

Reactive Milling of Organic Compounds

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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 nor material which to a substantial extent has been accepted for the qualification of any other degree or diploma of a university or other institution of higher learning, except where due acknowledgment is made in the acknowledgements.’

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Abstract

Persistent organic pollutants are a well-known threat to the environment. Substances such as polycyclic aromatic hydrocarbons and chlorinated organic compounds in contaminated soil and groundwater can have severe and long-lasting effects on health in animals and humans. There is an urgent need for the development of safe technologies for their effective removal.

Originally developed for mineral processing, mechanical treatment by ball milling is an extremely versatile technique for the degradation of toxic compounds. Reactive milling can rapidly destroy organic compounds without producing hazardous wastes. Complete breakdown of the organic molecules is achieved after relatively short milling times. Successful tests were conducted on polychlorobiphenyls (PCBs), DDT, DDD, DDE, Dieldrin and hexachlorobenzene with a conversion yield in the of greater than 99% (Hall et al., 1996; Monagheddu et al., 2000; Zhang et al., 2001; Zhang et al., 2002; Tanaka and Zhang, 2003; Pizzigallo et al., 2004; Nomura et al., 2005; Bellingham, 2006).

In this study reactive ball milling was used to investigate the destruction of two classes of persistent organic pollutants environmental contaminants. The compounds studied are either known environmental pollutants or simple analogues. These were chosen as being representative of pollutants to investigate the pathway using ball milling destruction and in most cases were relatively small molecules so that the intermediates could be more easily identified.

The first class of compounds was polycyclic aromatic compounds. Some smaller members of this class such as naphthalene, anthracene were investigated. The second class of compounds were some analogues of environmentally hazardous hydroxylated and halogenated compounds such as chloronaphthalene, bromonaphthalene, 1-naphthol, 2-naphthol and pentachlorophenol under reactive milling using GCMS analysis of the degradation pathway. Destruction efficiencies greater than 99% have been achieved for a number of organic compounds. Several different intermediates have been identified during the milling degradation.

There was also some evidence from this study that halogens could be transferred between compounds during milling. The final products of the milling destruction of these compounds are an amorphous carbon residue and inorganic chloride or bromides. It was proposed that large amounts of halogens could be found however the results showed that small amounts detected. At early stages of milling a number of intermediate breakdown products were detected which were destroyed on extended milling.

The core objective of this research was to clarify the reaction mechanisms pathways used of more complex polycyclic aromatic hydrocarbons and aromatic organ halogen compounds. This study is a part of a long-term research project on the destruction of toxic organic compounds by reactive milling.

Chapter 1

1. Introduction

1.1 Environmental Pollutants Background

New Zealand's tourist advertising promotes a pure natural environment that is so attractive to thousands of visitors from other countries each year. With open spaces filled with rugged landscapes, beautiful beaches, often spectacular geothermal and volcanic activity, a temperate climate and fascinating animal and plant life, it is no surprise that New Zealand is promoted as a clean green paradise. And the great benefit of New Zealand's economy is there are farming, horticulture and forestry.

The land is susceptible to the accumulation of toxic contaminants. Deposition of contaminants on particles settling from the air and in rainwater act as an ongoing source of many contaminants. In addition many toxic chemicals are applied to the land during normal agricultural practices. Water seeping through soils has the capacity to leach chemicals deeper into the soil and ground water. This movement of contaminants through soil is countered by contaminants to adhere to soil particles and so remain stationary. This balance between these leaching and absorption phenomena determines the rate of movement of a chemical through the soil (Lentz and Kennedy, 1998).

Soil contains many species and large numbers of bacteria, which are essential to the health, and function of the soil. Some of these bacteria are able to breakdown some contaminants and therefore reduce levels of soil pollution. The presence of contaminants in soils can lead to transfer of these chemicals into vegetation and animals. As many of these products are human food items there exists the possibility of exposure of humans as well as wildlife (Lentz and Kennedy, 1998).

The key causes of soil contamination in New Zealand fall into four groups: 1) Agricultural use of pesticides and fertilisers. 2) Roadside deposition of contaminants originating from motor vehicles. 3) Atmospheric deposition of contaminants from

short range (e.g., spray drift) or long-range atmospheric transport. 4) Local contamination caused by specific industrial activity (Lentz and Kennedy, 1998).

Although some pesticides and industrial wastes have undergone extensive toxicological testing, it is unclear whether this testing has been adequate to detect the potential for these chemicals and pesticides to disrupt metabolic pathways. There is widespread agreement that the development of investigating and testing programs is appropriate (Lentz and Kennedy, 1998). Primary category toxic contaminants in New Zealand are as following Metals (arsenic, cadmium, copper, chromium, lead, mercury, zinc), Polycyclic Aromatic Hydrocarbons (PAHs), Polychlorinated Biphenyls (Specific priority congeners), Organochlorine Pesticides (DDT, Dieldrin, Chlordane), Volatile Aromatic Hydrocarbons (Benzene, Ethylbenzene, Toluene, Xylene), Volatile Chlorinated Aromatics (Chlorobenzene) Chlorophenols (Pentachlorophenol), Oxygenated Compounds (2,3,7,8-Dioxin and Furan congeners), Miscellaneous Compounds (Cyanide, Nitrate, Ammonia) (Lentz and Kennedy, 1998).

1.1.1 Chlorinated Compounds

Persistent organic pollutants (POPs) are a set of chemicals that are toxic, persist in the environment for long periods of time, and they move up through the food chain. POPs have adverse effects on human health and animals, such as cancer, damage to the nervous system, reproductive disorders, and disruption of the immune system. Because they spread worldwide via the atmosphere, oceans, and other pathways, POPs released in one part of the world can travel to regions far from their source of origin. POPs contain the following group: 1) Certain insecticides, such as DDT and chlordane, which were once commonly used to control pests in agriculture and in building materials; 2) PCBs, which were used in hundreds of commercial applications, such as in electrical, heat transfer oils, and in hydraulic equipment, plastics, and rubber products; 3) Certain chemical byproducts, such as dioxins and furans, which are produced unintentionally from most forms of combustion, including municipal and medical waste incinerators, open burning of trash, and industrial processes (Vallack et al., 1998; Guzzella et al., 2005; Nomura et al., 2005).

1.1.1.1 Dieldrin

Dieldrin is the common set of isomers that were used as insecticides (Registry, 2002). It is chemical that is made in the laboratory and does not occur naturally in the environment. Dieldrin slowly evaporates in the air. Dieldrin can enter the environment from accidental spills or leaks from storage containers at waste sites. In the past, dieldrin entered the environment when farmers used these compounds to kill pests on crops and when exterminators used it to kill termites. Dieldrin is still present in the environment from these past uses. Dieldrin sticks to soil and may stay there unchanged for many years. Most dieldrin in the environment attaches to soil and to sediments at the bottoms of lakes, ponds, and streams. Dieldrin can travel large distances by attaching to dust particles. Plants can take up dieldrin from the soil and store it in their leaves and roots. Fish or animals that eat dieldrin contaminated materials store a large amount of the dieldrin in their fat. Residents who live near hazardous waste sites that contain dieldrin may have greater exposure as a result of contact with contaminated environmental media (Registry, 2002).

1.1.1.2 DDT (1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane)

DDT (1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane) is a pesticide that was once widely used to control insects on agricultural crops and insects that carry diseases like malaria and typhus, but is now used in only a few countries to control malaria (Registry, 2002). In 1972, DDT was banned in many parts of the world, except for use in controlling emergency public health problems (Registry, 2002). The release of DDT into the environment occurs primarily through spraying applications onto agricultural crops, forestlands, other nonagricultural land, and homes (for the control of disease-bearing vectors). Exposures in the home occurred through the use of DDT as a mothproofing agent, to control lice and, in some parts of the world, to control mosquitoes and other disease-bearing vectors. Both DDD and DDE are degradation products of DDT. DDD was also used as an insecticide, but to a much lesser extent than DDT. DDE is the result of thermal decomposition of DDT and has not commercial use (Hall et al., 1996; Registry, 2002).

1.1.1.3 Chlorodane

Chlordane was used as a pesticide in the United States from 1948 to 1988 (Registry, 1994). Chlordane is not a single chemical, but is a mixture of many related chemicals, of which about 10 are major components. Some of the major components are trans-chlordane, cis-chlordane, β -chlordane, heptachlor, and trans-nonachlor (Registry, 1994).

Chlordane is known to stay in the environment for many years and is still found in food, air, water, and soil. In soil, it attaches strongly to particles in the upper layers of soil and is unlikely to enter into groundwater. Most chlordane remains in the soil for many years (Registry, 1994). However, it is sufficiently long lived that it may travel long distances and be deposited on land or in water far from its source. Chlordane may be found in fish and shellfish caught in chlordane contaminated waters. People receive high exposure to chlordane from living in homes that were treated with chlordane for termites (Registry, 1994).

1.1.1.4 Polychlorobiphenyls (PCBs)

PCBs are a group of synthetic organic chemicals that can cause a number of different harmful effects. There are no known natural sources of PCBs in the environment (Hasegawa et al., 1995; Registry, 2000; Yoshiharumitoma et al., 2004; Guzzella et al., 2005). PCBs enter the environment as mixtures containing a variety of individual chlorinated biphenyl components, known as congeners, as well as impurities (Ikoma et al., 2001). PCBs also entered the environment from accidental spills and leaks during the transport of the chemicals, or from leaks or fires in transformers, capacitors, or other products containing PCBs. PCBs may be released into the environment by the burning of some wastes in municipal and industrial incinerators. PCBs remain in the environment for very long periods of time. PCBs are present as solid particles or as a vapor in the atmosphere. They will eventually return to land and water by settling as dust or in rain and snow. They do not break down in soil and may stay in the soil for months or years; generally, the more chlorine atoms that the PCBs contain, the more slowly they break down. PCBs accumulate in fish and marine mammals (such as seals

and whales) reaching levels that may be many thousands of times higher than in water. PCBs exposure to humans may also cause irritation of the nose and lungs, gastrointestinal discomfort, changes in the blood and liver, and depression and fatigue (Registry, 2000)

1.1.1.5 Chlorinated Dibenzo-*p*-Dioxin (CDDs)

Chlorinated dibenzo-*p*-dioxins (CDDs) are a family of 75 different compounds commonly referred to as polychlorinated dioxins. These compounds have varying harmful effects (Registry, 1998). CDDs enter the environment as mixtures containing a variety of individual components and impurities (Nomura et al., 2005). CDDs are naturally produced from the incomplete combustion of organic material by forest fires or volcanic activity. They are unintentionally produced by industrial, municipal, and domestic incineration and combustion processes. Currently, it is believed that CDD emissions associated with human incineration and combustion activities are the predominant environmental source (Registry, 1998; Nomura et al., 2005). Because CDDs remain in the environment for a long time, contamination from past pesticide and herbicide use may still be of concern. CDDs are released in wastewaters from pulp and paper mills that use chlorine or chlorine containing chemicals in the bleaching process (Registry, 1998; Borowski et al., 2001; Nomura et al., 2005). The movement of chemical waste containing CDDs through soil has resulted in contamination of groundwater. Soil erosion and surface runoff can also transport CDDs into surface waters. Most of the CDDs found on the parts of plants above the ground probably come from air and dust and/or previous use of CDD-containing pesticides or herbicides (Registry, 1998).

1.1.2 Polycyclic Aromatic Hydrocarbons (PAHs)

PAHs are a group of chemicals that are formed during the incomplete burning of coal, oil, gas, wood, garbage, or other organic substances, such as tobacco and charbroiled meat (Registry, 1995). There are more than 100 different PAHs. PAHs, such as naphthalene, anthracene, benzo[*a*]pyrene (BaP), phenanthrene and related polycyclic

aromatic hydrocarbons are ubiquitous environmental contaminants (Ake et al., 2003). PAHs generally occur as complex mixtures and not as single compounds. They are found throughout the environment in the air, water, and soil (Registry, 1995).

PAHs have been commonly used in various formulations of wood preservatives. These agents are applied to wood products using either spraying, dip tank, or pressure treatment techniques (Registry, 1995; Fang and Findlay, 1996; Theurich et al., 1997; Ake et al., 2003; Aracil et al., 2005). Polycyclic aromatic hydrocarbons (PAHs) in contaminated soil and groundwater can have severe and long-lasting effects on health. The evidence that these contaminants can cause adverse health effects in animals and humans is rapidly expanding. The frequent and widespread occurrence of PAHs in groundwater makes appropriate intervention strategies for their remediation highly desirable. PAHs commonly enter the environment as incomplete combustion byproducts of carbonaceous materials and may persist in groundwater, surface water, soil, air and foodstuffs. The PAHs are a major component of liquid creosote and are suspected carcinogens and immune altering agents (Ake et al., 2003). In addition, PAHs are well known hazardous by-products in the coal and petroleum industry. The effluent water of many petrochemical industries, particularly of cracking plants, very often contains a high load of these compounds, which are hardly biodegradable (Theurich et al., 1997).

1.1.3 Pentachlorophenol (PCP)

Pentachlorophenol (PCP), is highly chlorinated phenol derivatives, introduced into the environment through its use as a disinfectant, herbicide, insecticide, and fungicides (Ake et al., 2003; Pizzigallo et al., 2004). Pentachlorophenol is a synthetic substance, and does not occur naturally in the environment.

Pentachlorophenol is released to the air by evaporation from treated wood surfaces and factory waste disposal. It enters surface water and groundwater from factories, wood treatment facilities, and hazardous waste sites. It also enters the soil as a result of spills, disposal at hazardous waste sites, and its use as a pesticide. Movement of pentachlorophenol in soils depends on the soil's acidity. The compound can be present in fish or other species used for food. In air, soil, and surface water,

pentachlorophenol lasts for hours to days. The compound is broken down in soil and surface water by microorganisms, and in air and surface water by sunlight, to other compounds, some of which may be harmful to humans (Registry, 2001). Because of the intensity of this toxicity, attention has been focused on its presence in and removal from the environment. PCP is mainly used as a wood preservative for power line poles, cross arms, and fence posts, and this use leads to soil contamination (Fukushima and Tatsumi, 2001).

1.2 Methods of Destroying Environmental Contaminations

Hazardous polyhalogenated pollutants like PAHs, PCBs, DDT, dioxins, hexachlorocyclohexane (Lindane, HCH), pentachlorophenol (PCP), and like chlorinated compounds also threaten the environment worldwide, e.g. soils and drinking water resources, and represent especially serious problems mankind is faced with all over the world (Birke, 2002). Chloroaromatic pesticides are often used as preservatives, antimicrobials, herbicides, insecticides, and disinfectants. These compounds lead to environmental problems they are toxic and persistent. Their degradation is possible through chemical, thermal and biological processes. Both chemical and thermal degradations are difficult to apply to the disposal of these contaminants. Biological degradation and naturally occurring hydrolysis require long periods (Galadi et al., 1995).

There is a growing interest and necessity to find efficient and economic methods to treat man-made pollutants, of which the chlorinated compounds. Several methods such as incineration, thermal oxidation, and photodehalogenation mentioned below have been proposed for decomposing chlorinated and halogen compounds (Mio et al., 2002; Ake et al., 2003; Tanaka and Zhang, 2003; Tanaka et al., 2003; Inoue et al., 2004; Matsunaga and Yasuhara, 2005).

1.2.1 Incineration

Incineration is different from other thermal technologies in that it oxidizes bulk quantities of waste that may be in liquid and solid phase. Incinerators may release toxic chemicals from their stacks, including heavy metals, partly burned organic material such as polyvinyl chloride (PVC), herbicide residues, and other organic chemicals, including PAHs, and furans. Also, incineration often leads to the formation of more toxic oxygenated derivatives (Galadi et al., 1995; Monagheddu et al., 2000). There is an interest in the development of decomposition technologies for such chlorinated materials and wastes but it leads to problems with safety, reliability, operational costs (Cao et al., 1999).

Incineration is the most widely used technology for the destruction of polychloroaromatics such as PCBs (Galadi et al., 1995; Monagheddu et al., 2000). Incineration treats only the vapour phase of contaminants. High temperatures, 870 to 1,200 °C (1,400 to 2,200 °F), are used to volatilise and combust halogenated and other organics in hazardous wastes. The incineration of chlorinated organic compounds or halogen-containing substances has some potential to form hazardous compounds such as harmful gases and dioxins.

Combustion, which is one of applications of incineration, has been carried out at waste disposal facilities for a long time, but it is now prohibited in many parts of the world because of the emission of harmful substances, such as a group of dioxins and HCl gas. Landfills require a large amount of land area, which is not always available (Fukushima and Tatsumi, 2001; Ksandopulo et al., 2002; Inoue et al., 2004; Pizzigallo et al., 2004). Recently several disposal methods such as the blast furnace method and the liquefying method have been proposed. These methods are very effective but employ a dechlorination process that requires high-temperature facilities (Ksandopulo et al., 2002; Mio et al., 2002; Yoshiharumitoma et al., 2004). Combustion operations of such wastes without controlling the temperature have been facing strong public opposition at present because of the possible formation of toxic substances such as dioxins like polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) and PAHs. This has given more importance to the development of other safer and more reliable methods for disposing of such products (Ksandopulo et al., 2002; Tanaka et al., 2003).

1.2.2 Thermal Oxidation

Thermal oxidation, is a technique that uses extremely high temperatures (usually between 700-1300 °C) to promote the growth rate of oxide layers (Oxidation, 2005). Thermal oxidation is accomplished using an oxidation furnace (or diffusion furnace), which provides the heat needed to raise the oxidizing ambient temperature. A furnace typically consists of: 1) a cabinet; 2) a heating system; 3) a temperature measurement and control system; 4) fused quartz process tubes; 5) a system for moving process gases into and out of the process tubes; and 6) a loading station used for loading (or

unloading) wafers into (or from) the process tubes (Matsunaga and Yasuhara, 2005; Oxidation, 2005)

Chlorinated hydrocarbons represent the major toxic components of hazardous wastes. The thermal destruction of these toxic components via high temperature oxidation processes can release gas effluents containing stable toxic by-products with adverse effects on the human health and the environment. So it is of great importance to identify all intermediates and determining parameters involved in the oxidation processes in order to promote their destruction and reduce harmful effluents (Fadli et al., 1999).

1.2.3 Photodehalogenation

Photodehalogenation under sunlight exposure plays a key role in environmental degradation of haloaromatic pesticides. The photochemistry of these halides as a method for their destruction has been reviewed (Galadi et al., 1995; Theurich et al., 1997). In solvents able to donate a hydrogen atom, reductive dehalogenation is observed while in aromatics, direct photolysis leads to arylation. The UV photooxidation of some chloroaromatics was performed in water (Theurich et al., 1997). It showed that the rates of photodegradation were greatly increased by addition of hydrogen peroxide. Photodechlorination enhanced by an electron-transfer mechanism was also proposed (Galadi et al., 1995; Theurich et al., 1997). In any way, this process is unsatisfactory in that the light has to be absorbed by the aromatic pesticide to ensue photodecomposition. If, because of a poor solubility or at the end of its consumption, the pesticide would be present in low concentration little light would be absorbed (Galadi et al., 1995).

1.2.4 Summary

In conclusion, the above methods mentioned in Section 1.2 for degradation of organic compounds have been proposed, all these methods can be effective; however, they need highly controlled conditions in operation as well as facilities with devices and chemical reagents, leading to high cost. For this reason, there remains the need to

develop economical methods for the disposal and recycling of such wastes (Galadi et al., 1995; Theurich et al., 1997; Ksandopulo et al., 2002; Tanaka et al., 2003). Compared with these, a mechanochemical method offers both the advantages of simple operation and large capacity of material including organic chlorinated compounds and toxic other organic substances (Tanaka et al., 2005).

1.3 Mechanochemistry

1.3.1 Introduction of Mechanochemistry

The earliest application of a mechanochemical reaction was when man used flints to make fire in prehistoric times (Gilman, 1996; Boldyrev and Tkacova, 2000). Chemical reactions can be triggered by application of mechanical energy such as by friction or impact. An example is the corrosion of iron. It was found in the 18th century that the dissolution of metal is greatly accelerated when being subjected to friction on its surface (Gilman, 1996). The chemistry occurring at surfaces under impact has been investigated for a long time and has found numerous practical applications for more than 100 years, and it is still frequently used in many fields of human activity (Birke, 2002).

Such phenomena are commonly included by the two terms "mechanochemistry" and/or "tribochemistry". It has been shown recently that mechano- and/or tribochemical reactions can be utilized to destroy polyhalogenated pollutants (Mulas et al., 1997; Birke et al., 1998; Gock et al., 2001; Ikoma et al., 2001). The original aim of the application of mechanical energy on solids was their disintegration and the production of surface rich powders (Steinike and Tkacova, 2000).

Mechanochemistry is a branch of chemistry dealing with the chemical and physico-chemical changes of substances in all states of aggregation (Fernandez-Bertran, 1999). Mechanical influence plays an essential role in chemical reactions involving at least one solid. Solid-state mechanochemistry is concerned either with the study of chemical reactions, which occur under the action of mechanical forces, or with the study of reactions involving solids, which, after unloading, maintain certain properties gained during preliminary mechanical treatment (Fernandez-Bertran, 1999; Birke, 2002). Of most chemical interest have been some observations about mechanical treatment of polymers, wet reactions of lignin model compounds and recent reports concerning the "destruction" of toxic chlorinated compounds by mechanical processes (Field et al., 1997; Ikoma et al., 2001).

Tribochemistry covers chemical and physico-chemical changes of solids due to the influence of mechanical energy (Birke, 2002; Hsu et al., 2002), and while it not always used that way, generally refers to the chemistry that occurs between the lubricant (and/or environment) with the rubbing surfaces under boundary lubrication conditions (Hsu et al., 2002). This includes specific reactions that occur only under rubbing conditions and reactions that would occur independently under the temperatures and pressures in the contact. The reactions such as oxidation, thermal degradation, catalysis and polymerization that would occur independently can be defined as the contact chemistry (Hsu et al., 2002; Birke et al., 2004).

The rapid development of the investigations in mechanochemistry and mechanical activation have high lighted mechanochemical reactors for the mechanical treatment of solids and numerous evaluation of mechanochemical processes that occur (Urakaev and Boldyrev, 2000). Mechanochemical processing is the term applied to powder processing in which chemical reactions and phase transformations take place during milling due to the application of mechanical energy (Birke, 2002; Delogu et al., 2004; Suryanarayana, 2004). The mechanochemical reactions could result in the sythesis of novel materials, reduction/oxidation processes, exchange reactions, decomposition of compounds, and phase transformations in both organic and inorganic solids (Fernandez-Bertran, 1999; Boldyrev and Tkacova, 2000). The materials produced in this way have already found applications in areas such as hydrogen storage materials, gas absorbers, fertilizers, pharmacy, synthesis, preparation of catalyst, manufacture of pigments, and this technique has become a large effort in the general field of mechanical alloying and milling (Suryanarayana, 2004). In accordance with the above trend, mechanochemistry of dispersed solids has made an enormous contribution to the development of high-performance, and low-cost materials and to development of novel technologies (Boldyrev and Tkacova, 2000).

Mechanochemical treatments of soils contaminated with organochlorine molecules were conducted by grinding using a ball mill with different dechlorinating reagents (Mulas et al., 1997; Mio et al., 2002). The treatment provokes a solid-state transformation at the mineral surface without any deformation of the structure. The solid contact of the modified surface seems to induce the production of radicals, which are very active in subsequent oxidative coupling reactions. Thus, the

"mechanochemical" procedure could furnish a tool to start the reaction without any interference of organic solvents (Mulas et al., 1997; Mio et al., 2002).

1.3.1.1 Mechanochemical Dehalogenation

Mechanochemical dehalogenation is a novel method for the destruction of polyhalogenated compounds. Contaminated materials as well as highly concentrated or pure contaminants and their mixtures are treatable reactively low temperatures in a short time, regardless of their state (Birke, 2002). For instance, PCBs in contaminated soils, filter dusts, transformer oils, or as pure substances are dechlorinated to harmless chloride and their parent hydrocarbon biphenyl by using magnesium (Registry, 2000; Birke, 2002; Yoshiharumitoma et al., 2004; Matsunaga and Yasuhara, 2005; Matsunaga and Yasuhara, 2005). Recently, it was shown that polyhalogenated pollutants (pesticides such as hexachlorocyclohexane (HCH, lindane) or 1,1,1-trichloro-2,2-bis(4-chlorophenyl) ethane (DDT) as well as chemical agents can be well destroyed by mechanochemical reactions (Hall et al., 1996; Theurich et al., 1997; Birke et al., 2004).

In co-operation with several European companies over the last 3 years, projects using mechanochemical dehalogenation technology has been applied successfully to the decontamination of contaminated soils and contaminated oils (Birke, 2002). It also benefits from low maintenance costs (Birke, 2002). In addition, it has revealed both effectiveness and interesting economical features for the destruction of polyhalogenated pollutants in a wide range of contaminated materials without producing harmful by product.

It has been reported that the dehalogenation induced by radical and photo catalysis is deeply affected by the state of the surfaces of oxides. Co-absorbed water, for example, strongly diminishes the degradation of the chlorinated compounds on alumina (Birke, 2001). It is expected that such a water effect also occurs in the mechanochemical treatment (Monagheddu et al., 2000; Tanaka et al., 2005). On the other hand, by utilizing alkali or alkali earth metals like magnesium or sodium as dehalogenation reagents in mechanochemical conditions using vibratory mills, these toxic substances

are efficiently eliminated directly inside a contaminated complex material at room temperature and in a short time (Ikoma et al., 2001; Zhang et al., 2001). Moreover, detoxified materials like transformer oils can be readily recycled. No harmful emissions to the environment have to be expected (Birke et al., 2004).

However, few authors provided information on the mechanochemical technique applied to oxidative reactions. Some researches (Nasser et al., 2000) successfully tested the degradation of herbicides such as 2,4-D using very gentle grinding of the organic molecules and manganese dioxide (Nasser et al., 2000). The mechanism is thought to be the grinding of a reactive mineral in the presence of adsorbed organic molecules causes a surface alteration of the mineral structure producing structural defects. These defects produce a chemical activation, which promotes the break-up of chemical bonds and consequently the degradation of chlorinated compounds. Therefore, mechanochemical treatments provide a way to initiate a reaction between organic compounds and minerals (Pizzigallo et al., 2004).

1.3.1.2 Mechanochemical Dechlorination

The mechanochemical dechlorination has a high potential to dispose of PVC wastes at any desired locations with flexible operation due to its use of a portable facility composed of a mill and a washing tank with a filter. Mechanochemical dechlorination proceeds as the grinding progresses and is improved with an increase in both the mill speed and the number of balls in the mill (Mio et al., 2002). The following mechanism has been proposed for the mechanochemical dechlorination. First, the mechanical stressing induces the electron transfer from O^{2-} sites on the surfaces of the CaO particle to the organic compounds, the organic anion radicals then undergo the effective self-dissociation of the chlorine-carbon bond (Ikoma et al., 2001; Tanaka and Zhang, 2003). Recently, Mio et al. has used the mechanochemical method for dechlorinating PVC by grinding with oxides and hydroxides of Mg, Al and La using a planetary ball mill followed by washing with water. Tanaka also showed that other factors such as moisture and quartz addition also affect the dechlorinating process and investigation ways to improve the mechanochemical process toward the treatment of wastes containing chlorinated organics (Tanaka et al., 2005).

Zhang et al have proposed a method for dechlorinating such halogenated organic compounds: using a mechanochemical method based on grinding with an inorganic material such as CaO. The decomposition is induced through the solid-state reaction between the organic and inorganic compounds, and when the chlorinated organic compound is, for example, ground with CaO, the organically chlorine is board transformed into inorganic chloride (Tanaka and Zhang, 2003). An alternative method has been proposed for decomposing organic polymer wastes containing halogens such as F, Cl, and Br by means of mechanochemical treatment. Also, a mechanochemical milling with alkaline earth metals (Mg, Ca) (Mulas et al., 1997), or their oxides used as reactive substrates has attracted attention as a practically simple and useful process for degrading chlorinated organic compounds (Zhang et al., 2000; Ikoma et al., 2001).

1.3.1.3 Mechanochemical Degradation

Mechanochemical degradation has recently attracted attention in destruction of organo-chlorinated molecules (Mulas et al., 1997; Nasser et al., 2000; Mio et al., 2002). The toxicity of polyhalogenated compounds is due to the so-called "organic halogen" specifically bound to these compounds. Therefore, these substances can be detoxified by stripping off the "organic halogen" entirely via a chemical route. As the source of the high toxicity of polyhalogenated hydrocarbons, the organically bound halogen is removed from the molecule entirely, being transformed into inorganic chloride (Birke, 2002).

The process of mechanochemical degradation benefits from several features: It can be easily performed using ball mills that are readily available in different sizes and designs (treatment of materials up to several tons is possible). Mechanochemical degradation has been utilized in inorganic and organic synthesis, the preparation of alloys, ceramics, and nanocomposites, and the activation and disordering of alloys and compounds. If the reaction between the reactant powders is highly exothermic, milling can initiate a self-propagating thermal reaction after some activation time (Takacs and Sepelak, 2004).

1.3.1.4 Mechanochemical Polymerization

Because it may occur alongside destructive processes polymerization is also important. Mechanochemical polymerization is one of the most promising processes for the production of composite materials of inorganic compound and organic polymers, this process has promise as an effective way to form a chemical bond between the two (Boldyrev and Tkacova, 2000). The mechanochemical polymerizations initiated by the grinding of inorganic compounds such as metallic oxides and ionic salts have been studied by a few (Cao et al., 1999; Zhang et al., 2001; Mofa et al., 2002). However, in most of their studies the mechanochemical phenomenon was only reported qualitatively. The relationships between polymerization and grinding have hardly been investigated (Hasegawa et al., 1995).

The mechanical properties of the composite materials, which are composed of inorganic powder and organic polymers, depend greatly on the dispersibility of the inorganic powder in the polymer matrix and the interfacial interaction between the powder surface and the polymer molecules. The state of the fine powder surface is very important to improve the dispersibility and interaction. To effectively utilize mechanical energy in the grinding operations and to modify the surface property of fine inorganic powders (Hasegawa et al., 2002). The mechanical strength of the composite materials depends greatly on the interfacial interaction between the inorganic compound and organic polymer, and is improved if a chemical bond between them can be formed (Hasegawa et al., 1995).

In exception, a new mechanochemical treatment by high-energy impact is ball milling (BM) of powder mixtures composed by chloro-organics and reactive substrates can lead to a complete degradation of the organic compounds (Cao et al., 1999). Ca and Mg and their oxides were employed as reductive agents under either inert or hydrogen atmospheres. The specific use of calcium hydride as a substrate was found to more effective in determining highly selective and rapid dechlorination results (Cao et al., 1999).

1.4 Ball Milling

The ball milling methodology is highly attractive since it allows the process to be carried out in a confined and strictly controlled environment (Cao et al., 1999). Due to its commercial usefulness and to the unusual physical phenomena involved, ball milling is an interest from both the technological and the scientific point of view. Applications currently range from materials science and advanced technology to traditional mineral processing and alternative wastes degradation (Mulas et al., 1997; Delogu et al., 2003). Ball milling is one of the promising techniques to not only improve hydrogenation properties of hydrogen absorbing alloys, but also to form hydrides under various atmospheres (Hanada et al., 2004).

Ball milling is very versatile (Delogu et al., 2000). Since the mid 1980s ball milling has been widely applied to transform metals and inorganic compounds in order to obtain materials with good mechanical properties. This technique has been used for mechanical alloying of a mixture of elemental powders and mechanical milling of intermetallic compounds (Font et al., 1997). Solid solutions, amorphous phases, and nanocrystalline structures can be obtained. In contrast to the many studies done concerning transition metals and inorganic compounds, ball milling experiments on organic materials are scarce. For the here given application in the field of mechanochemistry, most important is the complete recovery of the milling product continuously or from various batches in a semi-continuous route without a significant contamination level from the milling tools which will be important for synthesis and industrial production (Kaupp et al., 2003).

The main advantages of ball milling in comparison with the traditional procedures are: Firstly, decrease in the number of stages thus a simplification of the process; Secondly, ecological safety of the method, resulting from excluding the operations that involve the use of solvents, intermediate fusion, etc.; Furthermore, ball milling requires a low energy input only. Because of the strikingly reaction conditions, toxic compounds can be converted to defined products (Birke et al., 2004). Finally, the possibility of obtaining a product in the metastable state, which is difficult to obtain

using traditional technological methods. An increase in the number of publications provides evidence for the growth of attempts to apply the results obtained in the laboratory to technology (Cocco et al., 1995; Font et al., 1997; Takacs, 1998; Boldyrev and Tkacova, 2000; Kaupp et al., 2003; Kaupp et al., 2004).

1.4.1 High Energy Milling

High-energy milling techniques, currently called mechanical alloying (MA) and mechanical milling (MM) have been applied to a wide range of metallic and inorganic systems to produce a variety of non-equilibrium phases such as amorphous alloys, nanocrystalline structures, composite materials as well as new compounds. It can be performed at the kg scale and can be scaled up to technical importance. It has been also shown that combustive syntheses and self-propagating reactions can occur in highly exothermic systems during the milling (Delogu et al., 2000; Delogu et al., 2003). Additionally High-energy milling has already been found to be very effective for the production of metal-flakes for paint-pigments, electrical conductive pastes, anti-corrosives and many others (Kaupp et al., 2004).

1.4.1.1 Mechanical Alloying

Mechanical alloying is normally a dry, high-energy ball milling technique that has been applied in the production of a variety of commercially useful and scientifically interesting materials (Delogu et al., 2000; Suryanarayana, 2004). Mechanical alloying is a scalable experimental technique, which is broadly used for the preparation and modification of metals, hydrides, and other inorganic solids (Kaupp et al., 2003). Mechanical alloying has been described as a process where powder particles are treated by repeated deformation, fracture and cold welding by highly energetic collisions of grinding media in a milling process (Cocco et al., 1995; Kaupp et al., 2004). This definition may be amplified in that Mechanical Alloying stands out by the transfer of high-levelled energy into powder and so mechanical alloying often leads to material transformation of the crystalline structure by solid-state reactions (Kaupp et al., 2003).

1.4.1.2 Mechanical Milling

Mechanical milling is one of the most common operations in the processing of solids. It has been defined as a process when powders of uniform composition, such as pure metals, intermetallics, or prealloyed powders, and milling in a high-energy ball milling, and material transfer are not required for homogenisation (Takacs, 1998; Suryanarayana, 2004). This technique could represent an important alternative to more oxidative processes in removing organochlorine compounds from heavily contaminated soils (Pizzigallo et al., 2004). Mechanical milling was successfully applied to various compounds through a large range of applications (Suryanarayana, 2004). Rougier (2002) showed that mechanical grinding under a control atmosphere could be an attractive route for the production of carbons for super capacitor applications among numerous examples in the field of electrochemistry. The advantage of Mechanical Milling over Mechanical Alloying is that since the powders are already alloyed and only a reduction in particle size and/or other transformations have to be induced mechanically, the time required for processing is short (Magini et al., 1998).

1.4.1.3 Reactive Milling

Reactive milling is the mechanical alloying process accompanied by a solid-state reaction (Kaupp et al., 2004). The definition of reactive milling is suitable if during milling a chemical reaction is required and observed (Suryanarayana, 2004). By this route, a dispersion of ultra-fine (nano-scaled) crystals and/or a homogeneous dispersion of transformed phases in a matrix can be achieved with respect to the starting materials (e.g. Ag_2O instead of Ag) (Cocco et al., 1995; Kaupp et al., 2003). The reactive milling technique is still not widely used, even though mechanical alloying has a long tradition and inorganic or more recently organic chemical syntheses (see section 1.3.1.4) are known to proceed to completion without producing wastes (Cocco et al., 1995).

Reactive milling in this kind of principle can show economical advantage. Often these processes are environmentally friendly as they avoid wastes e.g. in solid state

synthesis where organic solid-solid reactions and others can rapidly proceed without any wastes and in the absence of solvents (Kaupp et al., 2003). A further use of the same set-up is in organic solid-state reactions where the necessity for repeated contacts between the reacting crystals prevails for obtaining quantitative reactions without producing wastes (Kaupp et al., 2004; Yoshiharumitoma et al., 2004). Another application of reactive milling (milling under hydrogen) is milling of metal powders in the presence of reactive solids/liquids/gases which is done to synthesize metal oxides, nitrides, and carbides (Cocco et al., 1995; Cao et al., 1999; Akiba et al., 2001).

1.4.1.4 Other Methods

Several new methods have been developed in recent years to produce materials in a nonequilibrium condition. The majority of these methods produce effects very similar to those obtained in mechanically alloyed powders. The major difference is that while mechanical alloying produces the material in the powder form, most of these new methods deal with bulk materials. Another difference is that these new methods focus on producing noncrystalline and amorphous materials in view of their novelty and potential applications (Suryanarayana, 2004). Some of these new methods are briefly described below. Cryomilling, which the milling operation removes the powder from the mill in the form of a slurry and transferred to a glove box containing dry argon (Suryanarayana, 2004). Rod Milling, the grinding medium is in the form of rods rather spherical balls (Suryanarayana, 2004). Mechanically activated self-propagating high temperature synthesis is based on a combination of mechanical alloying and self-propagating high temperature synthesis processes (Cao et al., 1999). Oxidation attrition milling reduction, the commercially available powders (of micrometer size) are oxidized at appropriate temperatures to produce brittle oxide powders (Suryanarayana, 2004).

1.4.2 Type of Mills

Different types of high-energy milling equipment are used to produce mechanically alloyed/milled powders. They differ in their design, capacity, efficiency of milling, and additional arrangements for cooling, heating, and so forth (Takacs and Sepelak, 2004). Industrial mills of different types are in practical use for a number of commercial applications, such as Spex Shaker Mills, Planetary Ball Mills, Attritor Mills, Jet-Mills, Bead-Mills, Rod-Mills and with change only in parameter values (Inoue and Okaya, 1996). The following sections describe some of the most common mills currently in use for milling, which are available and can be purchased for stand milling operations (Suryanarayana, 2004).

1.4.2.1 Spex Shaker Mills

Shaker mills, such as spex mills, which mill about 10-20g of the powder at a time, are mostly commonly used for laboratory investigations and for alloy screening processes (Kaupp et al., 2003). The common version of the mill has one vial, containing the powder sample and grinding balls, secured in the clamp and swung energetically back and forth several thousand times a minute (Suryanarayana, 2004). The back-and-forth shaking motion is combined with lateral movements of the ends of the vial (Kaupp et al., 2003).

SPEX mills have certain disadvantages. First of all, the balls may roll around the end of the vial rather than hitting it; this decreases the intensity of milling. Secondly, the powder may collect in the eyes of the “8” and remain unprocessed. Last, the round-ended vial is rather heavy; the flat-ended vial is 30% lighter, the impacts at the ends of the vial dominate the milling action. However, some powder may collect at the edges and remain unprocessed (Kaupp et al., 2003; Suryanarayana, 2004).

1.4.2.2 Planetary Ball Mills

Laboratory planetary mills have been widely used by researchers the studying effects of mechanochemical activation (Magini et al., 1998). These mills are usually of the batch type have been used for various purposes including mechanical alloying experiments. The centrifugal force produced by the jars rotating around their own axes and that produced by the rotating support disk both act on the vial contents, consisting of the material to be ground and the grinding balls (Suryanarayana, 2004). The grinding balls in the planetary mills acquire much higher impact energy than is possible with simple pure gravity or centrifugal mills. In order to attain high productivity of the planetary mill, continuous feeding of a material into the jars moving at very high speeds and continuous unloading of the product should be provided (Field et al., 1999; Suryanarayana, 2004). A great number of processes in industry involve grinding of various materials and treatment of powders. These processes are traditionally performed in ball mills, which tend to be large and slow. The idea of using centrifugal acceleration field instead of gravitational field resulted in the advent of novel grinding equipment of the planetary type (Field et al., 1999; Suryanarayana, 2004).

1.4.2.3 Attritor Mills

An attritor mill is a conventional ball mill, which consists of a rotating horizontal drum half-filled with small steel balls (Suryanarayana, 2004). As the drum rotates the balls drop on the metal powder that is being ground; the rate of grinding increases with the speed of rotation. The dry particles are subjected to various forces such as impact, rotation, tumbling, and shear. This causes powder size reduction because of collisions between balls, between balls and container wall, and between balls, agitator shaft, and impellers. Attritors of different sizes and capacities are available (Suryanarayana, 2004). The grinding tanks or containers are available either in stainless steel or stainless steel coated inside with alumina, silicon carbide, silicon nitride, zirconia, rubber, and polyurethane. Compared with SPEX or planetary mills, the velocity of the grinding medium in the attritors is much lower, and consequently the energy of milling in the attritors is low (Suryanarayana, 2004).

1.4.2.4 Vibratory Mills

Vibration mills are commonly used for small scale applications (Inoue and Okaya, 1996). In vibratory mills hot spots are always present, and ignition takes place when propagation becomes possible due to sufficient mechanical activation. The influence of the ball-ball collisions can be considered negligible, if the ignition time is found to be proportional to the powder-to-ball mass ratio (Takacs and Sepelak, 2004). By means of utilizing base metals like magnesium or sodium and applying mechanochemical conditions using vibratory mills, these toxic substances are eliminated directly inside a contaminated complex material at room temperature and in a short time very efficiently (Birke, 2002). Vibratory mills have to move the mass of the grinding chamber. This limits their size and cannot to be operated under controlled conditions like atmosphere or closed circuit (Kaupp et al., 2003).

1.4.2.5 Other Mills

Several new designs of mills have been developed in recent years for specialized purpose. These include Jet Mills, Bead Mills, and Rod Mills (Suryanarayana, 2004). The jet mills use large streams of air or inert gas, which limits their use in reactive milling. Next to this the non-presence of grinding media does not lead to significant kinetic effects (Kaupp et al., 2003). Bead mills, horizontally or vertically, do not exhibit a significant kinetic impact as well, since no high-level relative acceleration of the grinding media occurs which leads to shear and friction effects but not to collision (Inoue and Okaya, 1996). The rod mills are very similar to the ball mills except that they use steel rods instead of balls as grinding medium. It has been claimed that the powder contamination during rod milling is much lower than during ball milling (Suryanarayana, 2004).

1.4.3 Milling Factor

Mechanochemistry, using mechanical energy to initiate chemical reactions, is an emerging technology in the field of waste disposal. While some heat is produced during milling, reactions often differ from those initiated thermally. Mechanochemical reactions occur through a number of mechanisms. Several factors affect the efficiency of a mill, including its type, speed or frequency, the shape, size and material of the milling bodies, temperature, atmosphere, etc. In many cases, the milling conditions influence the reaction route and the obtained products, not only the rate of the reaction. But even in such complex cases, it is useful to match the time scales using the relative milling intensities before searching for further effects (Takacs and Sepelak, 2004). Consequently, predicting the kinetics of a mechanochemical process is a challenging task (Takacs and Sepelak, 2004). In a ball mill intense mixing takes place and reactants are brought into contact with each other. Grinding reduces the particle size and increases the surface area available for reaction. New reactive surfaces are exposed during particle fracture and the introduction of dislocations increases the surface reactivity. Milling tends to create radicals, which can then go on to react with neighbouring compounds. All these effects combine to make mechanochemical reactions possible (Birke and Black, 2001).

1.4.4 Matrix Materials in Milling

During grinding in planetary and vibration mills, powder particles are subject to a combination of impact and shear, which produce surface strain localization regions, thereby initiating cracking. At the crack tip, there is also a strain localization zone, that is, a zone of converted material where the excess energy goes into bond breaking, defect generation and redistribution, and formation of free radicals and new chemical species. In particular, processing of oxide powders leads to crystallite decomposition and oxygen removal (Hasegawa et al., 2001; Mofa et al., 2002). All mechanochemical processes take place on the surface of the particles, altering the structure of the surface layer. This process includes not only the formation of new defects and bond breaking but also high energy electron emission, which results in local irradiation of the material (Mofa et al., 2002). The grinding of powders by ball milling consists in a

series of impacts during which powder particles become trapped between the external surfaces of two colliding bodies (Delogu et al., 2003). The immediate role played by milling bodies in the development of mechanochemical processes is as a rule treated as contamination of mechanical activation products by their material (Mofa et al., 2002).

It is known that through mechanical stress during the milling process, ultrasound or intensive stirring of polymer solutions, the C-C backbone chain is split with the formation of radicals. This allows for the degradation to shorter chains and in some cases subsequent reaction of the polymers (Schmidt-Naake et al., 2001). Further C-C forming reactions of highest synthetic potential are Knoevenagel condensations (Kaupp et al., 2003). Fine grinding of silicates leads to the formation of a surface phase distinct in structure from the bulk crystal. Composition of a newly formed surface phase also may differ from the bulk material due to the sorption of gas molecules from the environment. The formation of a surface phase is presumed to result from melting of crystalline mineral due to the local high temperature heating up at small contact spots of the colliding particles and/or from plastic deformations (Urakaev et al., 2003; Kalinkin et al., 2004).

Quartz is one of the most frequently used solids with respect to mechanical treatment (Hasegawa et al., 2001; Mako et al., 2001). Therefore, the structure of mechanically treated quartz is in a partially crystalline state; it still contains typical structural elements of the initial quartz, but the long-range order is absent during the mechanical treatment of quartz, Si-O bonds are broken, and different radicals are created (Mako et al., 2001; Mofa et al., 2002). The distribution of mechanically induced defects in quartz depends on the type of stress (Steinike and Tkacova, 2000). For example, sand consists of quartz (SiO_2), which forms an infinite covalent crystal lattice. If the crystal is split, all Si-O bonds are broken that existed between the two fragments and the freshly cleaved faces are completely unsaturated with free $\equiv\text{Si}\cdot$ and $\cdot\text{O}-\text{Si}\equiv$ surface radicals and other highly reactive species which react with CO , CO_2 , N_2 , and H_2 gases to form more stable, paramagnetic centres on the quartz surface (Steinike and Tkacova, 2000; Mofa et al., 2002; Urakaev et al., 2004). The resulting active centres also act as polymerization centres. They represent local plasma. This plasma tends to be saturated immediately (Steinike and Tkacova, 2000; Kaupp et al., 2003). The

purpose of this study was to theoretically study the influence of the material of milling bodies on the mechanical activation of quartz in a planetary centrifugal mill with steel fittings.

1.5 Choice of Methods in This Study

1.5.1 The Ball Mill

Many studies have been done concerning transition metals and inorganic compounds; ball milling experiments on organic materials are scarce (Magini et al., 1998; Takacs, 1998; Mofa et al., 2002; Suryanarayana, 2004). In this study, high energy ball milling was used to investigate the destruction of PAHs and selected chlorinated pesticides.

1.5.2 The Study Compounds

1.5.2.1 PAHs

Polycyclic aromatic hydrocarbons (PAHs) have received increased attention in environmental pollution studies because some of these compounds are highly toxic (William et al., 1999). A single strain of bacteria has been reported to utilize or co-oxidize more than one PAH, naphthalene, phenanthrene, biphenyl, anthracene, pyrene, chrysene, fluorine, fluoranthene and dibenzothiophene (Collina et al., 2005). Although the pathways of biodegradation are well known for PAHs (Registry, 1995; Theurich et al., 1997), however, mechanochemical degradation pathways for PAHs are largely unknown. Mechanism of degradation PAHs by ball milling includes the efficiency and the formation of intermediates through milling is less known. In this study, PAHs degradation was investigated naphthalene and anthracene as model compounds using ball milling. More investigations about the relationship between the ways different PAHs by a single strain are attractive (Kiyohara et al., 1994).

Naphthalene is the simplest polycyclic aromatic hydrocarbon. Information obtained from studies of milling degradation of naphthalene has been valuable for understanding and predicting the pathways used in the metabolism of the structurally more complex polycyclic aromatic hydrocarbons and related heterocyclic aromatic compounds (Richard et al., 1992; Yang and Lu, 2005). In this study, Naphthalene was used as the simplest PAH to investigate the pathway-using ball milling destruction.

1.5.2.2 Chlorinated Compounds

Pentachlorophenol (PCP) in soil is known to be transformed through degradation by several bacterial and fungal species (Yoshiharumitoma et al., 2004; Nomura et al., 2005). The mechanochemical method has recently attracted attention in the degradation of organo-chlorinated molecules the reaction of organo-chlorinated compounds (PCP, chloroanilines, and PCBs) and the comparison of the degradation efficiency between mechanochemical and batch procedures has been carried out (Yoshiharumitoma et al., 2004; Nomura et al., 2005).

Chlorobenzene is the simplest species of chlorinated aromatic compounds. The knowledge of the formation mechanism of its oxidation products and the one of operative conditions under which they can be completely destroyed, can contribute to a better understanding of the fate of higher molecular weight aromatics such as polychlorinated benzene, phenols, biphenyls, dibenzo-dioxins (PCDD) and dibenzofuranes (PCDF) which are often associated with the incineration of chlorinated hydrocarbons containing hazardous chemical wastes. Numerous laboratory studies were devoted to oxidation processes of chlorobenzene under different experimental conditions (Fadli et al., 1999). Chlorobenzene can form PCBs in pyrolytic conditions. Biphenyls can then generate PCDFs by oxidation with the loss of one or two chlorine atoms or two H atoms from the ortho position. Chlorophenols can be formed from chlorobenzene in the presence of oxygen via reaction of a chlorophenol radical with an OH radical. Chlorophenols can subsequently react to form both PCDDs and PCDFs. PCDD/Fs are one of the most toxic chemicals known. They have been demonstrated to occur in the environment and they appear as by-products of chemical processes (Aracil et al., 2005; Nomura et al., 2005).

Chlorobenzene decomposition is of interest as the chlorine atom is bonded strongly to the benzene ring (Burfeindt and Homann, 2001) and potentially contributes to dioxin formation. A number of studies have examined chlorobenzene reactions, focusing on the removal of the chlorine atom. Burfeindt and Homann (2001) stated that chlorination of the aromatic ring is not favoured. Higgins et al. (2001) studied chlorobenzene flames and detected chlorinated intermediates in both fuel-rich and fuel-

lean flames. The formation of chlorinated byproducts under post flame conditions has not been studied in depth (Higgins et al., 2001).

In this study, focused on investigating the mechanochemical treatment of PAHs and halogenated and hydroxylated aromatics because it is a noncombustion technology that requires no heating process or off-gas treatment that we expect will be more acceptable than conventional heating processes. In mechanochemical reactions, the compounds to be treated are milled with quartz sand by a planetary ball mill. Organochlorine compounds such as chlorinated benzenes, chlorinated naphthalene, and pentachlorophenol were degraded by ball milling treatment. Since mechanochemical reactions occur in the solid phase, to investigate the feasibility of mechanochemical treatment of organochlorine compounds, the degradation pathway would be determined.

1.5.3 The Study Matrix Materials

Quartz sand is utilized to mechanical processing in a planetary mill with steel balls in this study. Firstly, it's very common in many soils. Secondly, it's inexpensive and environmentally safe. Also, it has been shown to initiate free radical sites when it is fractured.

1.5.4 GCMS Identification of Reaction Products

The GC/MS method is applicable to the determination of PAHs compounds involving naphthalene, anthracene and intermediate products, and chlorinated compounds. The GCMS analysis of chlorinated compounds showed no trace products oxidation of any of the intermediates observed (Dilmeghani and Zahir, 2001). It offers rapid qualitative and quantitative analysis of complex mixtures with precision and sensitivity, yet the equipment is relatively cheap and inexpensive to operate (William et al., 1999).

Chapter 2

2 Materials and Methodology

2.1 Equipment and Materials

All the experiments were conducted at the Applied Science laboratories, Division of Applied Science, Auckland University of Technology, Wellesley Campus, Auckland, New Zealand.

2.1.1 Equipment

Retsch PM100

The Retsch PM100 is a planetary mill. The machine was used in all the experiments. The mill was equipped with a 500 ml grinding which was containing with 20 balls of 20 mm diameter.

Gas Chromatograph-Mass Spectrometer

Detection and identification organic compounds were done by a Shimadzu QP-5000 GCMS. The GCMS column used for this analysis was a DB5 fused silica capillary column with a length of 30 m, an internal diameter of 0.25 mm and 5 μm coating thickness.

Ultrasonic Bath

A Filli Cavalin ultrasonic bath made in Italy was used for extraction of treated samples into solvent.

Centrifuge

Centrifuge (MSE) was used to centrifuge treated samples from solvent.

2.1.2 Materials

Quartz Sand

Mataia silica sand was purchased from Sand Resources (NZ) Ltd in Auckland, New Zealand. The sand was examined under a microscope and identified as crystalline quartz. The typical chemical analysis, as provided by Sand Resources, is given in Table 2.1-1.

Table 2.1-1: Percentage of silica sands

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%

Laboratory Analysis Materials

Chemicals used includes: Na₂SO₄ (Scharlau), n-tridecane (SIGMA 99%), hexane (Scharlau, analytical grade), acetone (SIGMA 99.5%), CaO (BDH- laboratory reagent), D₂O (Aldrich- laboratory reagent), and ortho-Phosphoric acid (reagent grade).

Reactants used were: naphthalene (BDH- laboratory reagent), anthracene (MERCK-Schuchardt, Synthesis grade), pentachlorophenol (PCP) (BDH- laboratory reagent), 1-chlorobenzene (BDH- laboratory reagent), 1-bromobenzene (Scharlau, Synthesis grade), 1-chloronaphthalene (BDH- laboratory reagent), 1-bromonaphthalene (MERCK-Schuchardt, Synthesis grade), phenol (Riedel-deHaën), 1-naphthol (BDH- laboratory reagent), 2-naphthol (M&B-laboratory reagent).

2.2 Milling Process

In this study, most laboratory milling trials were operated by the PM100 ball mill. The mixtures (usually 50 g) were charged into a steel grinding jar of 500 mL capacity. 20 steel balls of 15 or 20 mm diameter were put into each jar together with the mixtures. The mill was operated at approximately 500 rpm under atmospheric conditions for different periods of time and the product was thoroughly removed from each pot after grinding by washing.

Time series trials were performed with 2 g treated of samples taken at regular intervals during milling to determine the concentration and identify breakdown products with respect to milling time. For these trials, the reactant was added to the quartz sand and milled for a number of hours. The grinding jar lid with the gas ports was used to extract headspace samples using a 1 mL syringe. Solid samples were taken at regular intervals for identification of breakdown products.

Two classes of organic compounds were investigated under reactive milling process. The first was representative of simple PAHs such as naphthalene, anthracene, and pentachlorophenol. Each organic compound has been conducted in low and high concentration trials. The low concentration trials were used to compare destruction efficiency with naphthalene, anthracene, pentachlorophenol, while the high concentration trials were used to analyse the degradation pathway. In the second class of compounds were halogenated and hydroxylated aromatics. All the organic compounds were operated in high concentration trials. A series of “cross-over” experiments were conducted to investigate whether halogens could be transferred between compounds during milling.

2.3 Extraction Procedures

EPA Ultrasonic extraction method (Method 3550C) (Agency, 1996) was used to extract organic compounds from treated samples into the 1: 1 hexane: acetone solvent for all analyses.

A summary of the method is:

2 g of treated sample was weighed directly into a 20 mL test tube with cap. Approximately 1 mL of 20% phosphoric acid was added into the test tube until the solid sample completely wet. The wet sample was left to digest for 30 minutes. 10 mL of solvent which was mixed with 1:1 hexane: acetone containing 500 ppm n-tridecane as internal standard was pipetted into the test tube followed by the addition of approximately 5 g of sodium sulphate anhydrous in order to absorb the moisture. The test tube was capped and shaken vigorously by hand to mix the solvent and sample. After that, the test tube was placed in the ultrasonic bath for 30 minutes at 15°C. The samples were taken out to shake vigorously by hand occasionally. Once the sonication has finished, the test tube was placed into centrifuge at 6000 rpm for five minutes. 1 µL of the extracted solvent was injected into the GCMS for analysis.

2.4 Analysis

Solid Samples were identified using a gas chromatograph/ mass spectrometer (GC/MS) System using DB-5 column. The carrier gas was Helium. The GCMS column was optimized for the following conditions: initial temperature, 40°C, ramp at 5°C/min to 240°C and hold for 10 minutes until the completion of the 60 minutes run. Column flow rate was maintained at 1.5 mL/min throughout the analysis. The injector split mode was 1/10 ratio. Injector port temperature was 260°C and interface temperature was 260°C. Identification was achieved by comparing the experimental spectra to library reference mass spectra of the database and, when possible, to spectra of purchased reference compounds. Retention times of chromatographic peaks were also compared with the ones of purchased compounds when available.

Headspace samples (500 µL) were taken from the grinding jar through gas sampling ports into the grinding jar lid using a syringe. Headspace samples were injected directly into the GCMS for detection of volatile compounds in the headspace. GC conditions were the same as for the solid samples analysis above.

2.5 Data Analysis

Quantitation of the analytes in the sample was performed on the basis of a comparison of the area of the compound to that of the standard calibration graphs.

The destruction efficiency is defined as the total mass of a chemical into a process, minus the mass of the chemical in all products, byproducts and environmental releases, divided by the input mass (to give a percentage). Only closed processes that achieve greater than 99.99% destruction efficiency can be considered (Rahuman et al., 2000). In these experiments the destruction efficiency is calculated based on mentioned above. As the grinding jar is sealed, gas and liquid emission are negligible and the destruction efficiency is calculated based on the concentration of each compound is the solid before and after milling according to Equation 1.

$$\text{Destruction Efficiency (DE)} = 1 - \frac{\text{Conc. in treated sample}}{\text{Conc. in untreated sample}} \quad \text{Equation 1}$$

2.6 Method

2.6.1 Preparation of Calibration Standards for PAHs and PCP

2.6.1.1 Naphthalene

Naphthalene standard solution of different concentration was made: 5000, 2000, 1000, 500, 200, 100, 50 ppm. Each contained n-tridecane as internal standard. These standards were made to use in the calculation of destruction rate of the contaminant in the soil after treatment. Standard solutions were stored in volumetric flasks tightly stopped.

2.6.1.2 Anthracene

Anthracene standard solution of different concentration was made following the same sample preparation as outlined for naphthalene in Section 2.6.1.1 above.

2.6.1.3 Pentachlorophenol (PCP)

Pentachlorophenol standard solutions were prepared in different concentration according to the procedure detailed in Section 2.6.1.1.

2.6.2 Preparation of Calibration Standards for Halogenated and Hydroxylated Aromatics

2.6.2.1 Halogenated Aromatics

2.6.2.1.1 1-Chlorobenzene

The standards preparation for halogenated and hydroxylated aromatics were chosen in different initial concentration based on minimal interference with the GC retention time and the solubility of the analytes in the following standard preparations. 1-Chlorobenzene standard solution of different concentration was made: 4400, 2000, 1000, 500, 200, 100, 50 ppm. The other procedures were following the naphthalene standard preparation detailed in Section 2.6.1.1.

2.6.2.1.2 1-Bromobenzene

1-Bromobenzene standard solutions were prepared in the usual way (see section 2.6.1.1) with different initial concentration 4500 ppm.

2.6.2.1.3 1-Chloronaphthalene

1-Chloronaphthalene standard solutions were made following the standard naphthalene preparation detailed previously in Section 2.6.1.1. But the initial concentration was made in 3000 ppm.

2.6.2.1.4 1-Bromonaphthalene

Following the standard naphthalene preparation procedure outlined above in Section 2.6.1.1. 1-Bromonaphthalene was made from 3000, 2000, 1000, 500, 200, 100, 50 ppm.

2.6.2.2 Hydroxylated Aromatics

2.6.2.2.1 Phenol

For phenol, the standard solutions of different concentration were prepared in the usual way as described in Section 2.6.1.1.

2.6.2.2.2 1-Naphthol

Again, the preparations of 1-naphthol standard solutions were made following the standard naphthalene procedure detailed above in Section 2.6.1.1.

2.6.2.2.3 2-Naphthol

2-Naphthol standard solutions were prepared according to the procedure outlined in Section 2.6.1.1. Additionally, the initial concentration was made in 2500 ppm.

2.6.3 Reactive Milling in PAHs and Pentachlorophenol

Introduction

The milling destruction of PAHs and PCP in quartz sand were investigated thoroughly below. The final products in the milling destruction of PAHs and PCP in quartz sand are determined. A number of low concentration trials were performed to compare overall destruction rate. A variety of high concentration trials were conducted to identify intermediate breakdown products and to elucidate possible destruction pathways.

2.6.3.1 Naphthalene

2.6.3.1.1 Low Concentration Trial

Naphthalene was added onto a batch of quartz sand to 1000 mgkg^{-1} . N-tridecane was used as internal standard. Identical trials were performed on each of the quartz sand samples; 50 g of quartz sand and twenty 15x20 mm steel balls were milled for 90 min taking samples after 0, 3, 5, 10, 15, 20, 25, 30, 40, 50, 60 and 90 min. The samples were extracted and analysed for naphthalene following the standard procedures detailed in Section 2.3 and 2.4.

2.6.3.1.2 High Concentration Trial

Naphthalene was added onto a sample of quartz sand to approximately 20000 mgkg^{-1} prior to milling. The quartz was homogenized and untreated samples taken for extraction and analysis. The quartz (50 g) was placed in a grinding bowl along with twenty 15x20 mm steel balls and clamped in the mill under an air atmosphere. Milling commenced and solid samples were taken after 0, 5, 10, 20, 30, 40, 50, 60, 90, 120 minutes and 3 hours of milling and were analysed for breakdown products on the GCMS. The headspace samples (500 μL) were taken from the grinding jar through the

gas port in the lid using a syringe and injected directly into the GCMS. Headspace samples were taken after 30 min and 1h and analysed on the GCMS. The solid samples were extracted and analysed according to the procedure outlined in Section 2.3 and 2.4.

2.6.3.2 Anthracene

2.6.3.2.1 Low Concentration Trial

Anthracene was added onto a batch of quartz sand in the usual way (see Section 2.6.3.1.1). A 50 g batch of the quartz was milled under mill speed at 500 rpm with twenty 15 mm steel balls. Samples were taken at regular intervals with the final sample after 90 minutes of milling and analysed on the GCMS.

2.6.3.2.2 High Concentration Trial

Anthracene was added onto a sample of quartz sand following the standard naphthalene spiking procedure detailed previously in Section 2.6.3.1.2.

2.6.3.3 Pentachlorophenol

2.6.3.3.1 Low Concentration Trial

Pentachlorophenol was prepared according to the procedure detailed in Section 2.6.3.1.1. The quartz was mixed well and untreated sample were taken for extraction and analysis. The remaining quartz (50 g) was milled under an air atmosphere at 500 rpm with twenty 15 mm steel balls. Samples were taken every 5 minutes with a final sample taken after 90 minutes. Samples were extracted and analysed using GCMS.

2.6.3.3.2 High Concentration Trial

The milling of PCP was investigated following the same sample preparation, milling and analysis procedures as outlined for naphthalene in Section 2.6.3.1.2 above.

2.6.4 Reactive Milling in Halogenated and Hydroxylated Aromatics

Introduction

The milling destruction of a number of halogenated and hydroxylated aromatics, namely 1-chlorobenzene, 1-bromobenzene, 1-chloronaphthalene, 1-bromonaphthalene, phenol, 1-naphthol and 2-naphthol, were investigated. High concentrations of these compounds in quartz sand were separately milled and intermediate and final breakdown products identified. A variety of “cross-over” experiments were conducted to investigate whether halogens could be transferred between compounds during milling.

2.6.4.1 Halogenated and Hydroxylated Aromatics separately Milling

2.6.4.1.1 High Concentration 1-Chlorobenzene in Quartz Sand

1-Chlorobenzene was added onto a 50 g sample of quartz sand to approximately 22512 mgkg⁻¹ following the procedure outlined in Section 2.6.3.1.2. The quartz (50 g) was placed in a grinding bowl along with twenty 20 mm steel balls and milled at 500 rpm in the PM100 under an air atmosphere. Duplicate solid sample were taken after 15, 30, and 60 minutes of milling and analysed on GCMS. Headspace samples were taken after 5, 15 minutes and at the conclusion of milling prior to taking to the respective solid samples. Also, headspace samples were analysed using GCMS.

2.6.4.1.2 High Concentration 1-Bromobenzene in Quartz Sand

1-Bromobenzene was prepared according to the procedure outlined in Section 2.6.4.1.1. The quartz (50 g) was milled to approximately 31404 mgkg⁻¹ under air atmosphere at 500 rpm with twenty 20 mm steel balls. Headspace and solid samples were taken at regular intervals and analysed on the GCMS.

2.6.4.1.3 High Concentration 1-Chloronaphthalene in Quartz Sand

1-Chloronaphthalene was added onto a batch of quartz sand to approximately 16262 mgkg⁻¹ in the usual way (see Section 2.6.4.1.1). A 50 g batch of the quartz sand was milled under an air atmosphere at 500 rpm with twenty 20 mm steel balls. Samples were taken at regular intervals with the final sample taken after 2 hours of milling.

2.6.4.1.4 High Concentration 1-Bromonaphthalene in Quartz Sand

A batch of quartz sand (50 g) was milled with approximately 20708 mgkg⁻¹ of 1-bromonaphthalene following the 1-chlorobenzene procedure in Section 2.6.4.1.1. The sample was loaded into the 500 mL grinding jar containing twenty 20 mm steel balls and milled at 500 rpm for 2 hours under an air atmosphere. The milled sample and analysed on the GCMS to detect and identify breakdown products.

2.6.4.1.5 High Concentration Phenol in Quartz Sand

Phenol (1 g) and quartz sand (50 g) were loaded into the 500 mL grinding jar and milled with twenty 20 mm steel balls at 500 rpm for 2 hours in the PM100 mill. Samples were prepared according to the procedure outlined in Section 2.6.4.1.1. At the conclusion of milling a sample of the headspace and solid samples were extracted and analysed on the GCMS.

2.6.4.1.6 High Concentration 1-Naphthol in Quartz Sand

1-Naphthol in quartz sand trials were also performed following the 1-chlorobenzene as detailed in Section 2.6.4.1.1. Samples were taken at regular intervals with the final sample taken after 2 hours of milling. Samples were extracted and analysed using the GCMS.

2.6.4.1.7 High concentration 2-Naphthol in Quartz Sand

The milling of 2-naphthol was investigated following the same sample preparation, milling and analysis procedures as outlined for 1-chlorobenzene in Section 2.6.4.1.1 above.

2.6.4.2 Halogenated and Hydroxylated Aromatics “Cross-Over”

Milling

Standard milling procedures (50 g of quartz sand, 500 mL steel grinding jar, twenty 20 mm steel balls, mill speed 500 rpm, air atmosphere) apply for all the trials detailed below unless otherwise stated. The concentration of mixture of halogenated and hydroxylated aromatics were made at the same molar ratio of 1:1 for the halo and hydroxyl atom. The Milling commenced and headspace samples were taken after 0, 5, 10, 15 minutes, while solid samples were taken after 15, 20, 30, 45, 60, 90, 120 minutes of milling were analysed for breakdown products on the GCMS. The standard extraction and analysis methods detailed in Section 2.3 and 2.4 were used in most of the trials below.

2.6.4.2.1 High Concentration Mixed 1-Chlorobenzene and 1-Bromobenzene in Quartz Sand

1-Chlorobenzene and 1-bromobenzene were mixed at the same molar ratio of Cl to Br in the mixtures, which was 0.01 mol. 1-Chlorobenzene were loaded onto a sample of quartz sand to approximately 22152 mgkg^{-1} , while bromobenzene were approximately $31,404 \text{ mgkg}^{-1}$. All trials were done under standard condition. Additionally, 3 hours of milling samples was performed to further investigate breakdown products.

2.6.4.2.2 High Concentration Mixed 1-Chlorobenzene and 1-Bromobenzene with CaO in Quartz Sand

1-Chlorobenzene, 1-bromobenzene and CaO were mixed at the molar ratio of Cl: Br: CaO in 1:1:12 in the mixtures in the usual way (see 2.6.4.2.1). Standard milling conditions applied.

2.6.4.2.3 High Concentration Mixed 1-Chlorobenzene and 1-Bromobenzene heating in the Reflux

To investigate whether any halogen exchange occurs without milling, 1-chlorobenzene and 1-bromobenzene were taken 5 mL respectively into 50 mL round bottom flask. Attach a reflux water condenser and reflux over a small flame for 5 minutes, 1, 2, 3 hours and were analysed for broken products on the GCMS.

2.6.4.2.4 High Concentration Mixed 1-Chloronaphthalene and 1-Bromonaphthalene in Quartz Sand

1-Chloronaphthalene and 1-bromonaphthalene were loaded onto quartz sand (50g) at the same molar ratio of Cl to Br, which was 0.005 mol. 1-Chloronaphthalene was added onto a small of quartz sand to approximately 16262 mgkg^{-1} , while 1-bromonaphthalene was approximately 20708 mgkg^{-1} . A number of trials were also done using standard milling conditions. The solid samples were taken after 15, 30, 45, 60, 90, 120 minutes and 2, 3, 4, 5 hours.

2.6.4.2.5 High Concentration Mixed 1-Chlorobenzene and 1-Naphthol in Quartz Sand

A mixture of 1-chlorobenzene and 1-naphthol were milled with quartz sand approximately at the same molar ratio of Cl to OH in the mixture, which was 0.01 mol. 1-Chlorobenzene was added onto a batch of quartz sand to approximately 22512 mgkg^{-1} , while 1-naphthol was approximately 28800 mgkg^{-1} . Samples were

investigated following the same sample preparation, milling and analysis procedures as outlined for standard milling procedures above.

2.6.4.2.6 High Concentration Mixed 1-Bromobenzene and 1-Naphthol in Quartz Sand

1-Bromobenzene (approximately 15702 mgkg^{-1}) and 1-naphthol (approximately 14400 mgkg^{-1}) were milled at the same molar ratio of 0.005 mol for Br and OH. Standard milling procedures applied.

2.6.4.2.7 High Concentration Mixed 1-Chlorobenzene and 2-Naphthol in Quartz Sand

Different concentrations of 1-Chlorobenzene and 2-naphthol were loaded onto a 50 g sample of quartz sand to approximately 11256 mgkg^{-1} and 14400 mgkg^{-1} at the same molar ratio of Cl to OH. Treated samples were prepared according to the standard milling procedures.

2.6.4.2.8 High Concentration Mixed 1-Bromobenzene and 2-Naphthol in Quartz Sand

1-Bromobenzene (0.005 mol) and 2-naphthol (0.005mol) were added on quartz sand and the mixture was performed following the standard milling procedures detailed above. At the conclusion of milling a sample of the headspace and solid samples were extracted and analysed on the GCMS.

2.6.4.2.9 High Concentration Mixed 1-Chloronaphthalene and 1-Naphthol in Quartz Sand

A mixture of 1-chloronaphthalene and 1-naphthol was milled at the same molar ratio of Cl to OH, which were approximately 16262 mgkg^{-1} and 14400 mgkg^{-1} respectively. Samples were made following the standard milling procedures detailed previously.

2.6.4.2.10 High Concentration Mixed 1-Bromonaphthalene and 1-Naphthol in Quartz Sand

1-Bromonaphthalene and 1-naphthol were loaded onto a batch of quartz sand to approximately 20708 mgkg⁻¹ and 14400 mgkg⁻¹. They were well mixed at the same molar ratio of Br to OH and following the standard spiking procedures stated above.

2.6.4.2.11 High Concentration Mixed 1-Chloronaphthalene and 2-Naphthol in Quartz Sand

1-Chloronaphthalene and 2-naphthol in quartz sand trials were performed as outlined for standard milling procedures previously. They were mixed at the same molar ratio of Cl to OH to approximately 16262 mgkg⁻¹ and 14400 mgkg⁻¹.

2.6.4.2.12 High Concentration Mixed 1-Bromonaphthalene and 2-Naphthol in Quartz Sand

1-Bromonaphthalene and 2-naphthol were performed according to the standard milling procedures and spiked at the same molar ratio of Br to OH to approximately 20708 mgkg⁻¹ and 14400 mgkg⁻¹.

Chapter 3

3 Results

3.1 Calibration Standards

3.1.1 PAHs and PCP Calibration Standards

3.1.1.1 Naphthalene

Naphthalene standard solutions of 5000, 2000, 1000, 500, 200, 100 and 50 ppm were prepared. 1 μ L of each sample was injected into the GCMS. The peak area obtained is presented in Table 3.1-1. Figure 3.1-1 shows the standard curve obtained from the area.

Table 3.1-1: Results of naphthalene standard solutions

naphthalene concentration (ppm)	Ratio (naphthalene/ISTD)
0	0.00
50	0.09
100	0.21
200	0.46
500	1.38
1000	2.96
2000	5.22
5000	10.88

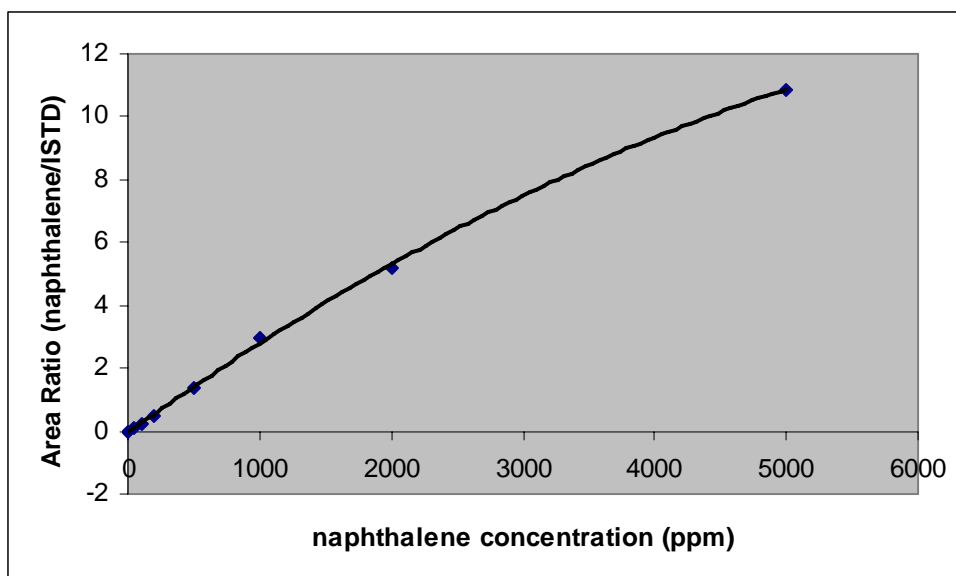


Figure 3.1-1: naphthalene standard curve

3.1.1.2 Anthracene

Anthracene standard solutions of 5000, 2000, 1000, 500, 200, 100 and 50 ppm were prepared. 1 μ L of each sample was injected into the GCMS. The peak area obtained is presented in Table 3.1-2. Figure 3.1-2 shows the standard curve obtained from the area.

Table 3.1-2: Results of anthracene standard solutions

anthracene concentration (ppm)	Ratio (anthracene/ISTD)
0	0.00
50	0.11
100	0.17
200	0.53
500	1.26
1000	2.32
2000	3.67
5000	5.33

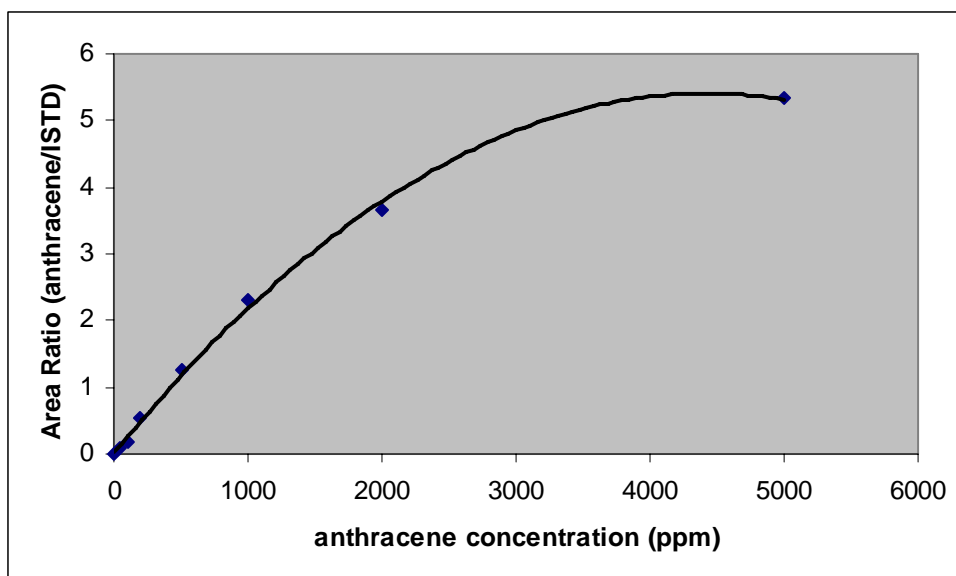


Figure 3.1-2: anthracene standard curve

3.1.1.3 PCP

Pentachlorophenol (PCP) standard solutions of 5000, 2000, 1000, 500, 200, 100 and 50 ppm were prepared. 1 μ L of each sample was injected into the GCMS. The peak area obtained is presented in Table 3.1-3. Figure 3.1-3 shows the standard curve obtained from the area.

Table 3.1-3: Results of PCP standard solutions

PCP concentration (ppm)	Ratio (PCP/ISTD)
50	0.06
100	0.17
200	0.68
500	0.98
1000	1.34
2000	2.19
5000	1.84

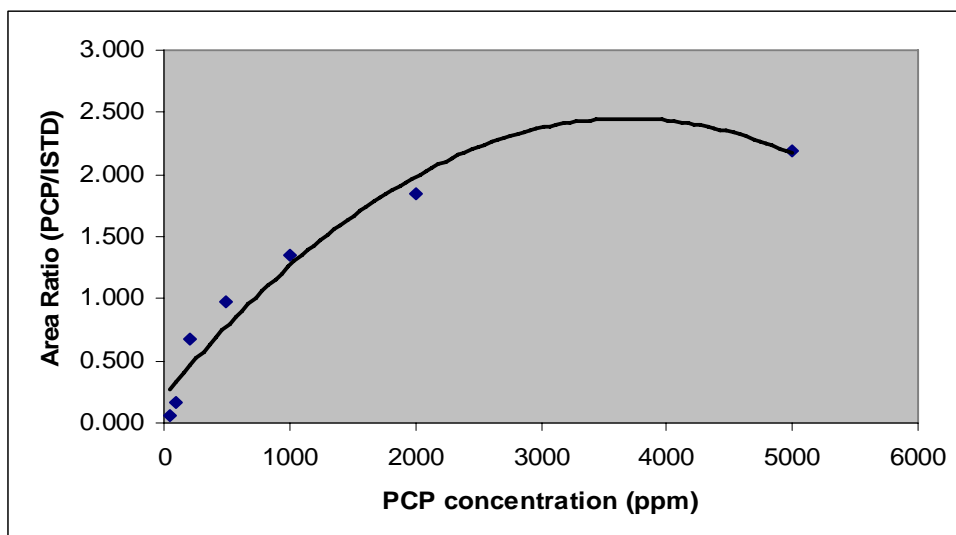


Figure 3.1-3: PCP standard curve

3.1.2 Halogenated and Hydroxylated Aromatics Calibration Standards

3.1.2.1 Halogenated Aromatics

3.1.2.1.1 1-Chlorobenzene

1-Chlorobenzene standard solutions of 4400, 2000, 1000, 500, 200, 100 and 50 ppm were prepared. 1 μ L of each sample was injected into the GCMS. The peak area obtained is presented in Table 3.1-4. Figure 3.1-4 shows the standard curve obtained from the area.

Table 3.1-4: Results of 1-chlorobenzene standard solutions

1-chlorobenzene concentration (ppm)	Ratio (1-chlorobenzene/ISTD)
0	0.00
50	0.07
100	0.14
200	0.28
500	0.56
1000	0.78
2000	1.26
4400	2.18

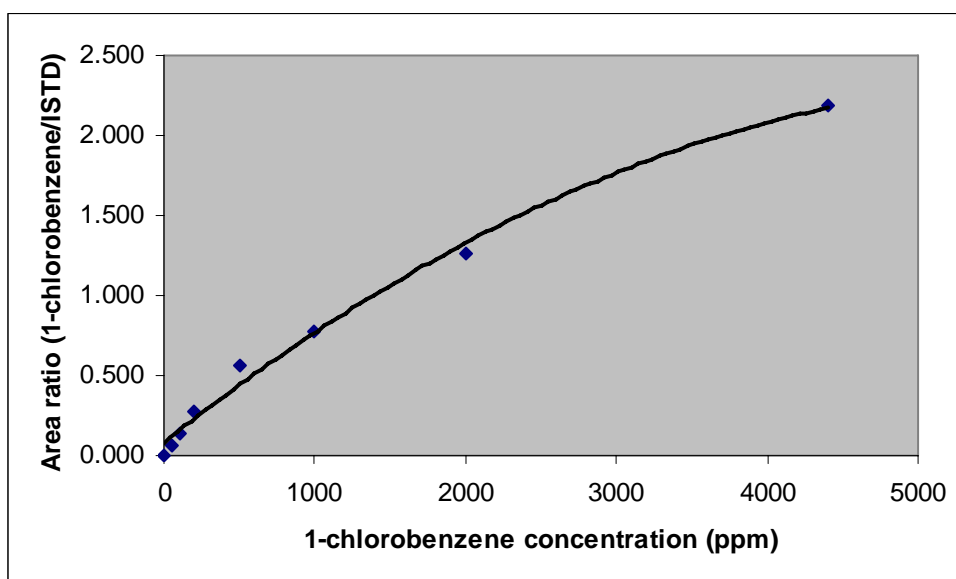


Figure 3.1-4: 1-chlorobenzene standard curve

3.1.2.1.2 1-Bromobenzene

1-Bromobenzene standard solutions of 4500, 2000, 1000, 500, 200, 100 and 50 ppm were prepared. 1 μ L of each sample was injected into the GCMS. The peak area obtained is presented in Table 3.1-5. Figure 3.1-5 shows the standard curve obtained from the area.

Table 3.1-5: Results of 1-bromobenzene standard solutions

1-bromobenzene concentration (ppm)	Ratio (1-bromobenzene/ ISTD)
0	0.00
50	0.06
100	0.14
200	0.29
500	0.56
1000	0.90
2000	1.17
4500	2.30

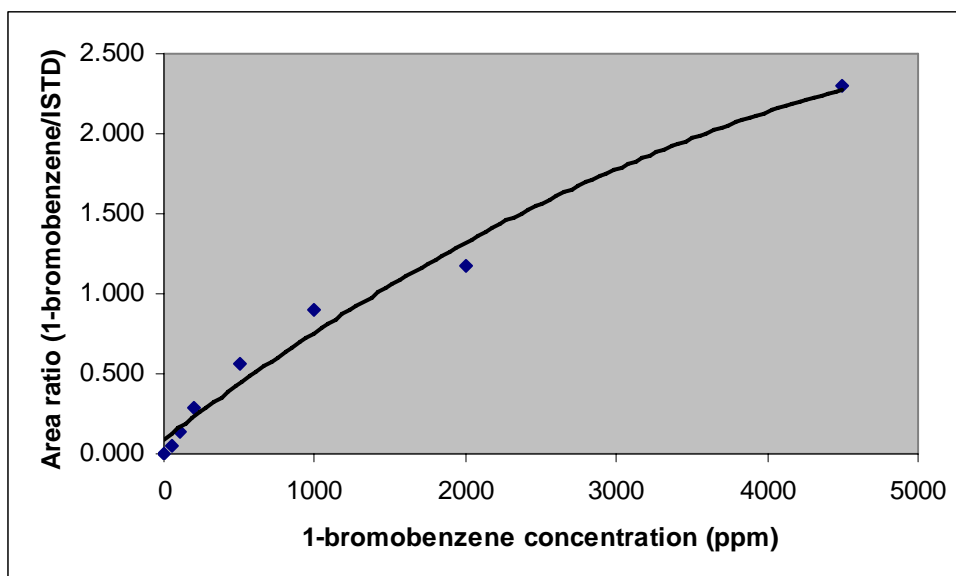


Figure 3.1-5: 1-bromobenzene standard curve

3.1.2.1.3 1-Chloronaphthalene

1-Chloronaphthalene standard solutions of 3000, 1500, 1000, 500, 200, 100 and 50 ppm were prepared. 1 μ L of each sample was injected into the GCMS. The peak area obtained is presented in Table 3.1-6. Figure 3.1-6 shows the standard curve obtained from the area.

Table 3.1-6: Results of 1-chloronaphthalene standard solutions

1-chloronaphthalene concentration (ppm)	Ratio (1-chloronaphthalene / ISTD)
0	0.00
50	0.20
100	0.35
200	0.60
500	1.11
1000	2.23
1500	3.02
3000	5.27

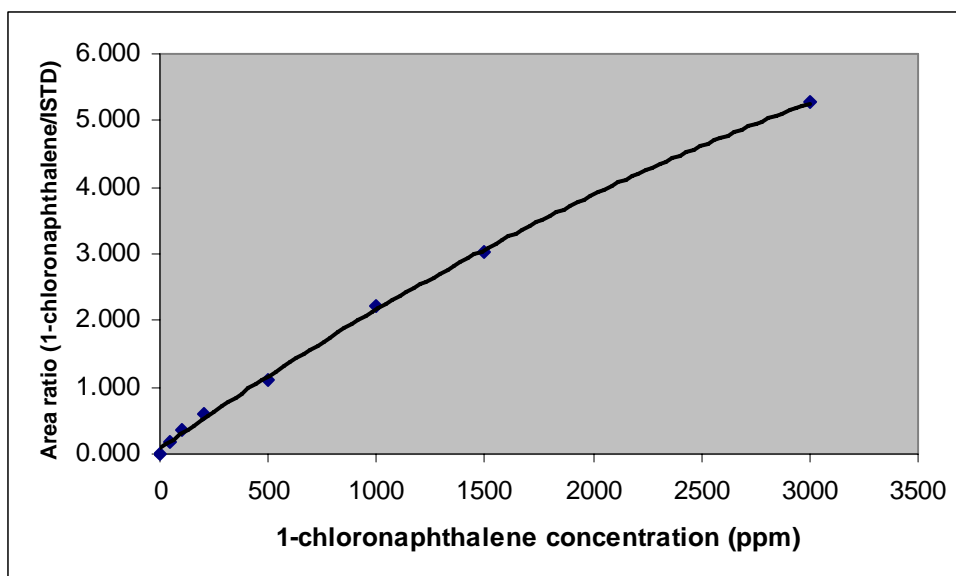


Figure 3.1-6: 1-chloronaphthalene standard curve

3.1.2.1.4 1-Bromonaphthalene

1-Bromonaphthalene standard solutions of 3000, 1500, 1000, 500, 200, 100 and 50 ppm were prepared. 1 μ L of each sample was injected into the GCMS. The peak area obtained is presented in Table 3.1-7. Figure 3.1-7 shows the standard curve obtained from the area.

Table 3.1-7: Results of 1-bromonaphthalene standard solutions

1- bromonaphthalene concentration (ppm)	Ratio (1- bromonaphthalene/ ISTD)
0	0.00
50	0.13
100	0.15
200	0.30
500	0.71
1000	1.08
1500	1.44
3000	2.60

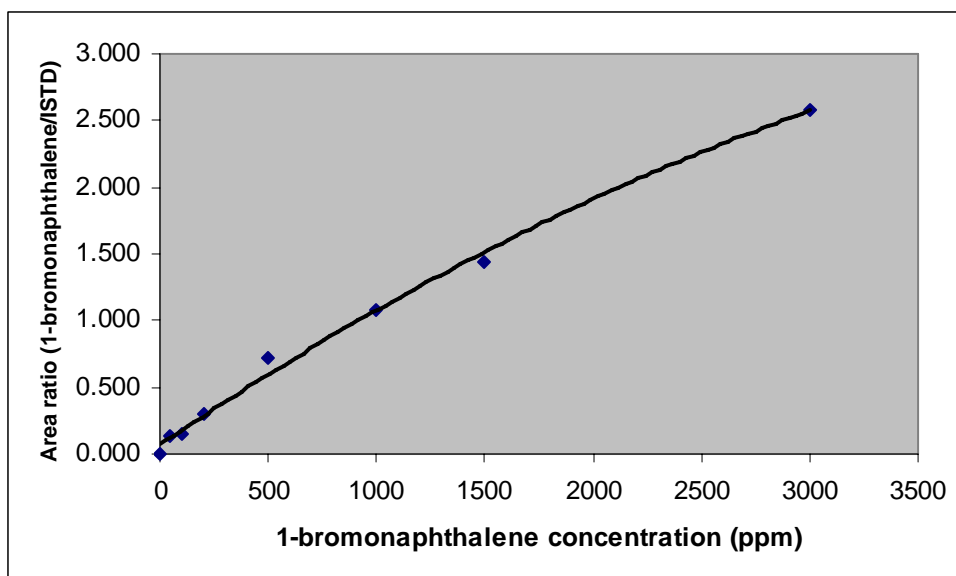


Figure 3.1-7: 1-bromonaphthalene standard curve

3.1.2.2 Hydroxylated Aromatics

3.1.2.2.1 Phenol

Phenol standard solutions of 5000, 2000, 1000, 500, 200, 100 and 50 ppm were prepared. 1 μ L of each sample was injected into the GCMS. The peak area obtained is presented in Table 3.1-8. Figure 3.1-8 shows the standard curve obtained from the area.

Table 3.1-8: Results of phenol standard solutions

phenol concentration (ppm)	Ratio (phenol/ISTD)
0	0.00
50	0.14
100	0.19
200	0.38
500	0.78
1000	1.33
2000	2.31
5000	3.85

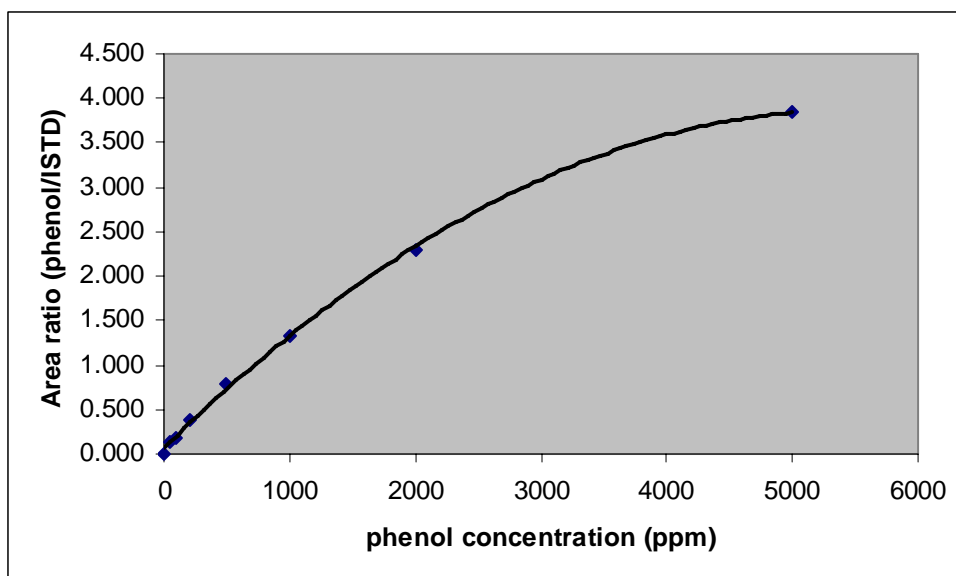


Figure 3.1-8: phenol standard curve

3.1.2.2.2 1-naphthol

1-Naphthol standard solutions of 5000, 2000, 1000, 500, 200, 100 and 50 ppm were prepared. 1 μ L of each sample was injected into the GCMS. The peak area obtained is presented in Table 3.1-9. Figure 3.1-9 shows the standard curve obtained from the area.

Table 3.1-9: Results of 1-naphthol standard solutions

1-naphthol concentration (ppm)	Ratio (1-naphthol/ISTD)
0	0.00
50	0.03
100	0.09
200	0.15
500	0.41
1000	0.84
2000	1.40
5000	3.68

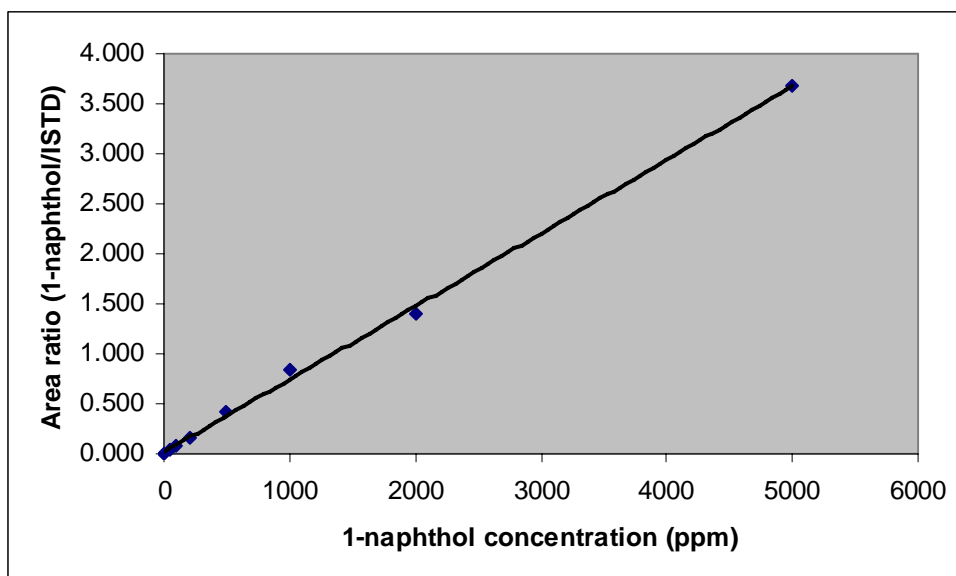


Figure 3.1-9: 1-naphthol standard curve

3.1.2.2.3 2-naphthol

2-Naphthol standard solutions of 2500, 1000, 500, 200, 100 and 50 ppm were prepared. 1 μ L of each sample was injected into the GCMS. The peak area obtained is presented in Table 3.1-10. Figure 3.1-10 shows the standard curve obtained from the area.

Table 3.1-10: Results of 2-naphthol standard solutions

2- naphthol concentration (ppm)	Ratio (2-naphthol/ISTD)
0	0.00
50	0.03
100	0.10
200	0.18
500	0.48
1000	0.88
2500	1.69

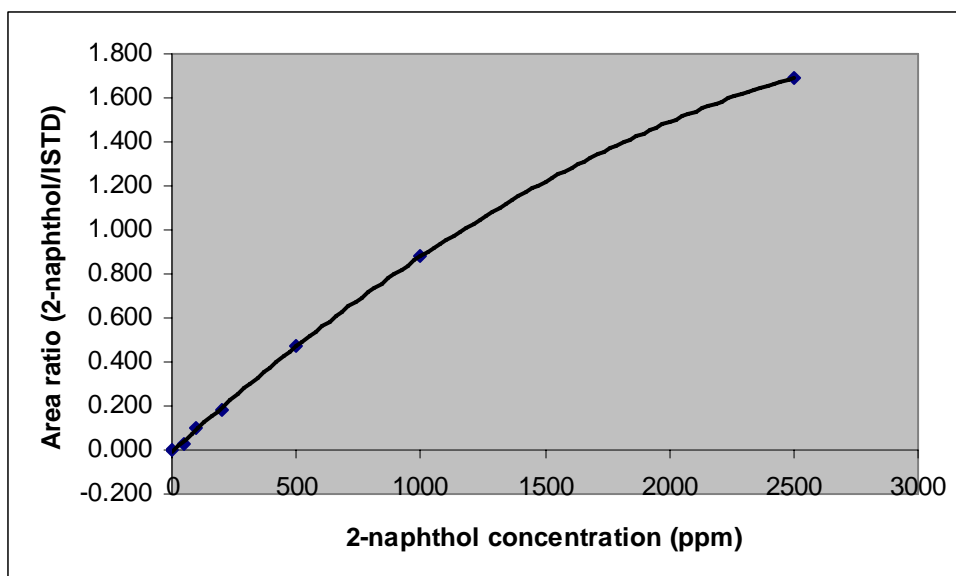


Figure 3.1-10: 2-naphthol standard curve

3.2 Reactive Milling in PAHs and Pentachlorophenol

3.2.1 Low Concentration Trials Naphthalene, Anthracene, PCP in Quartz Sand

Naphthalene, anthracene, PCP were quickly destroyed as milling progressed reaching < 5 ppm with 20 minutes as shown in Table 3.2-1. Anthracene, the most efficiency destruction products, reached a maximum of ~ 95 ppm after 3 minutes, before reducing to < 1 ppm with another 20 minutes of milling. PCP was totally destroyed after 20 minutes of milling. Naphthalene was found to destroy in a longest time compared with anthracene and PCP shown in Table 3.2-2. Its destruction efficiency was 100% after 60 minutes milling as shown in Figure 3.2-1. No intermediate breakdown products were detected by GCMS analysis.

Table 3.2-1: Results of low concentration naphthalene, anthracene, and PCP.

Milling time (min)	Concentration in naphthalene (ppm)	Concentration in anthracene (ppm)	Concentration in PCP (ppm)
0	1000.0	1000.0	1000.0
3	123.2	96.0	196.0
5	22.8	4.1	39.4
10	10.8	3.1	5.6
15	7.6	1.7	2.1
20	3.5	1.4	0.0
25	3.4	0.9	0.0
30	3.1	0.5	0.0
40	2.1	0.2	0.0
50	1.8	0.0	0.0
60	0.5	0.0	0.0
90	0	0.0	0.0

Table 3.2-2: Comparison destruction efficiency of naphthalene, anthracene, and PCP in low concentration trial

Milling time (min)	Destruction efficiency in naphthalene (ppm)	Destruction efficiency in anthracene (ppm)	Destruction efficiency in PCP (ppm)
0	0.0%	0.0%	0.0%
3	87.7%	90.4%	80.4%
5	97.7%	99.6%	96.1%
10	98.9%	99.8%	99.4%
15	99.2%	99.9%	99.8%
20	99.7%	99.7%	100.0%
25	99.7%	99.9%	100.0%
30	99.7%	100.0%	100.0%
40	99.8%	100.0%	100.0%
50	99.8%	100.0%	100.0%
60	100.0%	100.0%	100.0%
90	100.0%	100.0%	100.0%

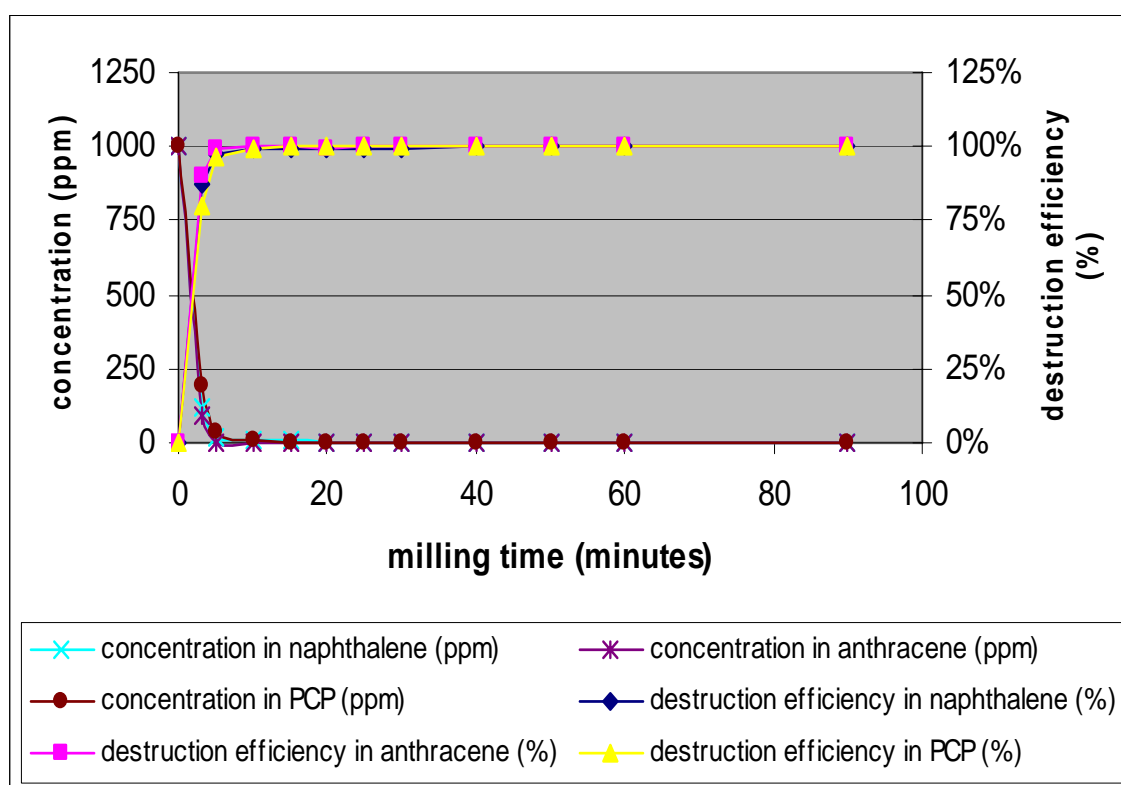


Figure 3.2-1: Concentration and destruction efficiency curve of naphthalene, anthracene, and PCP in low concentration trial.

3.2.2 High Concentration Naphthalene in Quartz Sand

Final Products

Naphthalene was destroyed during milling in the presence of quartz sand. No organic compounds were detected by GCMS analysis of the milled solid after 2 hours of milling. The colour of the spiked quartz sand changed from yellow to a grey colour that became increasingly dark as milling progressed. Mill of the clean quartz sand also resulted in a change in colour of the quartz to grey. This is due to the presence of fine iron and iron oxide particles in the milled quartz sand due to abrasion of the steel milling equipment (Bellingham, 2006).

Intermediate Breakdown Products

In the Headspace.

Volatile compounds benzene, toluene, xylene were detected in small amounts in the headspace gas after 1 hour of milling. 1,2,3,4-tetrahydronaphthalene was also detected in the headspace.

In the Solid.

A number of compounds were detected in the milled samples. Part of a typical chromatogram is shown in Figure 3.2-2. There were a number of peaks with mass spectra corresponding to cumene, 2-methylstyrene, 1,2,3,4-tetrahydronaphthalene, 1-methylnaphthalene, 1-naphthol, binaphthalene. All these intermediate breakdown products were completely destroyed as milling progressed, with none of them detected by GCMS in the final milled sample.

Figure 3.2-3 gives the structures of the breakdown compounds detected. Identification of compounds was achieved by comparing the experimental spectra to library reference mass spectra of the database. When possible, retention times of

chromatographic peaks were also compared with the ones of authentic standards when available.

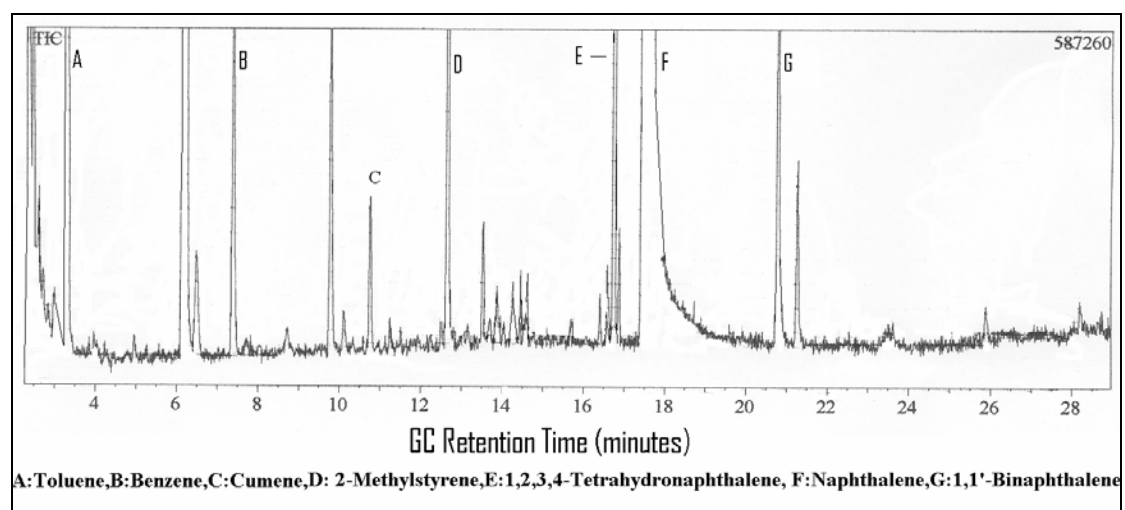


Figure 3.2-2: Typical chromatogram for naphthalene milled for 30 minutes.

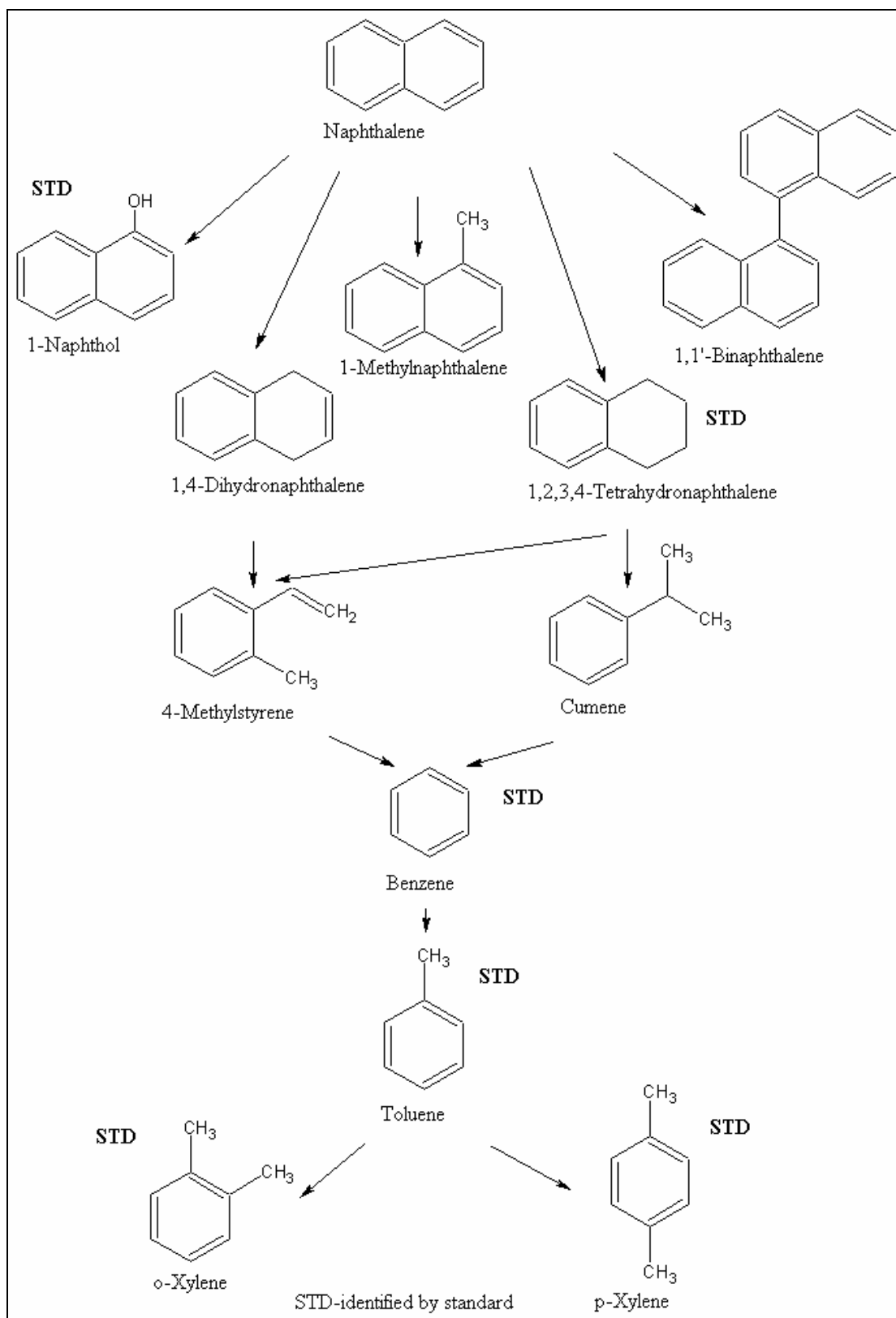


Figure 3.2-3: Intermediate breakdown products for naphthalene

At the conclusion of milling, the majority of breakdown products were never detected at more than 1% of the original naphthalene concentration as shown in Figure 3.2-4.

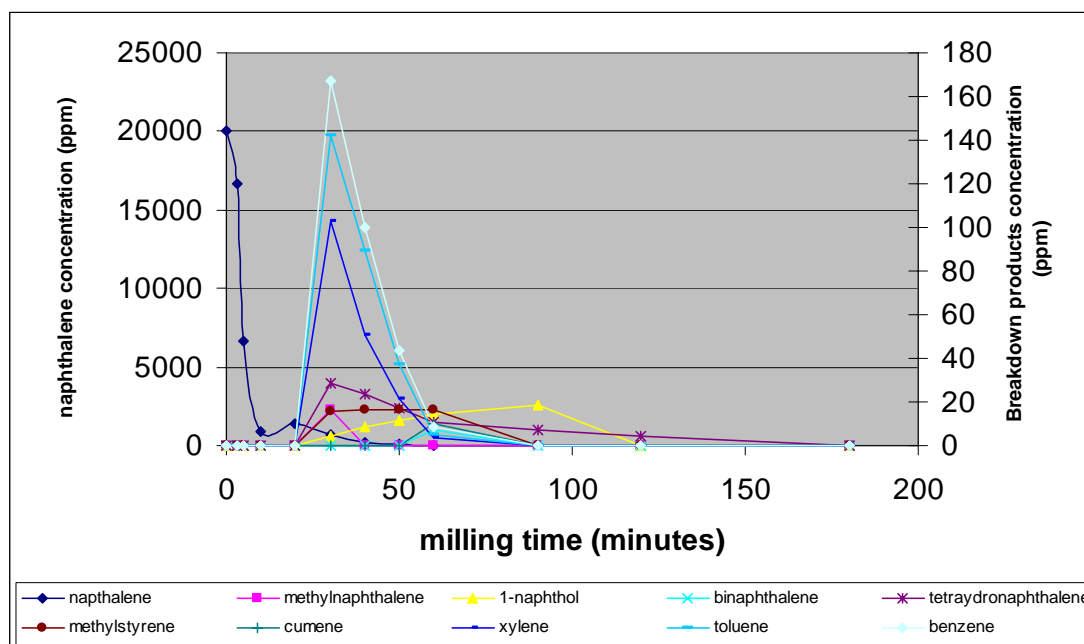


Figure 3.2-4: High concentration trial for naphthalene and breakdown products

3.2.3 High Concentration Anthracene in Quartz Sand

Final Products

On milling of anthracene in quartz sand, the colour of the sand changed from yellow to grey, as in the naphthalene experiment above. No final compound was detected by GCMS analysis of the treated samples after 2 hours milling.

Intermediate Breakdown Products

In the Headspace.

Volatile compounds benzene and toluene were detected in small amounts in the headspace gas at intermediate stages of milling. At the conclusion of milling however no volatiles could be detected in the headspace of the milling vessel indicating that any volatile fragments formed are destroyed through continued milling. Apart from

the original anthracene, small amount of naphthalene was found as a semi-volatile compound after 30 minutes milling.

In the solid

GCMS analysis of the solid samples taken at regular intervals during milling revealed a large number of peaks found apart from the original anthracene. Figure 3.2-5 shows a typical chromatogram with the larger peaks labelled. Various compounds such as naphthalene, methylanthracene, anthrone, anthraquinone, dihydroanthracene, tetrahydroanthracene were detected in the treated samples in small concentrations. Tetrahydroanthracene, anthrone, anthraquinone were detected in more than one isometric form. The identities of anthrone, anthraquinone were confirmed by analysis of standards. Figure 3.2-6 gives the structures of all the breakdown products.

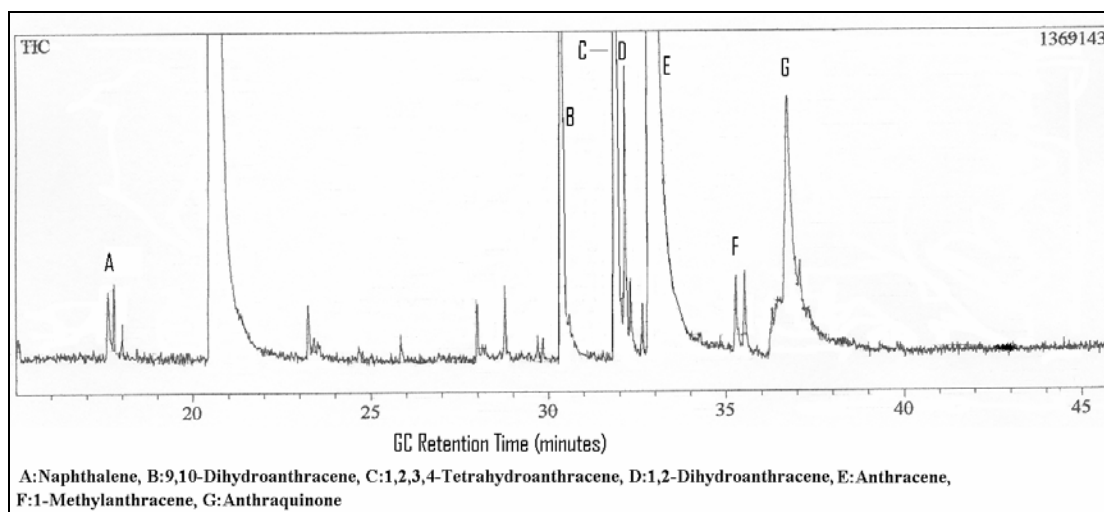


Figure 3.2-5: Typical chromatogram for anthracene milled for 60 minutes

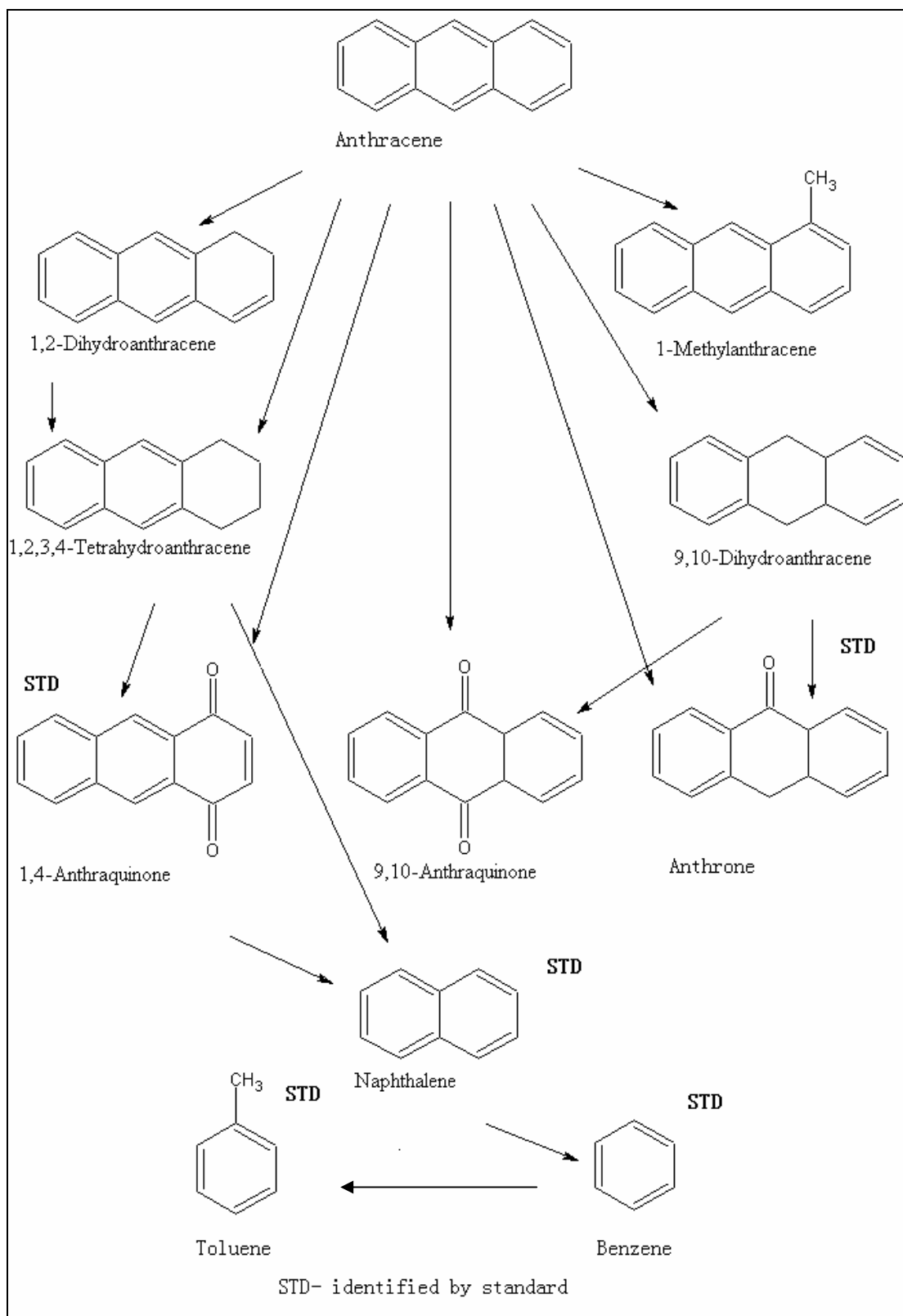


Figure 3.2-6: Intermediate breakdown products for anthracene

At the conclusion of milling, with the exception of anthracenedione, maximum concentrations of breakdown products were generally obviously less than 1% of the original anthracene concentration as shown in Figure 3.2-7.

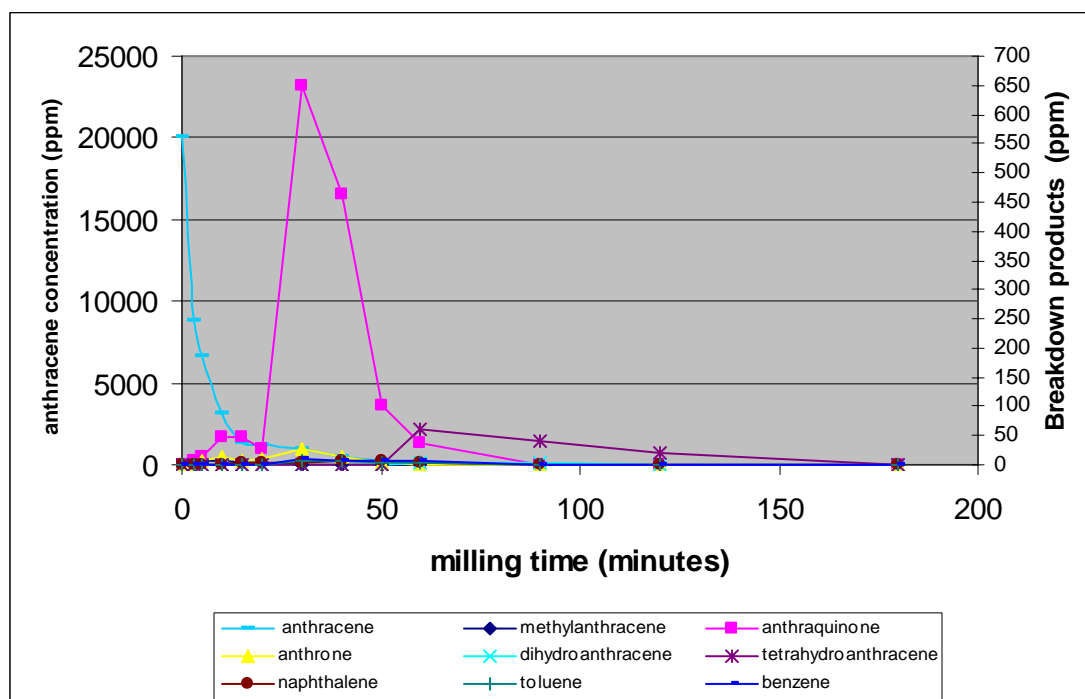


Figure 3.2-7: High concentration trial for anthracene and breakdown products

3.2.4 High Concentration PCP in Quartz Sand

Final Products

The final products in the milling destruction of PCP in quartz sand are assumed to be the usual carbon residue and inorganic chloride. The colour of the milled sample changes from pale yellow to dark grey.

Intermediate Breakdown Products

In the Headspace

Volatile compounds benzene, toluene, chlorobenzene, xylene and phenol were detected in small amounts in the headspace gas after 30 minutes and 1 hour of milling.

The presence of tetrachlorophenol is as expected for a semi-volatile compound. It should be mentioned that all chlorinated volatile compounds are destroyed through continued milling.

In the Solid

A large number of compounds were detected during GCMS analysis of milled samples. Part of a typical chromatogram is shown in Figure 3.2-8. Tetrachlorophenol was detected as an impurity in the original PCP quartz sand sample and hence its presence in the milled sample is most likely due to this rather than the formation of tetrachlorophenol from PCP. Figure 3.2-9 shows the structures of the breakdown compounds detected. Many of the breakdown products were detected in more than one isomeric form such as chlorobenzene, trichlorophenol, and tetrachlorophenol. Phenol was detected with its mass spectra corresponding to the standard compound. Trichlorophenol, and tetrachlorophenol were the more abundant intermediate breakdown products. All these intermediate breakdown products were destroyed as milling progressed.

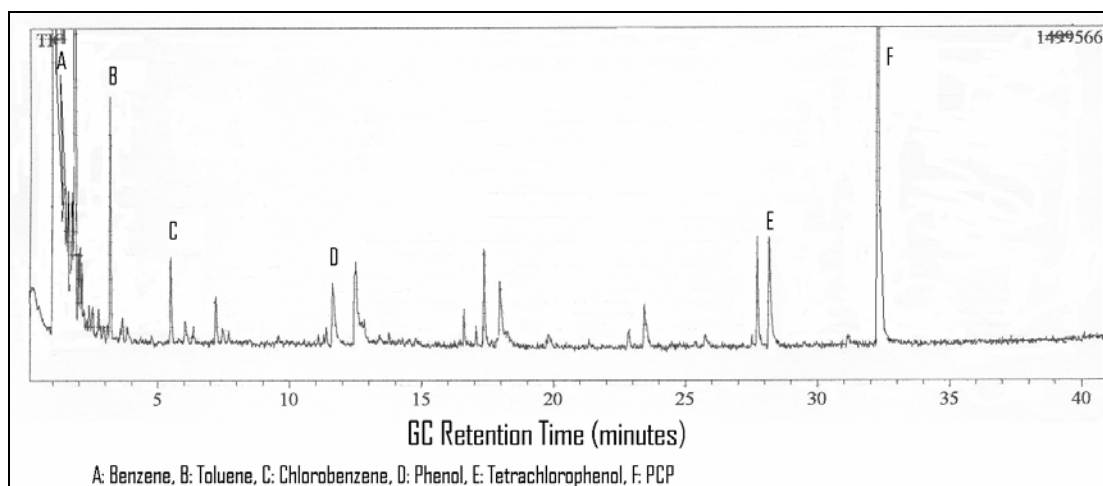


Figure 3.2-8: Typical chromatogram for PCP milled for 30 minutes

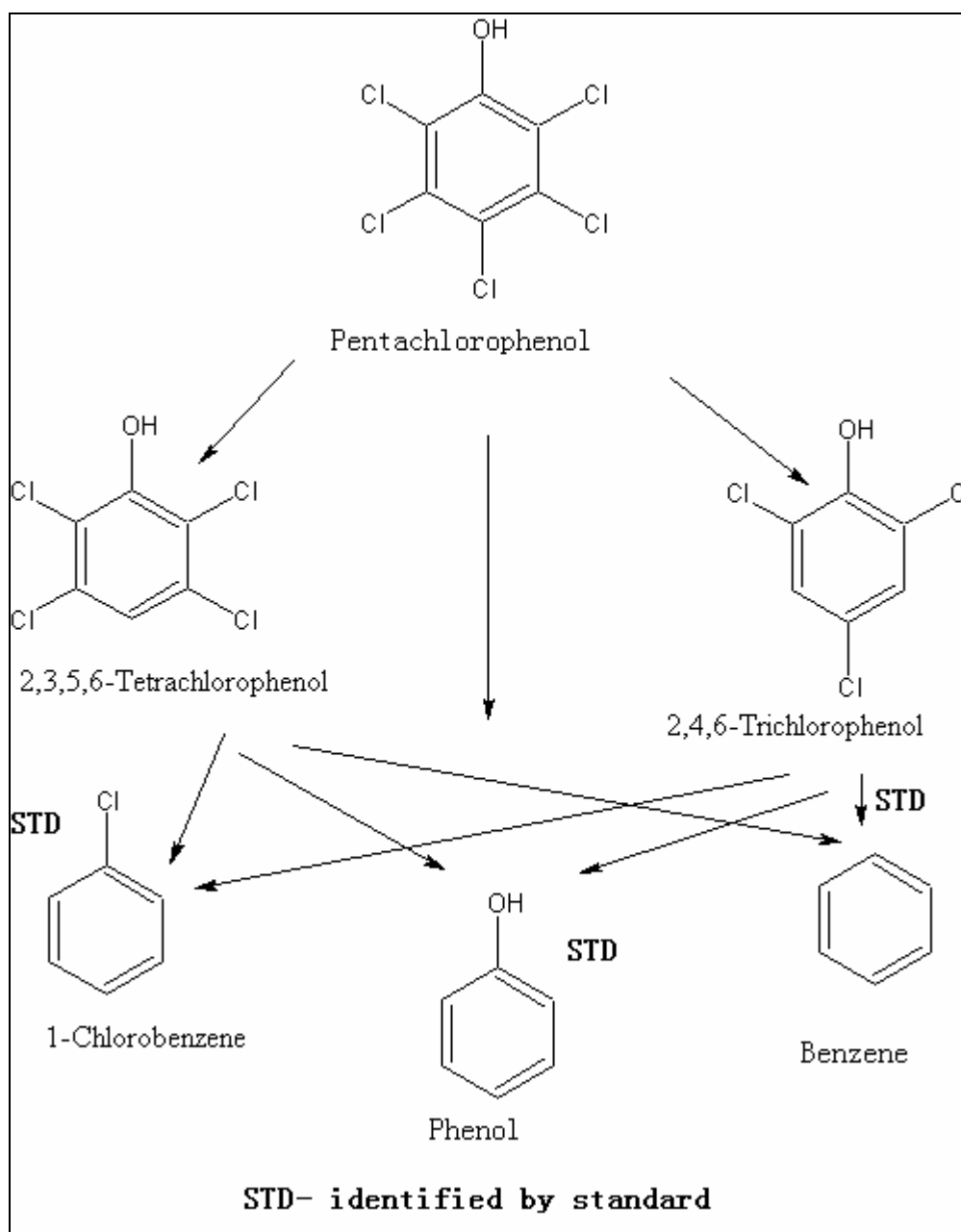


Figure 3.2-9: Intermediate breakdown products for PCP

At the conclusion of milling, with the exception of tetrachlorophenol, maximum concentrations of breakdown products were significantly less than 1% of the original PCP concentrations as Figure 3.2-10 shown as follows.

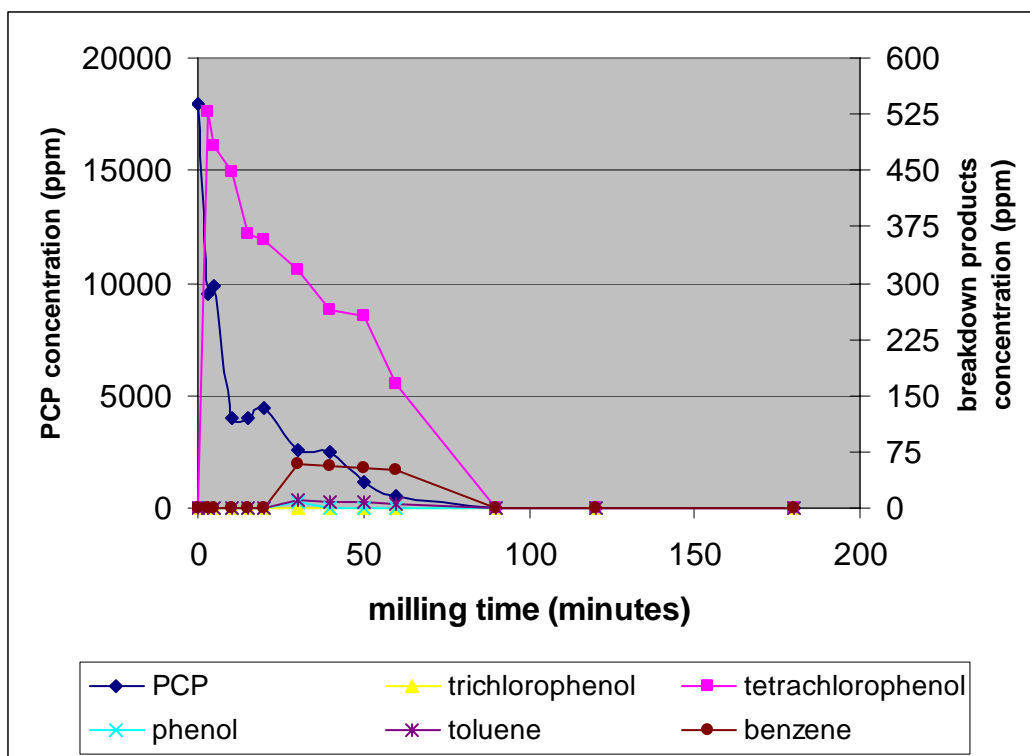


Figure 3.2-10: High concentration trial for PCP and breakdown products

3.3 Reactive Milling in Halogenated and Hydroxylated Aromatics

3.3.1 Halogenated and Hydroxylated Aromatics separately Milling

3.3.1.1 High Concentration 1-Chlorobenzene in Quartz Sand

No compounds were detected by GCMS analysis after 1 hour of milling. In this trial, the initial concentration of 1-chlorobenzene (22,512 ppm) is reduced to $< \sim 1$ ppm within 60 minutes of milling. The final products are assumed to be the carbon residue and inorganic chloride.

3.3.1.2 High Concentration 1-Bromobenzene in Quartz Sand

No compounds were detected by GCMS analysis after 1 hour of milling. In this trial, the initial concentration of 1-bromobenzene (31,404 ppm) is reduced to $< \sim 1$ ppm within 60 minutes of milling. The final products are assumed to be the carbon residue and inorganic bromine.

3.3.1.3 High Concentration 1-Chloronaphthalene in Quartz Sand

Milling of 1-chloronaphthalene resulted in the usual colour change of the quartz sand from yellow to dark brown. Products were detected in low concentrations (< 80 ppm). The major breakdown products detected were naphthalene. Other minor products detected are shown in Figure 3.3-1. All the breakdown products, with the exception of 1,2,3-trichlorotoluene, were identified by authentic standard.

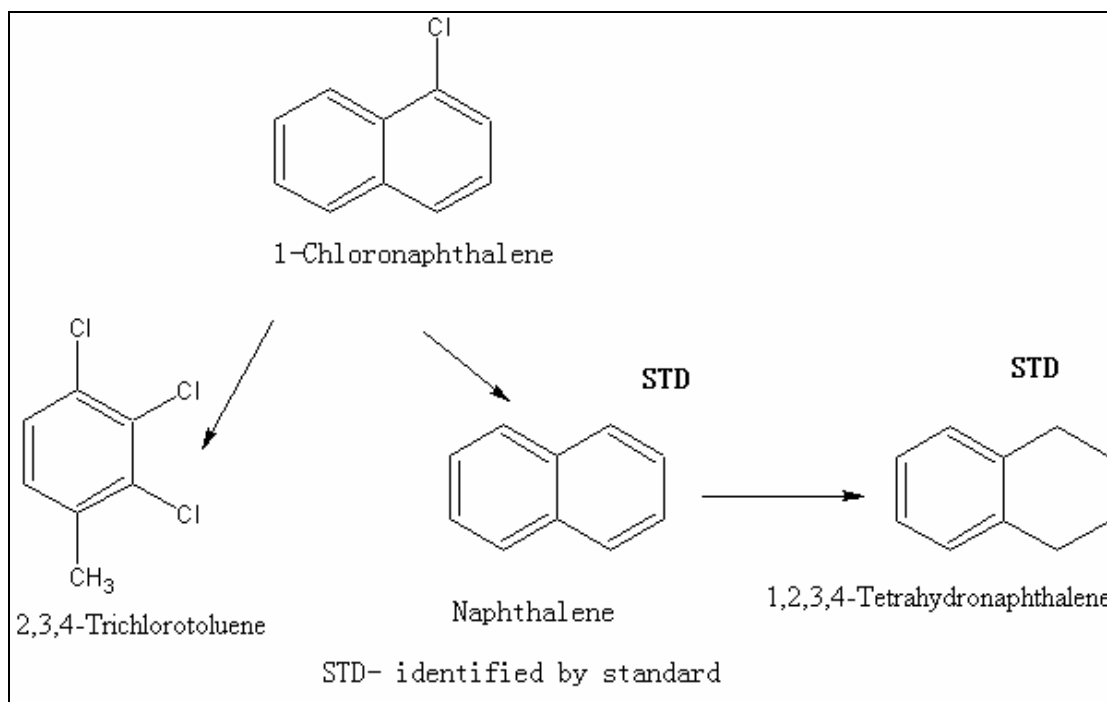


Figure 3.3-1: Intermediate breakdown products for 1-chloronaphthalene

3.3.1.4 High Concentration 1-Bromonaphthalene in Quartz Sand

On milling of 1-bromonaphthalene in quartz sand, the colour of the sand changed from yellow to brown. Naphthalene, dibromonaphthalene are found the most amounts. In particular, other major products are shown in Figure 3.3-2 with present in more than one isomeric form. All the breakdown products are detected in low concentrations (< 200ppm) and with the exception of naphthalene were identified by mass spectrum library match only.

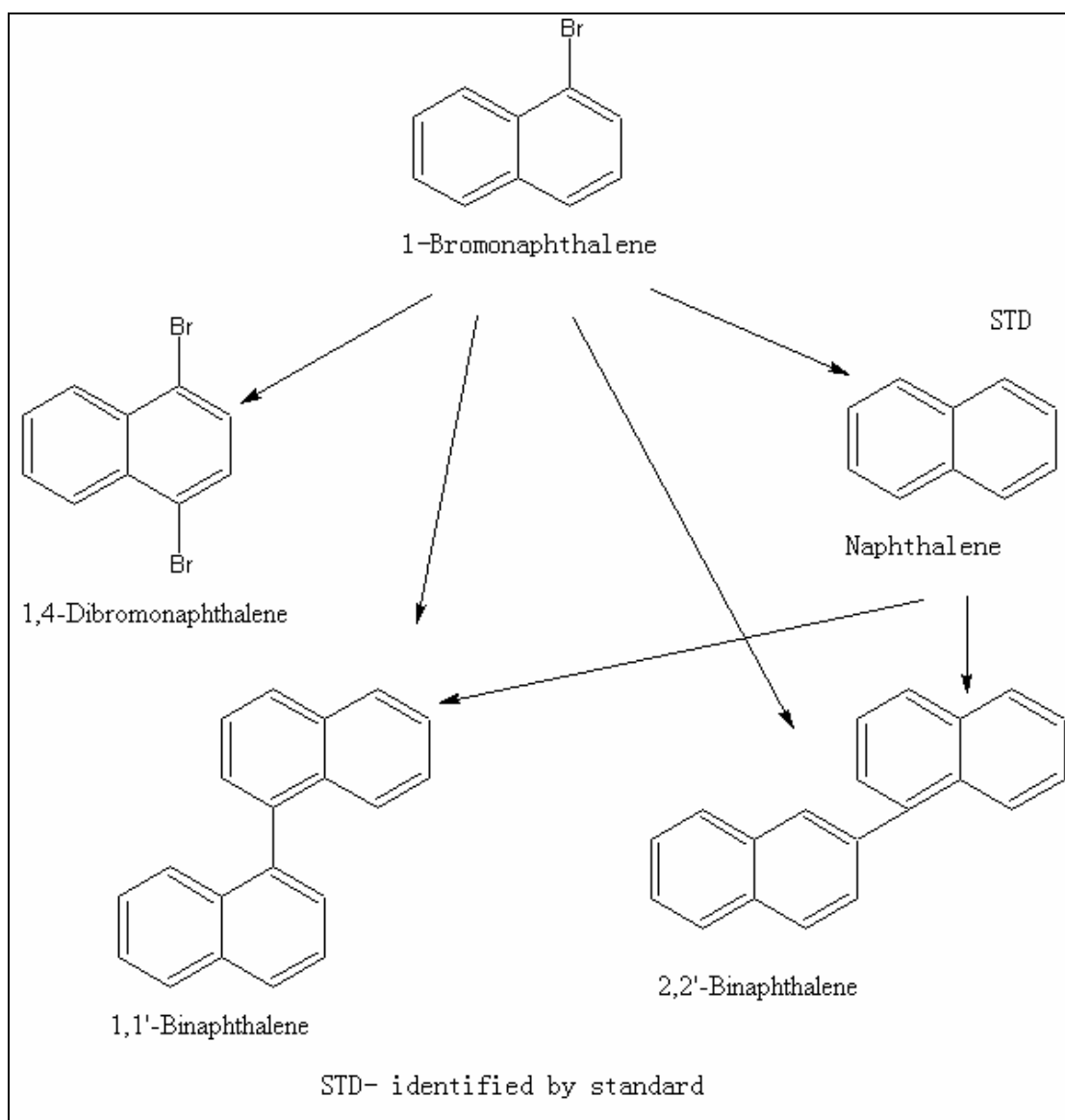


Figure 3.3-2: Intermediate breakdown products for 1-bromonaphthalene

3.3.1.5 High Concentration Phenol in Quartz Sand

Milling of phenol resulted in the usual colour change of the quartz sand from pale yellow to dark brown. Products that were detected in low concentrations are shown in Figure 3.3-4. Volatile compounds benzene, toluene, xylene, styrene, methylphenol were detected in small amounts in the headspace gas after 30 minutes of milling. Naphthalene and benzenediol were detected in the milled sample. Part of a typical chromatograph is shown in Figure 3.3-3.

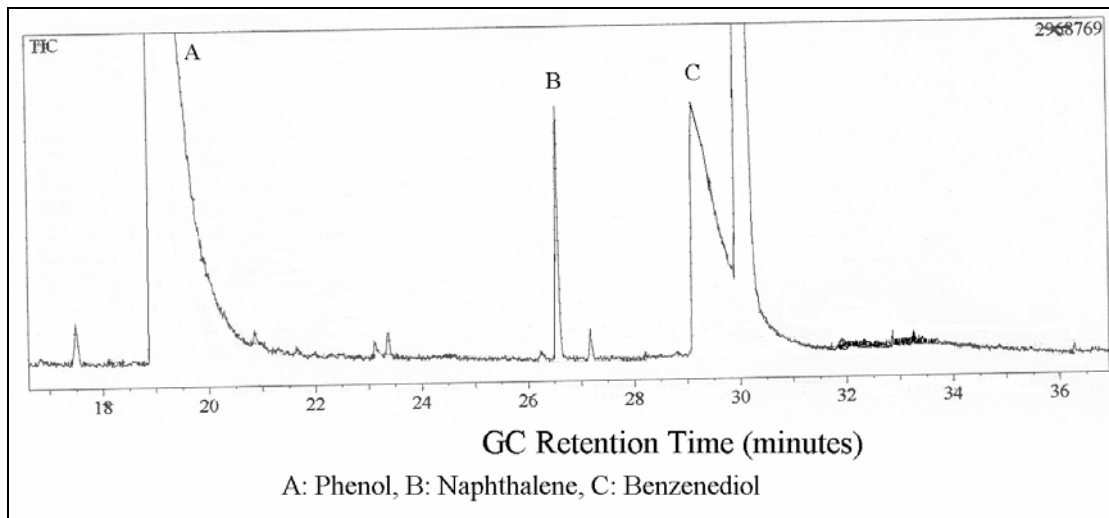


Figure 3.3-3: Typical chromatograph for phenol milled for 60 minutes

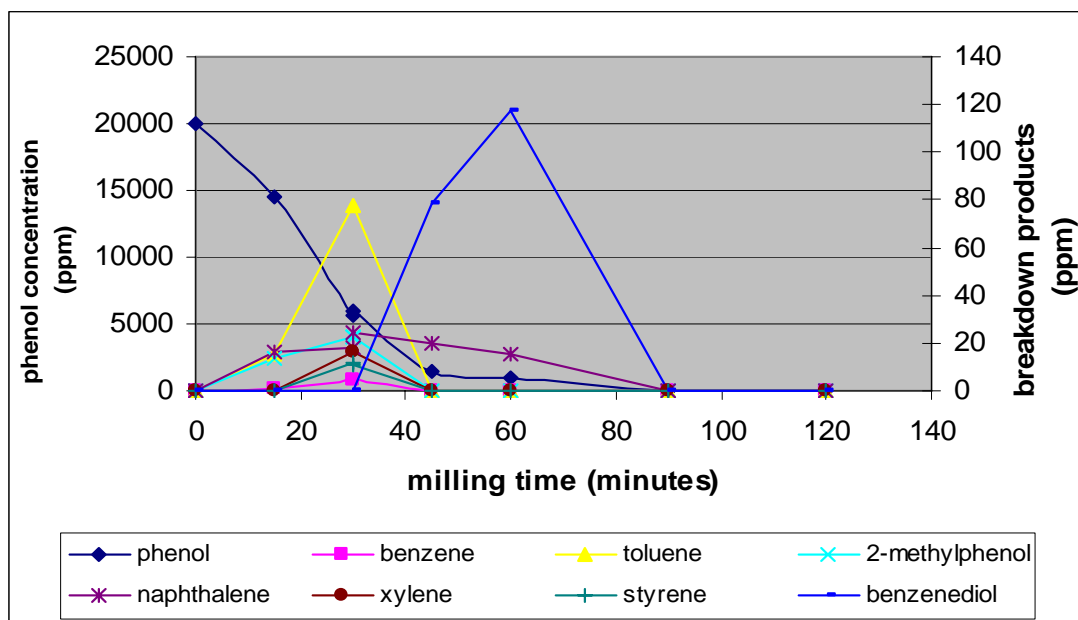


Figure 3.3-4: High concentration trial for phenol and breakdown products

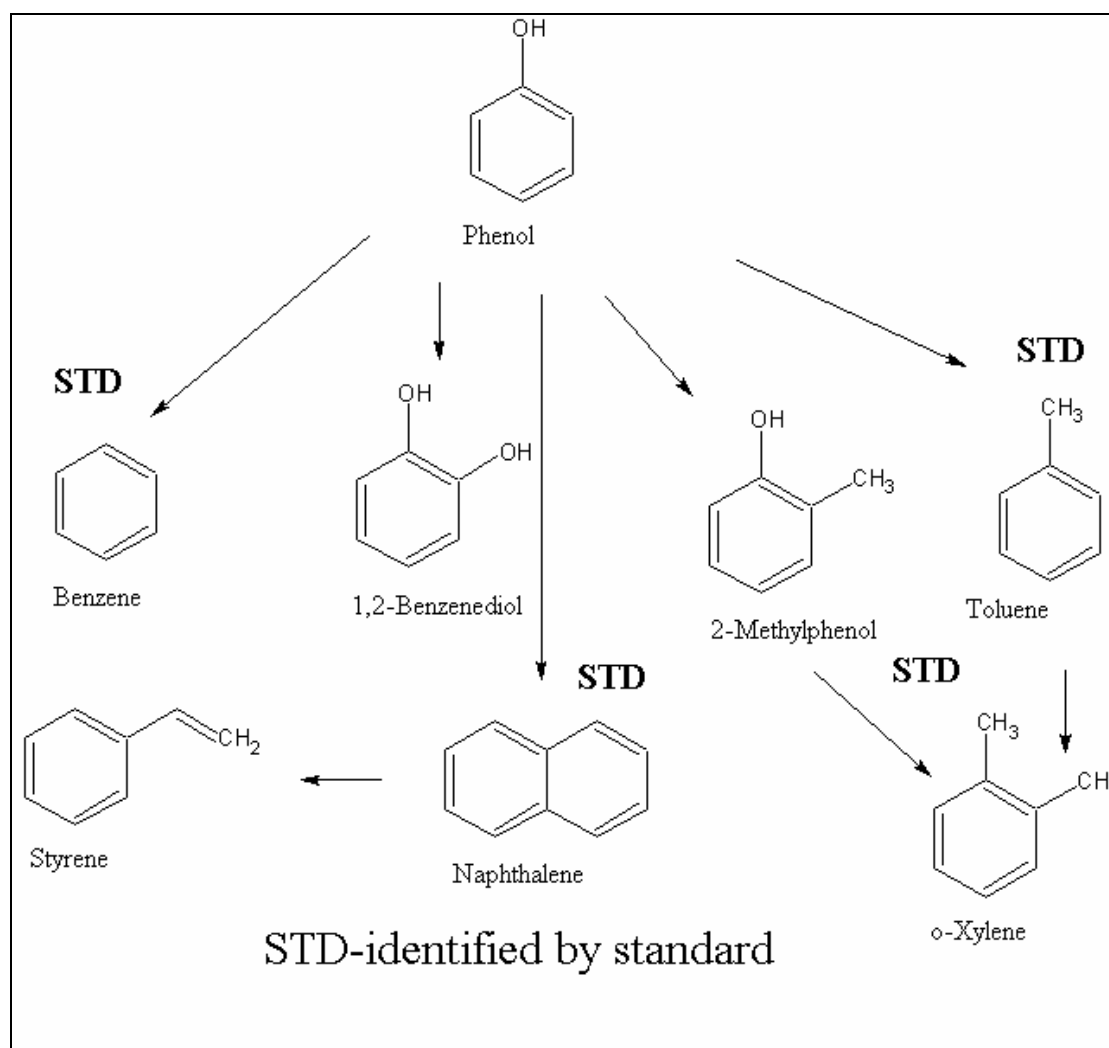


Figure 3.3-5: Intermediate breakdown products for phenol

3.3.1.6 High Concentration 1-Naphthol in Quartz Sand

Milling of 1-naphthol resulted in the colour change of the quartz sand from yellow to dark brown. With the exception of naphthalene, other minor products such as binaphthol and dinaphtho[1,2-b:1,2-d]furan detected are shown in Figure 3.3-6 with the present in more than one isomeric form and were identified by mass spectrum library match only. All the breakdown products were detected in low concentrations ($< 50\text{ppm}$).

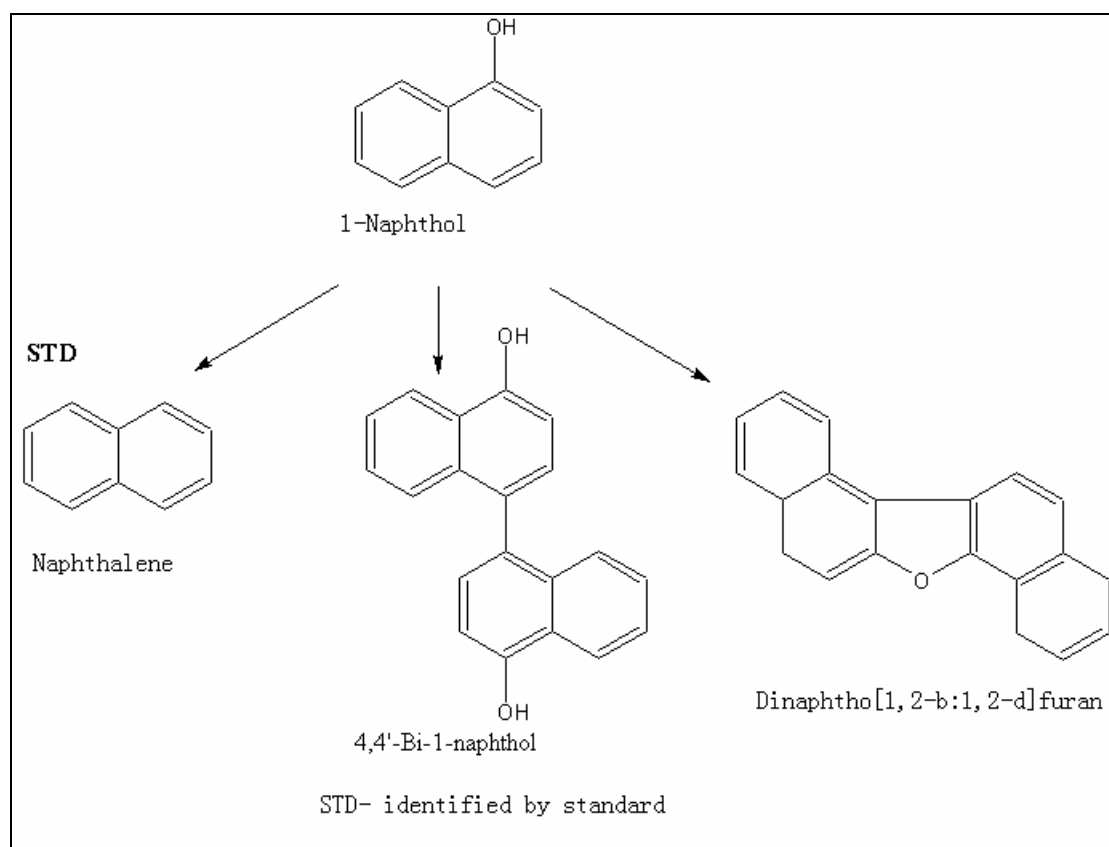


Figure 3.3-6: Intermediate breakdown products for 1-naphthol

3.3.1.7 High Concentration 2-Naphthol in Quartz Sand

On milling of 2-naphthol in quartz sand, the colour of the sand changed from yellow to dark brown. The major breakdown products shown in Figure 3.3-7 similar as 1-naphthol were naphthalene, binaphthol and dinaphtho[1,2-b:1,2-d]furan. The distinction between 1-naphthol and 2-naphthol is the presence of binaphthol with different isomeric form. All the breakdown products with the exception of naphthalene were identified by mass spectrum library match only.

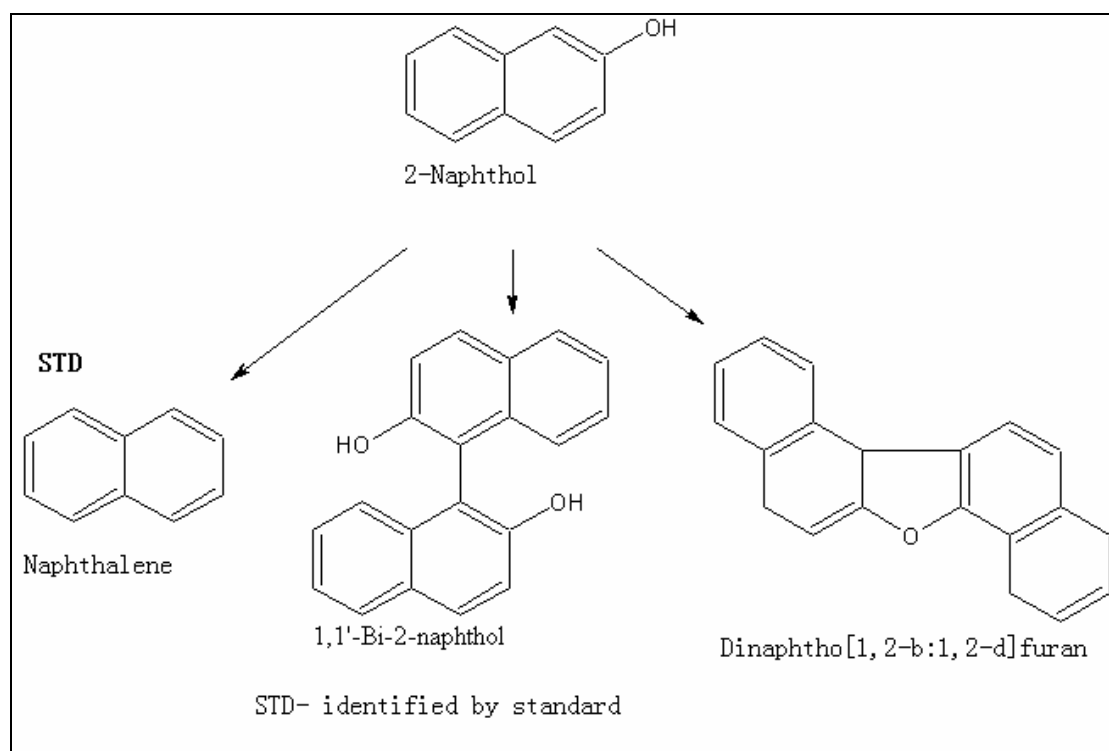


Figure 3.3-7: Intermediate breakdown products for 2-naphthol

3.3.2 Halogenated and Hydroxylated Aromatics “Cross-Over”

Milling

3.3.2.1 High Concentration Mixed 1-Chlorobenzene and 1-Bromobenzene in Quartz Sand

The detection of chlorobenzene and bromobenzene in the headspace after milling is expected based on their volatilities. A relatively large benzene peak, the result of dehalogenation of the starting halo-benzenes, was detected. No bromochlorobenzene was detected.

A number of compounds were detected in the milled solid including the compounds detected in the headspace. Only one halogenated compounds detected was bromobiphenyl. Other compounds detected were toluene and biphenyl. With the exception of benzene, the concentration of each breakdown products was much less than 1% of the original halobenzene concentration as shown in Figure 3.3-8. The identity of biphenyl was confirmed by analysis of authentic standards.

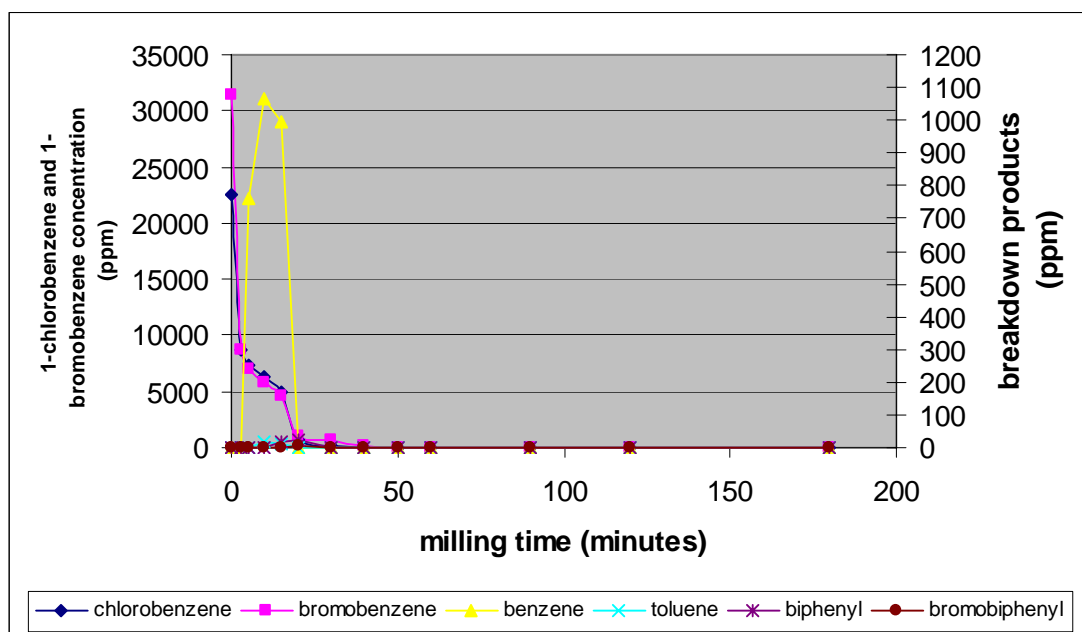


Figure 3.3-8: High concentration trial for 1-chlorobenzene and 1-bromobenzene

3.3.2.4 High Concentration Mixed 1-Chloronaphthalene and 1-Bromonaphthalene in Quartz Sand

The detection of 1-chloronaphthalene and 1-bromonaphthalene in the headspace after milling is expected based on their volatilities. Benzene, toluene, naphthalene were detected as a result of dehalogenation of the starting halo-naphthalenes. Other compounds detected were chlorobenzene, trichlorotulene, dibromonaphthalene were seen in the analysis of GCMS.

A large number of compounds were detected in the milled solid including the compounds detected in the headspace. Other compounds detected were bromomethylbenzene, tetrahydronaphthalene, methylnaphthalene, binaphthalene. No bromochloronaphthalene or dichloronaphthalene were detected. With the exception of naphthalene, the concentration of each breakdown products was much less than 1% of the original halonaphthalene concentration as shown in Figure 3.3-10. The identities of chlorobenzene, toluene, and naphthalene were confirmed by analysis of authentic standard. The structures of breakdown products are shown in Figure 3.3-12.

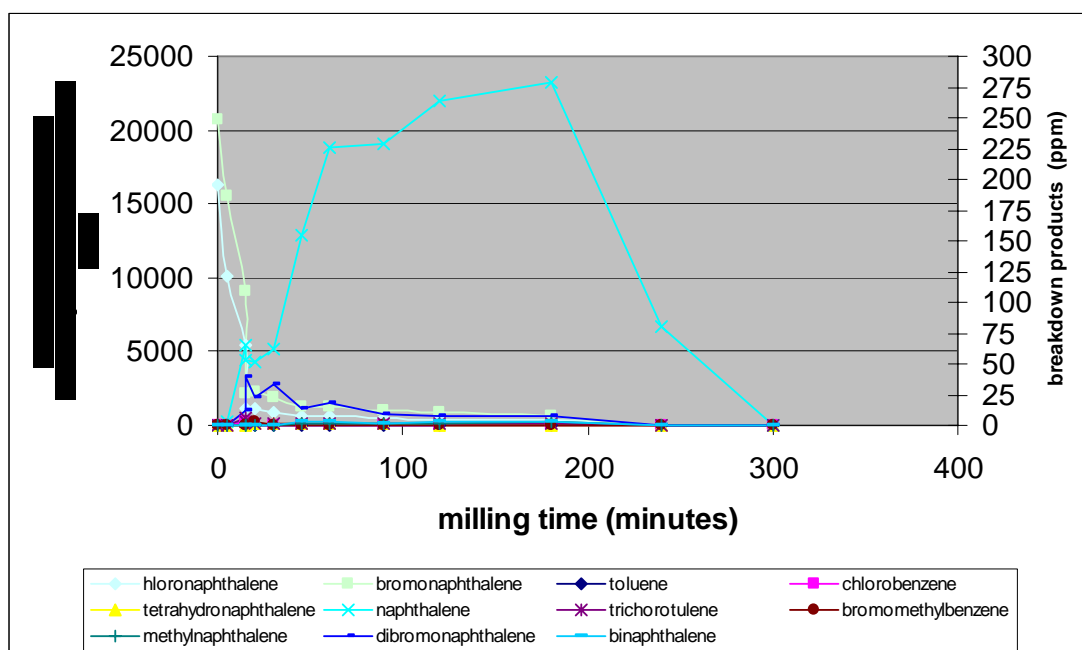


Figure 3.3-10: High concentration trial for 1-chloronaphthalene and 1-bromonaphthalene and breakdown products

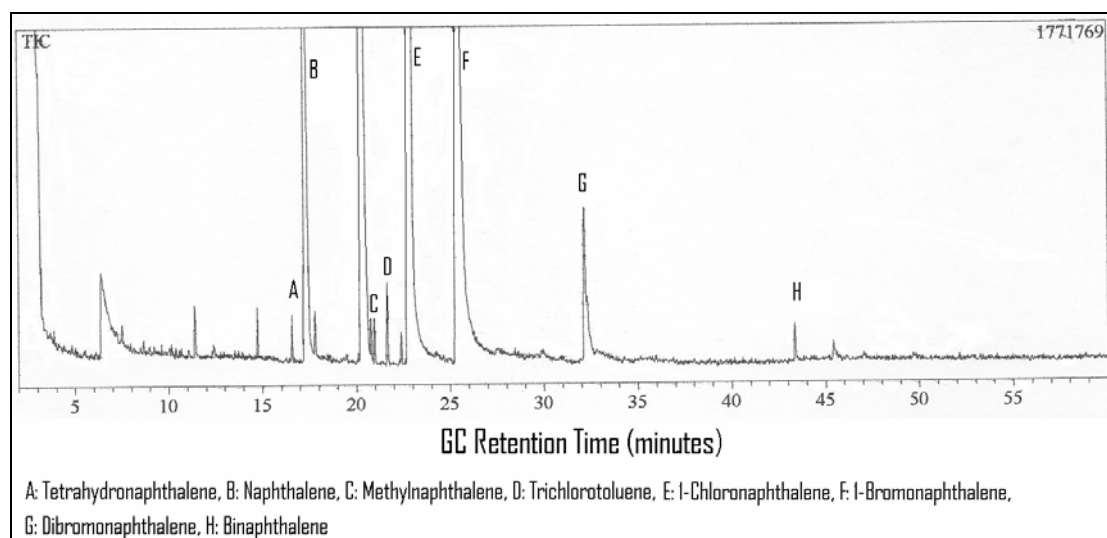


Figure 3.3-11: Typical chromatogram for 1-chloronaphthalene and 1-bromonaphthalene milled for 60 minutes

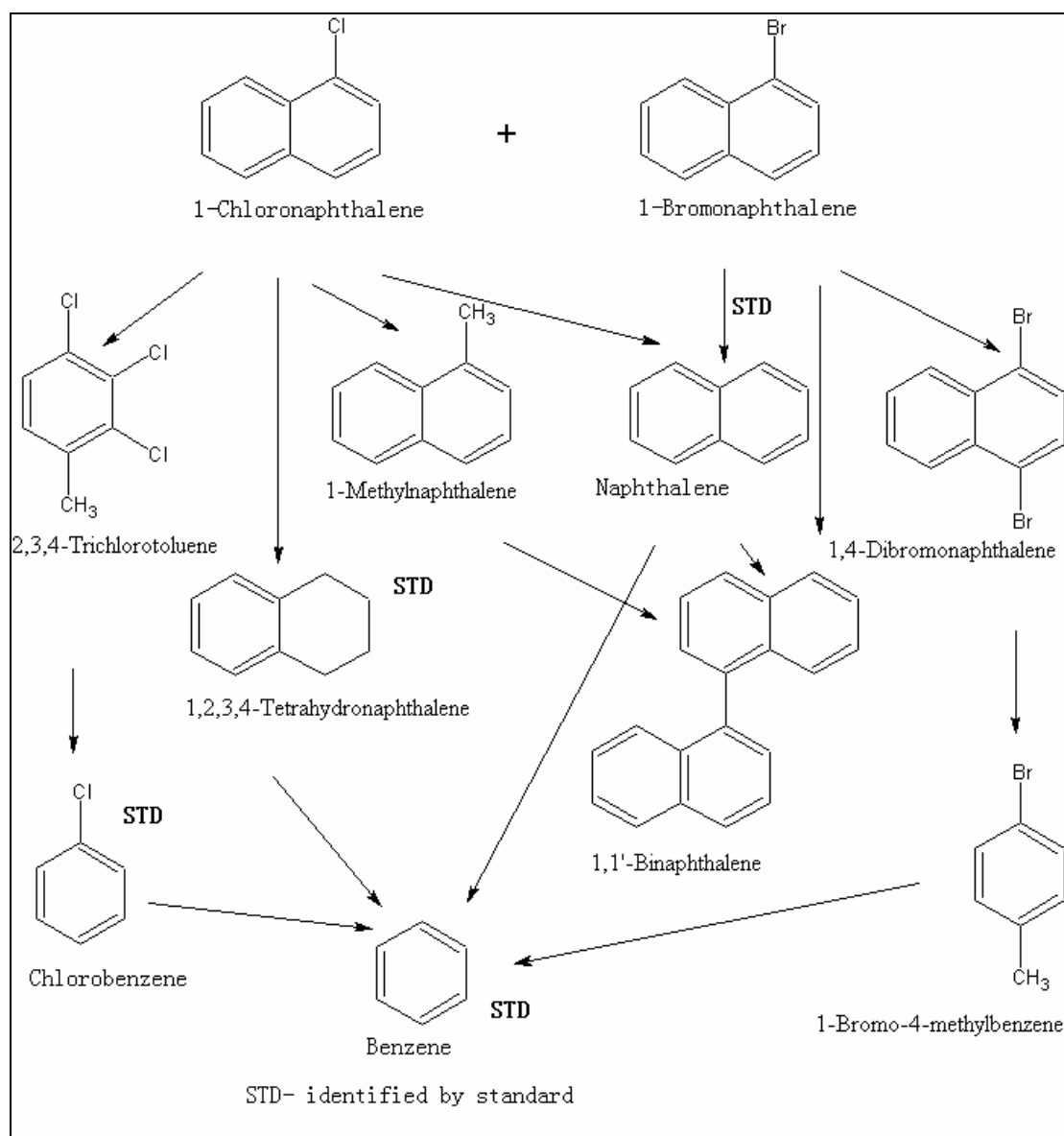


Figure 3.3-12: Intermediate breakdown products for 1-chloronaphthalene and 1-bromonaphthalene

3.3.2.5 High Concentration Mixed 1-Chlorobenzene and 1-Naphthol in Quartz Sand

Volatile compounds benzene, toluene, naphthalene was detected in the headspace after milling 1-chlorobenzene and 1-naphthol mixture. A small peak of tetrahydronaphthalene was also seen.

Apart from the original 1-chlorobenzene and 1-naphthol, toluene, naphthalene, 1-naphthalenone, 1,4-naphthalenedione were detected in the treated samples in small concentrations (less than 1%) shown in Figure 3.3-13. It can be assumed that during milling the carbon in the naphthalene reacts with oxygen in the air to form naphthalenone and naphthalenedione. No chloronaphthol or binaphthol were detected. Figure 3.3-15 gives the structures of the intermediate breakdown products. All breakdown products, with the exception of naphthalene, were identified by mass spectrum library match only.

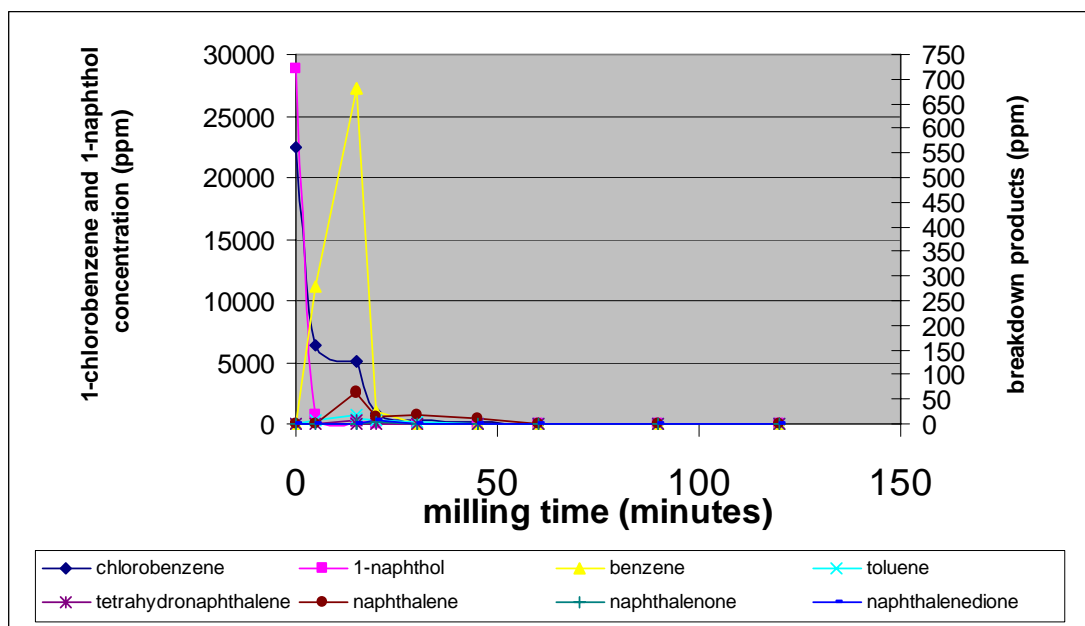


Figure 3.3-13: High concentration trial for 1-chlorobenzene and 1-naphthol and breakdown products

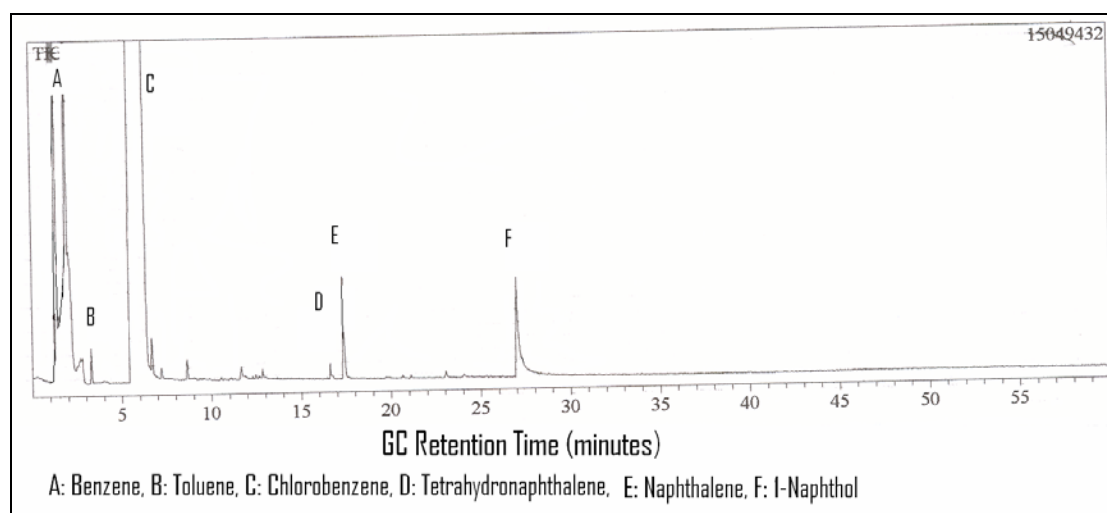


Figure 3.3-14: Typical chromatogram for 1-chlorobenzene and 1-naphthol milled for 15 minutes

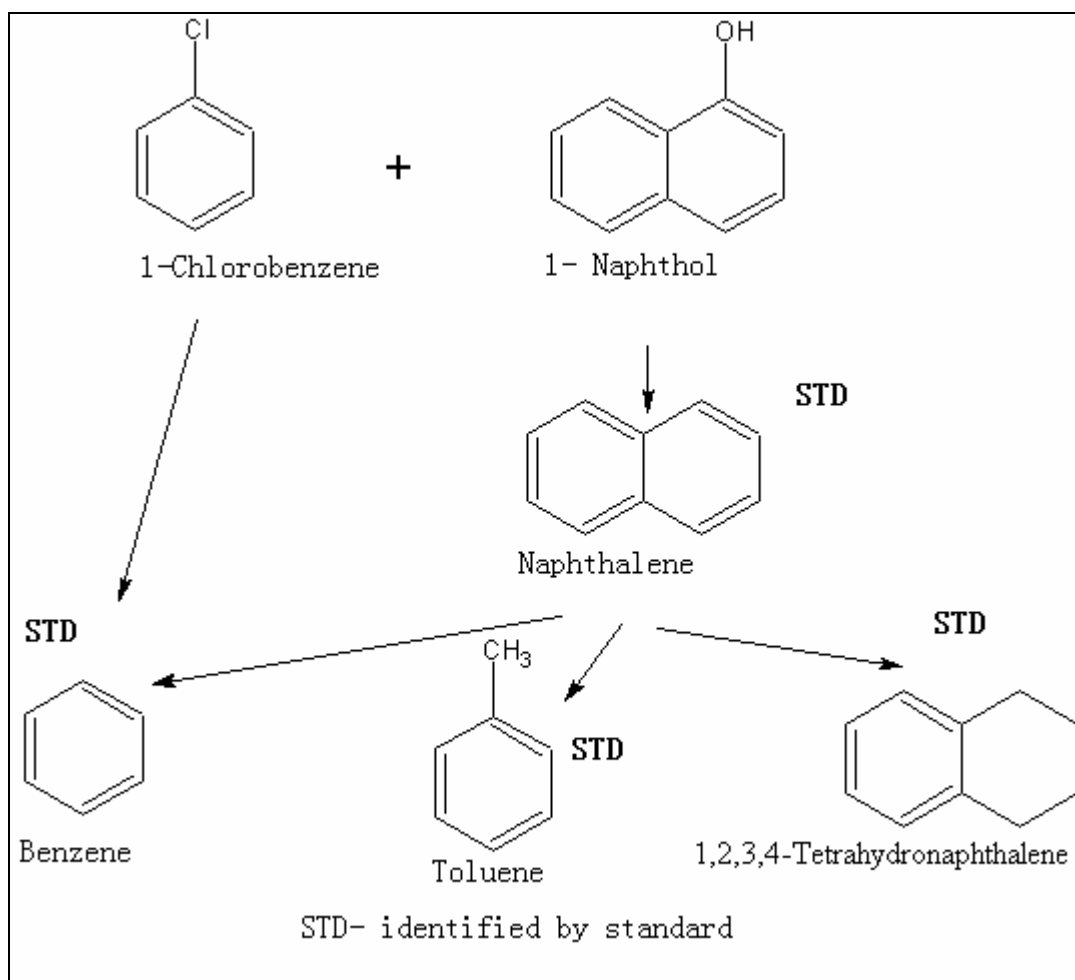


Figure 3.3-15: Intermediate breakdown products for 1-chlorobenzene and 1-naphthol

3.3.2.6 High Concentration Mixed 1-Chlorobenzene and 2-Naphthol in Quartz Sand

On milling of 1-chlorobenzene and 2-naphthol in quartz sand, benzene, toluene, naphthalene were all detected in the headspace gas.

Apart from the original 1-chlorobenzene and 2-naphthol, binaphthol was detected the most abundant. No halogenated compounds were detected as milling processed. Other compounds naphthalene, 2,6-naphthalenediol, dinaphtho[1,2-b:1.2-d]furan were detected in small concentrations as shown in Figure 3.3-16. Figure 3.3-18 gives the structures of the breakdown products detected. With the exception of naphthalene, the

identities of 2,6-naphthalenediol, binaphthol, dinaphtho[1,2-b:1,2-d] furan was confirmed by mass spectrum library match only.

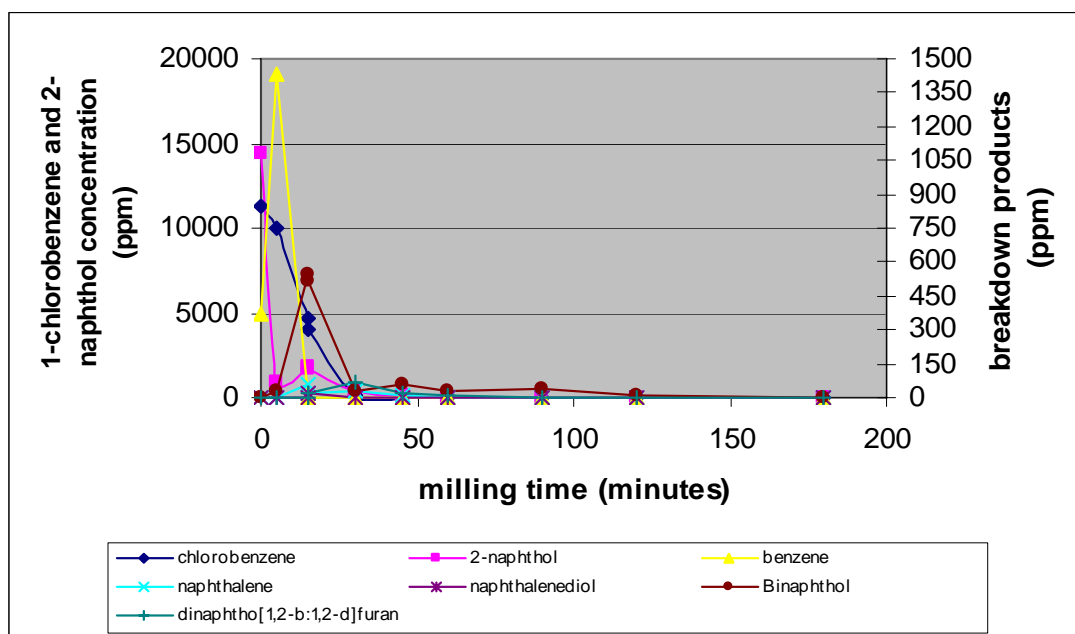


Figure 3.3-16: High concentration trial for 1-chlorobenzene and 2-naphthol and breakdown products

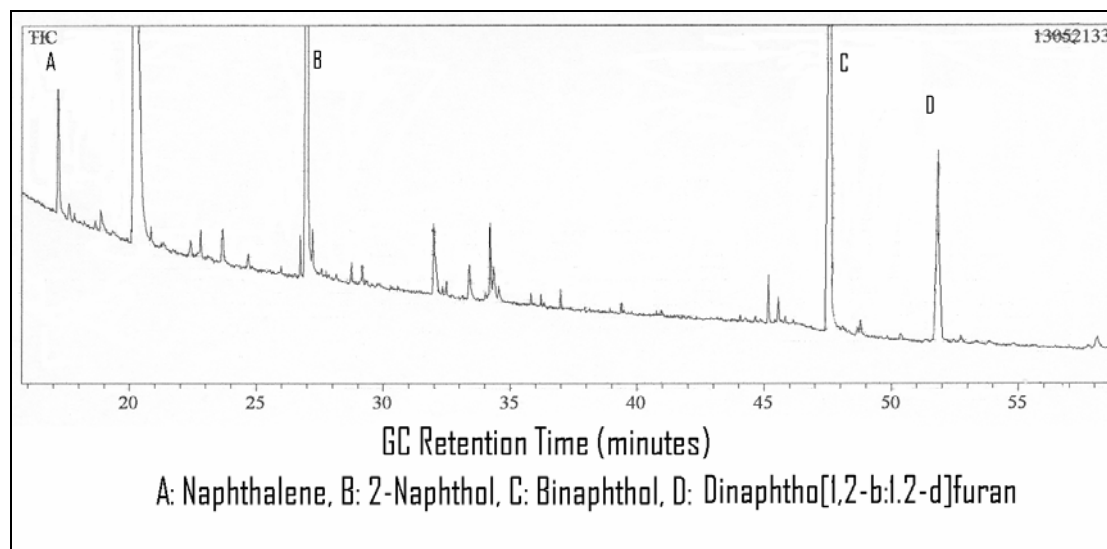


Figure 3.3-17: Typical chromatogram for 1-chlorobenzene and 2-naphthol breakdown products for 30 minutes

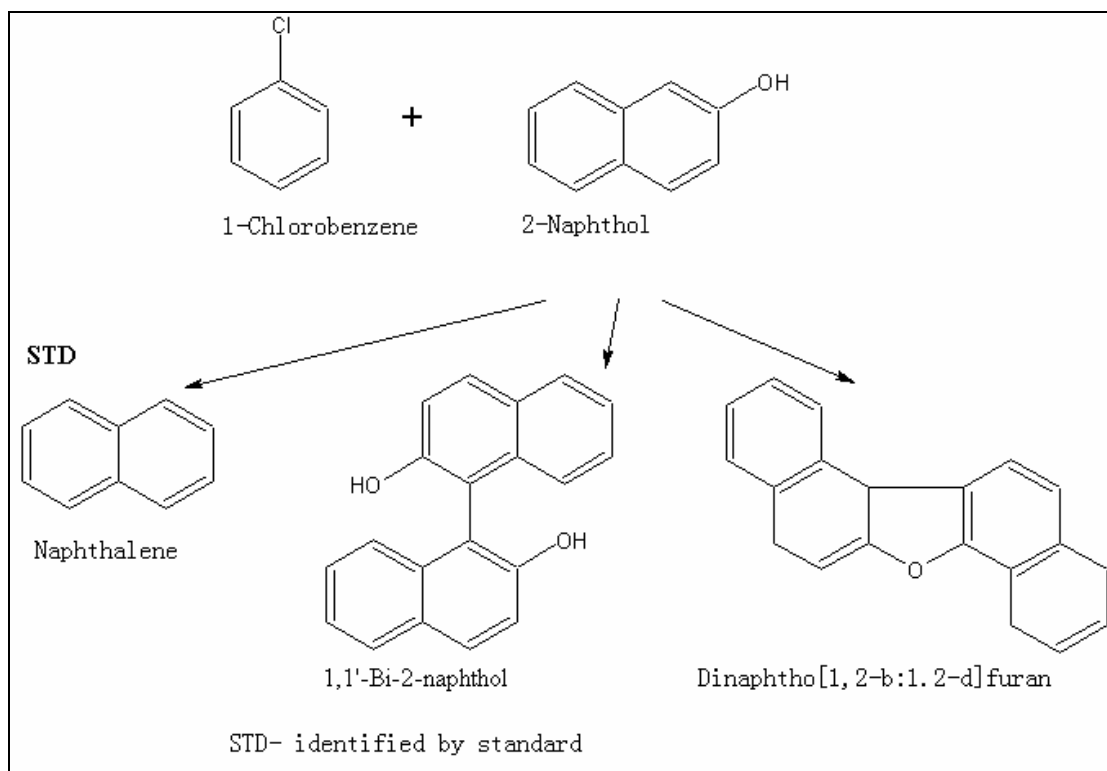


Figure 3.3-18: Intermediate breakdown products for 1-chlorobenzene and 2-naphthol

3.3.2.7 High Concentration Mixed 1-Bromobenzene and 1-Naphthol in Quartz Sand

No breakdown products were detected in the headspace gas after 30 minutes of milling. The only peaks shown in chromatograph were 1-bromobenzene and 1-naphthol.

The intermediate breakdown products detected were 1,4-naphthoquinone and dinaphtho[1,2-b:1.2-d]furan. Binaphthol was detected in more than one isomeric form (shown in Figure 3.3-21). It should be emphasised again that no other halogenated compounds was detected as milling progressed in this trial except 1-bromobenzene. Products that were detected in low concentrations (<50 ppm) are shown in Figure 3.3-19. All the breakdown products were identified by mass spectrum library match only.

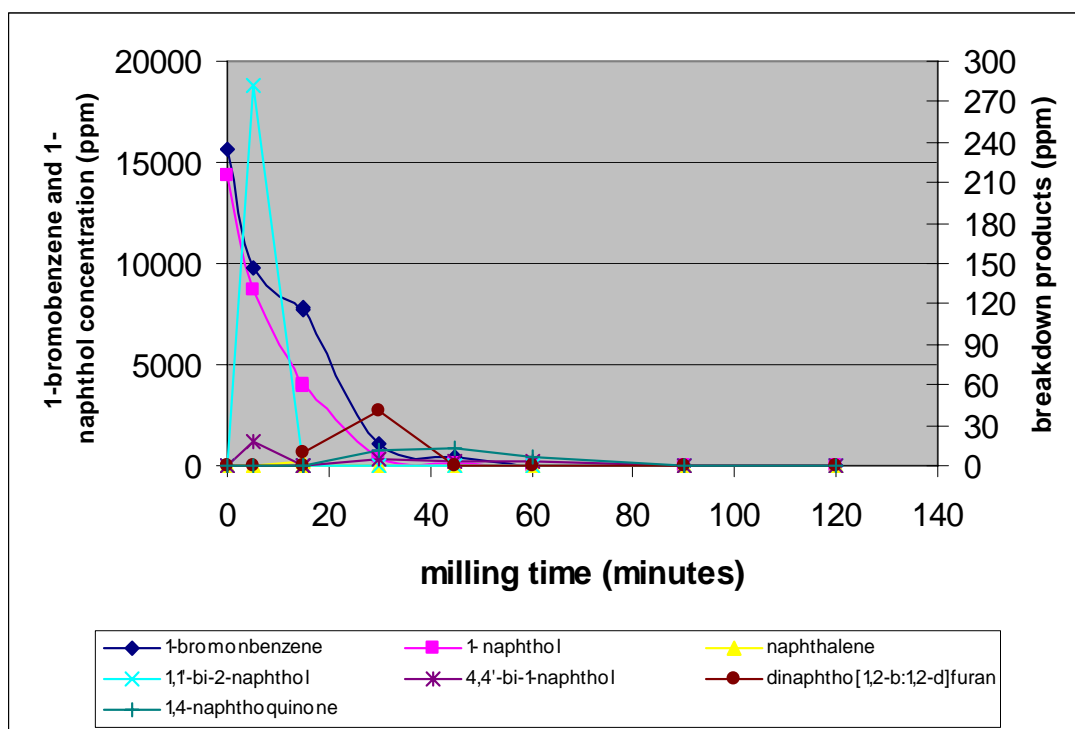


Figure 3.3-19: High concentration trial for 1-bromobenzene and 1-naphthol and breakdown products

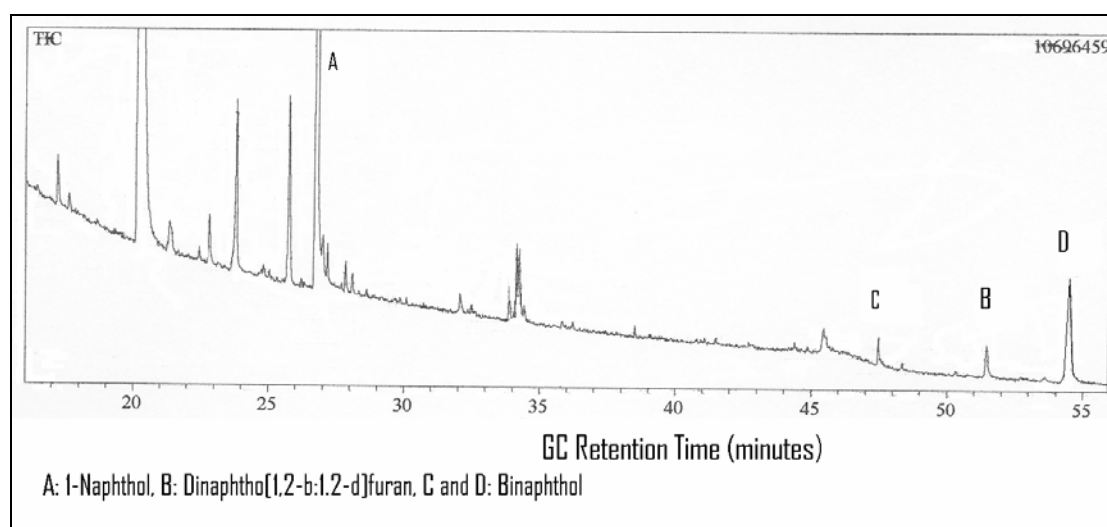


Figure 3.3-20: Typical chromatogram for 1-bromobenzene and 1-naphthol milled for 30 minutes

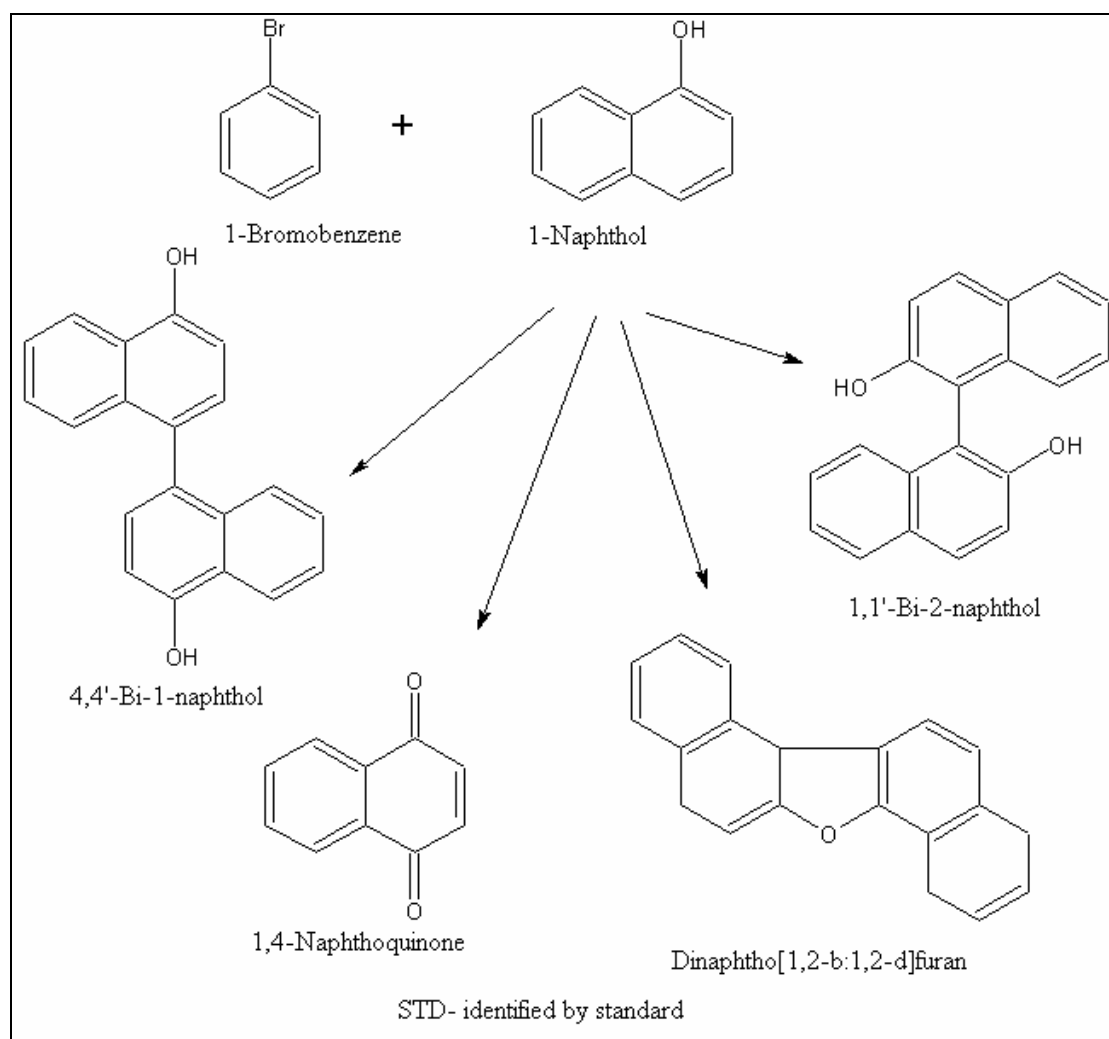


Figure 3.3-21: Intermediate breakdown products for 1-bromobenzene and 1-naphthol

3.3.2.8 High Concentration Mixed 1-Bromobenzene and 2-Naphthol in Quartz Sand

From the headspace samples after 15 minutes milling, small benzene and naphthalene peaks were detected by analysis of GCMS. No bromonaphthol was detected.

The intermediate breakdown products detected were similar to that obtained during the milling of 1-bromobenzene and 1-naphthol in quartz sand as reported in Section 3.3.2.7. Binaphthol was present in one isomeric form, while naphthalenediol in different isomeric form as shown in Figure 3.3-24. With the exception of binaphthol, the concentration of each breakdown products was much less than 50 ppm of the

original concentration seen from Figure 3.3-22. All the breakdown products except naphthalene were confirmed by mass spectrum library match only.

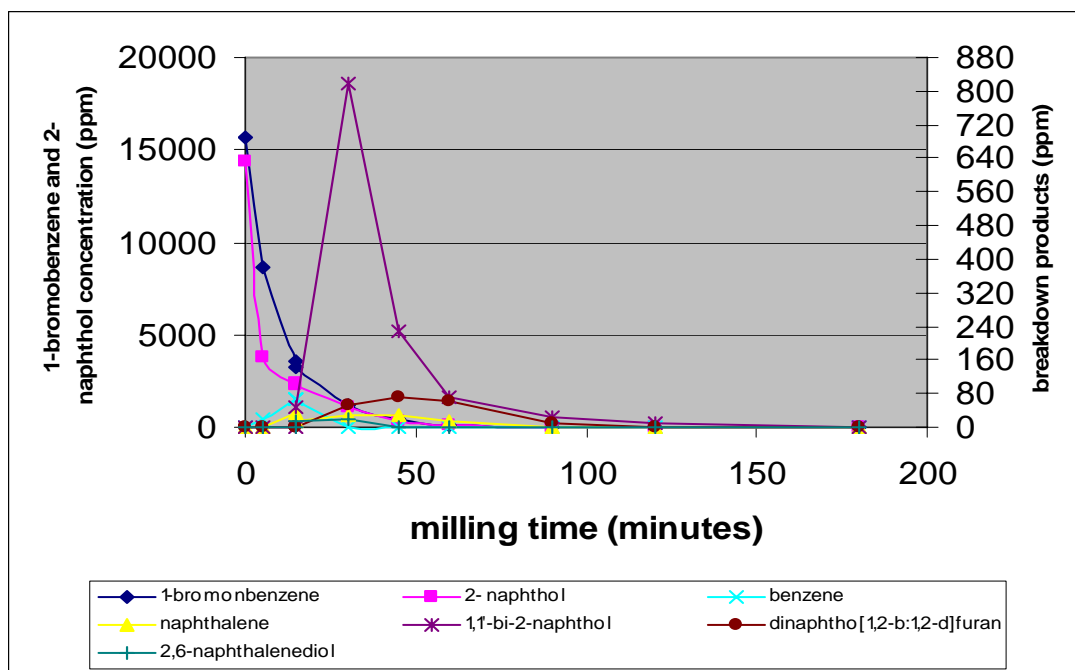


Figure 3.3-22: High concentration trial for 1-bromobenzene and 2-naphthol and breakdown products

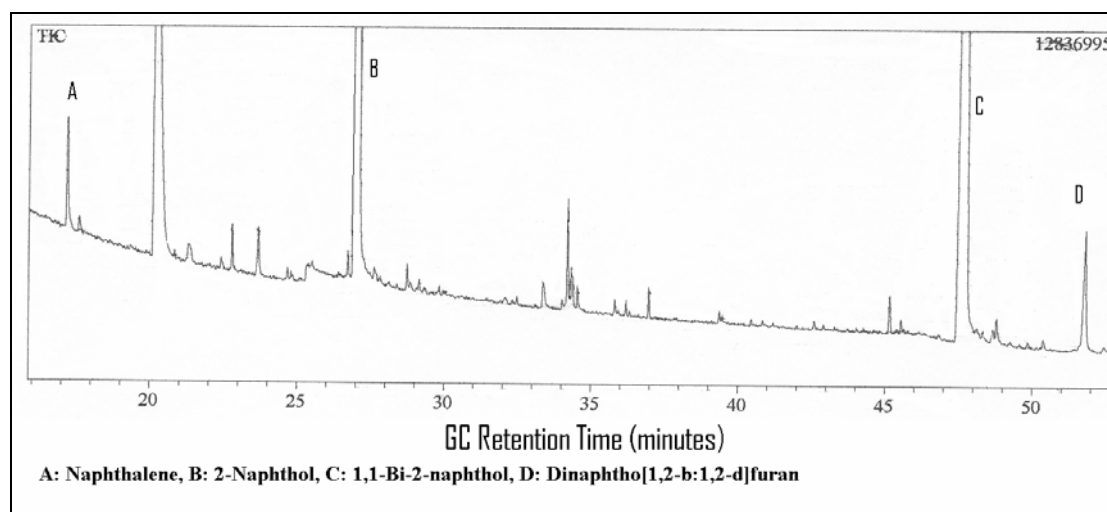


Figure 3.3-23: Typical chromatogram for 1-bromobenzene and 2-naphthol milled for 30 minutes

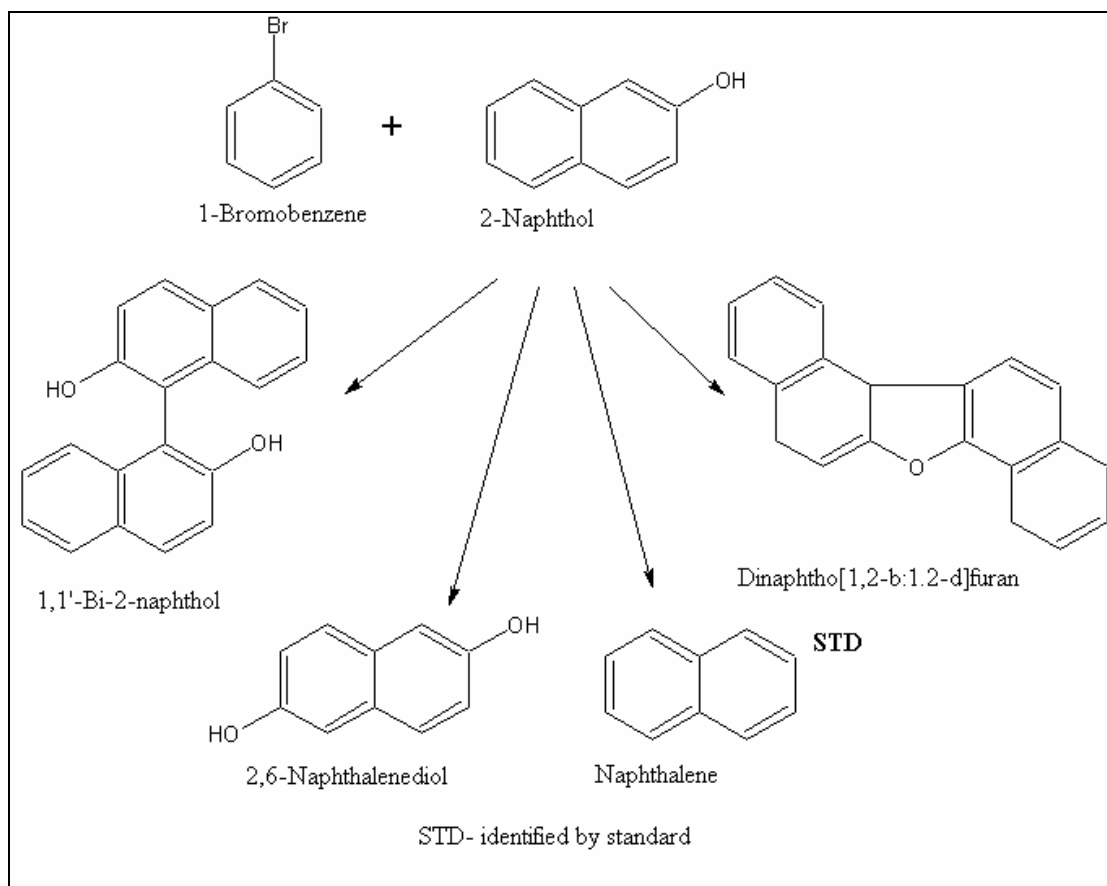


Figure 3.3-24: Intermediate breakdown products for 1-bromobenzene and 2-naphthol

3.3.2.9 High Concentration Mixed 1-Chloronaphthalene and 1-Naphthol in Quartz Sand

On the milling of 1-chloronaphthalene and 1-naphthol in the headspace sample, a relatively large naphthalene peak, the result of dehalogenation of the starting halonaphthalenes, was detected. Small trichlorotoluene and 1,4-naphthoquinone peaks were also seen. No chloronaphthol was detected.

A number of compounds were detected in the milled solid such as naphthalene, binaphthalene, dinaphtho[1,2-b:1.2-d]furan. Binaphthalene was present in more than one isomeric form. Other halogenated compound detected was chloronaphthol. Products detected are shown in Figure 3.3-27. With the exception of naphthalene, all the breakdown products were much less than 1% of the original concentration as shown in. The identities of all the breakdown products except naphthalene were confirmed by mass spectrum library match only.

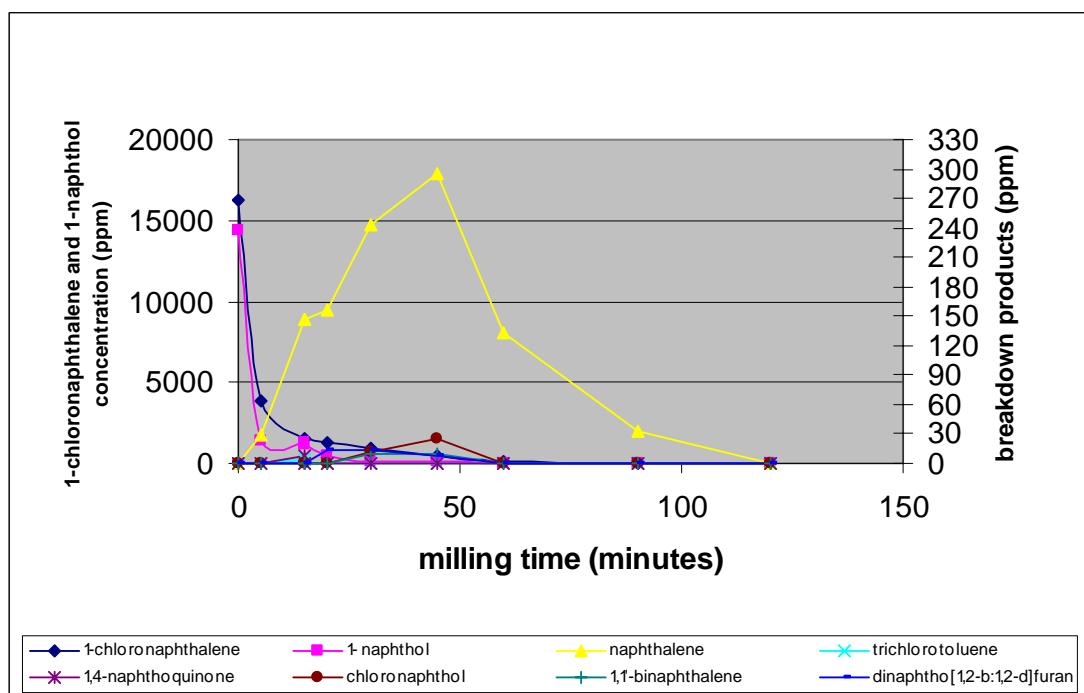


Figure 3.3-25: High concentration trial for 1-chloronaphthalene and 1-naphthol and breakdown products

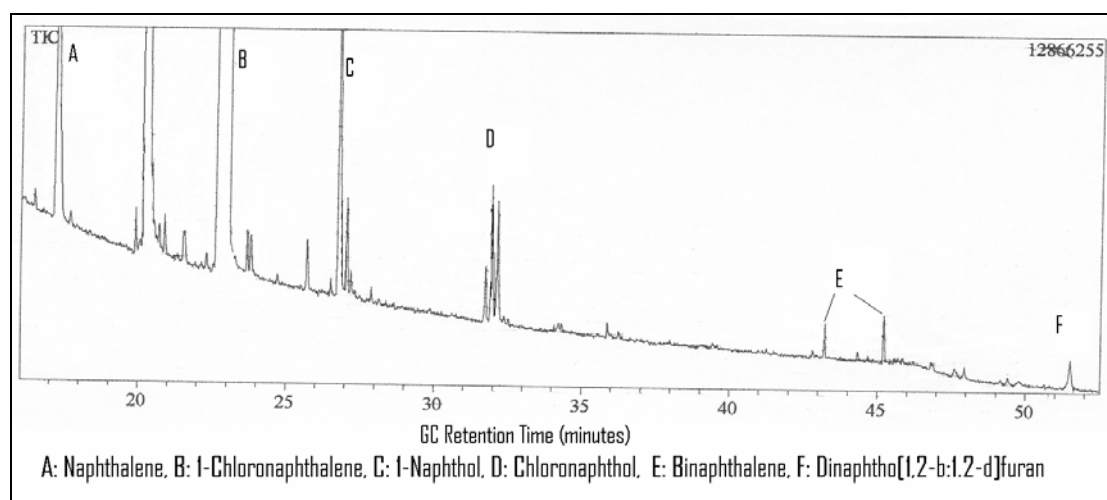


Figure 3.3-26: Typical chromatogram for 1-chloronaphthalene and 1-naphthol milled for 30 minutes

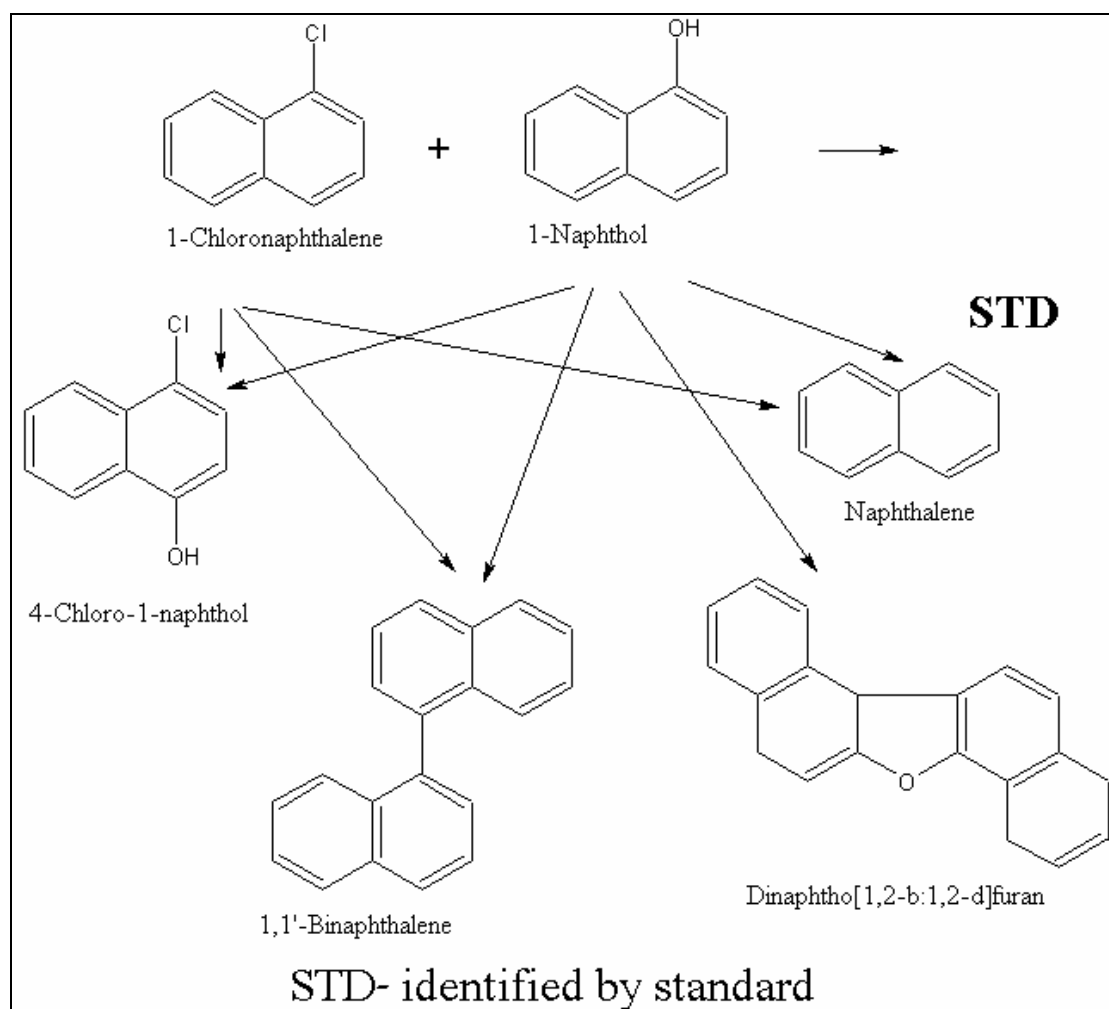


Figure 3.3-27: Intermediate breakdown products for 1-chloronaphthalene and 1-naphthol

3.3.2.10 High Concentration Mixed 1-Chloronaphthalene and 2-Naphthol in Quartz Sand

The detection of 1-chloronaphthalene and 2-naphthol in the headspace after milling is expected based on their volatilities. A large number of compounds detected were toluene, indene, xylene, tetrahydronaphthalene, dihydronaphthalene, naphthalene, and methylnaphthalene. Other halogenated compounds detected were chlorobenzene and trichlorotoluene. No chloronaphthol were detected.

A large number of compounds were detected in the milled solid including the compounds detected in the headspace. Other halogenated compound detected was chloronaphthol. Other non-halogenated compounds detected were

dihydronaphthalenone, binaphthalene, binaphthol and dinaphtho[1,2-b:1.2-d]furan. All of them were detected in more than one isomeric form as shown in Figure 3.3-30. Binaphthol was the most abundant intermediate breakdown products and its peak is best explained by the presence of hydroxyl groups attached to the base 2-naphthol. With the exception of binaphthol and naphthalene, maximum concentration of breakdown products were generally significantly less than 1% of the original 1-chloronaphthalene and 2-naphthol concentration (indicated in Figure 3.3-28). All the breakdown products with the exception of naphthalene were identified by mass spectrum library match only.

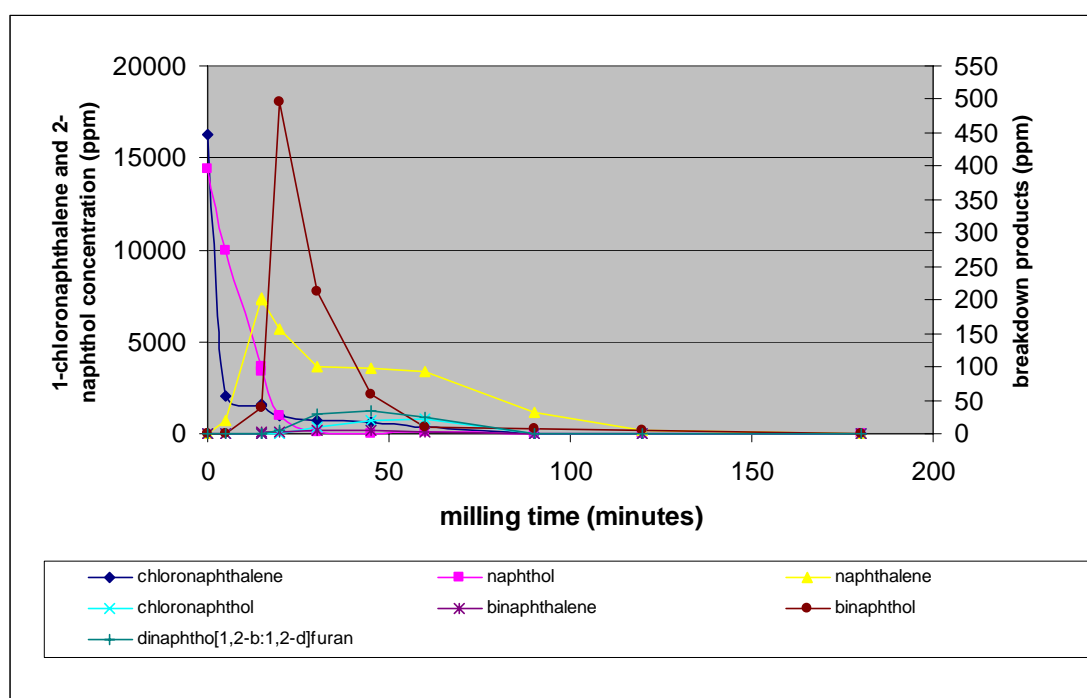


Figure 3.3-28: High concentration trial for 1-chloronaphthalene and 2-naphthol and breakdown products in solid samples

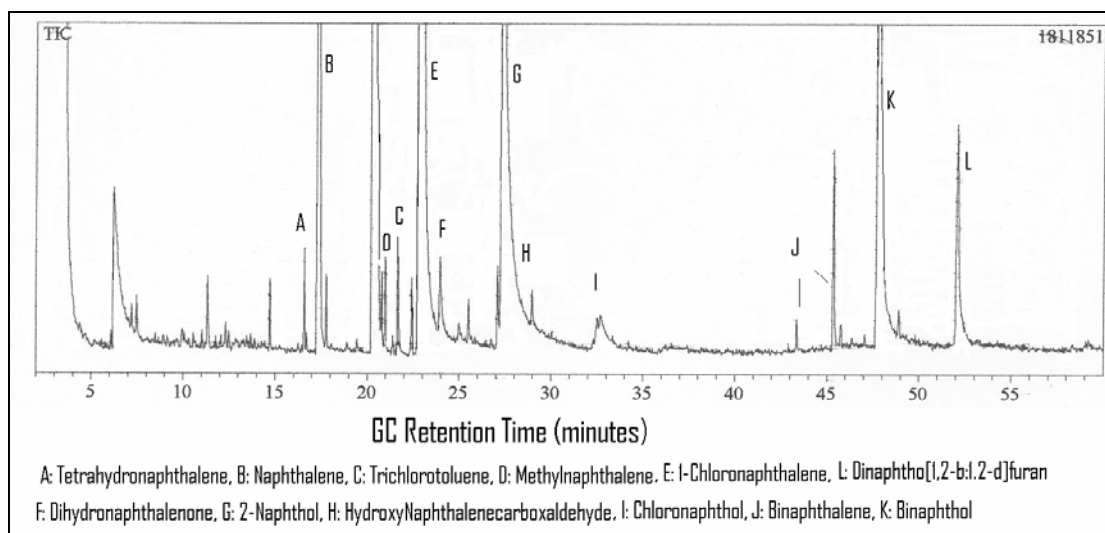


Figure 3.3-29: Typical chromatogram for 1-chloronaphthalene and 2-naphthol milled for 30 minutes

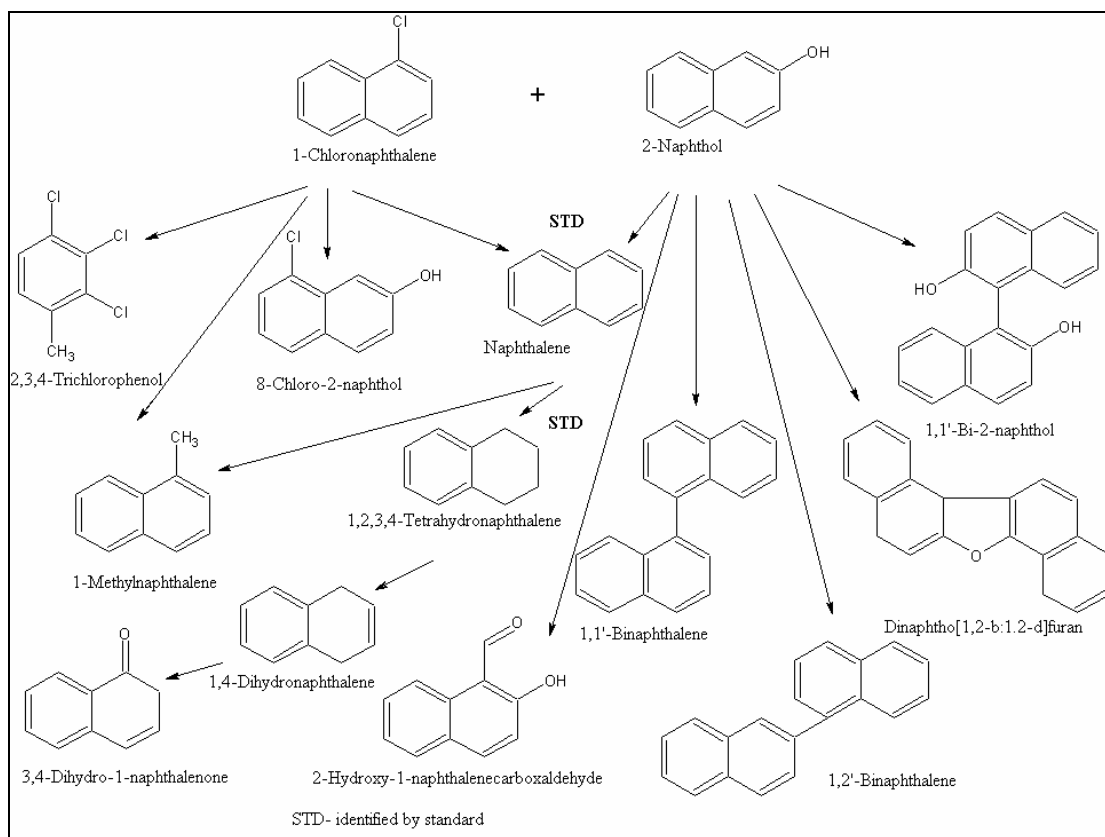


Figure 3.3-30: Intermediate breakdown products for 1-chloronaphthalene and 2-naphthol

3.3.2.11 High Concentration Mixed 1-Bromonaphthalene and 1-Naphthol in Quartz Sand

On the milling of 1-bromonaphthalene and 1-naphthol samples in the headspace gas, naphthalene and dibromonaphthalene were detected in small amount.

A large number of compounds were detected in the milled solid including the compounds detected in the headspace. The other halogenated compound detected was bromonaphthol. Other compounds detected were binaphthalene and dinaphtho[1,2-b:1,2-d]furan with the presentation in more than one isomeric form as indicated in Figure 3.3-33. With the exception of naphthalene, all the breakdown products were in small amount, reaching a maximum of 100 ppm (shown in Figure 3.3-31). Also, apart from naphthalene, the identities of breakdown products were confirmed by the mass spectrum library match only.

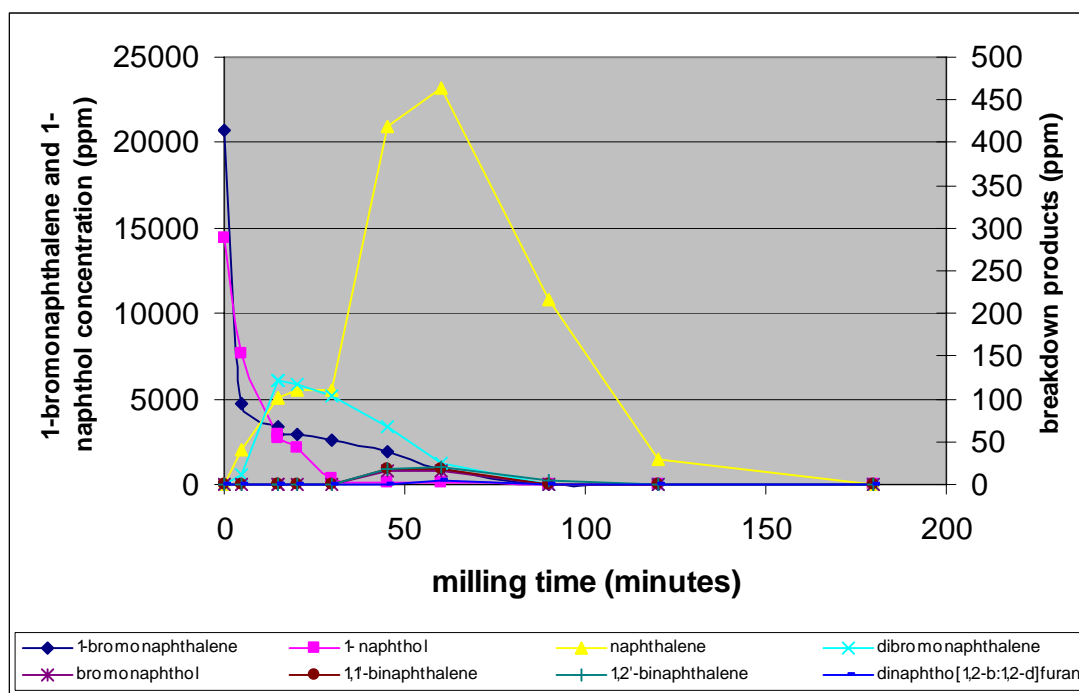


Figure 3.3-31: High concentration trial for 1-bromonaphthalene and 1-naphthol and breakdown products

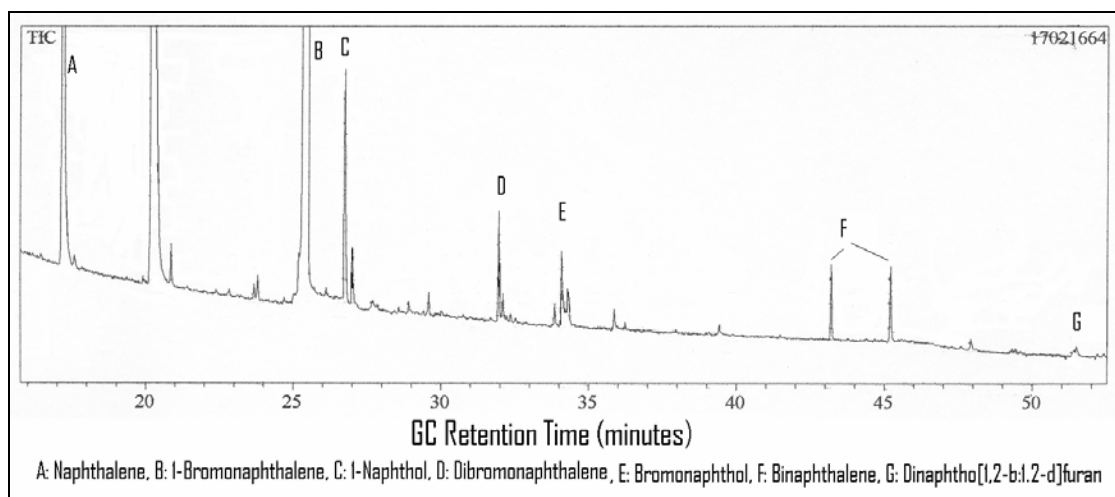


Figure 3.3-32: Typical chromatogram for 1-bromonaphthalene and 1-naphthol milled for 60 minutes

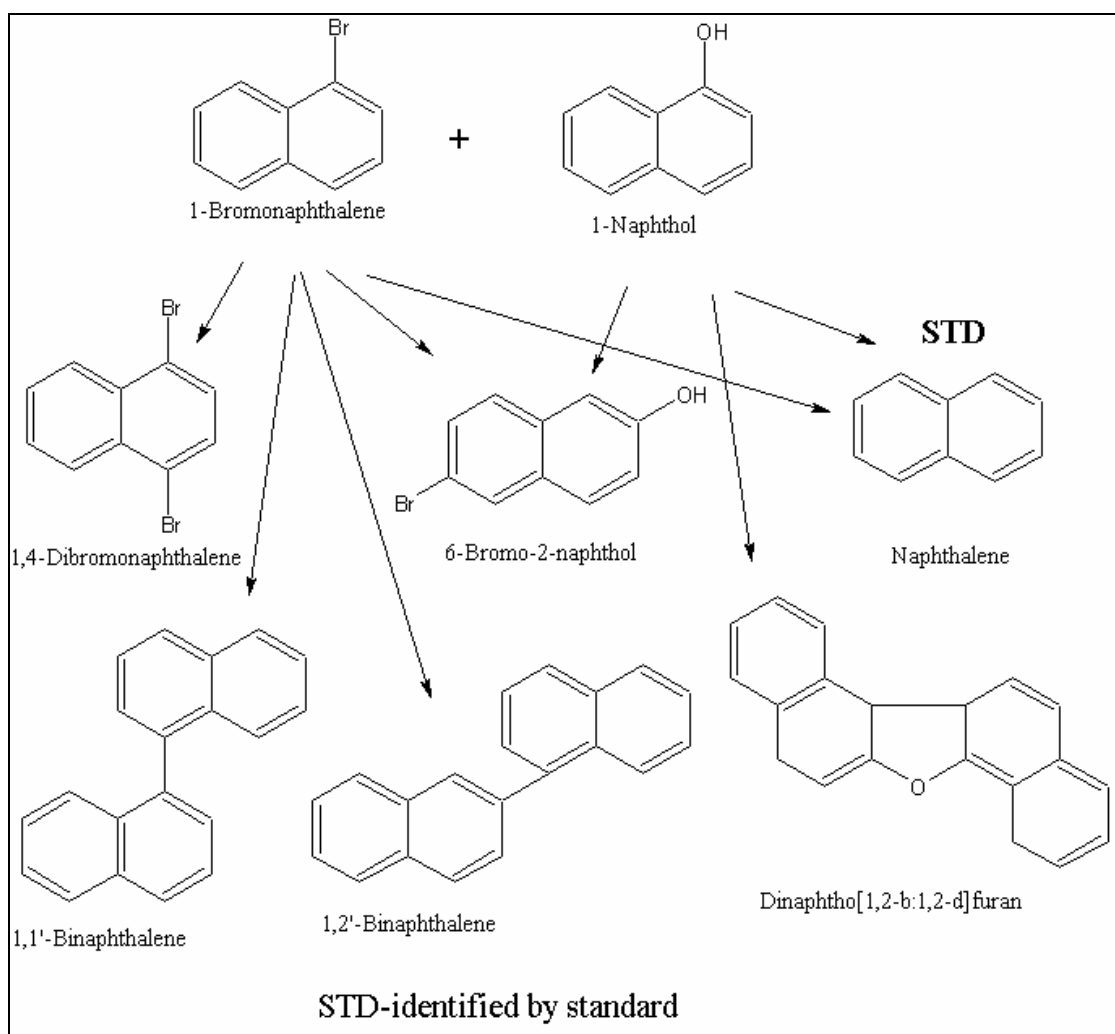


Figure 3.3-33: Intermediate breakdown products for 1-bromonaphthalene and 1-naphthol

3.3.2.12 High Concentration Mixed 1-Bromonaphthalene and 2-Naphthol in Quartz Sand

From the detection of 1-bromonaphthalene and 2-naphthol after milling in the headspace gas, a large number of compounds detected were toluene, indene, xylene, naphthalene. Other halogenated compound detected was dibromonaphthalene. No bromonaphthol was detected.

A large number of compounds were detected in the milled solid including the compounds detected in the headspace. The other halogenated compound detected was bromonaphthol. Other compounds detected were tetrahydronaphthalene, dihydronaphthalene, methylnaphthalene, dihydronaphthalenone, 2-hydroxy-1-naphthalenecarboxaldehyde, binaphthalene, binaphthol and dinaphtho[1,2-b:1,2-d]furan. Binaphthalene was present in more than one isomeric form as shown in Figure 3.3-36. With the exception of naphthalene and binaphthol, all the breakdown products were in small amount, less than 100 ppm (shown in Figure 3.3-34). Also, apart from naphthalene, the identities of breakdown products were confirmed by the mass spectrum library match only.

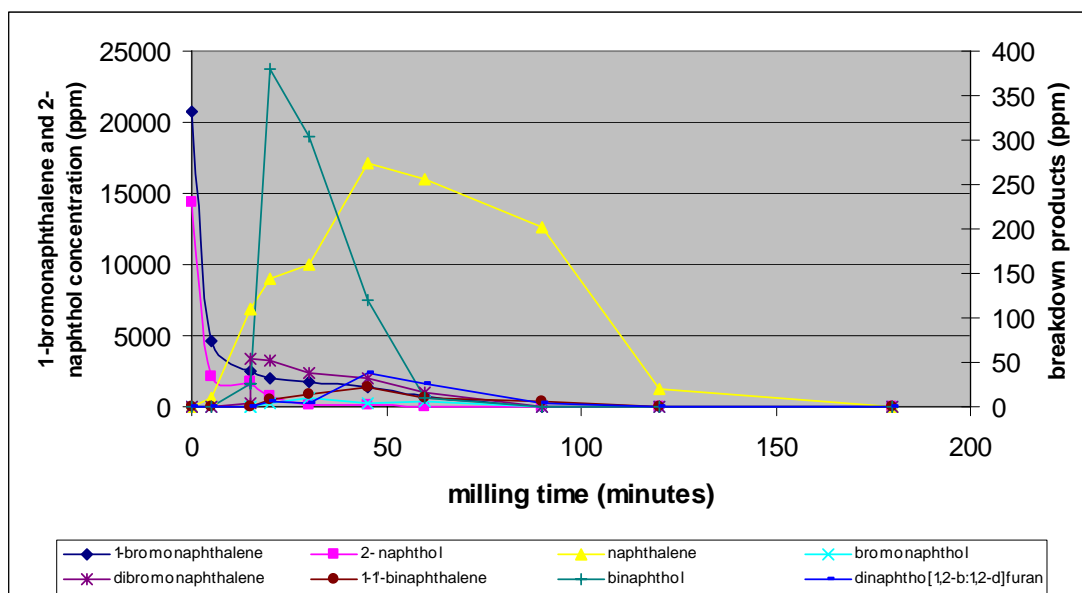


Figure 3.3-34: High concentration trial for 1-bromonaphthalene and 2-naphthol and breakdown products

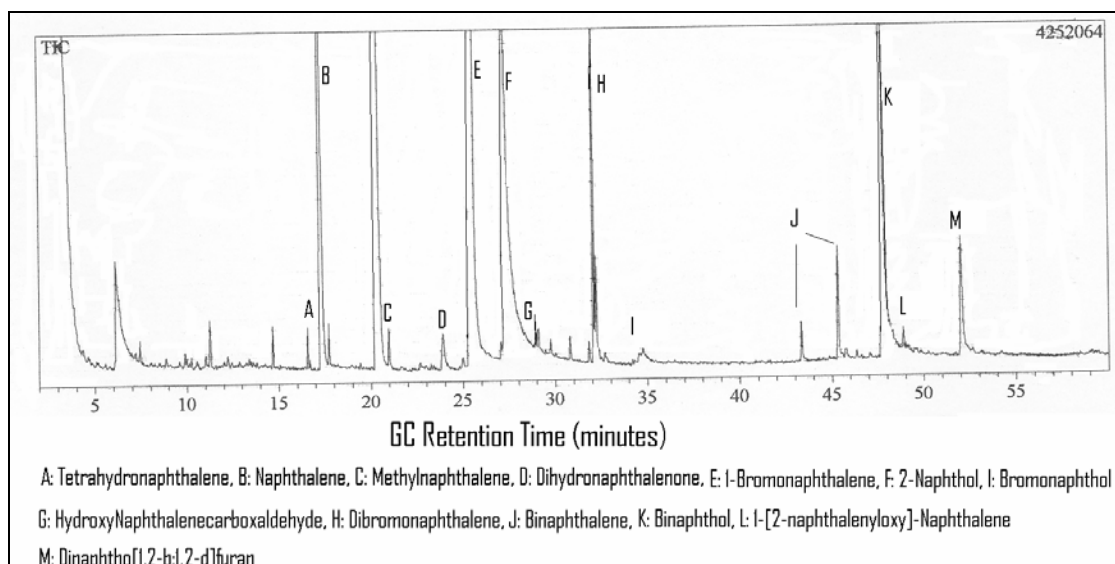


Figure 3.3-35: Typical chromatogram for 1-bromonaphthalene and 2-naphthol milled for 30 minutes

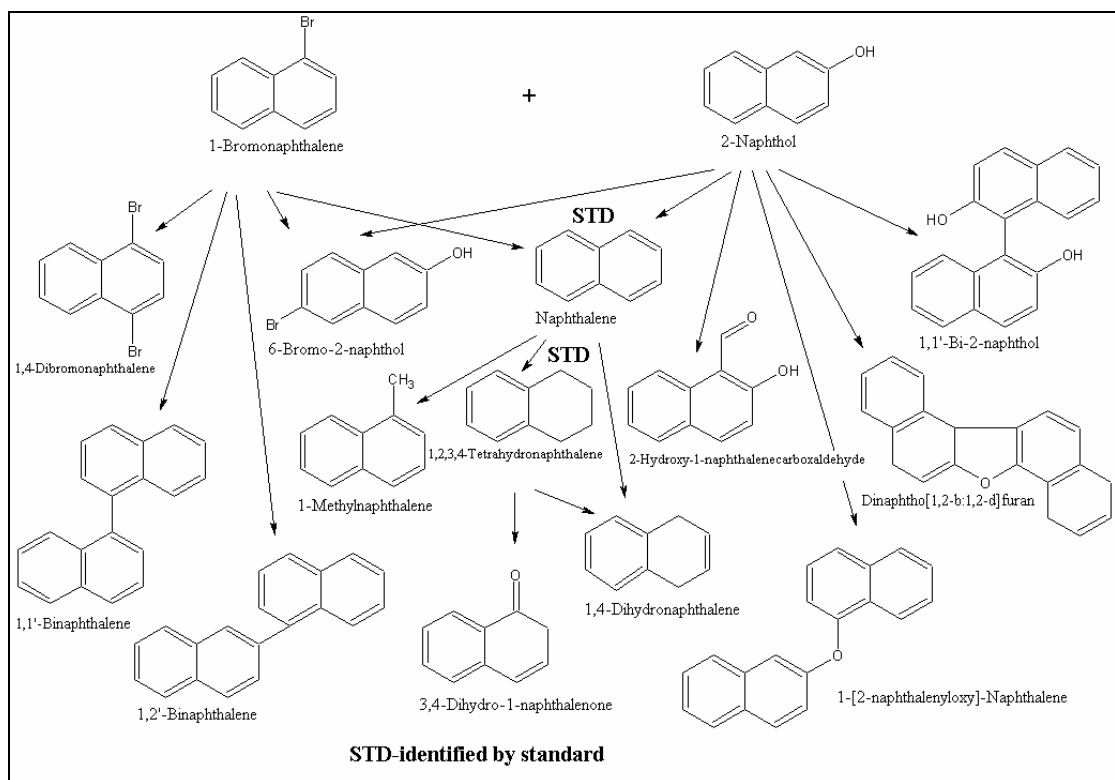


Figure 3.3-36: Intermediate breakdown products for 1-bromonaphthalene and 2-naphthol

Chapter 4

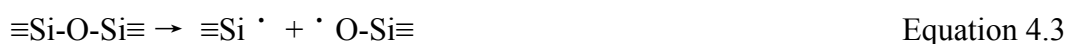
4. Discussion

Based on the experimental results detailed above, it is possible to discuss the aim and the achievement of this project. The aim of the project was to investigate the destruction of selected classes of compounds in quartz sand using ball milling as a mechanochemical reactor. The intermediate breakdown products were focus to be detected using GCMS.

During the milling process, chemical bonds are broken and ions or radicals are created (Hasegawa et al, 1995; Kaupp et al., 2003). They are shown in Equation 4.1 and 4.2.



According to these, the quartz during milling procedure reacts in two stages. The homolytic cleavage of Si-O bonds when quartz is milled is shown in Equation 4.3 while the heterolytic cleavage is shown in Equation 4.4 (Bellingham, 2006; Hasegawa et al.; 1995; Mofa et al., 2002).



The $\equiv Si^{\cdot}$ centre and $\cdot O-Si \equiv$ radicals are the main radicals produced during the milling process under an oxygen atmosphere as shown in equation 4.5 and 4.6 (Bellingham, 2006; Hasegawa et al.; 2001, Mofa et al., 2002).



In the absence of hydrogen, $\equiv\text{Si}^\cdot$ centre and $^\cdot\text{O-Si}\equiv$ radicals react during milling as shown in Equation 4.7 (Mofa et al., 2002; Steinike and Tkacova, 2000; Urakaev et al., 2004). In water ground silica generates hydroxyl radicals, and possibly hydrogen radicals, according to Equation 4.8 and 4.9 (Bellingham, 2006; Kaupp et al., 2003; Steinike and Tkacova, 2000).



4.1 Discussion of the Results

4.1.1 Naphthalene

The concentrations and chemical structures of the identified intermediates suggest that reactive milling of naphthalene mainly involved reduction, oxidation, addition, and fragmentation pathways. The following discussion is a review of different reduction, oxidation, addition, and fragmentation pathways proposed for naphthalene destruction.

4.1.1.1 Reduction Pathways- Hydrogenation of Naphthalene

The initial step of the naphthalene milling destruction was reduction which an attack of an H radical either at the 1 position, leading to form tetrahydronaphthalene or at the 2 position leading to form dihydronaphthalene. The latter will be easily reduced via a reactive hydrogen atom of dihydronaphthalene to tetrahydronaphthalene as Figure 4.1.1-1 shown below. Sayan and Paul (2002) pointed that tetrahydronaphthalene as an abundant intermediate was found during experimentally derived heats of formation of naphthalene hydrogenation, with dihydronaphthalene as short lived transient stages.

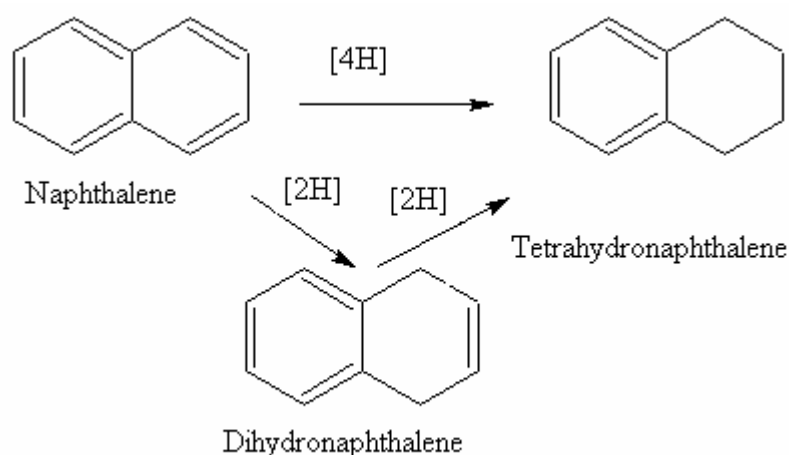


Figure 4.1.1-1: Hydrogenation of naphthalene

4.1.1.2 Addition Pathways – Alkylation of Naphthalene

The addition mechanisms in naphthalene during milling involved the attachment of alkyl substituents and combination of aromatic compounds. Figure 4.1.1-2 presents the possible alkylation pathways of methylnaphthalene as an example based on respective intermediate formation and free radical formation. The presence of methane/methyl components could account for the small hydrocarbon fragments generated through the milling destruction (Yang and Lu, 2005). Zhang et al. (2004) reported that naphthalene followed the similar pathways undertaken by benzene during selective gas-phase oxidation, in particular favoring the alkylation on the α -position. From hydrocarbons, C^\bullet radicals are formed through cleavage of C-H bonds, with the carbon radicals combining to form an amorphous carbon residue. While the naphthalene intermediate might either react with methane to form methylnaphthalene, or naphthalene may directly react with methyl radicals available during the mechanical destruction. The radicals were generated on naphthalene surface. This indicates that radical reactions free-radical reactions involving naphthalene have also been reported during a milling process (Yang and Lu, 2005).

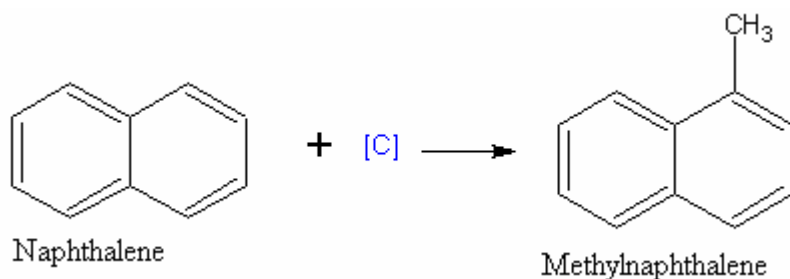


Figure 4.1.1-2: Alkylation of naphthalene

The subsequent milling destruction of naphthalene explained the formation of the ring cleavage products. Elimination of carbene radicals in naphthalene leads to formation of methylstyrene as illustrated in Figure 4.1.1-3.

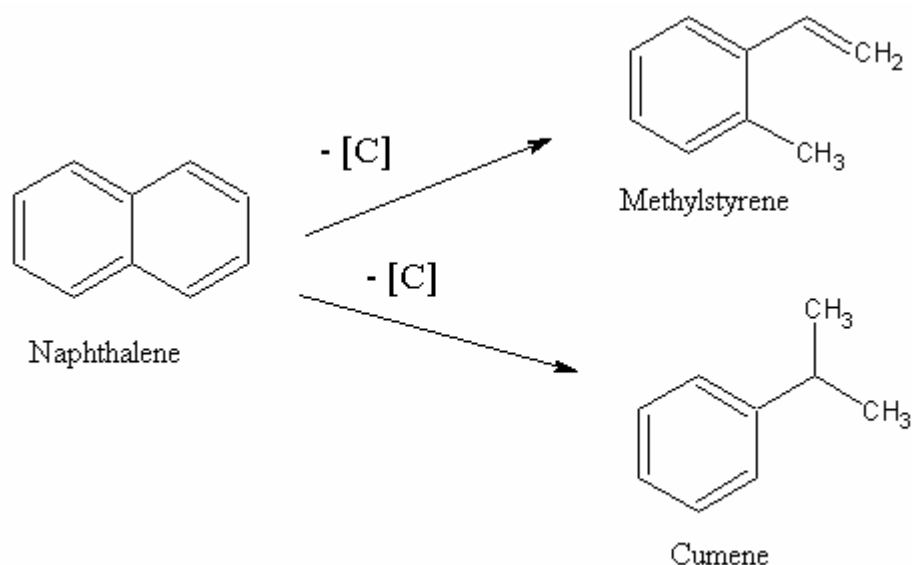


Figure 4.1.1-3: Cleavage products of naphthalene

The formation of toluene was from benzene, but once a significant amount of toluene was formed, it competed with the unsubstituted benzene in further methylation reactions according to Friedel-Crafts alkylations (Maitland Jones, 2005). As a result, toluene was made first, then the xylenes as outlined in Figure 4.1.1-4.

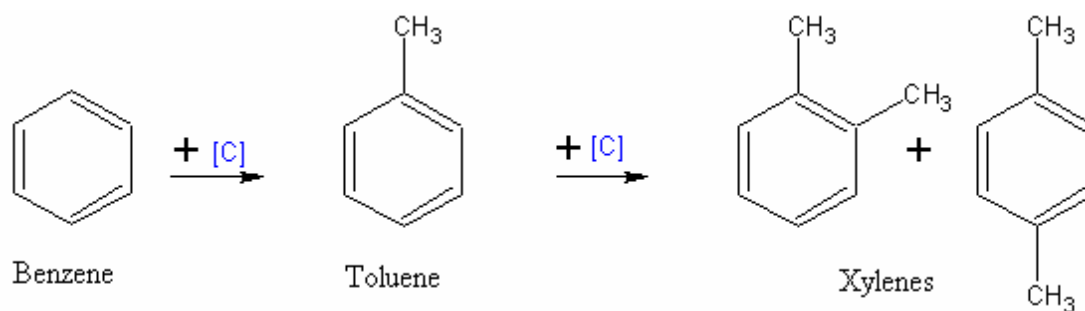


Figure 4.1.1-4: Alkylations of naphthalene

The presence of trace naphthol was generated as hydroxyl radicals replaced hydrogen atoms. The hydroxyl radicals were formed from oxygen, which dissociated into $O \cdot$ radicals combining $H \cdot$ radicals as presented in Figure 4.1.1-5. Naphthol was not detected when naphthalene reacted with nitrogen. Mihele et al. (2002) reported that the formation of naphthol was found during the reaction of naphthalene with OH radicals in a smog chamber.

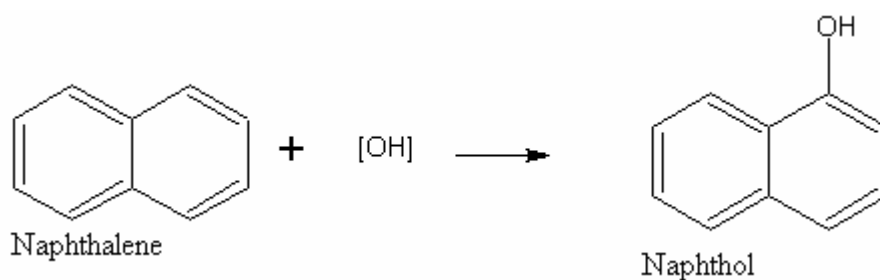


Figure 4.1.1-5: Hydrogenation of naphthalene

4.1.1.3 Addition Pathways – Dimerization of Naphthalene

Since naphthalene and benzene have aromatic structures and can form intermediates, the mechanisms used for binaphthalene formation during naphthalene oxidation may explain one of the possible pathways to form larger molecule during naphthalene decomposition. Following the addition pathway during Naphthalene milling in high temperature in the gas phase, Figure 4.1.1-6 displays possible addition reactions forming binaphthalene isomers presented in this study. Note that dimerization occurring through radical reactions was reported after 30 minutes milling of time the formation of binaphthalene was a result of substitution process. Here a naphthalene radical cation was generated by milling; it exchanged hydrogen radicals as presented in Figure 4.1.1-6.

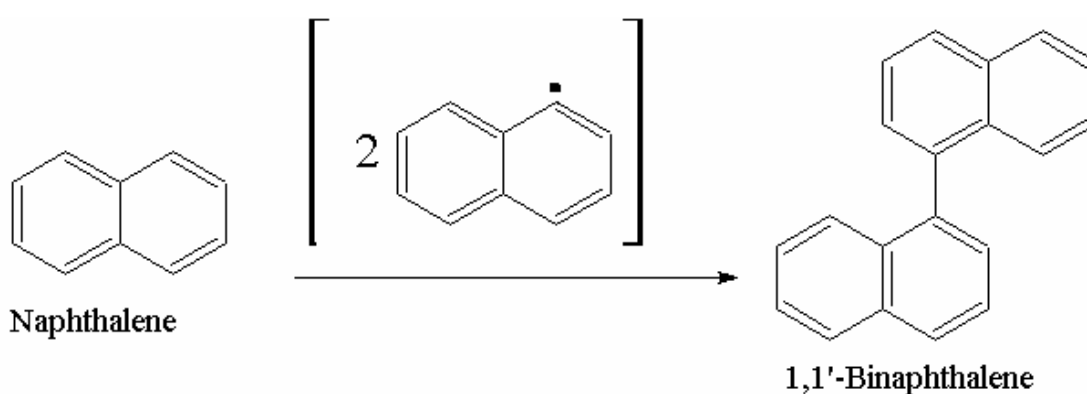


Figure 4.1.1-6: Dimerization of naphthalene

4.1.2 Anthracene

During the milling destruction experiments with anthracene, tetrahydroanthracene, and dihydroanthracene were found as intermediates, in agreement with naphthalene breakdown products as detailed in Section 4.1.1.1 above. The suggested mechanism, as presented in Figure 4.1.2-1, involves a $H\cdot$ radical attack at the 1,4 positions and 9,10-positions will probably react in two different pathways. In Tyurina's paper, the self-hydrogenation occurred in the anthracene to result dihydroanthracene found under the specified conditions and the presence of magnesium clusters (Tyurina et al., 2003). From Borowski et al. (2001) finding, anthracene was reduced to a mixture of 1,2,3,4-tetrahydroanthracene and dihydroanthracene. The total conversion of anthracene and the presence of these two products suggest that after hydrogenation of the first ring, the reaction proceeds with a slower rate to the hydrogenation of the second ring.

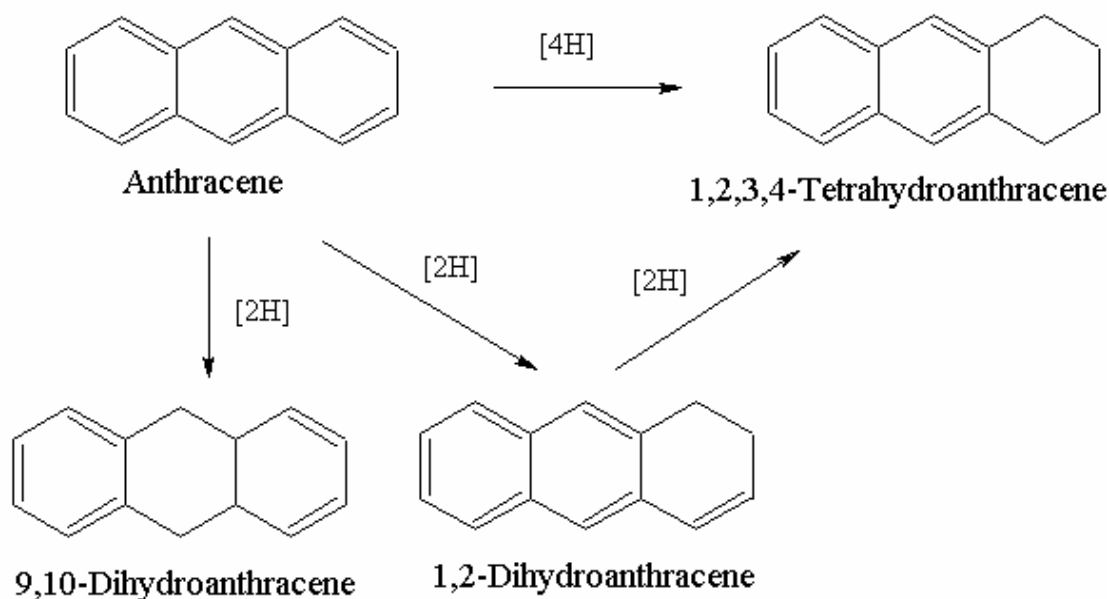


Figure 4.1.2-1: Hydrogenation of anthracene

Reactive milling of anthracene was generated a number of intermediate products. Their reaction mechanisms were described below. The formation of methylanthracene can also be explained by the mechanism explained as methylnaphthalene formed in the presence of Figure 4.1.2-2.

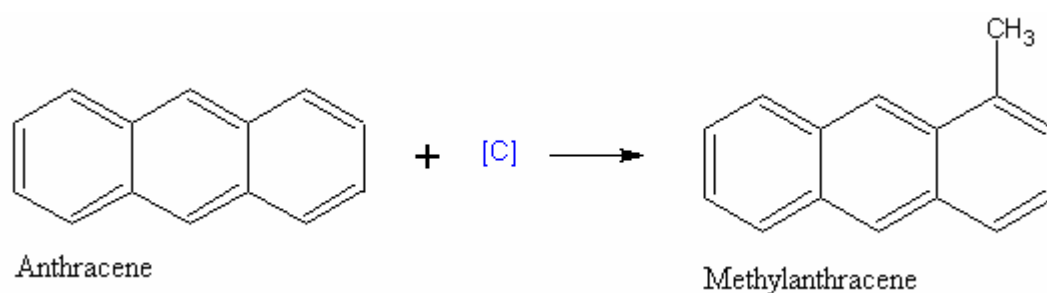


Figure 4.1.2-2: Alkylation of anthracene

Anthraquinone was generated from oxidation anthracene. It was identified by GCMS in two different isomers as shown in Figure 4.1.2-3. One was attacked at 9,10 positions, and the other was formed by an oxidation with O₂ at the 1,4-position. The formation of trace amounts of anthrone can be explained by a side reaction starting from 9, 10-anthraquinone with further oxidation. Small traces of anthrone were clearly identified by GCMS when anthraquinone was the model compound. Merlau ML et al. (2005) pointed that the dimer was capable of oxidizing anthracene to anthraquinone under Mn(III) porphyrin catalyst. Anthraquinone and anthrone were also found oxidation of anthracene by FeF₂₀TPPCl/Imidazole/m-CPBA and metalloporphyrin (Safari et al., 2005)

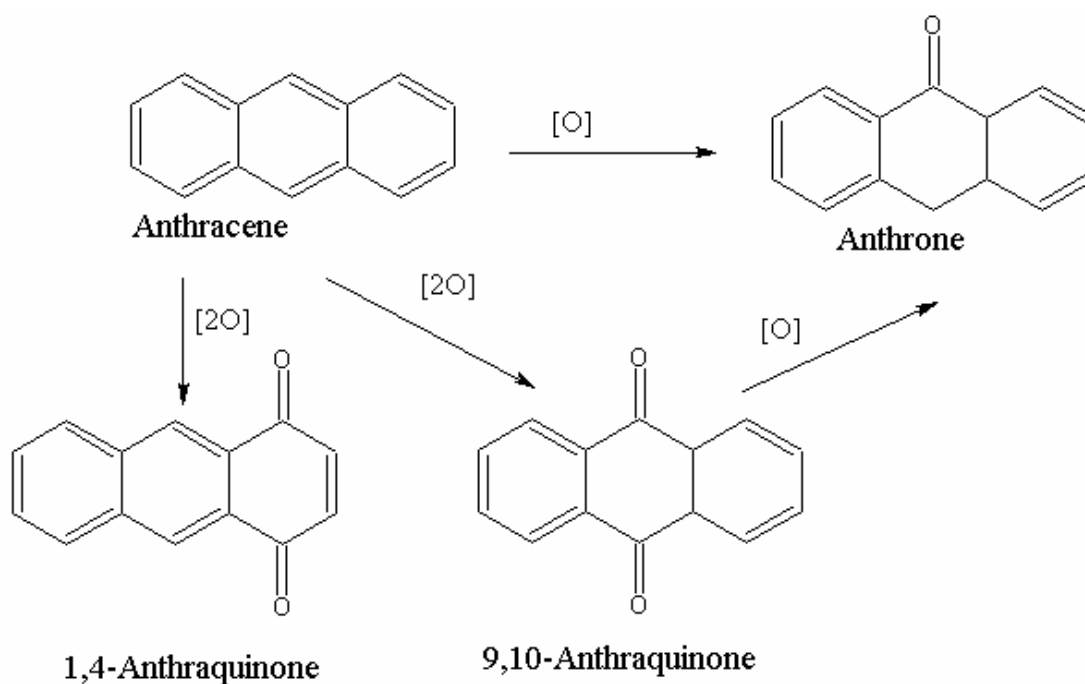


Figure 4.1.2-3: Oxidation of anthracene

The formation of naphthalene, toluene and benzene were a result of cleavage of anthracene. The mechanisms of these reactions were similar as the cleavage of naphthalene discussed in Section 4.1.1.2.

4.1.3 Pentachlorophenol

The intermediates detected during the milling of PCP with quartz sand mainly from dechlorination reactions. Removal of the OH group also appears to be possible based on the detection of benzene and chlorobenzene. In PCP reduction, GCMS revealed the disappearance of PCP after 1 hour milling, but large amounts of trichlorophenols was found to be present. The yield of phenol was only in trace amounts. As intermediates, tetrachlorophenols were detected by GCMS and identified as follows from their retention times. From these results, the proposed dechlorination steps of PCP are as shown in Figure 3.2-9. Chlorines ortho to hydroxyl groups are the most difficult to remove, and meta chlorines are a little more easily removed than the para chlorines. Ortho chlorines may interact with the hydroxyl group to cause low electron density in the carbon–chlorine bond. The concentrations of intermediates changed as is shown in Figure 3.2-10. PCP itself was removed quickly but intermediate chlorophenols were found in relatively large amounts. The formation of chlorophenols with low chlorine numbers was especially slow because of the low reaction rate of these chlorophenols with the naphthalene radical anion. The low reactivity of chlorophenols can be explained by the inductive effect of the hydroxyl group. Thus, chlorophenols appear to be difficult to be completely dechlorinated by our mechanical reduction system. We did not identify these products from reliable standards, but infer their existence from the experimental data and the chemical literature on the GCMS. Yu JJ and PE (2004) stated that the existence of a similar pathway for production of tetrachlorophenol and trichlorophenol from pentachlorophenol

4.1.4 1-Chloronaphthalene

Based on the experimental results detailed in Section 3.3.1.3, and on evidence from the literature, the following pathways are proposed for the milling destruction of chloronaphthalene in quartz sand. Firstly, the major reaction is the removal of chlorine groups from the chloronaphthalene to form naphthalene, which was further hydrogenation to form tetrahydronaphthalene. Secondly, a trace amount of trichlorotoluene was formed through dehydrochlorination, dechlorination, cleavage and rearrangement of the chloronaphthalene molecule.

4.1.5 1-Bromonaphthalene

The intermediate products formed during the milling destruction of bromonaphthalene in quartz sand are a result of debromination and addition of bromides and naphthalene groups based on the detection of naphthalene, binaphthalene and dibromonaphthalene.

4.1.6 Phenol

The destruction of phenol through milling in a quartz sand matrix appears to occur with 99% destruction achieved in 90 minutes under the experimental conditions described. The intermediate breakdown products formed during the reactive milling of phenol in quartz sand are a result of addition of hydroxy groups and removal of the OH groups. The presence of various methyls, ethyl attached to a benzene ring. The destruction of naphthalene is larger than the initial benzene containing two aromatic rings. This is likely to be the first step in the formation of the amorphous carbon residue.

4.1.7 1-Naphthol

It is clear from the results that the reactive milling destruction of 1-naphthol achieved 99% in 90 minutes under the milling conditions used. The intermediates naphthalene

detected during the milling of 1-naphthol with quartz sand mainly from removal of the OH groups. There are many reports on the oxidative coupling reaction of 1-naphthol. The formation process of binaphthol is generally believed to involve the naphthoxy radical (Takeya et al., 2004; Mizuki Tada et al., 2005). Oxidative coupling of 1-naphthol also appears to be possible in this study based on the detection of binaphthol and dinaphtho [1,2-b;1,2-d]furan. Initially, 1-naphthol coordinates to an unsaturated naphthol radical and then an O₂ molecule adsorbs on the quartz sand. In the third step, the activated oxygen extracts the H atom of the hydroxyl group of the coordinated 1-naphthol. Finally two dehydrogenated 1-naphthols couple together to form binaphthol shown in Figure 3.3-6. Dinaphtho[1,2-b;1,2-d]furan detected was as a result of further oxidation of 1-naphthol.

4.1.8 2-Naphthol

For 2-naphthol milled in quartz sand only a few intermediate breakdown products are detected in low concentrations. The compounds detected have very similar mass spectra to that of 1-naphthol and hence the chemical structures are likely to be similar to that of 1-naphthol too as shown in Figure 3.3-7. Based on the different isomeric forms between 1-naphthol and 2-naphthol, binaphthol was detected in another isomeric form too. Oxidative coupling in 2-naphthol proceeds more easily than in 1-naphthol to afford the corresponding binaphthol (Takeya et al., 2004).

4.1.9 1-Chlorobenzene and 1-Bromobenzene

The intermediate breakdown products detected during milling of 1-chlorobenzene and 1-bromobenzene probably is followed by two pathways, one is that the oxidative addition and the subsequent milling destruction are not rapid due to stronger C-Cl and C-Br bonds. As a result, the formation of benzene and biphenyl is possible to occur with these substrates. So, the nature of halogen is very important in determining the product distribution. The biphenyl was also produced in more quantities during the reaction and they supposed that the formation of biphenyl took place through a radical reaction. The nature of halogen would affect all the steps except for the reductive

elimination at the end of milling. On the other hand, addition of bromobenzene and benzene also appears to be possible based on the detection of bromobiphenyl.

4.1.10 1-Chloronaphthalene and 1-Bromonaphthalene

For chloronaphthalene and bromonaphthalene milled in quartz sand only a few intermediate breakdown products (shown in Figure 3.3-12) are detected in very low concentrations. The mixed milling of 1-chloronaphthalene and 1-bromonaphthalene should take place through the same pathways as for halobenzene, as illustrated in Section 4.1.8. Firstly, for chloronaphthalene and bromonaphthalene, it is assumed that the one being addition of naphthalene groups from breaking C-Cl and C-Br going through the reaction cycle producing naphthalene and binaphthalene. In the case of chlorobenzene or bromobenzene, the product is benzene and biphenyl. Secondly, the other intermediate breakdown products detected such as methylnaphthalene, tetrahydronaphthalene are followed the mechanisms of destruction naphthalene. Thirdly, a small number of trichlorotoluene, chlorobenzene, dibromonaphthalene, bromomethylbenzene are formed through dehaloriantion, oxidation, cleavage and rearrangement of the chloronaphthalene and bromonaphthalene as outlined in Section 4.1.4 and 4.1.5

4.1.11 1-Chlorobenzene and 1-Naphthol

The intermediates detected during the mixed milling of 1-chlorobenzene and 1-naphthol with quartz sand mainly dechlorination reactions. Removal of the OH group also occurs based on the detection of naphthalene.

4.1.12 1-Chlorobenzene and 2-Naphthol

The intermediate breakdown products formed during the mixed milling of chlorobenzene and 2-naphthol in quartz sand are different from the destruction pathway to the intermediate products from the mixture of chlorobenzene and 1-

naphthol. With the exception of naphthalene, binaphthol and dinaphthofuran detected are a result of addition and oxidation of naphthalene.

4.1.13 1-Bromobenzene and 1-Naphthol

The intermediates detected during the milling of bromobenzene and 1-naphthol mainly from oxidation, isomerisation and addition reactions occurring. The presence of naphthoquinone during milling indicated that oxidation of naphthalene by air is possible.

4.1.14 1-Bromobenzene and 2-Naphthol

There are a number of similarities between the destruction pathway to the intermediate products in Figure 3.3-24 and occurring during milling with bromobenzene and 1-naphthol as outlined in Section 4.1.13. In the case of milling the major products include naphthalene, naphthalenediol, binaphthol, and dinaphthofuran with removal of OH groups, oxidation, and addition reactions occurring. The bromobenzene and 1-naphthol pathway in particular contains the same breakdown products, namely, binaphthol and dinaphthofuran.

4.1.15 1-Chloronaphthalene and 1-Naphthol

For chloronaphthalene and 1-naphthol milled in quartz sand only a few intermediate breakdown products (shown in Figure 3.3-25) are detected in very low concentrations. The intermediate breakdown products formed during the milling treatment are a sequence of dechlorination, oxidation and removal and addition of hydroxyl groups. The presence of chloronaphthol during milling states that chlorine and hydroxyl groups in naphthalene are also likely to be formed.

4.1.16 1-Chloronaphthalene and 2-Naphthol

Based on the experimental results detailed above, and on evidence from the literature, the following pathways are proposed for the mixture milling of 1-chloronaphthalene and 2-naphthol in the quartz sand. Firstly, the major reaction is the removal of hydroxyl and chlorine groups from the chloronaphthalene and naphthol leaving carbon radicals, which combine to form the carbon residue. Secondly, a large number of intermediate breakdown products are formed through dehydrochlorination, dechlorination, oxidation, cleavage and rearrangement of the chloronaphthalene and naphthol molecule. Thirdly, chloronaphthol was formed as a result of combination with chloronaphthalene and 2-naphthol. Once again it should be emphasised that, with the exception of binaphthol, none of the intermediate breakdown products shown in Figure 3.3-28 are formed in concentrations greater than 1% of the original concentration.

4.1.17 1-Bromonaphthalene and 1-Naphthol

For 1-bromonaphthalene and 1-naphthol milled in quartz sand only a few intermediate breakdown products are detected in very low concentrations. The compounds detected have very similar chemical structures to that of 1-chloronaphthalene and 1-naphthol. Also, bromonaphthol was formed by bromides and hydroxyl groups. The differences were, binaphthalene was found in different isomers and dibromonaphthalene was formed.

4.1.18 1-Bromonaphthalene and 2-Naphthol

From the results outline in Figure 3.3-36, there are a number of similarities between the destruction pathways to the intermediate products presenting during milling with 1-chloronaphthalene and 2-naphthol stated in Section 4.1.15. First of all, in the case of milling major products of chloronaphthalene and 2-naphthol include naphthalene, tetrahydronaphthalene, dihydronaphthalene, dihydronaphthalenone, methylnaphthalene, hydroxynaphthalenecarboxaldehyde, binaphthalene, binaphthol,

dinaphthofuran with removal of OH groups, oxidation, and addition reactions occurring. The bromonaphthalene and 2-naphthol pathway in particular contains the same breakdown products with exception of binaphthalene occurring in different isomers. Secondly, bromonaphthol was formed as a result of bromine transferring into 2-naphthol which had the same reaction in chloronaphthalene and 2-naphthol forming chloronaphthol. However, bromine transferred into bromonaphthalene to form dibromonaphthalene. This pathway was not be detected in chloronaphthalene and 2-naphthol forming dichloronaphthalene.

Chapter 5

5. Conclusion

The object of this study was to investigate the mechanochemical destruction of PAHs and chlorinated compounds using the ball milling process. The investigation aimed to increase the understanding of the mechanisms using simple compounds whose products could be easily characterised and identified.

The results for the milling of PAHs and simple chlorinated compounds indicated that mechanochemical processing was very effective for the destruction of these compounds. The grinding of naphthalene and anthracene results similar intermediates found during the milling degradation. Based on this mechanisms found, mechanochemical destruction should be applicable to other PAHs compounds. For pentachlorophenol, 6 intermediates have been proved during the milling process.

The results from the halogenated and hydroxylated aromatics milling trials showed that for chloronaphthalene, bromonaphthalene, 1-naphthol, and 2-naphthol provide evidence that halogens and carbon fragments are transferred between compounds during milling.

The results of this research and from the literature suggest that more experiments are needed to investigate the ability of ball milling to destroy a wide range of hazardous organic compounds, including POPs. Further research is needed to understand the fate of the chlorine and the identity of any organochlorine compounds in the final milled product.

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