Thermal Treatment of Marine Soil Contaminated With Hydrocarbon

by

Razak Bin Mohd Sapiah

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
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Approved by,

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

RAZAK BIN MOHD SAPIAH

ABSTRACT

This report presents the work of thermal treatment of marine soil contaminated with hydrocarbon. The aim of the project is to determine the optimum temperature and to find the efficiency of thermal treatment in removing hydrocarbons contaminated in marine soil with different penetration depths of the contaminated marine soil.

Marine soil pollution normally is contaminated with hydrocarbon through many operations in petroleum exploration, production and transportation. In long term, the organic hydrocarbons have resulted in major environmental issue because of their adverse effect on human health and environment. The contaminated marine soil must be treated to avoid the problems. There are four categorizes of treating technologies available: chemical & physical treatments, biological treatments, solidification / stabilization and thermal treatments. Normally the treatment method has been chosen based on the efficiency of the treatments.

In the study, the soil samples were collected from one of the marine site in Malaysia with the different depth penetrations (surface area, 10cm, 20cm, 30cm, 40cm and 50cm) and were placed in the glass containers fitted with plastic screw lids. The contaminated soil analyzed to determine the hydrocarbon groups contaminated using the Gas Chromatography Mass Spectrum Unit (GCMS) and treated through thermal treatment method using Fixed Bed Activated Unit. The temperatures were used are 300°C, 400°C, 500°C and 600°C, with the residence time of 94 minutes. The amounts of hydrocarbon removing/reducing from the contaminated soil have been measured by UV/Visible Spectrophotometer. The efficiency of the thermal treatment method has been calculated based on the amount of hydrocarbon removal from the contaminated soils. After categorize these hydrocarbons into groups, the optimum temperature of the treatment have been found.

The result show that the thermal treatment method on the samples which have 76% containing hydrocarbon from alkanes group with their carbon chains between C_2 to C_{20} very efficient in removing hydrocarbon contaminants in the contaminated soil. The optimum thermal treatment temperature was obtained about 300°C.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Soil pollution is caused by the presence of xenobiotic (man-made) chemicals or other alteration in the natural soil environment. Soil degradation is defined as the decline in soil quality caused through its misuse by human activity (Barrow, 1991). A contaminated soil with hydrocarbon may be defined as a space where in the activity of production, transformation, transport or service is carried out and which due to negligence or defective design or improper maintenance, leads to the occurrence of damage and immediate or deferred risks for the users, the present and future inhabitants and for the environment (Ricour, 1993).

Many operations in petroleum exploration, production and transportation have the potential to affect the environment in different degrees. Leakages from pipeline, oil wells, underground storage tanks of gas stations, improper disposal of petroleum wastes and oil spills are the major causes of soil and ground water contamination (Amro, 2004). There are also cases whereby oil might be spilled purposely as what was happened in the Persian Gulf War in 1991 (Tajik, 2004).

Number of oil spills reported in the Arabian Gulf area was 550 oil spills incident with a total of 14,000 barrels in the period 1995 to 1999 and 11,000 barrels was spilled in the period of 2000 to 2003 (Saudi Aramco, 2001). As a result, when the oil spills penetrate into the shoreline, the effect of the contamination will remain for long period of time, thus the oil spill that reaches the shore will be more toxic (Singsaas et al, 2000).

However one barrel of crude oil can make one million barrels of water undrinkable (Amro, 2004).

Widespread use, improper disposal, accidental spills and leaks of organic hydrocarbons like petroleum hydrocarbons, organic solvents, and poly-aromatic hydrocarbons (PAHs) have resulted in long-term persistent sources of contamination of soil and groundwater, which becomes a major environmental issue because of their adverse effect on human health and environment (Santanu, 2008).

There are various levels of biological effects of hydrocarbon (Ibrahim, 2008):

- Human hazards through eating contaminated seafood.
- Decrease of fisheries resources and damage to wildlife such as sea birds and mammals.
- Decease of aesthetic value due to unsightly slicks and oiled beaches.
- Modification of marine eco-system by elimination of certain species with an initial decrease in diversity and productivity.
- Modification of habitats, delaying or preventing recolonization.

There are many technologies available for treating sites contaminated with petroleum hydrocarbon. The treatment selected depends upon contaminants and site characteristics, regulatory requirements, costs, and time constraints (Ram et al., 1993). The successful treatment of a contaminated site depends on designing and adjusting the system operation based on the properties of the contaminations, soils, performance of the systems and by making use of site conditions rather than force fitting a solution (Norris et al., 1994).

There are four popular major ways to remediate soils contaminated with petroleum hydrocarbon (Ibrahim, 2008):

- Chemical and physical treatment.
- Biological treatment.
- Solidification / stabilization.
- Thermal treatment.

1.2 PROBLEM STATEMENT

1.2.1 PROBLEM IDENTIFICATION

Soil pollution is a global problem. It has affected the lives of millions of people and caused several deaths and health problems. The effects of soil pollution are quite alarming and can cause huge disturbances in the ecological balance and health of living creatures on earth. Over the past 10-15 years, awareness of the problem, and the policy and the strategy to tackle the problem has radically changed. Initially the approach to tackle the problem of polluted soils was primarily focused on the clean-up of soil after excavation, this lead to the development of intensive and relatively expensive methods. At that time biological treatment and thermal treatment was considered not feasible (Stegmann, 2001).

The primary objective of the project is to study the effectiveness of removing the hydrocarbon contaminants in the contaminated marine soils by using the thermal treatment method. The efficiency of the thermal treatment method may depend on the several factors such as:

- The amount of soil contaminated with hydrocarbon.
- The penetration depth of the oil into the soil.
- The type of hydrocarbon and polluted soil.

The temperatures applied to the contaminated soils during the thermal treatment process have to be considered in finding the most efficient temperature in removing the contaminants in the contaminated soils.

1.2.2 SIGNIFICANT OF PROJECT

Petroleum products are some of the most widely used chemicals in society today. With the massive quantity of fuel required to power automobiles, heat homes, and the number of times each gallon of petroleum is stored, transported, or transferred, so the accidents and leakages are unavoidable. Today, Medias like newspapers, TV, internets, etc always reported that many petroleum contamination results from leaking aboveground and

underground storage tanks, spillage during transport of petroleum products, abandoned manufactured gasoline sites, other unplanned releases, and current industrial processes.

As petroleum contains hazardous chemicals such as benzene, toluene, ethylbenzene, xylene, and naphthalene, this contamination can be hazardous to the health of plants, animals, and humans (Vasudevan et al., 2001). Organic pollutant compound such as hydrocarbon are very serious soil pollutants because of the high toxicity of the polycyclic aromatic hydrocarbon (PAH) fraction. According to Environmental Protection Agency, 16 PAHs have been reported as carcinogenic and mutagenic. So it is necessary to remove them from contaminated site.

Rachel Carson (1962), has sparked environmental consciousness globally especially on the issues of groundwater and soil contamination. She highlighted the problem of chemicals use in agricultural activities which has affected the groundwater and soil quality as well as its habitat. Hence soil and groundwater contamination affecting environment and human health has become critical environmental issues.

Groundwater and soil pollution in Malaysia for the past has not been identified as key environmental issue in Malaysia. This is true since not many cases of environmental and human health incidents have been reported. However with increasing demand for agricultural and drinking water use, groundwater and soil vulnerability has become an important environmental and human health issue (Mohamed et al., 2009)

1.3 OBJECTIVES AND SCOPE OF STUDY

1.3.1 OBJECTIVES

The objectives and overall goal of this study is to evaluate the chemical and physical process relevant to thermal removal of hydrocarbon from soils. The specific objectives of this study are;

1. To utilize the thermal treatment method in treating the marine soil contaminated with hydrocarbon.
2. To find the optimum temperature for contaminated marine soil with hydrocarbon could be treated through thermal treatment.
3. To study the effectiveness of using thermal treatment in removing hydrocarbons from contaminated soil with different depth penetrations.

1.3.2 SCOPE OF STUDY

The scope of the study is to investigate the total petroleum hydrocarbon removal by using the thermal treatment methods at four different levels of temperatures which are 300°C, 400°C, 500°C and 600°C. The study also considers the different depth penetration of the contaminated soil. The contaminated soil samples are taken with different penetration depths which are at ground surface, 10cm depth, 20cm depth, 30cm depth, 40 cm depth and 50cm depth at one of the contaminated marine site in Malaysia.

To fulfill the goal and the objectives above:

1. Research and literature review on the theory and information from various resources like journals, articles and books relating to the study must be carried out.
2. This project is an experimental study where laboratory works will be performed based on the availability of equipments in the UTP laboratory.
3. The suitable contaminated soil with hydrocarbon samples has to find within Peninsular Malaysia.
4. Research and find the suitable equipments in the UTP laboratory, the most efficient methods in thermal treating for contaminated soil with hydrocarbon and

to analyze the hydrocarbon components in the contaminated soil before and after it been treated.

In the UTP laboratory facilities, the contaminated marine soil with hydrocarbon could be treated through thermal treatment by using Gas Chromatography Mass Spectrometry Unit. The equipment located at Block 4 of the chemical engineering academic building. The advantages of this equipment is able be manipulated in the temperature and also can detect the type and the amount of hydrocarbons removed from the process of thermal treatment.

1.3.3 THE RELEVANCY OF PROJECT

The rapid economic development of many countries since World War II has caused a considerable increase in marine transportation of raw materials, especially of crude oils and in offshore activities. However a significant amount of oil comes into the sea from operation discharges of ships as well as from incidents. The first large oil spills were caused: in 1967 by grounding of the tanker "Torrey Canyon" (117,000 tons), and in 1969 by a blow-out of the offshore platform "Santa Barbara" (13,600 tons) (Doerffer, 1992). In late 19^{th} centuries health officials from England and France have recognized the importance of soil and groundwater contamination and its effect to human health (Colten et al., 1996).

In the modern days, Love Canal tragedy in the City of Niagara, USA has become the main reference of soil and groundwater contamination. The long term exposure of contamination has revealed more than 248 types of chemicals in the Love Canal dump site, hence shows the critical problem of such contamination (Fletcher, 2002).

In Malaysia, groundwater and soil pollution for the past has not been identified as key environmental issue. This is true since not many cases of environmental and human health incidents have been reported. However with increasing demand for agricultural and drinking water use, groundwater and soil vulnerability has become an important environmental and human health issue (Mohamed, 2009).

Traditional method of treating soil and groundwater contamination has relied upon removal or containment (Brown et al., 1986). These were found to be the most common techniques in a survey of 169 remedial actions (Neely et al., 1981). Traditional remediation effort at hazardous waste sites have been partially effective 54% of the time and completely successful only 16% of the time (Neely et al., 1981). Most of this treatment scheme are not completely effective and do not offer permanent solutions. Some methods may even create additional uncontrolled hazardous waste.

There are four main alternatives for the treatment of contaminated soils (Stegmann, 2000):

1. Leave the contamination as it is, but restrict the utilization of the land.
2. Complete or partial encapsulation of the contamination.
3. Excavation of the contaminated soil and land filling.
4. Treatment of the contaminated soil in-situ or ex-situ either at an onsite or central plant.

CHAPTER 2

LITERATURE REVIEW

Contaminated soil with hydrocarbon brings up critical issues regarding worldwide environment and health concerns. With progress and advanced technology, and growing interest in soil remediation, various approaches have been proposed for treating the contaminants from the contaminated soil sites. There are many technologies are available for treating soil sites contaminated with hydrocarbon. One of the practical and best contaminated soil treatments is trough thermal treatment. However the treatment selected normally depends on several factors like, contaminants and sites characteristics, costs of the treatment and time constraints (Ram et al., 1993).

2.1 REMEDIATION TECHNOLOGIES

The following are some of techniques that might employ to treat contaminated marine soil with hydrocarbon. There are four classes of remediation are known (Ibrahim, 2008):

1. Chemical and physical treatment.
2. Biological treatment.
3. Solidification / stabilization.
4. Thermal treatment.

The examples of the four classes remediation as per listed in the Table 2.1. Several technologies have been developed and applied to the remediation of hydrocarbon contaminated soil, including physical/chemical, thermal and biological technologies. The choice of treatment depends on toxicity removal efficiency, detoxification of soils and energy consumption rates. Of these, the thermal remediation process is usually

preferred, due to advantages of reliability, high capacity and lower cost (Kasai et al., 2000).

Table 2.1: Four Classes of Remediation Technologies

Chemical and Physical Treatment
Ion exchange, Oxidation, Reduction, Precipitation, Neutralization, Photolysis, Carbon adsorption, Dechlorination, Soil vapor extraction, Washing and Flushing
Biological Treatment
Aerobic bioremediation, Anaerobic bioremediation and Phy-bioremediation
Solidification / Stabilization
Cement solidification, Vitrification, Lime solidification and Thermoplastic microencapsulation
Thermal Treatment
Incineration, Thermal desorption and Plasma high temperature treatment

2.1.1 CHEMICAL AND PHYSICAL TREATMENT

The aim of all chemical and physical methods of remediation is to change the chemical environment in a way that prevents the transport of toxic substances to other elements of the soil system (Ibrahim, 2008).

Chemical and physical methods of remediation include the followings: Oxidation, Ion Exchange, Chelation and Precipitation, Photolysis, Adsorption on Granulated Active Carbon (GAC), Reductive Dechlorination, Soil Vapor Extraction (SVE), Soil Washing, and Soil Flushing. The layout of soil vapor extraction is shown in Figure 2.1.

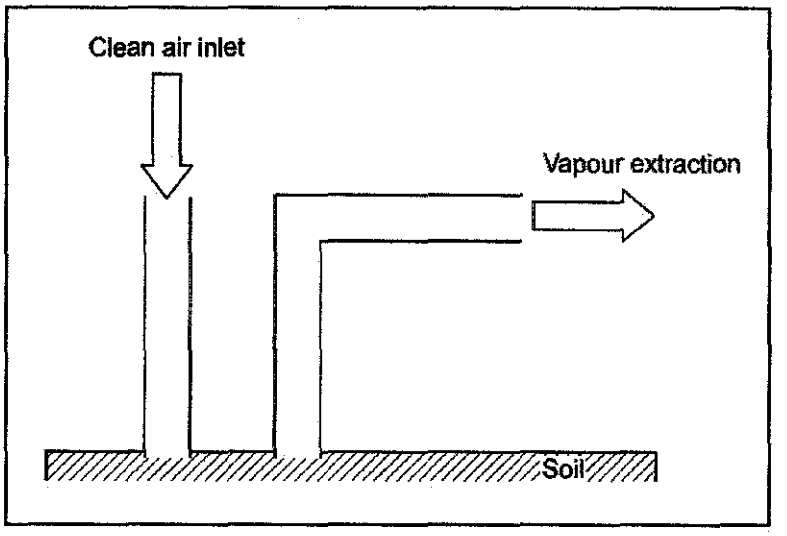


Figure 2.1: Soil Vapor Extraction (Ibrahim, 2008).

2.1.2 BIOLOGICAL TREATMENT

Biological treatment of contaminated soils is a remedial technique making use of naturally occurring microorganisms in the soil, which are capable of degrading toxic materials while carrying out their daily biological activities (Ibrahim, 2008). In bioremediation method, this can be divided into two categories as shown in Figure 2.2;

1. In situ bioremediations.
2. Ex situ bio remedial methods

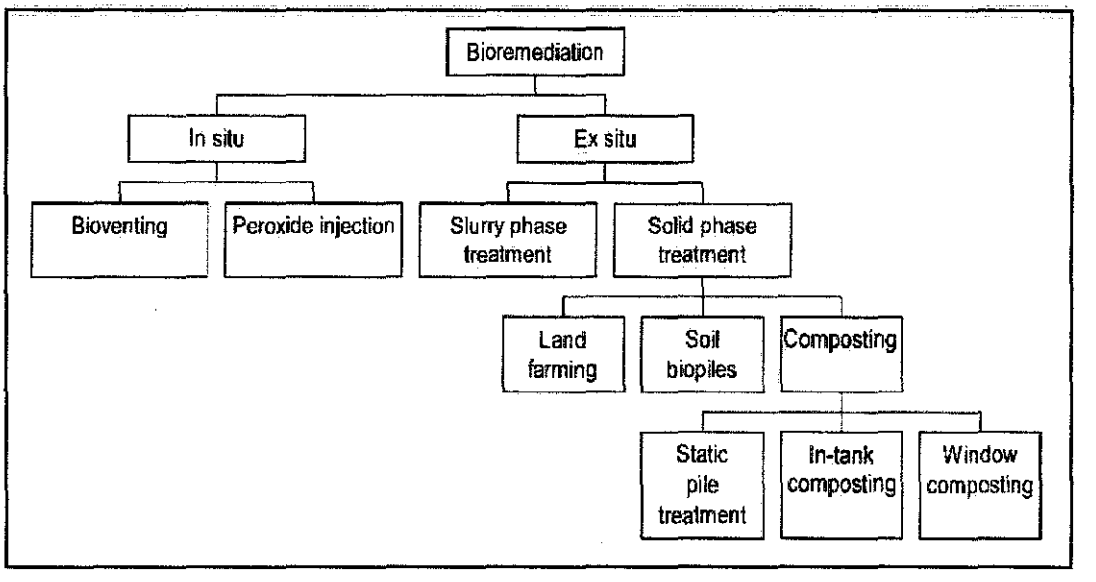


Figure 2.2: Technologies of Bioremediation (Ibrahim, 2008)

In situ bioremediation techniques are used to treat non-halogenated semi volatile organics, such as diesel fuel and heavy oils, beside other materials that are vulnerable to metabolism by microorganisms (Ibrahim, 2008). The technique some known as aerobic bioremediation is accomplished by introducing oxygen and nutrients to the soil in order to enhance the biodegradation of the contaminants. Two techniques normally used are: Bioventing, and Peroxide Injection.

Ex Situ bioremediation technique is the methods carried out away from the pollution site, are normally faster than the in situ methods. The technique is applicable for a wider range of contaminants, but more expensive. It has consists of two main technologies are: slurry phase treatment, and solid phase remediation.

2.1.3 SOLIDIFICATION / STABILIZATION

The technology aimed at immobilizing or stabilizing contaminants is the soil and to prevent them from entering the environment, either by enclosing them into a solid mass or converting them to the least soluble, mobile or toxic form (Ibrahim, 2008).

The most successful technologies are known that secure safe performances of these processes are: Bitumen-based solidification, Encapsulation in thermoplastic materials, Polyethylene extrusion, Pozzolan/Portland cement, and Vitrification.

2.1.4 THERMAL TREATMENT

Volatilization and destruction of contaminants by thermal treatment is a very effective technique. It is achieved by heating the contaminated soil in kilns to temperature 400°C to 700°C, followed by further treatment of the kiln off gas at higher temperatures 800°C to 1200°C to secure total oxidation of the organic volatile matter (Ibrahim, 2008).

2.2 THERMAL TREATMENT OF CONTAMINATED SOIL WITH HYDROCARBON

There are marine soils contaminated with hydrocarbons in many industrial sites and oil refineries. The most popular techniques are thermal treatment methods because they can be effectively applied to a wide range of organic contaminants (Merino et al., (2007). Thermal treatments methods can be classified into desorption and destruction techniques depend on their operational temperatures which are normally between 150°C to 500°C. If the treatment involves working at high temperature usually 600°C to 1000°C the contaminants often suffer chemical modification.

The most efficient industrial treatments to eliminate the soil contamination are thermal processes (Costes et al., 1997). The thermal destruction consists in exposing the soil to high temperature to destroy the organic compounds by cracking (Oppelt, 1986).

Thermal treatment technologies are based on the principle, namely heating the contaminated materials to extract the pollutants and a physical separation that transfers the pollutants to a gas stream. These methods can be applied on site or away from the site which is more often of the case.

Thermal methods represent a major option amongst the plans of remediation. Thus to 1992 incineration was the method selected for treating contaminated materials on nearly one-third of the sites remediated in the USA (EPA, 1993).

Contaminated soils with hydrocarbon exist in many industrial sites, gas plants, oil refineries, petrochemical plants, etc. To date, thermal processes have been the primary means for decontaminating such solid wastes (Oppelt, 1986). In particular, thermal treatment of waste soil in anaerobic conditions has been suggested as an environmentally acceptable method for decontamination (Yang et al., 1997).

Thermal treatment includes various technologies are (Ibrahim, 2008):

i. Incineration
ii. Thermal desorption
iii. Plasma high temperature metals recovery

Merino J. et al., (2007) in their research using thermal treatment method to study the effect of temperature on the release of hexadecane from soil. In the study, the properties of the contaminant, the characteristics of the soil and the operating conditions have been considered as the parameters for thermal decontamination process. The soil samples were artificially contaminated with *n*-hexadecane and thermal treatment of neat and contaminated soil samples was carried out. The results obtained at different temperatures from 150°C to 800°C showed that the hexadecane almost completely can be removed from the soil at operating temperature at about 300°C.

2.2.1 INCINERATION

Incinerator uses high temperature to destroy contaminating substances, which are converted into carbonic gas and steam, leaving behind various other products of combustion. Incinerator is generally carried out in two steps are:

i. Volatilization (temperature about 400°C), and
ii. Destruction (temperature about1000°C).

In this technology, contaminants are combusted at high temperatures (970°C to 1200°C). It is particularly effective for halogenated and other refractory organic pollutants (Ibrahim, 2008). For complete destruction of the contaminants, incineration is one of the most effective treatments available. Greater than 99.99% destruction of carbon tetrachloride, chlorinated benzenes, and polychlorinated biphenyls (PCBs) was achieved by a trial burn with an EPA mobile incinerator (Yezzi et al., 1984).

Wen J.L. et al., (2008) use thermal treatment (incineration) technology to remove polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) from heavily contaminated soil. The research project investigated the behaviour of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) when the contaminated soil was explored in a thermal treatment system (incineration). The effects of two temperatures 750°C and 850°C on the polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) contents of contaminated soils were evaluated. The laboratory-scale thermal treatment system consisted of a primary furnace and a secondary furnace. The experiments were performed by raising the primary furnace temperature at 5°C/min from room temperature and maintaining at 750°C or 850°C, respectively, for 1 hour to

ensure that after the thermal process; more than 99.95% of the contaminant was removed from the feed soil. The temperature of the secondary furnace was constant at 1200°C. The research found that thermal treatment is an effective technology to remove polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) from heavily contaminated soils. The removal efficiency was more than 99.99% was obtained at two primary furnace temperatures750°C and 850°C, while more than 98% of decomposition efficiency was achieved by using a secondary furnace at 1200°C.

2.2.2 THERMAL DESORPTION

This is the process by which organic contaminants are volatilized under controlled condition by heating the contaminated soil to temperatures up to 600°C. Under these conditions, contaminants of low boiling points vaporize to be afterwards collected and further treated. Other than incineration, this technology aims to physically separate the contaminants from the soil. The process comprises two steps:

i. Vaporization of pollutants, and
ii. Treatment of extracted gases.

During thermal desorption, the soil is heated at lower temperatures (from 150 to 650 °C) to eliminate the volatile and semi-volatile compounds (Merino et al., 2003) which are then either condensed and recovered or destroyed in passing through a high temperature afterburner (Oppelt, 1986).

Low temperature thermal stripping is effective as a decontamination method for soils contaminated with VOC. Thermal desorption is an innovative, non incineration technology for heating soil contaminated with organic compound (Fox et al., 1991). This method can be used for VOC-contaminated soils that cannot be managed by other methods (IT Corporation, 1987). The layout of thermal desorption system is shown in Figure 2.3.

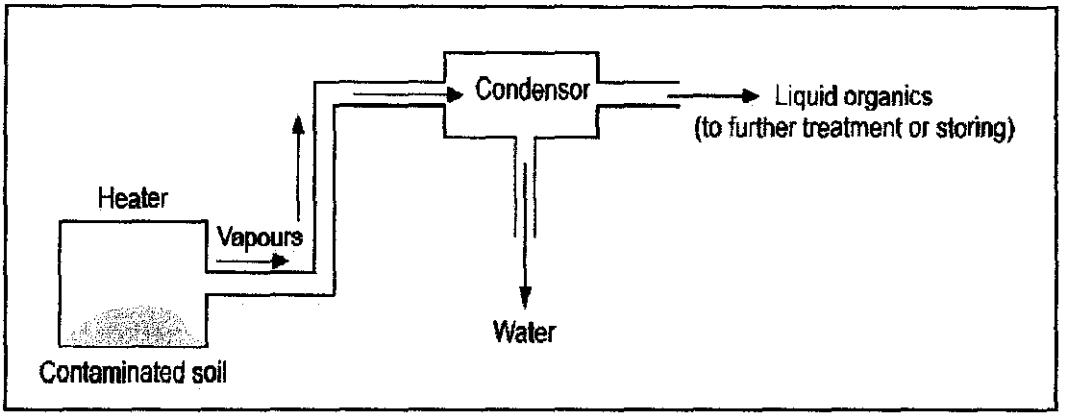
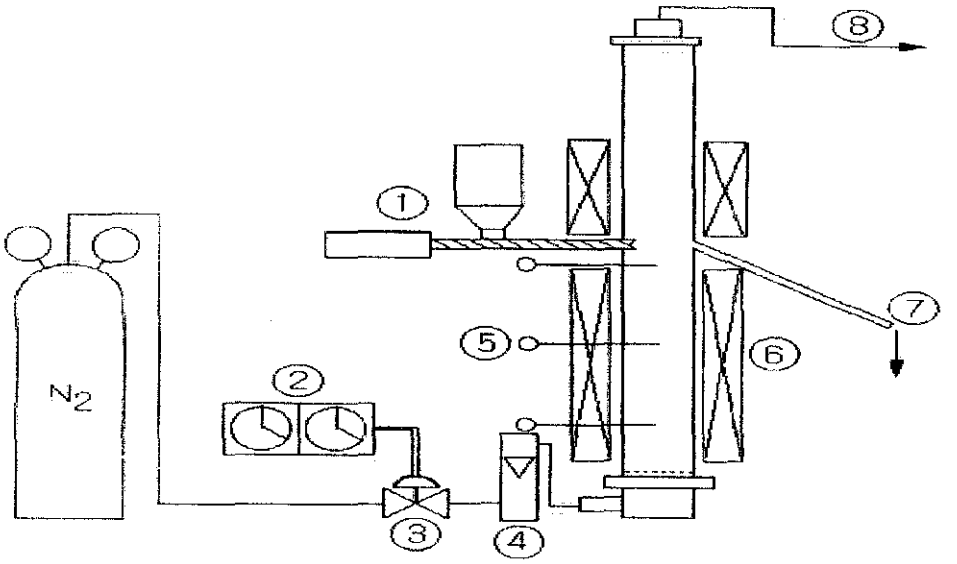


Figure 2.3: Thermal Desorption System (Ibrahim, 2008).

Joong et al., (1998) develop fluidized bed desorber for the remediation of petroleum contaminated soils at low temperature with high efficiency. The research is to investigate the thermal desorption behavior of soils contaminated by various hydrocarbons. Hence the performance of the fluidized bed desorber was investigated at different operating temperature and operating modes. The fluidized bed desorber could be run either for batch or continuous operation. For batch operation mode, a small amount of treated soils was taken through a sampling port by a vacuum pump at every 10 minutes. For continuous operation, contaminated soils were fed into the fluidized bed desorber through a screw feeder at a predetermined rate, and decontaminated soils were continuously discharged through the outlet. The schematic diagram of fluidized bed desorber has shown in figure 2.4. The machine showed that there were two stage of removing the contaminants. The first represents release of volatile organic compounds and water. Then the second stage represents slower release of oil with temperature increase. From the research they found that for batch operation result shows that the time to achieve the available efficiency depends on temperature and for continuous operation, the operating temperature must be kept over 294°C to accomplish the desorption efficiency over 95%.



1. Screw feeder
2. On-off twin timer
3. Solenoid valve
4. Rota meter
5. Thermocouples
6. Electric heater
7. Overflow
8. Ventilation.

Figure 2.4: Fluidized Bed Desorber. (Joong et al, 1998).

2.2.3 PYROLYSIS

Pyrolysis consists of heating the polluted materials in the absence of oxygen to a temperature of a few hundred degrees.

Pyrolysis transforms hazardous organic materials into gaseous components, small quantities of liquid, and a solid residue (coke) containing fixed carbon and ash. Pyrolysis of organic materials produces combustible gases, including carbon monoxide, hydrogen and methane, and other hydrocarbons. Pyrolysis typically occurs under pressure and at operating temperatures above 430 °C (800 °F). The pyrolysis gases require further treatment. The off-gases may be treated in a secondary combustion chamber, flared, and partially condensed.

Veronique R et al., (2005) use this method in their research regarding effects of temperature and soil components on emissions from pyrolysis of pyrene contaminated soil. The objective of the study was to explain how bioactive PAH are generated from a

non-bioactive PAH contaminant during soil thermal treatment. The specimens were heated in a ceramic boat contained within a quartz tube horizontally mounted within tubular electric furnace. A continuous flow of helium conveyed vaporized products from the boat to collection station throughout heating. Gases recovered from the gas sampling bag at collection station were analyzed by gas chromatography (GC) using a flame ionization detector (FID). The experiments show that at temperature 500°C and 650°C, pyrene is totally volatilized from the sample boat. The research shows that essentially all of an exogenous PAH contaminant, example pyrene, can be removed from soil or sand, by heating for a few tens of seconds to a temperature as low as 500 °C for soil or 750 °C for sand.

2.2.3.1 PYROLYSIS GAS CHROMOTOGRAPHY MASS SPECTROMETRY (GC-MS)

GCMS is the equipment used for treating the contaminated marine soil and also to determine the type and amount of hydrocarbons removed from the treatment process. Pyrolysis Gas Chromatography Mass Spectrometry is an analytical technique used in studies on organic matter in soil (Bracewell et al., 1989). During pyrolysis, a sample is rapidly heated in a vacuum of inert gas (e.g., helium). Volatile molecules evaporate, and nonvolatile molecules thermally crack into volatile fragments which can be analyzed by mass spectrometry (MS), gas chromatography (GC)/MS, or infrared spectroscopy (IR) (Bracewell, 1989).

The two most common techniques are curie point and controlled temperature programming pyrolysis. In Curie point pyrolysis, a sample is fixed in a bucket or on a coil of ferromagnetic metal which is inductively heated to its curie point (ferromagnetic limit). When the metal is heat up, volatile molecules in the sample evaporate and non-volatile molecules crack into volatile fragments. All compounds can be collected, separated, and identified by GC/MS.

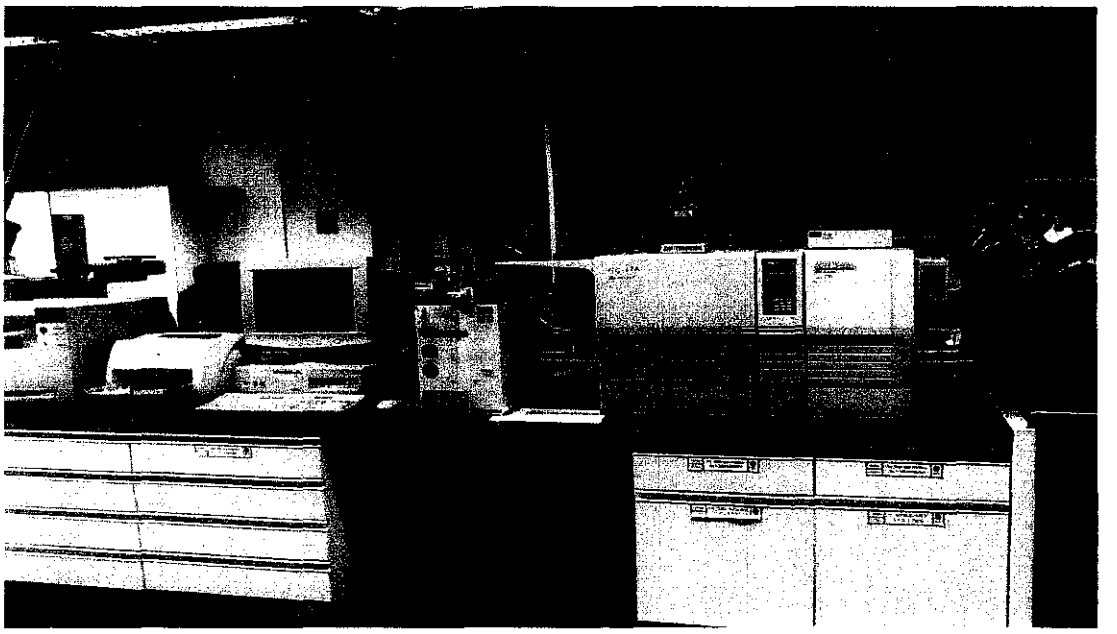


Figure 2.5: Gas Chromatography Mass Spectrometry (GC-MS)

2.2.4 PLASMA HIGH TEMPERATURE METALS RECOVERY

At high temperatures (plasma activated) metal fumes are purged, and then later recovered and recycled. This is suitable for soil as well as for groundwater.

CHAPTER 3

METHODOLOGY

3.1 MATERIAL

3.1.1 SOIL SAMPLES.

The samples of contaminated soil used for the study were collected from one of the petrochemical industry in Malaysia. The samples were taken at different depth penetrations; 0cm, 10cm, 20cm, 30cm, 40cm and 50cm. Then the samples had placed in glass containers fitted with plastic screw lids. The samples were labeled immediately after placing the sample into the container and placed in the chiller room at 5°C to prevent any light material vaporize from the samples.

The most effective shallow soil sampling method including scoop, hand auger, slide hammer, open tube, split tube, solid tube and thin walled tube (Byrnes, 2009). The samples were taken at different layer of depth penetrations; 0cm, 10 cm, 20 cm, 30cm, 40cm and 50cm. The steps of collecting the contaminated soil sample at site:

1. Cut 1 feet diameter hole of contaminated soil.
2. Collect the sample using scoop until the desired sampling depth is reached.
3. Lift up and transfer the soil from the scoop directly into a sample bottle.
4. Fill up the soil sample into the sample bottle is full.
5. Then, the sample bottle is capped and labeled.

3.2 METHODS

In the study, the treatment and analysis processes for contaminated soil with hydrocarbon at different depth penetration and at different temperature will be performed using Gas Chromatography Mass Spectrum (GC-MS). In general, the thermal treatment method is to remove the contaminants by heating the contaminated soil. The heat applied will destroy or evaporate the contaminants. Then the destroyed or evaporated hydrocarbon change into gases which move more easily through the soil. In this work, the contaminated marine soil with hydrocarbon will heat up at temperature ramp from 300°C to 600°C at 94 minutes time interval using Gas Chromatography Mass Spectrum (GC-MS).

3.2.1 GAS CHROMATOGRAPHY MASS SPECTRUM ANALYSIS

The experiment performs by using SHIMADZU PYR-4A pyrolysis unit (Chemical Data System) interfaced to a gas chromatograph (Shimadzu) coupled to a mass selective detector (Shimadzu) operating in electron impact mode (EI) at 70 eV. Samples were weighted (2 mg) in a 3 mm x 3 mm platinum (Pt) bucket.

In order for identifying possible hydrocarbon present, the pyrolysis gas chromatography study was conducted using SHIMADZU GCMS-QP5050 with the following condition: Electron impact ionization, electron energy 70 eV, scan range 40 to 500 amu at 1 scan/s. Nitrogen gas at a flowrate of 1.5cm³/min was used as a carrier gas. Figure 3.1 is shown the SHIMADZU PYR-4A pyrolysis unit.

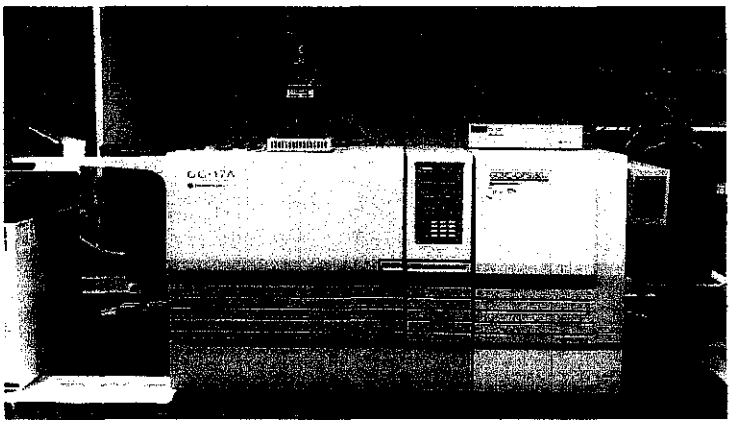


Figure 3.1: SHIMADZU PYR-4A Pyrolysis Unit.

The hydrocarbon contaminated soil samples were placed in 3 mm x 3 mm platinum bucket as shown in figure 3.2. The amount of samples placed in the bucket estimated about 2mg per bucket. Since the size is too small, to put the soil sample carefully into the bucket for ensuring to have the right results.

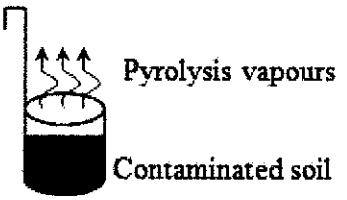


Figure 3.2: Platinum Bucket.

The full bucket was placed in the sample holder, which was affixed to the top of the PYR-4A pyrolysis unit as shown in figure 3.3 and keeps the bucket with the samples for 5 minutes at room temperature at under a helium gas stream.

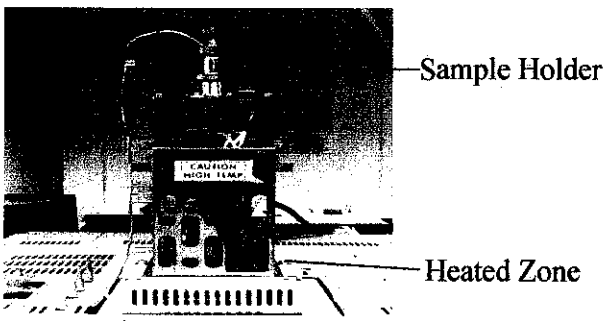


Figure 3.3: Sample Holder and Heated Zone

For starting the analysis the sample bucket was dropped into the heated zone.

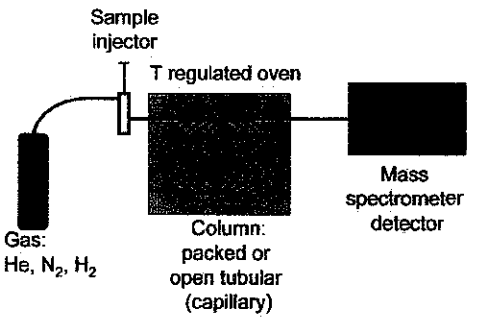


Figure 3.4: GCMS Analysis

The pyrolysis vapors were carried by small flow rate of helium into the GC capillary column. The temperature of the GC-MS injector was held at 290 °C. Figure 3.4 shows the location of column in the gas chromatography mass spectrometry. The experiments were conducted for different samples at four different temperatures; 300°C, 400°C, 500°C and 600°C. The temperatures were programmed at the mentioned degrees for 94 minutes for each experiment.

3.2.2 THERMAL TREATMENT USING FIXED BED ACTIVATION UNIT

The hydrocarbon contaminated soil sample treated by thermal treatment using fixed bed activation unit as shown in figure 3.5. The unit is able to treat the hydrocarbon contaminated soil sample from 100°C to 1100°C. For the project study, the soil samples treated at four levels of temperature which were at 300°C, 400°C, 500°C and 600°C. The fixed bed activation unit use automatic electrical heater. The heater automatically turn ON/OFF based on the temperature setting.

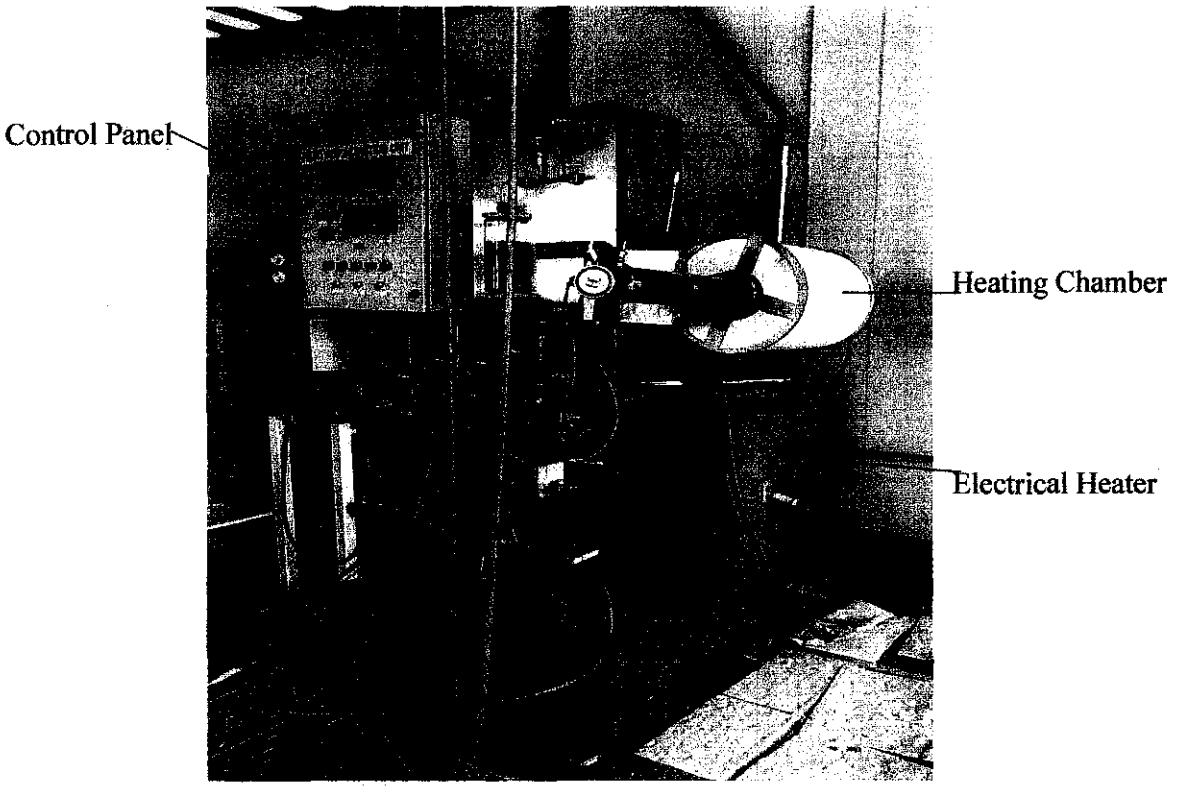


Figure 3.5: Fixed Bed Activation Unit

At about 30g of contaminated soil samples with hydrocarbon put into the ceramic cup and placed it inside the furnace (heating chamber). Inside the furnace/heating chamber, continuous nitrogen was injected at flowrate 2.5cm^3/s. Temperature at the furnace was gradually increased from ambient temperature at 30°C to heating (thermal treatment) temperature at 300°C. When the furnace temperature stable and maintain at 300°C, the heating process kept for 1 hour (residence time). After I hour gone through the thermal treatment process, the sample removed from the heater for hydrocarbon reduction analysis using UV/visible spectrophotometer.

3.2.3 UV/VISIBLE SPECTROPHOTOMETER ANALYSIS

The oil remaining in the soil was determined by solvent extraction using n-hexane. N-hexane (10 cm^3) was added to the rinsed soil and shaken laterally for 5 min as shown in figure 3.6 and then the n-hexane/hydrocarbons extract was removed. This process was repeated four times, the fourth extract gave the same absorbance reading as pure n-hexane (zero absorbance) as proposed by (Urum, 2004). All the n-hexane/hydrocarbons extract was collected into one volumetric flask and made up to 50 cm^3 with n-hexane

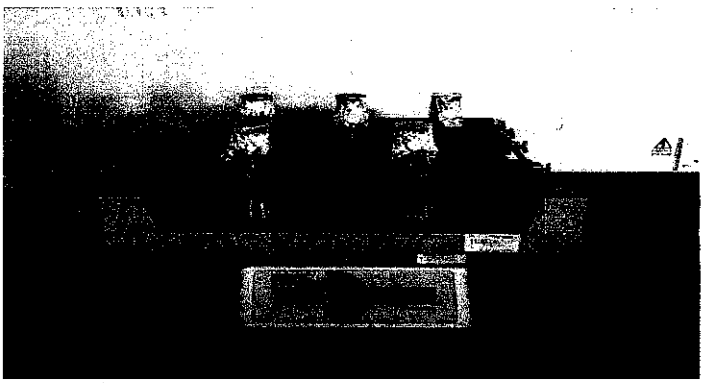


Figure 3.6: Soil Samples Extraction

A sample from the 50cm^3 extract was centrifuged for 20 min at a speed of 3000 rpm. This was to remove any suspended particles, which may interfere with the absorbance measurement. Although n-hexane is a highly non-polar solvent, it was selected due to low toxicity and case of availability in comparison with other solvents.

Absorbance of the centrifuged extract was measured at 400nm using SHIMADZU UV-3150 UV-VIS –NIR Spectrophotometer as shown in Figure 3.4. The 400-nm wavelength was chosen based on investigation using a stock solution of n-hexane/crude oil mixture, which showed that the highest absorbance occurred at 400nm. The concentration of crude oil at this absorbance was determined from the function obtained from the calibration curve of the stock solution of n-hexane/crude oil at 20°C given by (Urum, 2004).

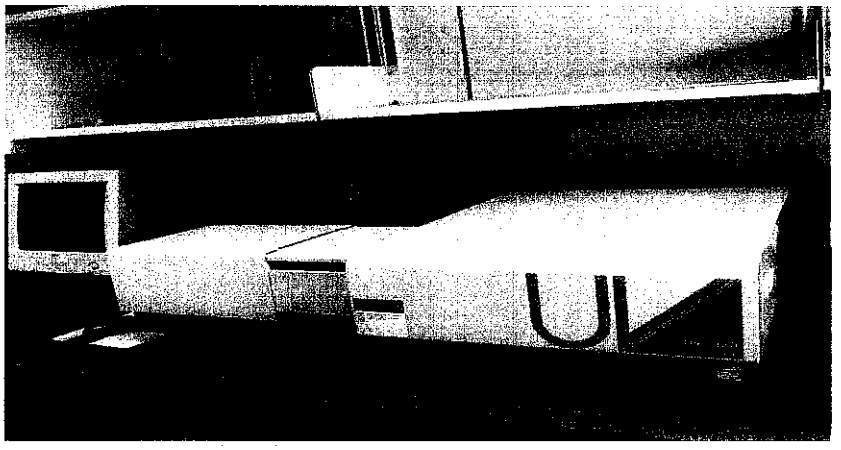


Figure 3.7: UV/ Visible Spectrophotometer

CHAPTER 4

RESULT AND DISCUSSION

4.1 RESULTS

4.1.1 GAS CHROMATOGRAPHY MASS SPECTRUM ANALYSIS

This analysis conducted to identify the major hydrocarbon components contain in the samples. The major functional group for these samples of contaminated soil determine in the experiments. The contaminated soils normally have a complex mixture, containing hundreds of thousands of hydrocarbons.

The pyrolytic GC-MS can determine the contaminated hydrocarbon components in the contaminated soil samples. All the compounds detected in the pyrolysis GC-MS vapours were classified into grouping. According on the chromatograms resulted from the analysis; the main pyrolytic products detected from the pyrolysis of the contaminated soil samples are identified. The peak identifications were based on mass spectral interpretation and published libraries of mass spectra of lignocellulose pyrolyzates.

Pyrolysis GC-MS have been conducted for twenty-four samples using the short run GC program. The pyrolysis GC/MS results demonstrate the extensive sorption of petroleum hydrocarbons components.

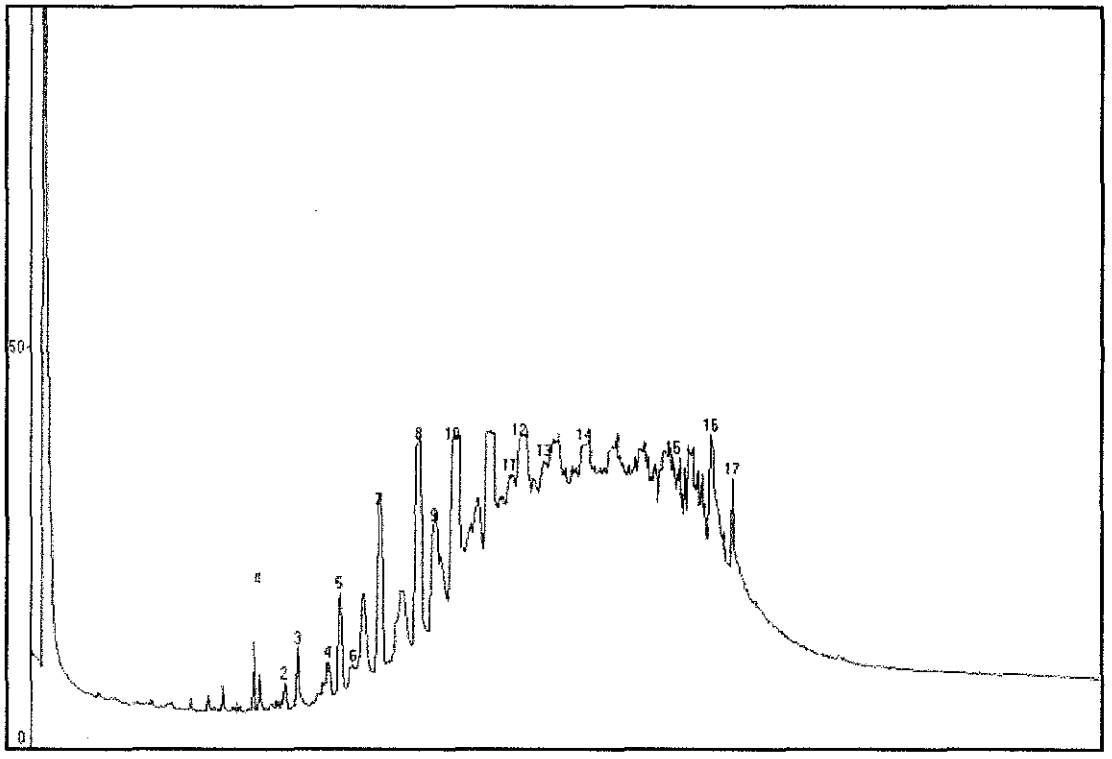


Figure 4.1: Peaks of the components from the GC-MS Analysis.

PKNO	R.TIME	I.TIME	F.TIME	A/H(sec)	AREA	HEIGHT	%Total	NAME	M. FORMULA	GROUPING
1	1	1	3	27	313935454	11676429	66	Water	H20	Water
2	22	22	23	13	5205489	404417	1	Dodecane	C15H32	alkane
3	24	23	24	12	9175349	781522	2	n-Tridecane	C13H28	alkane
4	26	26	27	21	8651865	406299	2	Dodecane	C15H32	alkane
5	27	27	27	12	8703171	704444	2	n-Pentadecane	C15H32	alkane
6	28	28	29	30	5542168	185715	1	IH_Indene	C15H28	Alkene
7	31	30	31	7	7832381	1180849	2	Pentadecane	C15H32	Alkane
8	34	34	34	68	22530266	330000	5	Nonane	C13H28	Alkane
9	35	35	35	23	9127496	392210	2	2-Propenoic Acid	C10H10O4	Acid
10	37	37	37	20	28188774	1426942	6	1,6-Dimethyl-4-isopropylnaphthalene	C15H18	Aro
11	42	42	42	19	5980862	321793	1	Octane	C10H22	alkane
12	43	43	43	16	6867016	427063	1	Tricyclo[2.2.1.0(2,6)]heptane	C7H10	alkane
13	45	45	46	29	10302899	355119	2	Nonadecane	C20H42	alkane
14	49	48	49	36	7135643	200987	1	n-Octacosane	C28H58	alkane
15	56	56	57	10	6810001	692894	1	Nonadecane	C19H40	alkane
16	60	60	60	10	12746642	1219536	3	1,4-Dicyclohexylcyclohexane	C18H32	alkane

Figure 4.2: List of the components from the GC-MS Analysis

4.1.2 HYDROCARBON GROUPING

From the Gas Chromatography (GC) analysis for the sample taken at 0cm depth penetration, the result shows that the content of contaminated hydrocarbon components chain ranging from C_7 to C_{28}. The major functional group in the sample are 75% is alkane group which contain straight chain, branched alkanes, as well as cyclic alkanes with varying number of saturated rings and side chains. 5% of this contaminated soil sample is from aromatic hydrocarbon including one or more aromatics rings ranging from simple mono-aromatics compound, such as benzene and toluene to poly-aromatic compound such as pyrene. The rest of the fraction for this sample is carboxylic acid which is about 14% whereas alcohol is about 5%. The functional group distribution has shown in Figure 4.3.

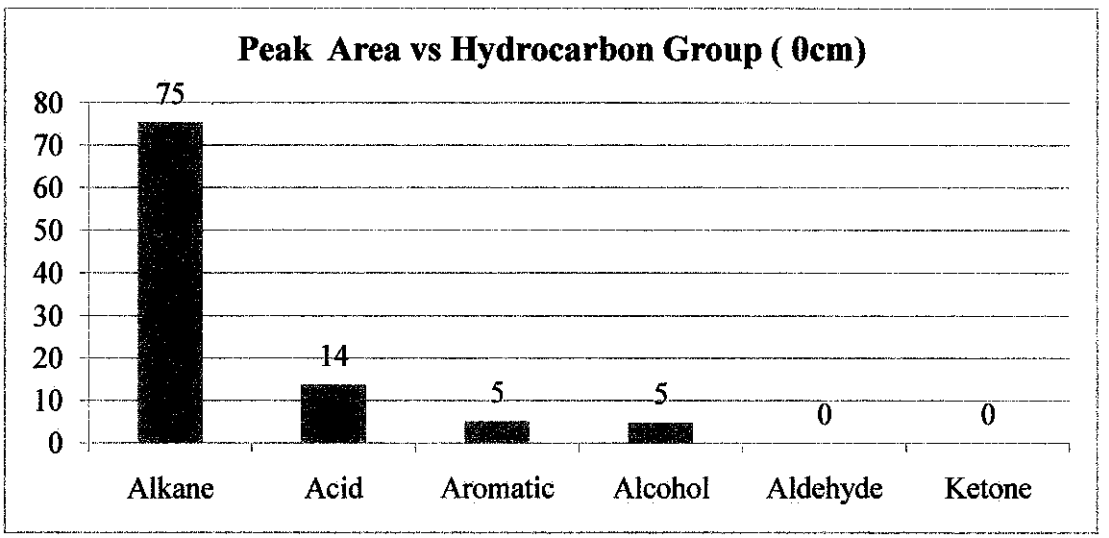


Figure 4.3: Functional group distribution for the samples at 0cm depth penetration

The Gas Chromatography (GC) results for the sample taken at 10cm depth penetration, show that the content of contaminated hydrocarbon compounds containing carbon chain ranging from C_2 to C_{44}. However, there is only 2% of hydrocarbon components chain ranging from C_{31} to C_{44}. The major functional group in the sample are 74% is from alkane group which contain straight chain, branched alkanes, as well as cyclic alkanes with varying number of saturated rings and side chains. 1% of this contaminated soil sample is from aromatic hydrocarbon including one or more aromatics rings ranging from simple mono-aromatics compound, such as benzene and toluene to poly-aromatic compound such as pyrene. The rest of the fraction for this sample is carboxylic acid which is about

3% whereas alcohol and aldehyde is about 7% and 2%. The functional group distribution for contaminated soil sample collected at 10cm depth penetration shows in Figure 4.4.

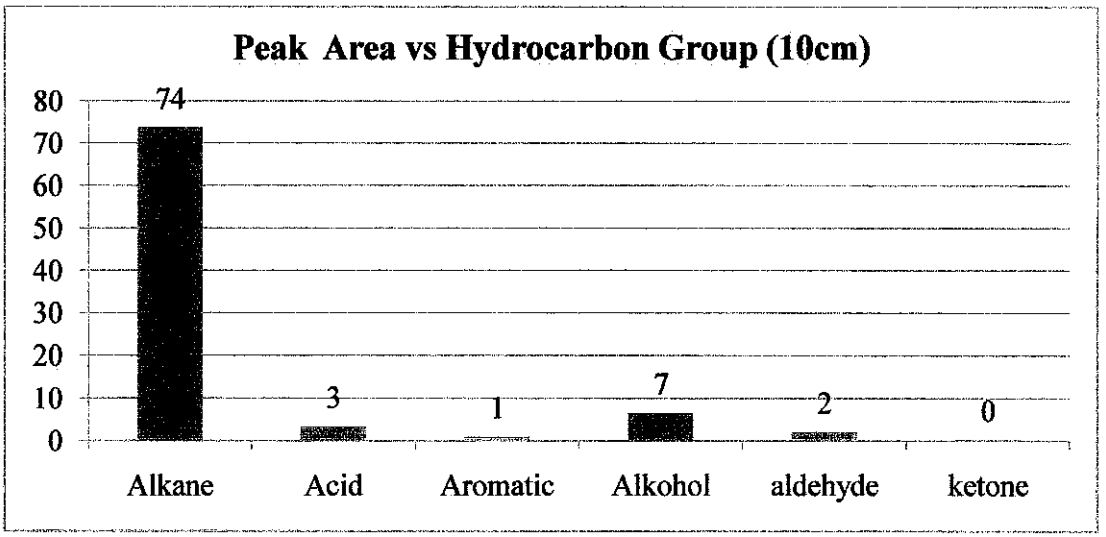


Figure 4.4: Functional group distribution for the samples at 10cm depth penetration

The Gas Chromatography (GC) result for the sample taken at 20cm depth penetration, the content of contaminated hydrocarbon components chain ranging from C_2 to C_{28}. The major functional group in the sample are 82% is from alkane group, 1% of this contaminated soil sample is from aromatic hydrocarbon, 5% is carboxylic acid whereas alcohol and ketone is about 4% and 8%. The functional group distribution for contaminated soil sample collected at 20cm depth penetration shows in Figure 4.5.

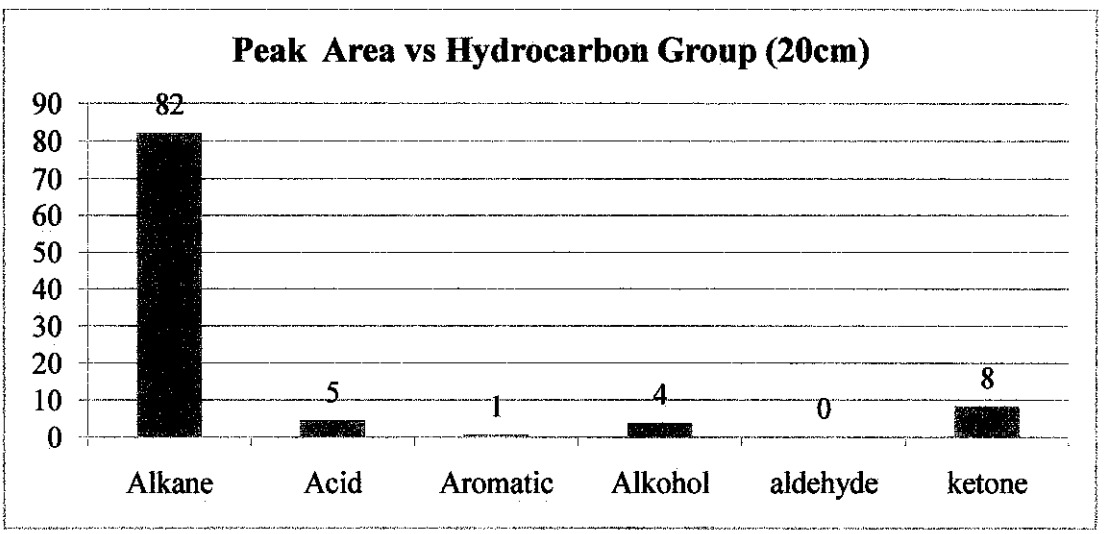


Figure 4.5: Functional group distribution for samples at 20cm depth penetration

The Gas Chromatography (GC) result for sample taken at 30cm depth penetration show that the content of contaminated hydrocarbon components chain ranging from C_2 to C_{20}. The major functional group in the sample are 82% is from alkane group, 1% of this contaminated soil sample is from aromatic hydrocarbon, 22% is carboxylic acid whereas alcohol is about 1%. The functional group distribution for contaminated soil sample collected at 30cm depth penetration shows in Figure 4.6.

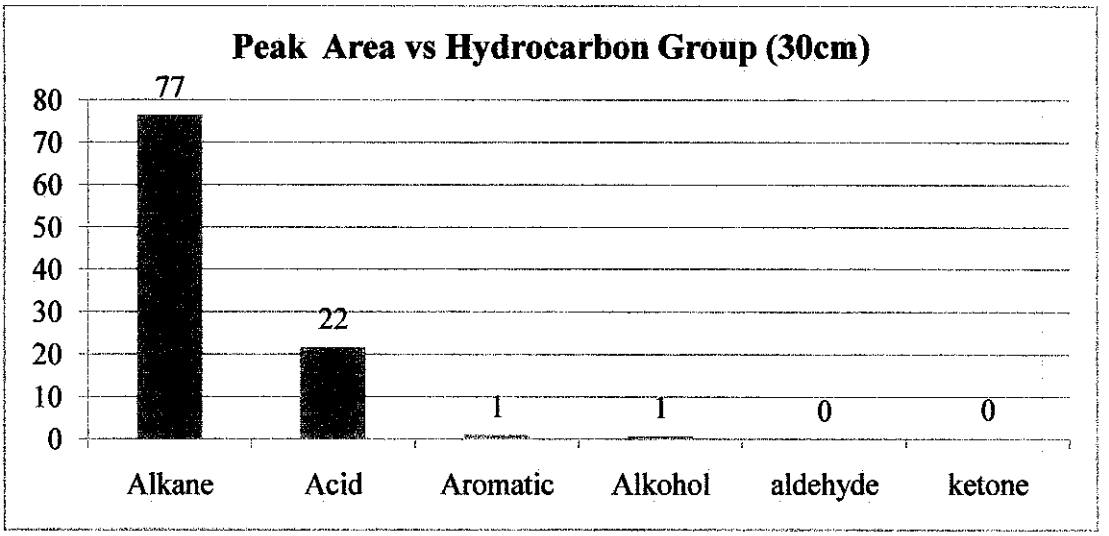


Figure 4.6: Functional group distribution for the samples at 30cm depth penetration

The Gas Chromatography (GC) result for sample taken at 40cm depth penetration show that the content of contaminated hydrocarbon components chain ranging from C_2 to C_{20}. The major functional group in the sample are 77% is from alkane group, 1% of this contaminated soil sample is from aromatic hydrocarbon, 12% is carboxylic acid whereas alcohol and ketone is about 1% and 4%. Besides that 5% of this contaminated soil sample is from aldehyde group. The functional group distribution for contaminated soil sample collected at 40cm depth penetration shows in Figure 4.7.

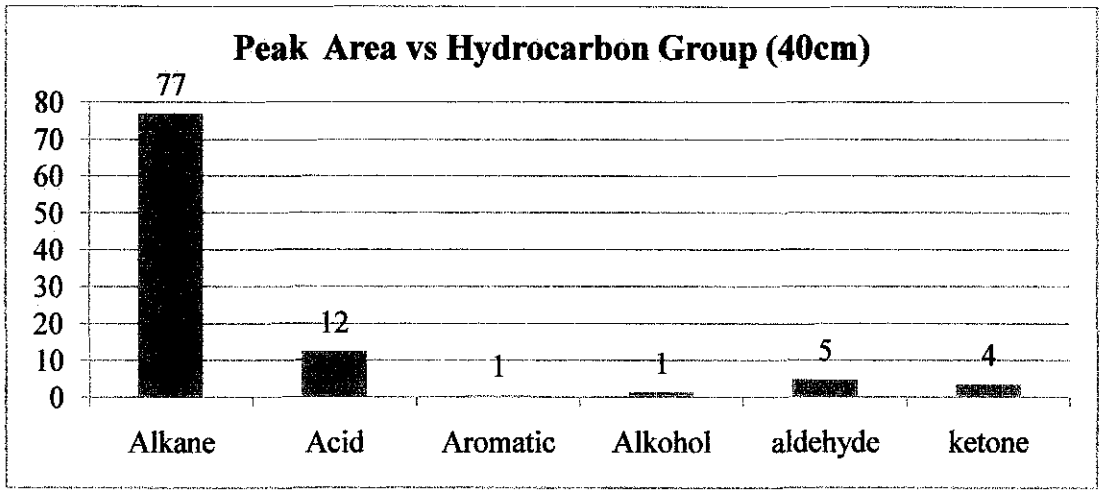
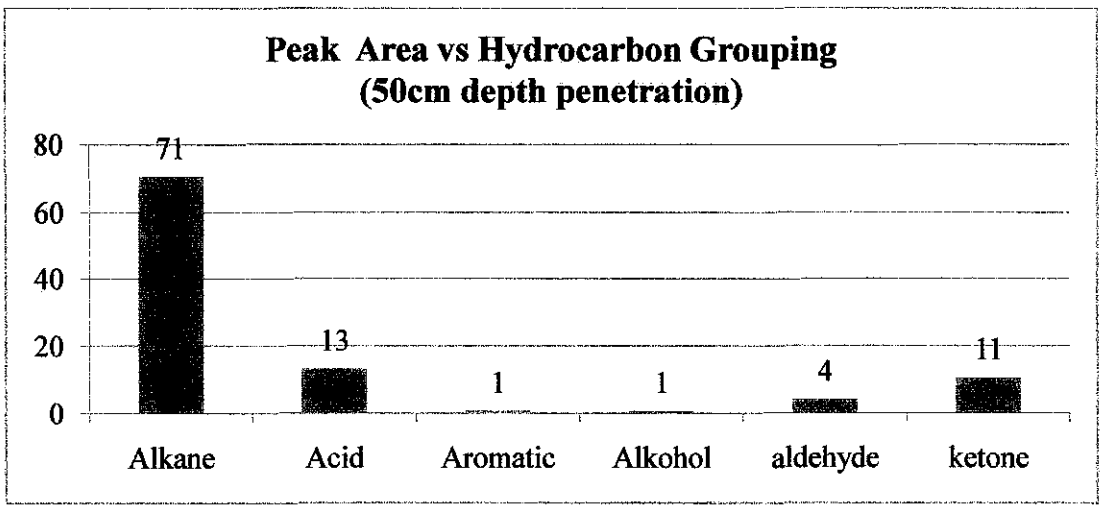


Figure 4.7: Functional group distribution for the samples at 40cm depth penetration

The Gas Chromatography (GC) result for sample taken at 50cm depth penetration show that the content of contaminated hydrocarbon components chain ranging from C_2 to C_{44}. However there is only 0.5% of hydrocarbon components chain ranging from C_{31} to C_{44}. The major functional group in the sample are 71% is from alkane group, 1% of this contaminated soil sample is from aromatic hydrocarbon, 13% is carboxylic acid whereas alcohol and ketone is about 1% and 11%. Besides that 4% of this contaminated soil sample is from aldehyde group. The functional group distribution for contaminated soil sample collected at 50cm depth penetration shows in Figure 4.8

Figure 4.8: Functional group distribution for the samples at 50cm depth penetration



4.1.3 UV/VISIBLE SPECTROPHOTOMETER ANALYSIS

This analysis conducted to identify the hydrocarbon reduction from the treated samples of contaminated soil with hydrocarbon. The percentage of hydrocarbon reduction from these samples determine in the experiments. The percentage of hydrocarbon reduction normally related to the treated temperature during thermal treatment.

The UV/Visible Spectrophotometer analyses determine the percentage of hydrocarbon reduction through absorbance at determined wavelength. The wavelength for the experiments fixed at 400Nm based on the major functional group which is alkanes group. The wavelength also normally used for many petroleum hydrocarbons especially for crude oil analysis. According on the absorbance resulted from the analysis; the hydrocarbon reductions detected from the analysis of the contaminated soil samples were identified.

4.1.4 HYDROCARBON REDUCTION

Analysis on the contaminated soil samples before treatment conducted 3 times using UV/visible spectrophotometer. As the average of the results, the absorbance for the sample is 0.4683 as shown in Figure 4.9. The higher value absorbance determines the higher hydrocarbon concentration in the solution. Hence the higher hydrocarbon extracted from the soil samples.

The slope of the chart also determines the concentration of the hydrocarbon in the solution. The higher gradient show in the chart is the higher concentration of hydrocarbons in the solution. Hence higher hydrocarbon extracted from the soil samples. The slope of graph for soil samples before the thermal treatment is 0.01 as shown in Figure 4.9. The experiments for other soil samples after thermal treatment at different level of temperatures expected were much lower compared to the soil samples before the thermal treatment.

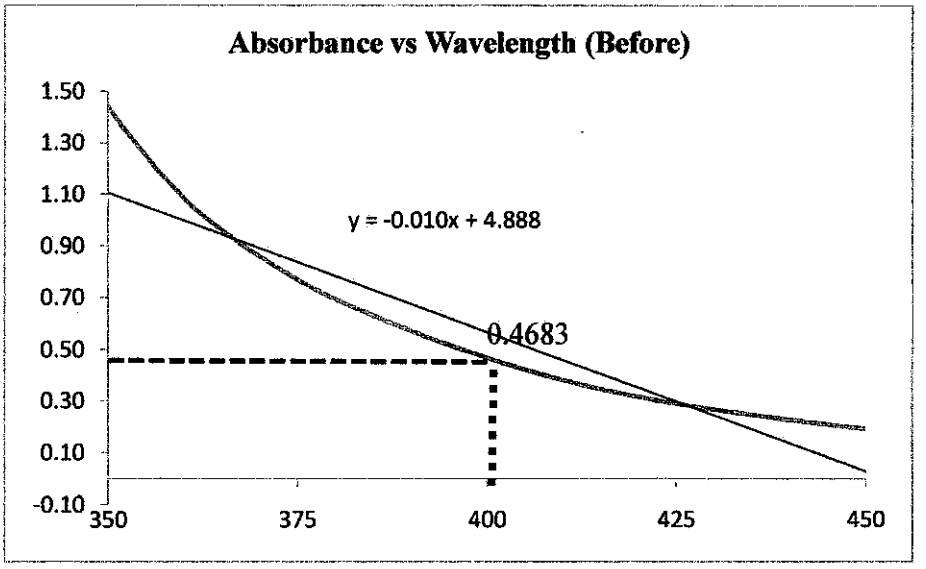


Figure 4.9: Absorbance on the samples before treatment.

The experiment on the contaminated soil samples with hydrocarbon which was treated through thermal treatment at temperature 300°C detected the absorbance on the liquid solution is at 0.0617 as shown in Figure 4.10. The result shows that the absorbance is much lower compared to absorbance for soil samples before treatment. Hence shows that the concentration of hydrocarbon in the extracted solution is lower than the concentration for extracted solution from soil samples before treatment. The slope for the graph also shows that the gradient is less compare to the gradient of the graph for soil samples before thermal treatment. From the results, the hydrocarbon containing in the soil sample reduce after went through thermal treatment.

The reduction of hydrocarbon in the soil samples can be calculated as:

Percentage of Hydrocarbon Reduction

= *((Absorbance before Treatment – Absorbance after Treatment) / Absorbance after Treatment) x 100*

For the sample which treated at temperature 300°C, the reduction of the hydrocarbon in the soil samples in about 86.82%.

Absorbance	0.0617
Slope	0.001
Hydrocarbon Reduction (%)	86.82

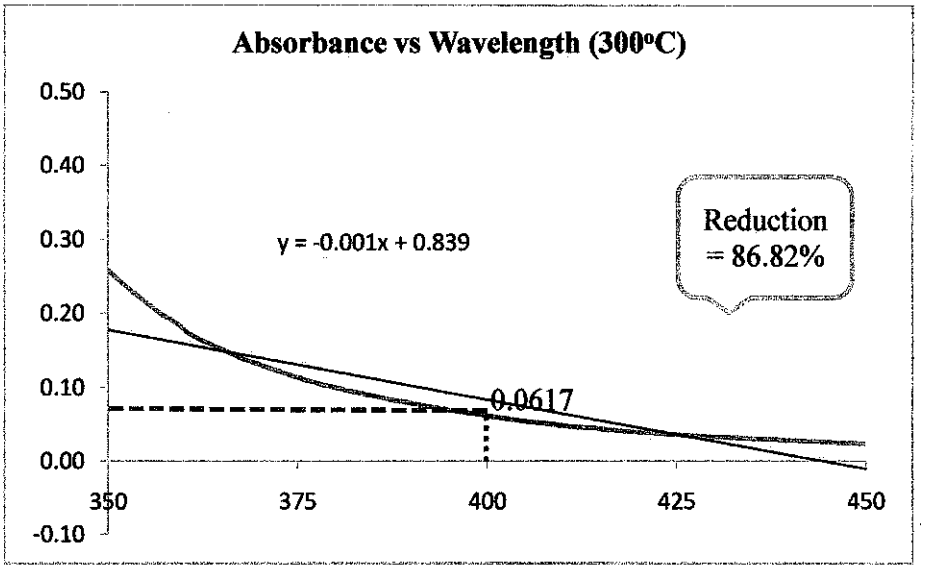


Figure 4.10: Absorbance on the sample after thermal treatment at temperature 300°C.

The results shown in Figure 4.11 indicates that the samples after thermal treatment at 400°C.

Absorbance	0.0513
Slope	0.001
Hydrocarbon Reduction (%)	89.05

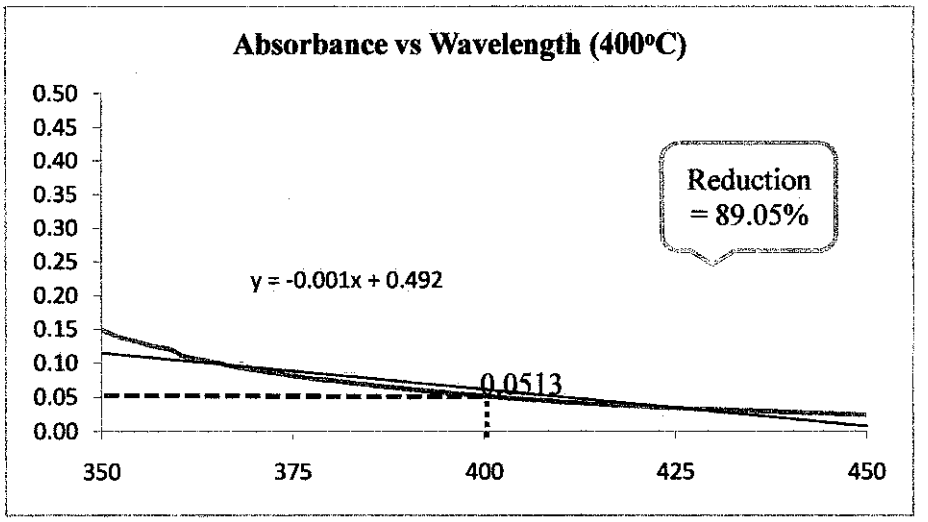


Figure 4.11: Absorbance on the sample after thermal treatment at temperature 400°C.

The results shown in Figure 4.12 indicates that the samples after thermal treatment at 500°C.

Absorbance	0.0393
Slope	0.000
Hydrocarbon Reduction (%)	91.61

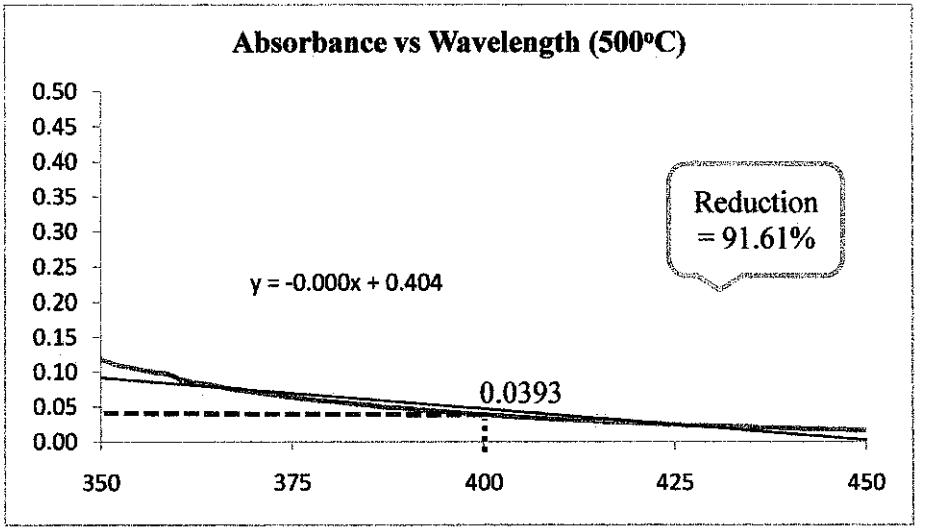


Figure 4.12: Absorbance on the sample after thermal treatment at temperature 500°C.

The results shown in Figure 4.13 indicates that the samples after thermal treatment at 600°C.

Absorbance	0.0383
Slope	0.000
Hydrocarbon Reduction (%)	91.82

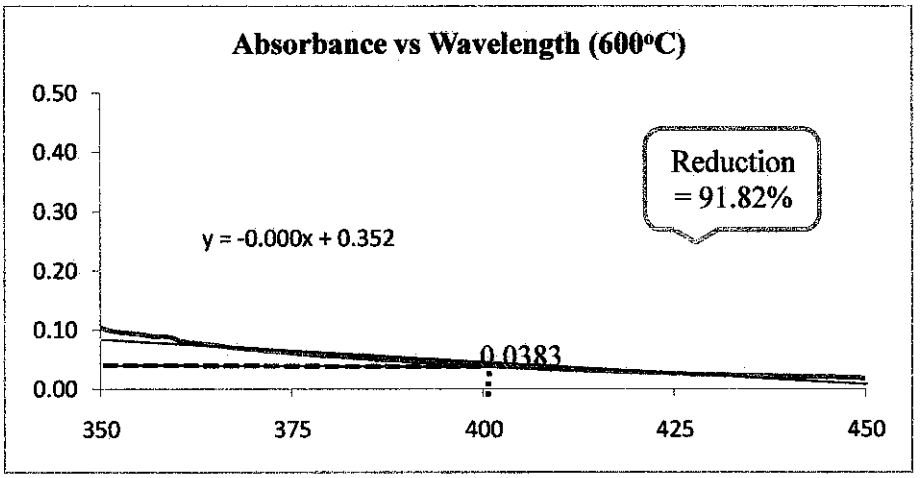


Figure 4.13: Absorbance on the sample after thermal treatment at temperature 600°C.

4.2 DISCUSSION

4.2.1 HYDROCARBON GROUPING

The major functional group in the samples is coming form the alkane group which is about 76% which contain straight chain, branched alkanes, as well as cyclic alkanes with varying number of saturated rings and side chains. The amount of alkanes group contains in the contaminated soil samples at different level of depth penetration shows that the alkanes group contain about the average at76%.

The contaminated soil sample at 0cm depth penetration contains about 75% of alkanes group compare to others contaminated soil samples which are at the depth penetration 10cm, 20cm, 30cm, 40 cm and 50cm contain 74%, 82%, 77%, 775 and 71% of alkanes group. The percentage of alkanes group in contaminated soil samples at different depth penetrations are shown in Figure 4.14.

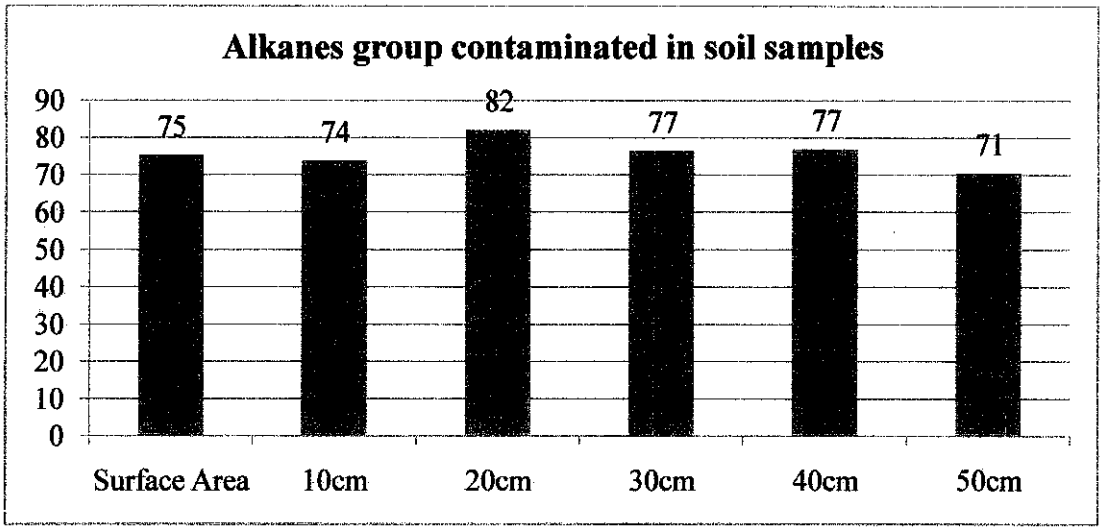


Figure 4.14: Percentage of alkanes group contaminated in the soil samples

Aromatic hydrocarbon contributed about 2% in this contaminated soil sample; including one or more aromatics rings ranging from simple mono-aromatics compound, such as benzene and toluene to poly-aromatic compound such as pyrene.

The contamination of aromatic hydrocarbon is slightly different where the aromatic group found higher at soil samples collected from ground surface area compare to soil samples collected at other areas (depth penetration). At 0cm the aromatic group contaminated in the soil at about 5% whereas other areas: 10cm, 20cm, 30cm, 40cm and 50cm depth penetrations are about 1% only. The percentage of alkanes group in contaminated soil samples at different depth penetrations are shown in Figure 4.15.

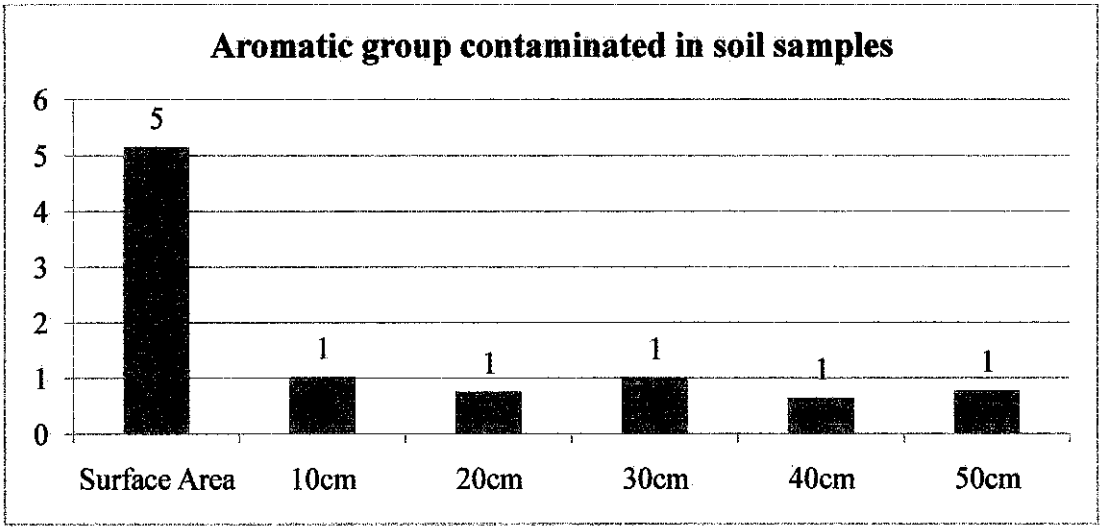


Figure 4.15: Percentage of aromatic group contaminated in the soil samples

The other hydrocarbon group found in the contaminated soil is carboxylic acid which is about 12%. The distribution of the acid group is varying based on the different of the sample depth penetrations. The acid group found contaminated into the soil higher at ground surface area and at depth penetration of 30cm to 50cm compare to at depth penetration 10cm to 20cm. The distribution of acid group in contaminated soil samples at different depth penetrations are shown in Figure 4.16.

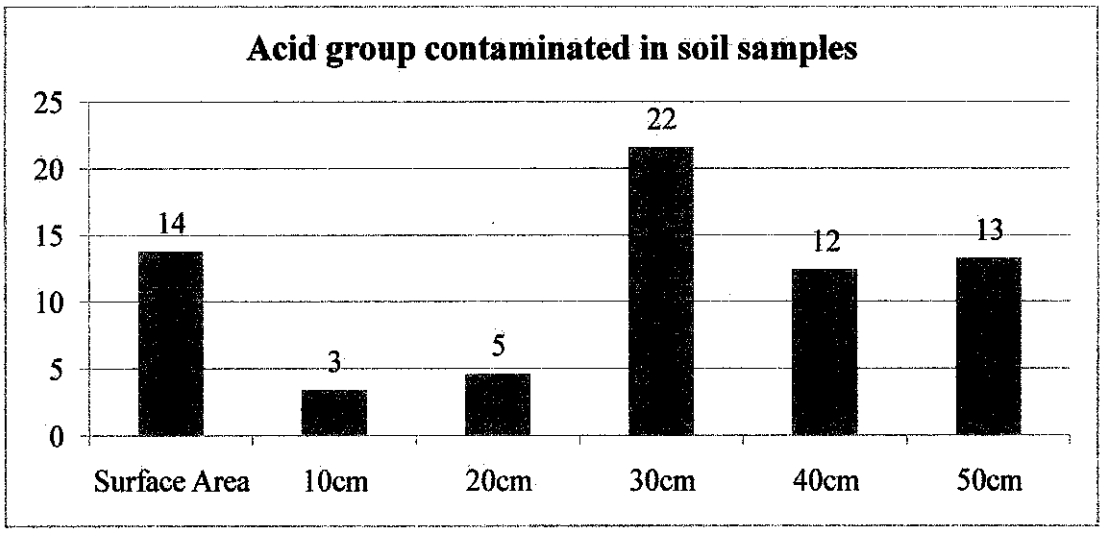


Figure 4.16: Percentage of acid group contaminated in the soil samples

The rest of the fraction for this sample is alcohol which is about 12% whereas aldehyde and ketone is about 2% and 4%. The hydrocarbon group of alcohol seen contaminated at all the soil samples but contaminated higher into the soil samples collected at surface area to sample at depth penetration 20cm compare to soil samples collected at depth penetration between 30cm to 50cm whereas this phenomenon is opposite for ketone group which is more contaminated for samples at depth penetration between 20cm to 50cm compare to samples collected at surface area until soil sample located at depth penetration 50cm. There are no ketone contaminated in the samples at surface area, 10cm depth penetration and 30cm depth penetration. At 20cm depth penetration, the contamination of ketone group detected at 8% whereas at 40cm and 50cm depth penetrations, the contamination of the group are about 4% and 11%.

The soil contamination of aldehyde group is little bit different where the contamination is scattered from surface area to depth penetration at 50cm. There is no aldehyde group contaminated at 0cm, 20cm and 30cm depth penetrations but it were detected contaminated with the samples collected at 20cm, 40cm and 50cm depth penetrations which are about 2%, 5% and 4%. The contamination of alcohol group, aldehyde group and ketone group in the soil samples are shown in the Figure 4.17.

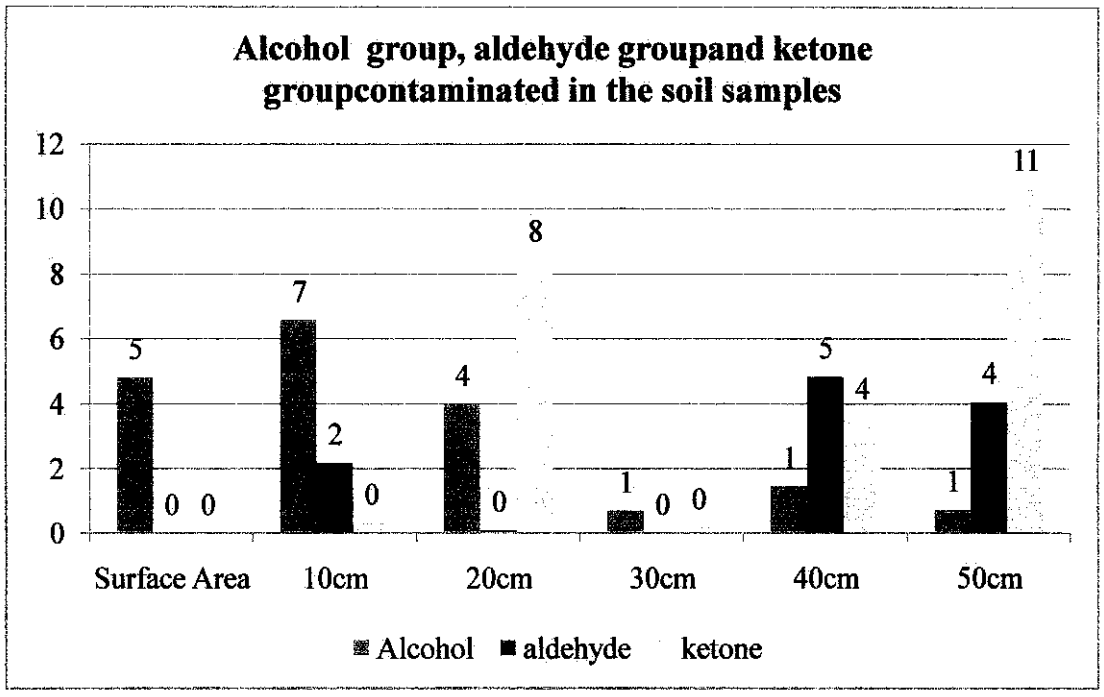


Figure 4.17: Percentage of alcohol, aldehyde and ketone groups contaminated in the soil samples

The soil contamination samples with hydrocarbon are grouping in the hydrocarbon groups as shown in the Figure 4.18. The major contamination is alkanes group followed by acid group which contaminated about 76% and 12% into the soil. The rest of the fraction is 2% aromatic, 3% alcohol, 2% aldehyde and 4% ketone.

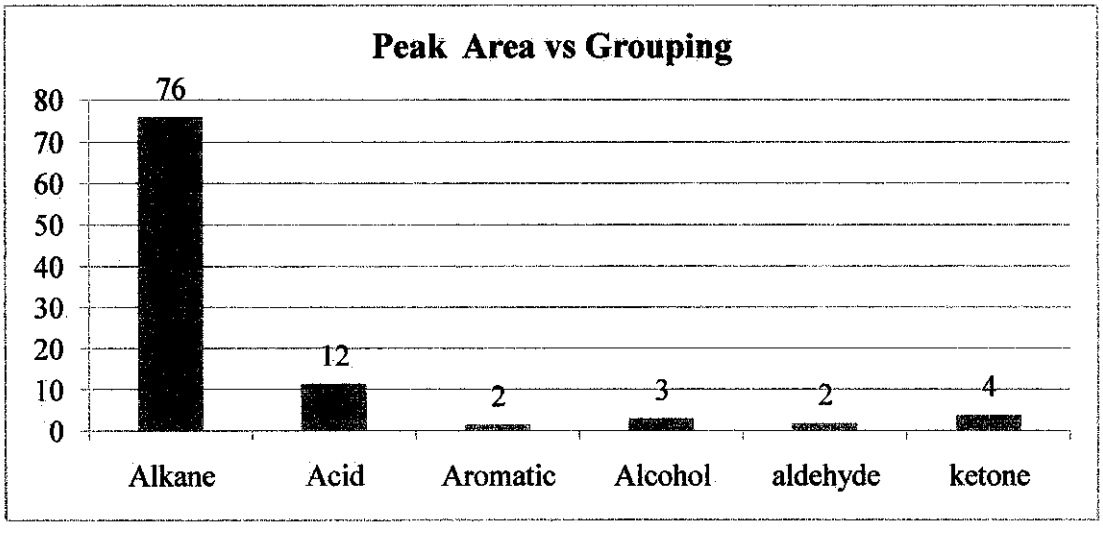


Figure 4.18: Functional groups contaminated in the soil samples.

4.2.2 HYDROCARBON REDUCTION (REMOVAL)

UV/visible spectrophotometer analysis on the contaminated soil samples shows that the content of contaminated hydrocarbon components reduces after went through thermal treatment. The thermal treatment process on the contaminated soil samples were treated by using fixed bed activation unit. During the heating process the continuos nitrogen with flowrate at 2.5cm^3/s flow through the heater to prevent soil from burning. The hydrocarbon contaminated in the soil removed by vaporization of the hydrocarbon components.

The soil samples contain main hydrocarbon form alkanes group which is about 85% of the contaminants and have their carbon chains between C_2 to C_{20} were experimented in treating the contaminations through thermal treatment at four different level of temperature. The temperatures were set at 300°C, 400°C, 500°C and 600°C. These were to find and determine the optimum temperature in the thermal treatment process. From the experiments, the percentage hydrocarbon removal calculated based on the hydrocarbon reduction detected form extracted solutions. The non-removal hydrocarbons in the soil samples extracted to solution using n-hexanes. From analysis on the solutions using UV/visible spectrophotometer, the reduction of the hydrocarbon in the soil samples were determined.

The hydrocarbon reduction for the contaminated soil samples for thermal treatment at temperature 300°C, 400°C, 500°C and 600°c were 86.82%, 89.04%, 91.61% and 91.82% as shown in figure 4.7. From the results, the different efficiency of thermal treatment for temperature at 300°C compared to 400°C can be calculated as:

Percentage Different Efficiency of Thermal Treatment between 300°Cand 400°C;

= *((% HC Reduction at 400°C - % HC Reduction at 300°C) / % HC Reduction at 400°C) x 100*

= *((89.0455 – 86.8247) / 89.0455) x100*

= *2.494%*

Percentage Different Efficiency of Thermal Treatment between 300°C and 500°C;

= *((% HC Reduction at 500°C - % HC Reduction at 300°C) / % HC Reduction at 500°C) x 100*

= *((91.6079 – 86.8247) / 91.6079) x100*

= *5.22%*

Percentage Different Efficiency of Thermal Treatment between 300°C and 600°C;

= *((% HC Reduction at 600°C - % HC Reduction at 300°C) / % HC Reduction at 600°C) x 100*

= *((91.8215– 86.8247) / 91.8215) x100*

= *5.44%*

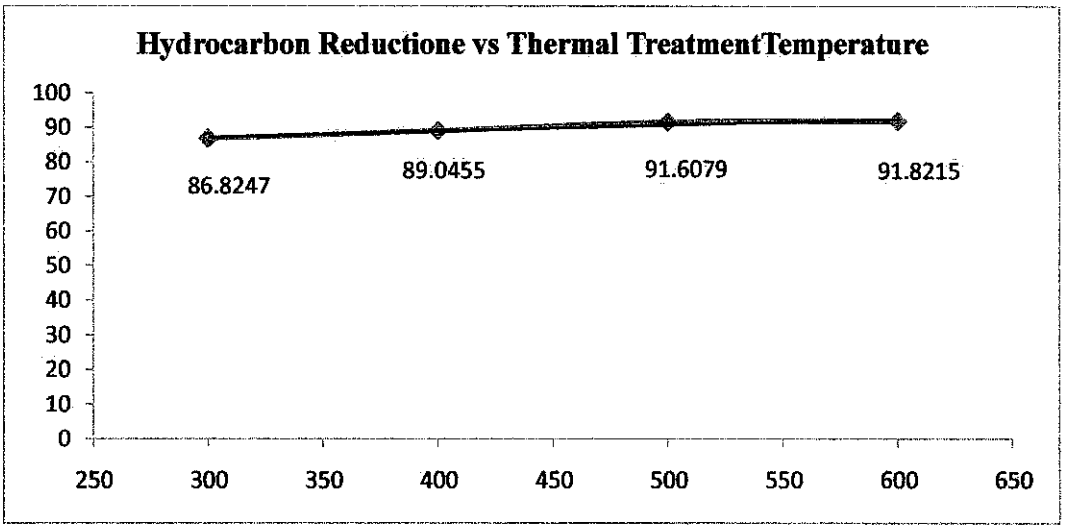


Figure 4.19: Hydrocarbon Removal Based on Temperature Treatment.

From the calculation above the different efficiency of thermal treatment at 300°C compared to 400°C is about 2.494%. It is about 5.44% of different efficiency of thermal treatment on the soil samples treated at 300°C and 600°C. The 5.44% efficiency of thermal treatment may small when we compared to the different amount of operation cost for thermal treatment at 300°C and 600°C.

CHAPTER 5

CONCLUSION

5.1 CONCLUSION

The objectives of this research are to determine the optimum temperature for thermal treatment, to study the effects of absorption of contaminants in soil depth and to find the suitable treatment for the marine soil contaminated with hydrocarbons. A part from that established methods which are contaminated soils sampling, hydrocarbon components analysis, thermal treatment process and the determination of hydrocarbon removal have been conducted successfully.

In a nutshell, the research had covered the determination of hydrocarbon compound group. The major of hydrocarbon group from the samples taken found was form alkanes group which contributed about 76% of the contaminants in the contamination soil samples. The percentage amount of alkanes group in the contamination soil samples also average for all the samples taken at different level of depth penetration which were at 0cm, 10cm, 20cm,30cm, 40cm and 50cm depth penetration. Others hydrocarbon groups found in the contamination soil samples were; acid and aldehyde which was 12% and 2% of the contaminants. The amount of these two hydrocarbon groups shown average at all the samples. Besides that, the aromatic group found 2% in the contamination especially at surface area. The amount of aromatic group becomes less for samples at 10cm to 50cm depth penetration. Alcohol group and ketone group found about 3% and 4% contaminated in the contamination soil samples. However the amount of alcohol group found contaminated higher for samples taken at surface area until 20cm depth penetration, and the contamination of ketone group found higher for samples taken at 30cm depth penetration until 50cm depth penetration.

This research project had shown that the hydrocarbon compounds removed from the thermal treatment which calculated based on the percentage hydrocarbon reduction in the treated soil

are; 86.82% for treating temperature at 300°C. The hydrocarbon reduction shown an increment as treating temperatures were increased. The hydrocarbon reduction for treating temperature at 400°C, 500°C and 600°C are 89.04%, 91.61% and 91.82%. From the result, efficiency of thermal treatment on the samples is not much different between amount the treating temperature between 300°C to 600°C. The different efficiency between 300°C and 600°C is only 5.44% and may consider small if compared with the different operation cost between 300°C and 600°C.

As the conclusion, the major hydrocarbon contaminated in the soil samples which contributed about 85% of the contaminants is from alkanes group which contain carbon chain at C_2 to C_{20}. The contaminants indicated the same hydrocarbon compounds found at each level of soil samples taken at different depth penetration from 0cm until 50cm depth penetration. With the contaminants, the optimum temperature for thermal treatment in removing the contaminants in the contaminated soil is 300°C. With an average of 90% hydrocarbon removal the experiment determined that the thermal treatment is one of the best and suitable for treating the marine soil contaminated with hydrocarbons.

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APPENDICES

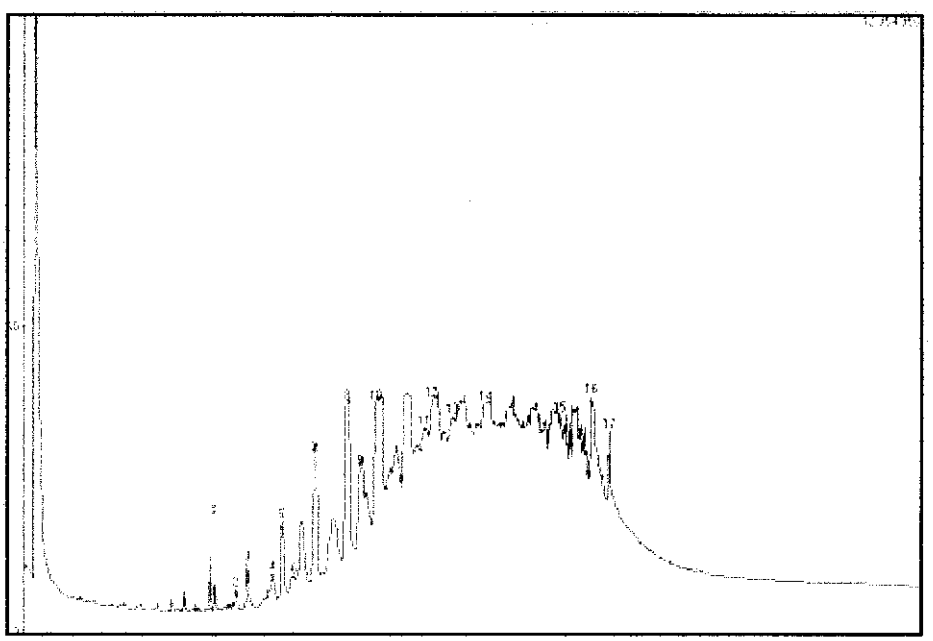
APPENDIX A:

GAS CHROMATOGRAPHY MASS SPECTROMETRY

Samples / Pyrolysis Temperature : Surface Area / 300°C

PKNO	%Total	NAME	M. FORMULA	GROUPING
1	66	Water	H20	Water
2	1	Dodecane	C15H32	alkane
3	2	n-Tridecane	C13H28	alkane
4	2	Dodecane	C15H32	alkane
5	2	n-Pentadecane	C15H32	alkane
6	1	IH_Indene	C15H28	Alkene
7	2	Pentadecane	C15H32	Alkane
8	5	Nonane	C13H28	Alkane
9	2	2-Propenoic Acid	C10H10O4	Acid
10	6	1,6-Dimethyl-4-isopropylnaphthalene	C15H18	Aro
11	1	Octane	C10H22	alkane
12	1	Tricyclo[2.2.1.0(2,6)]heptane	C7H10	alkane
13	2	Nonadecane	C20H42	alkane
14	1	n-Octacosane	C28H58	alkane
15	1	Nonadecane	C19H40	alkane
16	3	1,4-Dicyclohexylcyclohexane	C18H32	alkane

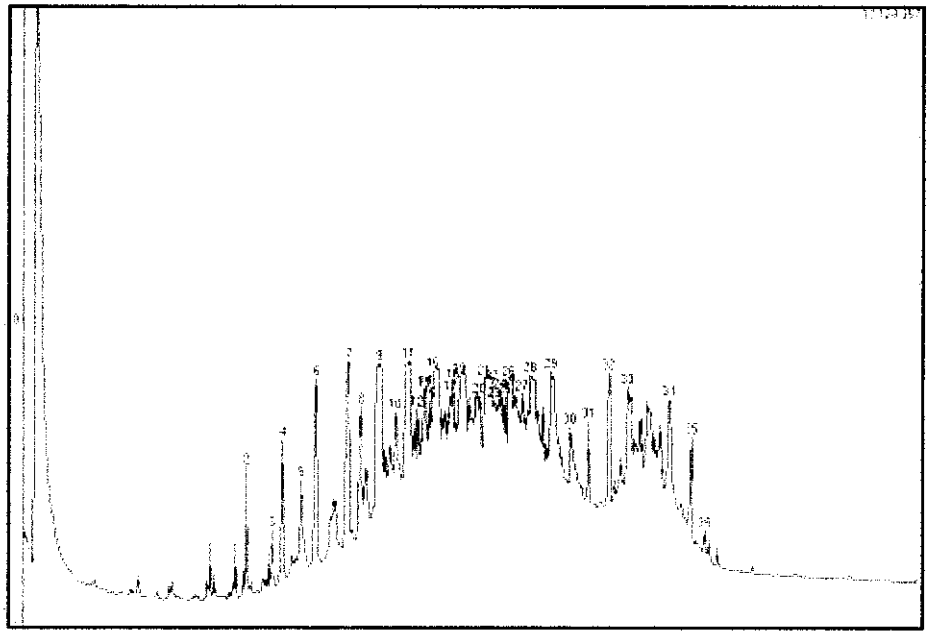
Peak Components for GCMS at 300°C



Samples / Pyrolysis Temperature : Surface Area / 400°C

PKNO	%Total	NAME	M. FORMULA	GROUPING
1	50	Water	H2O	Water
2	1	n-Tridecane	C13H28	alkane
3	1	Dodecane	C15H32	alkane
4	3	n-Tridecane	C13H28	alkane
5	2	Decane	C12H26	alkane
6	6	Heptadecane	C17H36	alkane
7	8	Heptadecane	C17H36	alkane
8	4	Dodecane	C14H30	alkane
9	2	3-Oxy-4-Octane	C8H14O	alkane
10	1	Undecane	C13H28	alkane
11	3	1-Hydroxy-2-pentanone	C5H10O2	CO
12	1	Hexadecane	C16H34	alkane
13	1	2-Methyltridecane	C14H30	alkane
14	1	Dodecane	C18H36	alkane
15	1	n-Octacosane	C28H58	alkane
16	1	Methyl 4-methylheptane-1,7-dioate	C10H18O4	ester
17	1	2-Methyltridecane	C14H30	alkane
18	1	n-Nonadecane	C19H40	alkane
19	1	3-Oxy-4-Octene	C8H14O	ether, alkene
20	1	I-Cyclohexyleicosane	C26H52	alkane
21	1	6-Cyclohexyl-2-hexenoic Acid	C12H20O2	acid
22	0	Hexadecane	C20H42	alkane
23	1	n-Nonadecane	C19H40	alkane
24	1	Tridecane	C14H30	alkane
25	1	n-Pentadecylcyclohexane	C21H42	alkane
26	1	3-Oxy-4-Octane	C8H14O	alkane
27	1	Eicosane	C20H42	alkane
28	1	3-Oxy-4-Octane	C8H14O	alkane
29	1	3-Oxy-4-Octane	C8H14O	alkane
30	1	n-Tetracosane	C24H50	alkane
31	1	n-Tetracosane	C24H50	alkane
32	1	3-Oxy-4-Octane	C8H14O	alkane
33	2	3-Oxy-4-Octane	C8H14O	alkane
34	3	Docosene	C22H46	alkene
35	1	n-Octacosane	C28H58	alkane
36	0	Trispiro[4,2,4,2,4,2]heneicosane	C21H36	alkane

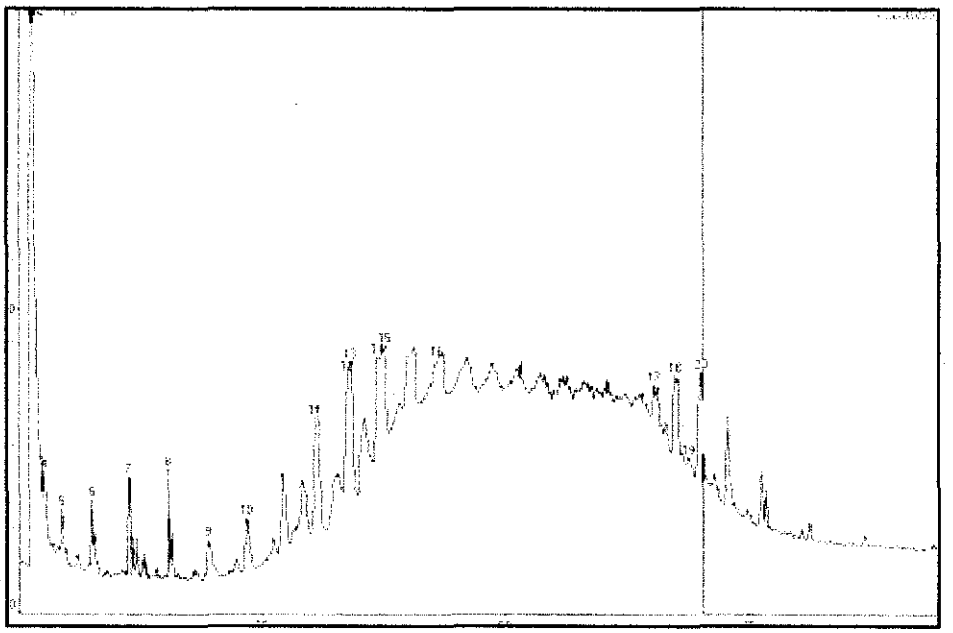
Peak Components for GCMS at 400°C



Samples / Pyrolysis Temperature : Surface Area / 500°C

MARK	%Total	NAME	M. FORMULA	GROUPING
1	14	Ethanedioic Acid	C2H2O4	acid
2	15	Carbamic Acid	CH3NO2	acid
3	36	Water	H20	water
4	2	Cyclopropane	C7H14	alkane
5	1	I-Octene	C8H16	alkene
6	2	I-Nonene	C9H18	alkene
7	2	I-Decene	C10H20	alkene
8	2	I-Undecene	C11H22	alkene
9	1	I-Decene	C10H20	alkene
10	1	1-Chlorooctadecane	C18H37Cl	alkane
11	2	3-1-Butyl-oct-6-en-1-ol	C12H24O	ene, OH
12	2	Nonane	C11H24	alkane
13	4	n-Hexadecane	C16H34	alkane
14	1	3-Oxy-4-Octene	C8H14O	alkene
15	1	Hexadecane	C16H34	alkane
16	1	I-Hexanol	C9H20O	OH
17	1	Trispiro[4,2,4,2,4,2]heneicosane	C21H36	
18	9	n-Docosane	C22H46	alkane
19	1	n-Octacosane	C28H58	alkane
20	1	n-Docosane	C22H46	alkane

Peak Components for GCMS at 500°C



Samples / Pyrolysis Temperature : Surface Area / 600°C

MARK	%Total	NAME	M. FORMULA	GROUPING
1	10	Ethylene	C2H4	ene
2	8	2-Amino-1-butanol	C4H11NO	NH2, OH
3	2	Cyclopropane	C6H12	alkane
4	2	I-Hexane	C6H12	alkane
5	1	I-Heptane	C7H14	alkane
6	1	Bicyclo[4,1,0]heptane	C7H12	alkane
7	1	Toulene	C7H8	aro
8	3	I-Octane	C8H16	alkane
9	0	Bicyclo[5,1,0]octane	C8H14	alkane
10	1	I-Heptene	C9H18	alkene
11	1	o-Dimethylbenzene	C8H10	aro
12	5	I-Nonene	C9H18	alkene
13	1	1,3-Decadiyne	C10H14	yne
14	0	I-Octane	C10H20	alkane
15	0	1,2,3-Trimethylbenzene	C9H12	aro
16	0	1,9-Decadiene	C10H18	alkene
17	6	I-Decene	C10H20	alkene
18	1	I-Decene	C11H22	alkene
19	0	1,12-Tridecadiene	C13H24	alkene
20	6	Cyclopropane	C11H22	alkane
21	0	Undecane	C11H24	alkane
22	6	I-Dodecene	C12H24	alkene
23	5	Cyclopropane	C12H24	alkene
24	3	I-Tetradecene	C14H28	alkene
25	2	Cyclooctane	C9H18	alkane
26	11	I-Chlorooctadecane	C18H37Cl	alkane
27	2	2-Butyl-1-octanol	C12H26O	OH
28	1	Hexadecane	C16H34	alkane
29	1	Pentadecane	C15H32	alkane
30	1	9,12-Octadecadienoic Acid	C18H32O2	acid
31	0	4-Phenanthrenol	C15H16O	aro, OH
32	1	Pentadecane	C15H32	alkane
33	0	Docosane	C22H46	alkane
34	1	13-Heptadecyn-1-ol	C17H32O	Yne, OH
35	1	Cyclohexane	C15H28	alkane
36	2	n-Docosane	C22H46	alkane
37	1	n-Tetracosane	C24H50	alkane
38	1	n-Tetracosane	C24H50	alkane
39	2	n-Docosane	C22H46	alkane
40	1	n-Tetracosane	C24H50	alkane
41	2	Docosane	C22H46	alkane
42	1	n-Tetratetracontane	C44H90	alkane
43	3	n-Octacosane	C28H58	alkane
44	1	Octacosane	C28H58	alkane
45	0	Octacosane	C28H58	alkane

Peak Components for GCMS at 600°C