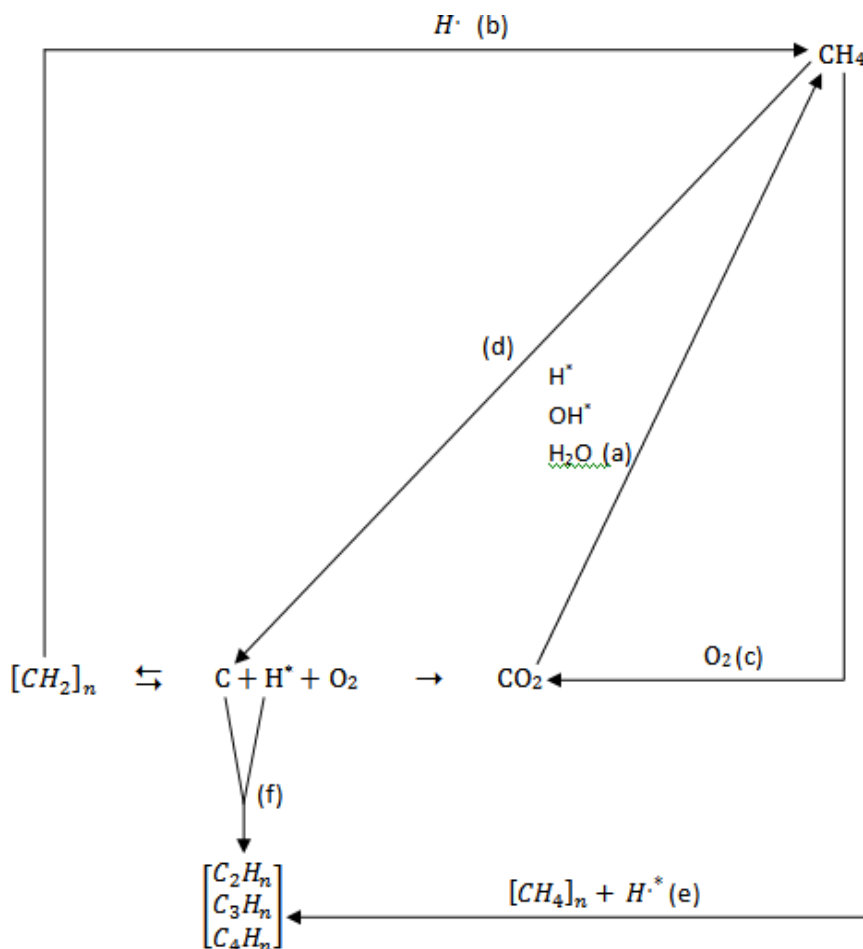
During the milling of carbon dioxide gas in standard quartz milling conditions the formation of methane dominates; other volatile product formed being ethane, propane and hexane were detected at lower amounts. This find suggests that methane is not solely formed from intermediates and a pathway should be proposed.

The results from the milling of oleic acid, naphthalene and quartz in modified atmospheres suggest:

1. Excess amounts of oxygen can increase the destruction of intermediates to amorphous carbon or increase formation of carbon dioxide.
2. Milling of samples under carbon dioxide has a similar methane production trend as that observed from samples having intermittent opening. This trend will be seen during the saturation of carbon dioxide formation.
3. Oxygen is involved in the destruction of intermediates forming carbon dioxide and methane first as determined from milling of organics and quartz in nitrogen atmospheres.

It has to be acknowledged gas formation will be influenced by temperature variations, based on the Arrhenius equation as temperatures increases the constant gets bigger and mathematically we will expect reactions to proceed more forward than backwards. Therefore competing reactions can be driven forward from the increase of temperature during longer periods of milling time. Temperature was measured for majority of samples analysed and yielded range of temperatures from 77°C to 140°C. This justifies the eventual conversation of organics to methane and methane to amorphous carbon.

Based on the above analysed results and the normalized data obtained for all the samples milled with intermittent opening; there are 6 reactions of which 2 are competing.



* Not a major pathway, but is highly possible based on equation 4

The first proposed pathway is the formation of carbon dioxide then methane from organic compounds pathway a, the origins of hydrogen are most likely from water and organic

compounds during the reduction of carbon dioxide it is also possible water is formed due to the presence of hydrogen radicals.

Pathway **b** is inclined for more rapid destruction of organics where amorphous carbon is formed, this could be found in milling of aromatic structures such as benzene or short chained volatiles like ethane. Amorphous carbon is reacted with hydrogen radicals forming methane. This pathway was derived from the milling of organic compounds in nitrogen conditions. In these conditions oxygen concentrations would be reduced and therefore detection of methane would omit the formation of carbon dioxide.

A competition pathway **c** has been proposed based on the milling of organic compounds in oxygen conditions. Very low concentrations of methane were detected indicative of carbon dioxide production due to the abundance of oxygen or possibly rapid destruction to amorphous carbon. The formation of amorphous carbon was unlikely as this would indicate the formation of water, which was not observed.

The tail end pathway **d**, is the destruction of methane to amorphous carbon and their analogy. This pathway was further elaborated to include the formation of small graphitic structures as determined by Raman and digestion trials.

The final two pathways **e** and **f** propose possible routes of formation small chain hydrocarbon such as ethane, propane and to a lesser extent hexane; the mechanics and variables effecting hexane formation was not investigated therefore not understood, also the reasons for propagation to cease at propane is not known.

Pathway **e** comes about from the possible formation of carbocation CH_5^+ which can react with methane resulting in ethane analyte adduct ion. A more detailed explanation on small chain volatile formation can be found in section 1.10.

Pathway **f** is based on the rapid breakdown of organics into carbon and hydrogen radicals it is similar to pathway **b** but takes into account the possibility of carbon propagating and then forming small chained volatiles as opposed to methane then propagation formation.

Sole carbon products add more intrigue to the substances analysed, they are formed at the highest concentration as final products during prolonged times of milling as expected. The two types of carbon allotropes were amorphous and graphitic which was verified by Raman

a broad peak at 1580 cm^{-1} and disordered 1350 cm^{-1} due to the smaller graphite crystals (refer to the Raman spectrum in the milling matrix composition section). The smaller graphitic structures can come about from methane and ethane formation on the “armchair” edges of the graphene layer due to the intense ball milling conditions (Espinal, Mondragón, & Truong, 2005). Silicate oxide along with other compound peaks was not seen based on personal inference and personal communication with Ms Michel Nieuwoudt from the University of Auckland.

The initial expectation was that it would be unlikely for amorphous carbon to form graphitic carbon but when we compare the heats of formation of amorphous carbon to graphite it is more stable 716.67 kJ/mol (Ribeiro da Silva & Santos, 2010) thus the carbon to graphite formation is exothermic and probably preferred.. Also, following the carbon phase diagram (Jan M. Jazula, 1997) of carbon allotropes it is clear that the formation of graphite is highly likely with a mean surface jar temperature of 77°C to 140°C and pressures $<0.01\text{ GPa}$.

Other sets of products which were not initially thought off and therefore were not analysed in detail for include the formation of PAHs and nitrogen containing compounds. The formation of PAH can occur in the presence of methane and ethane. When these gases are ionised PAHs can be formed; the heats of formation which can be used to determine stability for PAHs but would require a predefined pathway based on the number of carbons being present. Possible pathways for PAH formation from methane and ethane during combustion has been proposed by Selim Senkan and Marco Castaldi (Senkan & Castaldi, 1996). No doubt milling does not involve the bulk temperatures of combustion, but high energy planetary ball milling could result in similar reactions.

The formation of gaseous amine including NH_3 and NH_4 , which could come about from similar mechanisms involving nitrogen gas as those being proposed for methane formation from atomic carbon. Initial parameter standardisation for detection of ammonia were undertaken and it was found based on the same program used in the GC to analyse volatile gases that the retention time of ammonia overlapped that of methane at 1.10 minutes. A blank quartz sample milled in air was then analysed by FTIR for NH type of compounds indicated by a 1000cm^{-1} band, this experiment confirms that NH type bonds (basically ammonia) are not being formed in the background of quartz milling in air. Due to time

constraints NH bonds being proposed as being a possible pathway were not further investigated, but FTIR data from milled naphthalene and xanthine suggests NH type of bonds were not detected.

With respect to methane wise a change of carboxylic acid to an ester of 1 methyl unit can increase the length of time methane is produced as seen in methyl benzoate versus palmitic acid. It could be speculated the carboxyl group is cleaved off with the methyl group leaving a C18 linear chain which is cleaved into smaller hydrocarbons eventuating into methane, the carboxyl methyl would be stabilised by resonance thus the persistence till the 45th minute. The reason behind a more stable structure comes about from the possible elution of methane, if degradation of the carboxyl methyl group were to occur readily it would have contributed to the initial methane produced during the 10th to 30th minute intervals.

A similar trend observed by carbonyl containing linear hydrocarbons showed a cleavage of 3 – 5 carbon units from the end of the molecule. For example with methyl stearate producing the intermediate heptadecanoic acid; a similar process is seen in electron impact induced fragmentation in the mass spectrum.

Ionisation involves the bombardment of the sample in most cases organic compounds with a cloud of electrons; these electrons can knock electrons out of the samples particles causing the sample to attain a positive ion. These positive ions moved from the ionisation chamber by a positively charged plate known as the ion repeller. The positive ions now pass through 3 slits which initially are very positive eventually reaching to the last slit with 0V. This causes the ions to concentrate together resulting in a mixed ion stream which is subjected to magnetic forces causing ions of different masses to bend differently, lighter ions are deflected more and heavier ions are deflected less due to the curvature of the electromagnets used to induce the magnetic forces ions which are too heavy to too light will collide onto the electromagnet rather than passing through. Whatever ion streams make it through the electromagnet are then analysed using an ion detector, the ion detector neutralises the positively charged ions on contact with its surface due to electrons jumping from the metal to the ion (Ashcroft, 2010; Clark, 2000). Organics subjected to ionisation fragment resulting in similar intermediates formed when subjected to planetary ball milling in standard conditions.

5.2 Benzene derivatives

Benzenes are known with their stability due to aromaticity, one could think of benzene as the smallest resonance stabilized ring. Due to aromatic stability they have been adopted for use as core compounds for pesticides, where a ring would have been made to a PAH of desired size which would resemble a compound in a biochemical pathway; this PAH would then be heavily substituted with chlorine. The resistance of these types of pesticides allows them to persist in the environment making them extremely efficient a more lengthy discussion on pesticides can be found in section 1.3 Pesticides.

The presence of substituted groups dramatically alters the mechanochemical destruction pathway. The kinetics are possibly similar to fragmentation observed in mass spectra where organics are bombarded with electrons breaking compounds apart due to the single unpaired electron resulting in a positive ion and an uncharged free radical. This was illustrated by the linear aliphatic hydrocarbons like octadecane, where shorter chain aliphatic hydrocarbons were found by GCMS.

Similar mechanisms are observed regardless of substituent it is more of the “readiness” a substituent is to usually cleave itself from the longest alkyl chain. No doubt this process may differ in more highly aromatic structure such as anthracene it prevails when speaking in terms of preserving its aromaticity and cleaving off its longer alkyl chains like that observed by dibutyl phthalate. The above is summarised in equation 5.

When more aromatic rings are joined together like that in phenanthrene we can expect more resilience to high impact energies and free radical attack. This is expressed as the heat of hydrogenation where cyclohexene has an energy of 118 kJ/mol therefore 1,3-Cyclohexadiene with 2 double bonds we would expect to be double the energy of cyclohexene in fact the energy is 230kJ/mol slightly less than double of cyclohexene as conjugated dienes are more stable than sole dienes. When we compare benzene we would expect the energy of 356 kJ/mol which is 3 times that of cyclohexene. Benzene has energy of 206 kJ/mol which leaves a discrepancy of 150 kJ/mol which is attributed to extra stability, this comes about from all the carbon atoms have the same bond length and are sp^2 hybrids with p orbitals perpendicular to their ring. Therefore benzene cannot be expressed by one structure but in fact two structures representing resonance (McMurry, 2004). The stability from resonance was observed from mass spectra data of phthalates and anthracene

derivatives which persisted up until 10 minutes of standard ball milling. After this initial attack, intermediates are not seen; this could be due to the extreme fragility of benzene when attacked by high energies we can speculate a rapid break down of the once stable aromatic rings. This was observed by all benzene type structures after 30 minutes of milling.

Even at higher concentrations when 2% naphthalene was milled under standard conditions for 10 minutes the elution of naphthalene at lower concentrations indicating the likely hood of intermediates being seen but this was not the case, the formation of intermediates detectable by GCMS were absent further validating my speculation that these kinds of aromatics would instantaneous fragment to smaller pieces quickly yielding methane and amorphous carbon.

Solvents used for GCMS elutions was a 50:50 mixture of hexane and acetone giving the possibility of C6 intermediates or even C3 intermediates being foreshadowed by the solvent peaks. Oxidation of these solvents was also observed as some samples were stored for several days before analysis, when compared to a solvent mixture without exposure to a milled sample oxidation of the solvents was not observed. In fact the stability of these formed radicals last up to 30 hours in air and up to 3800 hours in vacuum. These radicals are discussed further in the section 1.6.3.

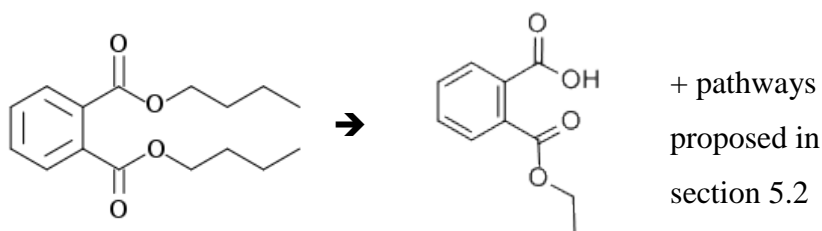
5.3 Esters, phthalates and carboxylic acid

Esters and carboxylic acids share a carboxyl group which is resonance stabilized via both oxygen groups. One ester of interest analysed with symmetric number of carbons on both sides of the ester was benzyl benzoate, which is comprised of 2 benzene rings affixed by the 2 methyls on both ends of the carboxyl group. The aromatic benzenes are then allowed to spin freely when subjected to physically inflicted forces such as high impact forces of the balls experienced during ball milling.

Increased stability would explain the presence of benzyl benzoate at the initial 10th minute interval of milling; further milling results in no traceable intermediates. An expected intermediate after milling would be a toluene derivative, but was not seen which was not unexpected as compounds of similar structure were milled under standard conditions did not yield detectable intermediates. The absence of intermediates could further validate my

speculation about benzene fragmenting into short hydrocarbon chains of C1 – C3 lengths when broken.

Dibutyl phthalate demonstrated longest chain alkyl cleavage at the one of the carboxyl groups whilst the other alkyl chain had 2 carbon unit degradation; each alkyl chain was initially four carbons long making up and is connected to an oxygen group. The degradation of 2 carbon units suggests partial cleavage of the longest chain and could result in total alkyl chain removal during extended periods of milling. Equation 7 below depicts the fore mentioned degradation.



Equation 7 Demonstrates the degradation of dibutyl phthalate into monoethyl phthalate.

Data obtained by GCMS it is clear that esters were more prone to yielding detectable intermediates when subjected to standard milling conditions as opposed to carboxylic acids and single benzene aromatics. Sadly out of the samples analysed esters of symmetry such as ethyl acetate and octadecanote were not included in the data set due to availability and time constraints.

5.4 Linear aliphatic hydrocarbons

Before starting it has to be mentioned that linear organic compounds can twist around resulting in numerous conformations, in fact these conformations can result in folding of the molecule without breaking their bonds (McMurry, 2004). This can result in numerous possibilities for fragmentation and even rearrangements when free radicals attack.

Out of the milled samples, linear aliphatic hydrocarbons yielded the least amounts of intermediates detectable by GCMS. They also produced the least amounts of intermediates under standard conditions detectable by GCMS. Due to the reduced amounts of intermediates being detected by GCMS and persistence of the original organic compound during early to late stages of milling, it would be fair to assume linear aliphatic hydrocarbons as having more resilience to degradation by planetary ball milling.

The resilience noted could be attributed to several characteristics working in synergy firstly the length of the linear hydrocarbons range from C16 to C18, inclusive of sole linear alkanes to carboxylic acids and esters. The length of these hydrocarbons could cause a lubrication effect similar to that seen in motor oil another attribute which could be considered is the extensive coiling these long chain hydrocarbons can undergo. A similar effect was experienced by Happy whom was analysing the destruction of PAH and aliphatic hydrocarbons in soil using ball milling (Magoha, 2004). Coiling and bending during the milling process could be considered as methods linear hydrocarbons try to mitigate the extra energy placed on them, when the carbon carbon bond exceeds the energy tolerance they will break.

The presence of ester groups affect the decomposition of the compounds as indicated by the abundance of intermediates detected by GCMS and therefore can be considered to drastically alter the mechanochemical interactions a compound undergoes, in essence linear aliphatic hydrocarbons persist for longer periods of time. The intermediates formed may resemble ionisation in a mass spectra where bits of a long chain are broken off bit by bit, indicated by the presence of the shorter chained hydrocarbons such as the C16 compound hexadecanol found in both carboxylic acids analysed. The formation of an alcohol under similar free radical conditions was seen by Mihele with naphthalene forming naphthol (Mihele, Wiebe, & Lane, 2002).

The formation of alcohols are debatable they could form instantaneously as intermediates but they could also come about from the storage of the intermediates with the milled quartz which has surface active free radicals which persist for 24 hours (Tristan, 2005), this was validated as a method of oxidation by a trial experiment of the 50:50 acetone hexane solvent kept in the same glass vial for 24 hours resulting in the formation of hexanone. To further confirm that hexanone did not come from the hexane solvent itself, the same jar of hexane acetone solution was analysed using the same ramp program in the GCMS showing the absence of hexanone. When considering the hydrogen radical its origins are most likely from water and therefore would yield hydroxide radicals which could also tack onto intermediates.

5.5 Composition analysis

Composition analysis can assist the understanding of the milled sample matrix. A further reason for doing composition analysis was to account for total carbon found in the system. Earlier trials starting with hydrofluoric acid followed by aqua regia were unsuccessful in fully digesting the milled samples; this was determined by the average mass left after digestion and presence of grey partially water soluble solids indicative of fluorosilicic acid formed from the hydrofluoric acid digestion of quartz (Karen E. Haneke, 2001). When the sequences of acids used were switched and subjected again to hydrofluoric acid, the amount of sample retained decreased indicative of more efficient successful digestion of inorganic substances such as iron and chromium originating from the ball milling equipment as well as silicon dioxides from quartz.

Based solely on the acid sequence used and mass data obtained it suggests the inner core could house small amounts of amorphous carbon $<0.0005\text{g}$, the quartz house is mechanochemically alloyed by the steel of the mill from extensive milling. The results obtained were as expected with majority of the milled samples being silicon derivatives making up $< 77\%$ followed by inorganic metals $<22\%$. This leaves a very small amount of carbon $<2\%$ to be present in a milled sample. When the digested black mass was further subjected to hydrofluoric acid digestion very fine particles of black particles float and stuck to the side of the polypropylene tube which were not seen initially. After repeating the progressive dilution and drying steps, the sample was weighted again and was $<0.0005\text{g}$ lighter for all 3 samples weighted. This may be indicative of amorphous carbon being trapped within the quartz matrix.

Previous research has suggested the presence of iron silicate complexes which may occur on the surface of the quartz and was theorised to act as a site for reactions to occur but XRD work done by Bellingham Bellingham and John Robertson (personal communication) have disproved the formation of iron silicate type of bonds with majority of the of the iron as being metallic (Robertson, 2010; Bellingham Bellingham, 2005). This would indicate accelerated destruction or organics with quartz is attributed to the fragmentation of quartz during milling yielding free radicals, the formation of free radicals of quartz is explained in Interaction of soils in planetary ball milling section. A separate hypothesis based on surface grain chemistry on metallic iron suggests that metallic iron may play a role in volatile formation.

Chapter 6. Conclusion

Intense ball milling of organic compounds in quartz is a complex process where subtle changes in variables such as air, water and soil compositions can all affect the final products. Because of the apparent feedback mechanisms that operate, it is perhaps unrealistic to try and obtain constant reproducible conditions in a “real world” context in which this technology is to be applied. In this study, using a defined set of milling conditions in air, 97% of the organics were totally destroyed in less than 60 minutes of milling time, eventually yielding amorphous carbon and graphite, methane, carbon dioxide and although these were not measured, some hydrogen and water is also expected to be formed. Although the carbon dioxide and methane are greenhouse gases, they are environmentally benign which makes the use of ball milling as a mitigation technology a green and attractive process.

The initial goal of this work was to quantitatively measure the formation of elemental carbon and to identify the ratios of graphitic to amorphous carbon. For practical reasons this proved to be considerably more difficult to do than was expected. Because it is not possible to mill with high concentrations of organic material and because the carbon is formed closely associated with sub-micron sized quartz particles it proved extremely difficult to quantitatively separate. While it has been possible to measure the formation of carbon and to show that it is a mixture of both graphitic and amorphous carbon, the quantitation of these results has been unsatisfactory.

A previously unexpected pathway in the conversion of carbon dioxide to methane and traces of ethane, propane and hexane. This was an unexpected and an almost counter intuitive result. This appears to be formed in an environment which is rich in hydrogen radicals from either the organic material being milled, or traces of moisture in the reaction. These radicals react with carbon dioxide to give methane, or at least methyl radicals which by hydrogen addition from the matrix or from other organic molecules can form methane or elaborate to larger hydrocarbons and presumably water. This needs more investigation, the formation/destruction pathways are clearly interconnected in a constantly changing equilibrium which is difficult to investigate. This observation indicates an initially strong

drive for reduction as intermediates are forming. Methane production from carbon dioxide can at times be remarkably high.

The measurement of methane and carbon dioxide for a range of compounds showed, not surprisingly, some variation in rate and given what has been found about the carbon dioxide/methane equilibrium the details of this gas formation could be expected to be quite variable and difficult to compare from run to run.

Trace amounts of nitrous oxide were detected by FTIR during the milling of xanthine. The significance of nitrous oxide and reasons for the low amounts were not investigated. Interestingly, no nitrogen dioxide or nitric oxide or ammonia was detected, indicating the formation of nitrous oxide may have a different pathway of formation to that of carbon monoxide and carbon dioxide. Imidazole was also milled in earlier experiments but the presence of nitrogen oxides was not investigated.

Nitrogen containing rings such as xanthine and imidazole also delayed the formation of methane from carbon dioxide as detected by FTIR and GC. The exact reasons and mechanisms for this are not known. Milling of other organic compounds in nitrogen atmospheres only increased the rate of methane formation but showed no signs of nitrogen oxides. When the milling of xanthine was compared to that of naphthalene, it was observed that the rate of methane production was significantly slower and higher levels of carbon dioxide were found in the early stages of the reaction

A practical consequence of this variability in gas formation is that necessary pressure venting of full scale mills and the formation of flammable gases needs to be taken into account when milling contaminated soils.

One of the important goals of this thesis was to examine a wide range of compounds with the goal of finding any compounds, or classes of compounds that were particularly resistant to mechanochemical destruction using “standard” milling conditions. The only compounds that seemed to show some slowness to react were long chain fatty acids. This behaviour has been seen before in long chain hydrocarbons. Whether this is a chemical feature or possibly some mechanical artefact such as ball lubrication or as a coating inducer is uncertain but it does raise a small warning about the expected milling times if these sorts of compounds are involved in full scale milling.

Ball milling is a very complicated process where fluidised clouds of solids and gases are interaction in what is now know to be a complex set of equilibria. The number of potential pathways free radicals can follow, a diversity of organic materials and the effects of moisture and soil types suggest that it is not possible to develop a simple model for the reactions of organic compounds during the mechanochemical destruction process.

Chapter 7. Recommendation

The standard milling conditions are intense, in most cases destruction of the original compound was complete at 10 minutes but more research needs to be done at lower milling speeds therefore reducing the intensity of the milling. This will help us further understand the pathways basic structures undergo.

This research has shown an unknown equilibrium between carbon dioxide and methane. This new pathway needs more investigation as it may explain some of the lack of reproducibility observed in many experiments.

The increased resistance of molecules containing linear hydrocarbon structures needs more investigation.

The total carbon values were unsatisfactory. Either a new method or the use of a Teflon bomb and laboratory microwave may address the problems faced.

As the milling progresses the formation of carbon allotropes could be observed throughout milling. It is possible that this may have an inverse relationship to the amount of methane formed. This has yet to be investigated and would help us understand this end part of the process.

Gas leaking was a continuing problem throughout the work. A specially designed jar with sampling ports and better seals is necessary to give reliable results for gas generation.

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