# CONVENTIONAL AND MICROWAVE PYROLYSIS REMEDIATION OF CRUDE OIL CONTAMINATED SOIL

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# ABSTRACT

The Nigerian economy has relied heavily on crude oil production since independence in 1960. As a consequence, it has seen an influx of multinational petroleum companies with oil exploration and associated activities having significant environmental impacts, particularly oil leakage and spillage into soil and the overall degradation of the ecosystem in the Niger Delta area. This study aims to find a viable solution to the remediation of polluted soil by comparing two thermal remediation techniques, namely microwave pyrolysis and traditional pyrolysis, which has been investigated using a Gray-King retort.

The polluted soil was first examined to ascertain the distribution of the soil organic carbon (SOC) with 78% found to be solvent extractable in dichloromethane/methanol, while 95 % was thermally labile and removed under hydropyrolysis (HyPy) conditions at 550 °C. The remaining 5 % of the SOC was composed of a recalcitrant residue being defined as the black or stable polyaromatic carbon fraction. The solvent extractable organic matter (EOM) was then further separated into the maltene (free phase) and asphaltene (bound phase) fractions together for comparison with a sample of Nigerian crude oil provided by the Shell Petroleum Development Company (SPDC), Nigeria. The Nigerian crude oil is a light crude oil with the percentage of maltene (95.2 %) was far higher than the asphaltene (4.8 %). A closer margin was observed in the percentage between the maltene (88.3 %) and asphaltene (11.7 %) in the soil EOM due to biodegradation.

The biomarker profile of the EOM was compared with that of a Nigerian crude oil to confirm that the EOM contains the crude oil in the soil. Their biomarker profiles revealed that the source inputs were terrigenous from deltaic settings, of Late Upper Cretaceous age and deposited under oxic conditions. Oleanane (a pentacyclic triterpene, abundant in oils from the Niger Delta) was present in both the crude oil and EOM and the hopane and the sterane distributions (*m/z* 191 and *m/z* 217 respectively) were similar in every respect, which indicates that the probable source of the pollutant crude oil in the soil is similar in composition to the Nigerian crude oil. Accordingly, the polluted soil was treated with microwave pyrolysis and Gray-King pyrolysis to remove the crude oil pollutant.

The maximum average recovered products from the thermal remediation process with Gray-King pyrolysis is 99.4 % TOC and maximum crude oil pollutant removed by Gray-King pyrolysis was 85.3 % TOC with maximum oil recovery of 70 % TOC from all the different treatment conditions, while the shortest treatment time condition gave the lowest gas yield of 10.2 % TOC. This implies that 100 % removal with respect to EOM and 89 % removal with respect to HyPy as discussed above. Furthermore, the polluted soil was also treated with microwave pyrolysis with maximum pollutant removal of 77 % TOC, which is 98.7 % removal with respect to EOM and 81 % with respect to HyPy.

In conclusion, Gray-King pyrolysis removed more of the soil organic carbon than microwave pyrolysis, but the latter does have advantages regarding operability and greater output within a short treatment time.

## CONFERENCE PRESENTATIOIN

1. **23rd meeting of British Organic Geochemistry society conference 2012, Leeds, Uk**
   Oral presentation: *The characterisation of crude oil and oil contaminated soil from the Niger Delta by catalytic hydropyrolysis*

2. **20th International Symposium on Analytical and Applied pyrolysis 2014, Birmingham, Uk**
   Poster presentation: *Gray-King pyrolysis of contaminated soil to remove crude oil contaminants*

3. **Energy Research Accelerator (ERA) postgraduate conference 2015 Leicester University, Uk**
   Poster presentation: *Remediation of Oil polluted soil, using conventional and microwave pyrolysis*

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# DECLARATION

I hereby attest that the work reported in this thesis is my own, except where otherwise acknowledged, and has not been submitted previously for a degree at this, or and other university.

Akinyemi Ogunkeyede

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## NOMENCLATURES/ABBREVIATIONS

| | |
|---|---|
| DPR | Department of Petroleum Resources |
| NNPC | Nigerian National Petroleum Corporation |
| OPEC | Organization of Petroleum Exporting Countries |
| SPDC | Shell Petroleum Development Company |
| SARA | saturated, aromatic, resin and asphaltene |
| HyPy | Hydropyrolysis |
| GC-MS | Gas chromatography-mass spectrometry |
| EOM | Extractable organic matter |
| C20 | Carbon number 20 |
| $C_{29}$ | Total number of carbon present in a biomarker |
| m/z | Mass to charge ratio |
| c | Velocity |
| f | Frequency |
| $\lambda$ | Wavelength |
| $E$ | Strength of the electric field |
| $\varepsilon'$ | Dielectric constant |
| $\varepsilon''$ | loss factor |
| j | An imaginary component. |
| $\tan \delta$ | Loss tangent |
| $\alpha$ | Asymmetric carbon in ring with functional group (usually H) down or into the page |
| $\beta$ | Asymmetric carbon in ring with functional group (usually H) up or out of the page |
| R | Asymmetric carbon that obeys clockwise conventions |

| | |
|---|---|
| S | Asymmetric carbon that obeys anticlockwise convention |

## Characteristic Fragment Ions of Biomarkers

Characterization of major biomarker groups is largely achieved using the following MS fragment ions.

| | |
|---|---|
| Aliphatic | m/z 71 |
| alkyl-cyclohexanes: | m/z 83 |
| methyl-alkyl-cyclohexanes: | m/z 97 |
| isoalkanes and isoprenoids: | m/z 113, 127, 183 |
| sesquiterpanes: | m/z 123 |
| adamantanes: | m/z 135, 136,149,163,177 and 191 |
| diamantanes: | m/z 187, 188, 201, 215 and 229 |
| tri-, tetra-, penta-cyclic terpanes: | m/z 191 |
| 25-norhopanes: | m/z 177 |
| 28,30-bisnorhopanes: | m/z 163, 191 |
| steranes | m/z 217, 218 |

## Target compounds for oil-spill studies

### Aliphatic biomarker

| | |
|---|---|
| Pr | Pristane |
| Ph | phytane |

### Hopanoid Biomarkers

| | |
|---|---|
| Ts | 18α-22,29,30-Trisnorneohopane |
| Tm | 17α-22,29,30-Trisnorhopane |
| $C_{29}$ | 17α,21β(H)-30-Norhopane |
| $C_{29}$Ts | 18α,21β(H)-30-Norneohopane |
| $C_{30}$ | 17α,21β(H)-hopane |
| $C_{30}$ | 17β, 21α(H)-hopane |
| $C_{3}$ | 17α,21β(H)-30-homohopane 22S |
| $C_{31}$ | 17α,21β(H)-30-homohopane 22R |
| $C_{32}$ | 17α,21β(H)-30-bishomohopane 22S |
| $C_{32}$ | 17α,21β(H)-30-bishomohopane 22R |
| $C_{33}$ | 17α,21β(H)-30-Trishomohopane 22S |
| $C_{33}$ | 17α,21β(H)-30-Trishomohopane 22R |
| $C_{34}$ | 17α,21β(H)-30-Tetrakishomohopane 22S |

| | |
|---|---|
| $C_{34}$ | 17α,21β(H)-30-Tetrakishomohopane 22R |
| $C_{35}$ | 17α,21β(H)-30-Pentakishomohopane 22S |
| $C_{35}$ | 17α,21β(H)-30-Pentakishomohopane 22R |
| $C_{30}$ | 18α-Oleanane |
| Steroid Biomarkers | |
| $C_{27}$ | 20*S* − 5α(H),14α(H),17α(H)-cholestane |
| $C_{27}$ | 20*R* − 5α(H),14β(H),17β(H)-cholestane |
| $C_{27}$ | 20*S* − 5α(H),14β(H),17β(H)-cholestane |
| $C_{27}$ | 20*S* − 5α(H),14α(H),17α(H)-ergostane |
| $C_{28}$ | 20*R* − 5α(H),14β(H),17β(H)-ergostane |
| $C_{28}$ | 20*S* − 5α(H),14β(H),17β(H)-ergostane |
| $C_{28}$ | 20*R* − 5α(H),14α(H),17α(H)-ergostane |
| $C_{29}$ | 20*S* − 5α(H),14α(H),17α(H)-stigmastane |
| $C_{29}$ | 20*R* − 5α(H),14β(H),17β(H)-stigmastane |
| $C_{29}$ | 20*S* − 5α(H),14β(H),17β(H)-stigmastane |
| $C_{29}$ | 20*R* − 5α(H),14α(H),17α(H)-stigmastane |

# Chapter 1: Background and motivation for the research

## 1. Scope

This opening chapter will briefly outline the background and motivation for this work. This section seeks to provide answers to questions on the remediation of crude-oil-contaminated soil by the use of pyrolysis technology, the interaction of pyrolysis with the contaminant, how findings are expected to contribute to the science of remediation of soil, and the essential geochemistry and petroleum composition of Nigeria. This chapter will highlight the aims and objective of this study and close with a summary on the fundamental importance of this chapter to the rest of the research work.

## 1.1 Background

Nigeria is the biggest petroleum producer in Africa, with 180 trillion cubic feet (Tcf) of proven natural gas reserves as of the end of 2015, and it was the world's fourth-largest exporter of liquid natural gas (LNG) in 2015 (USEIA, 2016). Nigeria produced 1.55Tcf of natural gas in 2014, and most of the natural gas reserves are located in the Niger Delta region of the country (USEIA, 2016). The density and sulphur content of crude oil are essential in shaping the market value. These parameters are applied to describe oil as either light or heavy (based on density) and as either fresh or sour (based on sulphur content). Light and sweet crude oils are desirable because they can be processed with far less sophisticated and energy-intensive refining techniques, giving them high market value. Nigerian crude oil is an example of the light, sweet oils around the world, with others such as Libya-Es Sider, United States-LLS, WTI and Malaysia-Tapis. In 1977, the Nigerian government created the Nigerian National Petroleum Corporation (NNPC) to oversee the regulation of the oil and natural gas industries, with secondary responsibilities for upstream and downstream development (USEIA, 2016).

In 1985, the DPR was established under the supervision of the Ministry of Petroleum Resources. DPR's function is to regulate general compliance, leases and permits, and environmental standards for the major international oil players (Shell, ExxonMobil, Chevron, Total, and Eni) in the oil and gas sector in Nigeria. Despite the relatively large volume it produces, Nigeria's oil production is hampered by instability and supply disturbances, which have resulted in unplanned outages as high as 500,000 barrels per day (bbl/d) (Khusanjanova, 2011). Nigeria became a member of the Organization of Petroleum Exporting Countries (OPEC) in 1971, decades after oil production began in the oil-rich

Bayelsa state in the Niger Delta region in the 1950s (USEIA, 2016). Crude oil production in Nigeria reached its peak in 2005 (2.44 million bbl/d) but began to drop significantly as constant violence from militant groups increased, forcing the companies to withdraw staff and shut down operations (USEIA, 2016).

Production recovered somewhat after 2009–2010, but it remained lower than its peak because of ongoing supply disruptions. Supply disruption escalated in 2013, mostly stemming from pipeline damage associated with oil theft, which resulted in the shutdown of the Trans Niger Pipeline and Nembe Creek Trunkline and misfortune on the shipments of multiple crude grades. Average crude oil production between January to October 2013 was approximately 2.0 million bbl/d of crude oil, similar to the level in 2008–2009 when disruption hit its highest record (USEIA, 2013). Pipeline sabotage from oil theft as well as poorly maintained and aging pipelines have caused oil spills. The oil spills have resulted in land, air, and water pollution, severely affecting surrounding villages by decreasing fish stocks and contaminating water supplies and arable land (USEIA, 2013).

Oil and gas production in Nigeria is concentrated in the Niger Delta region, and consequently it is here that problems associated with the industry are found. Local groups seek a share of the wealth by conducting frequent attacks on the oil infrastructure. This forces the companies to declare force majeure (a legal clause that allows a party to not satisfy contractual agreements because of circumstances that are beyond their control and prevent them from fulfilling contractual obligations) on oil shipments. Oil bunkering (oil theft) leads to vandalisation of pipelines, which often causes pollution and loss of production and forces companies to shut down production. Aging infrastructure and poor maintenance on the part of  companies have also resulted in oil spills.

Achebe *et al.* (2012) mentioned that the gas and oil pipeline standards (GOST) of Nigeria stated that the lifetime of a pipeline is 33 years, which led to the study to ascertain the causes of oil pipeline failures. It was observed that 42% was caused by mechanical failure, 18% by corrosion of the pipelines, 10% through operator error, 24% third-party activity (sabotage and acts of vandalism) and 6% natural hazards (floods, bush burning, etc.) (Figure 1-1). It was observed that the reliability of the pipeline decreased with the aging of the pipeline; the reliability of a pipeline aged around 20 years in service was 46% while those above 30 years were 25% reliable. It was noticed that Rivers State of the Niger Delta area has the highest occurrence of oil spill (32% ) while Cross-Rivers State has the lowest occurrence with 2% (Figure 1-2).

A total of 4,647 oil spill incidents occurred between 1976 and 1996, which is equivalent to 2.4 million barrels of oil being released into the environment. Only 23.17% of this total oil spill into the environment was recovered according to the Department of Petroleum Resources (DPR) (Nwilo and Badejo, 2007). Vidal (2014) reported that 7,000 oil spills occurred between 1970 and 2000 according to the Nigerian government. In addition, the report stated that there have been 2,000 official major spills with thousands of smaller spills still waiting to be cleared up, many going back to decades. Ordinioha and Brisibe (2013) estimate that the 7,000 oil spills have a value of 13 million barrels with a yearly average of about 240,000 barrels. Amnesty International (2012) reported that the livelihood of thousands of Bodo villagers in the Niger Delta region, who depend on fishing and farming, were severely affected by two oil spillages in 2008. These were found to be between 1,440 and 4,320 barrels of oil per day, so the total amount for the period of 72 days of the spill would be between 103,000 and 311,000 barrels of oil.

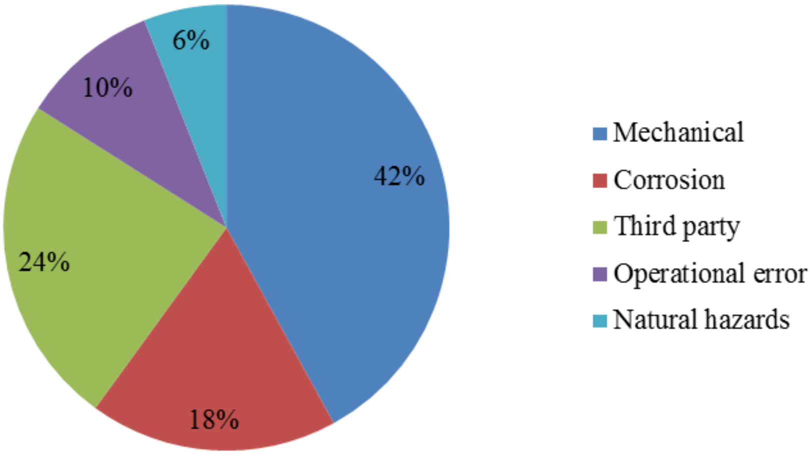

Figure 1-1: Factors causing pipeline failures (in percentages) (from Achebe *et al*., 2012).

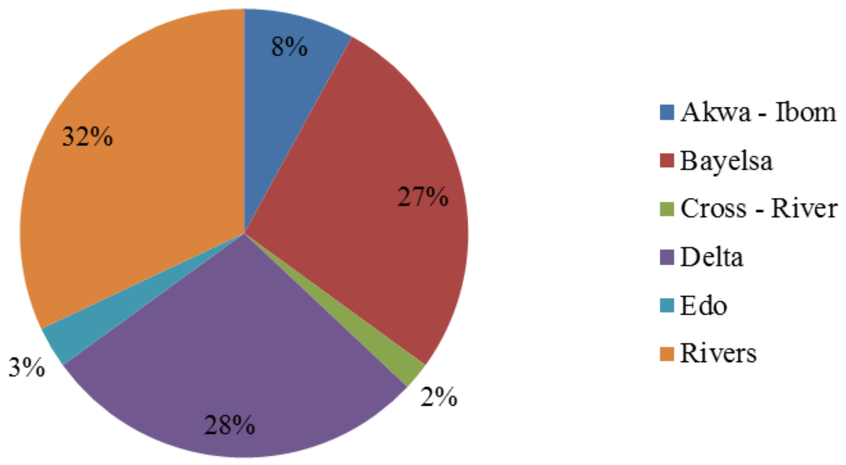

Figure 1-2: Rate of oil spill per state in Niger Delta for the period of 1999–2005 (from Achebe *et al*., 2012).

Unfortunately, little information has emerged concerning the suffering caused by the activities of the operating companies as compared to the wider coverage of the Gulf of Mexico oil spill (Vidal, 2010). The oil spillage in the area was reported to have negative consequences on the communities’ health, such as a high rate of child mortality, lower life expectancy and higher malnutrition rate, and a corollary study on women showed skin mycosis, tiredness, itchy nose, sore throat, headaches, red eyes, ear pain, diarrhoea, and a risk of spontaneous abortion as a result of drinking polluted water and eating contaminated food (Sebastian and Hurting, 2004; Omorede, 2015). In addition to the negative health challenges, the economic crises and reforms have deepened the exploitation and impoverishment of the Niger Delta, while the democratic institutions have failed to address the roots of the widespread grievances in the region (Obi, 2009). Consequently, there is a need to provide an effective remediation technology to meet the needs of the Niger Delta community.

## 1.3 Novelty of this research

This study seeks to address the prevailing soil contamination problem in the Niger Delta region of Nigeria through the use of an efficient soil remediation technique. To this end, techno-economic analyses were considered to decide the best remediation techniques for petroleum-polluted soils in Niger Delta. Knowledge from past work on techno-economic analysis of remediation treatment technologies for persistent organic pollutants in soil in developing countries by Li (2007) (see details in Chapter 2) favours the use of pyrolysis as a method of choice for this current research. Although the financial, health and environmental implications of other methods such as natural attenuation, phytoremediation, and bioremediation is lower, they require longer treatment times and have high space requirements with lower efficiency (60–80 %) compared to pyrolysis (99.9%) (Li, 2007). In addition, pyrolysis has the ease of equipment control, independence of the climatic factor, high product value, high throughput and a good return on investment. This study is novel because it produces comparative data on thermal and microwave pyrolysis in treatment of petroleum-polluted soils, covering a range of experimental process variables that influence hydrocarbon removal from soils. In addition, it shows comparative data on output per time and the implication on the techno-economic analysis of the two pyrolytic processes. Another novelty in this study lies in the fact that this is the first time microwave pyrolysis would be used on crude-oil-polluted soil after a successful treatment of drill cutting (Robinson *et al*., 2008). Likewise, the Gray-King process is an established assay method for coal (Adeleke *et al*., 2007; Zhang *et al*., 2014) but it has never been modified for the treatment of crude-oil-polluted soil as a thermal pyrolytic process. This study shows for the first time the use of the Gray-King process in the treatment of petroleum-contaminated soils.

## 1.4 Aims and objectives

The aim of this research is to detail a comparative investigation on conventional pyrolysis (Gray-King retort) and microwave pyrolysis as remediation techniques for treatment of crude-oil-polluted soil from the Niger Delta region of Nigeria. To accomplish this purpose, the following objectives would be considered:

1. An in-depth review of geology, bio-geochemistry and petro-chemistry of petroleum and their direct relation to petroleum-contaminated soils to ensure proper interpretation of experimental data from hydrocarbon compositions obtained from the two pyrolytic processes and Nigerian crude oil (provided by Shell Petroleum Development Company (SPDC), Nigeria). An in-depth review of established soil remediation techniques and techno-economic analysis to justify the use of pyrolysis in this current study.

2. An in-depth review of established soil remediation techniques and techno-economic analysis to justify the use of pyrolysis in this study.

3. The use of several analytical techniques to characterise the petroleum-polluted soils, original condensable oil hydrocarbons, incondensable gases evolved and the interpretation of experimental data on the chars produced, with techno-economic analysis of the two pyrolytic processes. Also, method validation would be carried out and analytical works repeated to ensure reproducibility of the reported data.

4. The comparative study of the final results with old and recent literature would be considered to explain the effectiveness of the results obtained and used to suggest areas in which further works or research would be conducted to benefit the stakeholders (community and government).

## 1.5 Nigerian petroleum geochemistry

Geochemical investigation gives valuable understanding of the petroleum system concept. It reveals the geological elements and processes essential for petroleum accumulation, identification, correlation and geographical map of the extent of the petroleum system. The investigation considered in this section of the thesis ensures proper interpretation of the experimental data that will be obtained on hydrocarbon chemical compositions from the two pyrolysis processes and Nigerian crude oil samples provided by SPDC, Nigeria.

The Niger Delta basin is the home of crude oil production in Nigeria, with principal deposition formed from allochthonous material (sediment material that moves from its original site of formation) in a marine deltaic environment (Lehne and Dieckmann, 2010). The Delta was formed during the continental breakup in the Cretaceous era, with the delta developing from the Paleocene (Onyema and Ajike, 2010). The three rock units from youngest to oldest in the stratigraphy of the basin are the Benin, Agbada and Akata formations. The Agbada forms found in the delta front and lower delta plain environments are alternating sequences of sandstones and mudrocks with interbedded shale to provide reservoir seals (Lehne and Dieckmann, 2010). The primary source rock is the upper Akata Formation, the marine-shale facies of the delta, with possible contribution from interbedded marine shale of the lowermost Agbada formation. The petroleum system of the

Niger Delta basin is called the Tertiary Niger Delta (Akata-Agbada) petroleum system (Adedapo et al., 2014; Onojake et al. 2015). Rocks within the petroleum system are from Paleocene to Recent in age, and the deposition of the overburden rock began in the middle Eocene and continues to the present day. Organic matter with geologic material deposited at the same time during the Agbada formation, with subsequent sedimentation and progressive burial, provided significant pressure and temperature gradient. Geopolymers subjected to sufficient geothermal pressures of sufficient geologic time begin to undergo changes to become kerogens. The kerogens are part of the organic matter in the sedimentary rocks, which consist of a mixture of organic chemical compounds with varying molecular weight. The Nigerian crude oil has a great abundance of kerogens and the Tertiary deltaic petroleum system of the Niger Delta basin sources rocks consisting of Type II, II-III and Type III kerogen (Nyantakyi et al., 2014).

### 1.5.1 Kerogens

Kerogen is a naturally occurring, solid insoluble organic matter found in source rocks that can yield oil upon heating (Speight, 2014). It was suggested that they are formed by a combination of the selective preservation of biopolymer and formation of new geopolymers to produce a finely disseminated organic material in sedimentary rocks (Gupta, 2015).

An important process during kerogen formation is the selective preservation of resistant macromolecules, particularly those formed at very early stages of diagenesis. It is assumed that kerogens were derived from humic substances during diagenesis. The organic materials in the aquatic environment could be attacked by microbial actions and be broken down into smaller constituents, followed by condensation reaction to give rise to humic substances. These two processes continue to increase in burial depth for a time period, and most humic material formed becomes insoluble due to an increase in polycondensation as the superficial hydrophilic functional groups (OH, COOH) are removed. The insolubility could continue at a significant depth as long as there is abundant terrestrial detrital material.

The condensation and defunctionalisaton of the humin-like materials results in kerogen (Wolicka and Borkowski, 2012). Vandenbroucke and Largeau (2007) suggested that kerogen can be generalised as a combination of various macromolecular structures, comprised, in various quantities, of recombined biodegradation products and resistant biomacromolecular products, depending on depositional environment and biological precursors. Chemical, biochemical and biological inputs exert strong control over kerogen composition, which results in clear compositional differences between the marine (amorphous organic material) and terrestrially (humus, woody material) derived kerogen (Vandenbroucke and Largeau, 2007).

Kerogen is the primary source of oil and gas. The quantity of oil generated from kerogen depends overwhelmingly on the hydrogen content. Kerogens are by far the most abundant organic matter on earth by volume (ca. $10^{16}$ tons of C compared to ca. $10^{12}$ tons of living biomass), and a great amount of time and money has been invested in the characterisation of kerogen and thermal evolution to provide a more accurate prediction of its oil and natural gas stockpiles (Vandenbroucke and Largeau, 2007).

Kerogen over time has been classified by visual grouping as macerals (organic components of coal analogous to the mineral rocks) and elemental composition (C, H and O) (Bruggeman and De Craen, 2012). Maceral grouping of kerogens is based on the organic optical properties, while the elemental composition has been used to group the kerogen into four types (Type I, II, III and IV). The elemental compositional grouping of the kerogen has been used in estimating petroleum potential or reserves and understanding the kinetic of its generation, which gives a more detailed understanding of the Tertiary deltaic petroleum system of the Niger Delta basin source rocks mentioned above. These types of kerogens originate because of the different kinds of debris deposited in the sediment and the conditions that prevail in that sediment over a geological time (Speight, 2014).

#### 1.5.1.1 Type I kerogen

Type I kerogen is derived from algal material preserved in anaerobic environments. It is commonly lacustrine and sometimes from a marine source. It is the most hydrogen-rich, oxygen-deficient kerogen, with a dominantly aliphatic character. It is mostly an oil-prone kerogen type at an appropriate maturity level (Bruggeman and De Craen, 2012). Type I kerogen is the chemical equivalent of the alginate maceral, with an atomic H/C ratio of >1.5, an O/C ratio of <0.15 and hydrogen indices of between 600 and 950, typical of an immature sample. The Type I kerogen is the most hydrogen-prone type but only provides 2.7% of global petroleum reserves (Vandenbroucke and Largeau, 2007). It is formed mainly from proteins and lipids.

#### 1.5.1.2 Type II kerogen

Type II kerogen is predominantly composed of degraded phytoplankton debris preserved in anaerobic or aerobic environments, an example is the Kimmeridge Clay formation from the North Sea. It is the second most hydrogen-rich kerogen, which is aliphatic in nature with a bias towards more cyclic or naphthenic compounds in comparison to the Type I kerogen (Speight, 2014). The aromatic system of the Type II kerogen increases with maturity. It is equivalent to the liptinite or exinite maceral groups with an atomic H/C ratio of about 1.5, an O/C ratio of around 0.15 and hydrogen indices of between 400 and 600 which are typical for an immature sample (Bruggeman and De Craen, 2012). It tends to produce a mix of gas and oil.

#### 1.5.1.3 Type III kerogen

Type III kerogen is relatively hydrogen poor and polyaromatic in nature in comparison with Types I and II. It is frequently associated with a deltaic setting derived from higher plant debris. The O/C ratio is relatively high due to the level of oxidation associated with the detrital sedimentation (Vandenbroucke and Largeau, 2007). The low atomic ratio of <1.25, O/C ratio is 0.03–0.3 and hydrogen indices between 50 and 300 are typical for an immature sample. This kerogen is thick, resembling wood or coal, and tends to produce coal and gas. It has very low hydrogen due to the extensive ring and aromatic systems. It is a form of cellulose, carbohydrate polymer that forms the rigid structure of terrestrial plants, lignin that binds the strings of cellulose together, and terpenes and phenolic compounds in the plant, but it is lacking in lipids or waxy matter (Speight, 2014).

#### 1.5.1.4 Type IV kerogen

Type IV kerogen has little or no potential to produce hydrocarbons with a H/C ratio <0.5, as it contains organic materials in the form of polycyclic aromatic hydrocarbons. It is highly oxidised kerogen (Speight, 2014).

## 1.6 Petroleum composition

The studies of petroleum geochemistry of the pyrolysis oil products and crude oil provided gives a proper understanding of petroleum composition and the preparation process required to separate their components in order to have a good interpretation of the clear signal-to-noise ratio obtained from instrumental analysis. This is relevant based on the petroleum-wide spectrum and the range in size of the organic molecules component. The petroleum composition could be a direct reflection of the diversity and structure of the parent kerogen (Seewald, 2003). Crude oil is a complex mixture of hetero-elements (nitrogen, sulphur, oxygen) and hydrocarbon compounds consisting of 80% by weight for light, sweet petroleum, less than 50% for heavy crude oil and much lower for tar sand bitumen. The carbon content of various types of petroleum is usually between 83% and 87% by weight, and the hydrogen content is 11–14% by weight (Speight, 2015).

The fate of crude oil in the soil depends on many factors such as microbial degradation, photooxidation, and interaction between the soil properties and the oil (Vinothini *et al.*, 2015). Despite the conflict in the geological formation processes of petroleum oil, it has chemically complex structures which consist of varieties of dissimilar cases of chemical compounds. The physical state of the crude oil (gas, liquid or solid) depends on the temperature, pressure and the proportion of the constituents of the oil which gives it variation in terms of heavy or light oil.

With the exception of some sulphur-containing compounds, the acidic compounds in crude oils all contain oxygen, and the main proportion of oxygen in petroleum is accounted for by carboxylic acids (Speight, 2015). Therefore, the oxygen content of oil is a direct indication of its acidity. The main descriptive form of hydrocarbon of interest to geochemists is saturated, aromatic, resin and asphaltene (SARA) (Keshmirizadeh *et al.*, 2013). The major noticeable change in the concentration among the group will be seen in asphaltene because it increases with biodegradation (Vinothini *et al.*, 2015).

### 1.6.1 Saturated hydrocarbons

The saturated hydrocarbons in crude oil can be divided into normal alkanes, branched alkanes (isoalkanes) and cycloalkanes (Rojo, 2009). Normal alkanes ($C_4$–$C_{20}$) account for up to 50% of the crude oil, though it depends more on the nature of the original organic matter or source (Rojo, 2009). Isoalkanes are usually present in the light and middle boiling point fractions in petroleum. The most abundant isoalkanes are pristane (tetramethylpentadecane $C_{19}$) and phytane (tetramethylhexadecane $C_{20}$), and they are 55% of the acyclic isoprenoids in crude oil. However, pristane is more abundant than phytane in crude oil (Tissot and Welte, 2012).

The last part of the saturated hydrocarbon fraction is cycloalkanes, a very important constituent of crude oil. The mono- and di-cyclic amounts from 50–55% of the total cycloalkanes of molecular mass >$C_{10}$, however, the abundance of the various mono- and dicycloalkanes decreases regularly as a function of molecular weight (number of carbon atoms) (Tissot and Welte, 2012). The steranes range mainly from 27 to 29 carbon atoms, while the pentacyclic triterpanes' maximum ranges from 27 to 35 carbon atoms (Onojake and Osuji, 2015). Tetra and pentacyclic cycloalkanes are generally most abundant in young and immature crude oils, and are also rich in resins, asphaltenes and polyaromatics (Tissot and Welte, 2012). In summary, aliphatic hydrocarbons are non-polar, non-aromatic hydrocarbons and can be eluted from petroleum mixtures via column chromatography, using hexane.

Over the years, the ratio of normal to branch alkane (*n*-$C_{17}$/pristane and *n*-$C_{18}$/Phytane) has been used for measuring biodegradation in oil, until research showed that it is not reliable or is of limited use. The rate of biodegradation of the branch alkanes approaching normal alkanes is too rapid, which causes a change of focus to hopane for biodegradation observation in oil (Hasinger *et al*., 2012).

### 1.6.2 Aromatic hydrocarbons

Petroleum contains a high amount of aromatic compounds called polyaromatic hydrocarbons (PAH). The concentration of aromatic hydrocarbon in crude oil depends on the source of the organic matter and the maturity of the oil. They all contain aromatic rings, side chains and aliphatic bridges (Abdel-Shaft and Mansour, 2016). They can easily be eluted via column chromatography using dichloromethane. Common aromatics are alkylnaphthalenes and alkylphenanthrenes, while the larger compounds such as pyrene (four-member ring) and benzopyrene (five-member ring) are less common. The aromatic hydrocarbons have more resistance in terms of degradation than the less polar aliphatic hydrocarbon (Pampanin and Sydnes, 2013).

### 1.6.3 Resins

Resins are compounds with two end groups, namely, the polar end and the non-polar paraffinic group. The saturated and the aromatic polarity and molecular weights are less than that of resin (Boukir, 2001). The uniqueness of the resin is the polar end group that contains heteroatoms with nitrogen, sulphur and oxygen (NSO). The polar end group is essential for the resin/asphaltene interaction (hydrogen bonding, dipole-dipole interactions) (Boukir, 2001). Asphaltene has a low hydrogen/carbon ratio of resin, but has a similar structure with resin (small in molecular weight compared to asphaltene) (Andersen and Speight, 2001; Aske *et al*., 2001).

### 1.6.4 Asphaltene

Asphaltene is a constituent of crude oil that is insoluble in a light alkane such as *n*-heptane but soluble in toluene (Jarrell *et al.*, 2014) (Figure 1-3). It plays an important role in the physical and chemical behaviour of crude oil (Idris and Okoro, 2013). The molecular weight of asphaltene is currently considered to be in the range of 500–1000 Da, which impacts properties such as colour of the asphaltene (black or brown), hardness, non-plasticity, and non-malleability (Oyekunle, 2006; Choi *et al.*, 2016). They are agglomerations of the most highly polar molecules, and they are responsible for the classification of crude oil such as light and heavy crude oil (Aske *et al.*, 2001; Oyekunle, 2006).

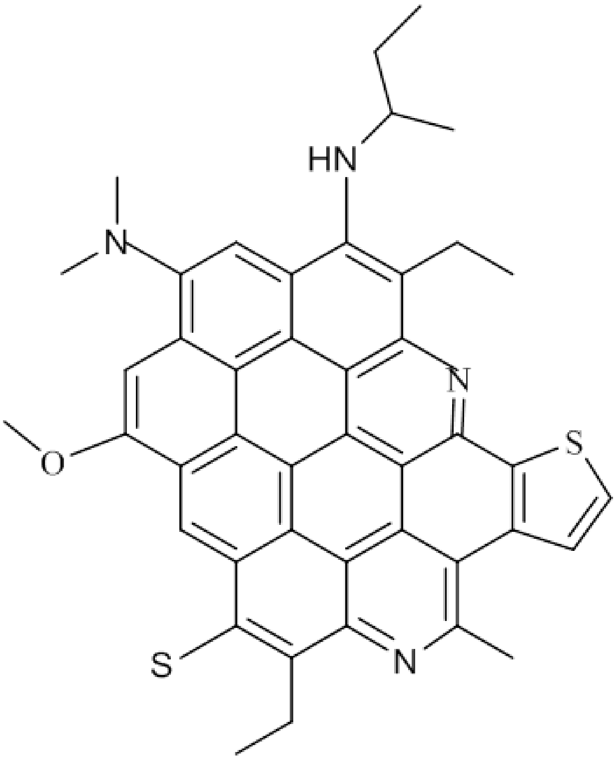

Figure 1-3: The molecular structure of asphaltenes (Hashmi *et al.*, 2012).

### 1.6.5 Biodegradation parameters and maturity parameters

Crude oil alteration occurs in reservoirs, and it modifies the composition of crude petroleum from its original state. The alteration may be related to the relative instability of crude oil and/or to the fact that traps are open systems, or it may also be due to a change in crude oil burial level caused by either subsidence or erosion (Tissot and Welte, 2012). The crude oil alteration can be altered by two processes: chemical and physical. Chemical alteration might be thermal maturation or microbial degradation of the reservoir oil, while physical alteration might be via the preferential loss of light compounds by diffusion, or the addition of new compounds to the reservoir due to further migration. The two processes could occur simultaneously to alter the crude oil composition. Two important alteration processes discussed in this work are biodegradation and thermal alteration (Tissot and Welte, 2012).

#### 1.6.5.1 Biodegradation

Biodegradation is the chemical dissolution of materials by bacteria or other biological means. Biodegradable matters are mostly organic materials. Biodegradation has been practised with interest in microbial degradation of petroleum hydrocarbon. Therefore, petroleum biodegradation is the modification of crude oil by living organisms (Peters *et al.*, 2005). Tissot and Welte (2012) described the biodegrading process as the microbial alteration of crude oil, by selective utilisation of certain types of hydrocarbons by micro-organisms, leading to the formation of degraded oil. Degradation of crude oil could be an aerobic or anaerobic process. Aerobic degradation occurs as a result of oxygen-rich meteoric water (water derived from precipitation (snow and rain) or from water bodies or ice melt) utilised by bacterial and certain preferentially metabolised types of hydrocarbons in the spill site of crude oil. However, anaerobic condition is assumed to result from supply of oxygen from dissolving sulphate ion (Little *et al.*, 2011). The degradation of oil requires conditions that support the microbial life. Also, a large volume of oil could be degraded within a short time if the condition is ideal compared with geologic and geochemical processes (Peters *et al.*, 2005). Some conditions that encourage petroleum biodegradation are:

1. There must be sufficient access to petroleum, electron acceptors (molecular oxygen, sulphate ion), water and inorganic nutrients (e.g. phosphorous).

2. The rock fabric must have sufficient porosity and permeability to allow diffusion of nutrient and bacteria motility.

3. Microorganisms that can degrade crude oil must be present.

Evaluation of the hydrocarbon degradation from the oil spill site is achievable by biomarkers (Peters *et al.*, 2005). Biomarkers are complex organic compounds in the crude oil that provide information on the crude oil source material, environmental conditions during its deposition, the thermal maturity experience of the oil, and the degree of degradation. Some of the biomarkers are pristine, phytane, steranes, triterpanes and porphyrin. Details on the biomarkers are discussed in Section 1.6.5.3.

Table 1-1: Assessing the degree of biodegradation of oil (Larter *et al.*, 2012).

| Level or Rank | Characteristic Change in Composition | Degree of Biodegradation |
|---|---|---|
| 0 | No alteration | Undegraded |
| 1 | Lower homologues of *n*-alkanes depleted | Light |
| 2 | General depletion of *n*-alkanes | |
| 3 | Only traces of *n*-alkanes remain | |
| 4 | No *n*-alkanes, acyclic isoprenoids intact | Moderate |
| 5 | Acyclic isoprenoids absent | |
| 6 | Steranes partly degraded | Heavy |
| 7 | Steranes degraded, diasteranes intact | |
| 8 | Hopanes partly degraded | Very Heavy |
| 9 | Hopanes absent, diasteranes attacked | |
| 10 | C26-C29 aromatic steroids attacked | Severe |

It is this class of compounds which is most widely used in assessing the degree of biodegradation an oil has undergone. Many researchers have published scales to classify the degree of biodegradation of a given oil with complete classifications being that of Larter *et al.* (2012), as shown in Table 1-1. This demonstrates the order in which the compound classes of the oil are removed, but it is an approximate classification, as the order in which certain compound groups are removed is "quasi-stepwise", as some components of more biodegradable compound classes may remain after degradation has already begun on the next most resistant class of compounds (Peters *et al.*, 2005).

The *n*-alkanes are removed at a faster rate than the acyclic isoprenoids. Therefore, it is possible to use ratios such as *n*-$C_{17}$/pristane and *n*-$C_{18}$/phytane to assess initial changes in the degree of biodegradation of oil. Table 1-1 has shown that *n*-alkanes are rapidly removed in the crude oil composition. Therefore, caution should be applied in the use of these ratios (Peters *et al.*, 2005).

The changes in the physical properties of a crude oil due to microbial degradation as described above will occur throughout the range of biodegradation shown in Table 1-1. The increase in viscosity and density will be most significant in the early stages of degradation due to the removal of compounds such as the *n*-alkanes as shown in Table 1-1.

In addition to clearly classifiable biodegraded oils, there are numerous occurrences of oils that are mixtures of biodegraded and non-biodegraded components, which comprise a saturated hydrocarbon fraction that appears to be non-degraded when analysed by gas chromatography (i.e. dominated by *n*-alkanes). In such situation, it is potentially difficult to identify the presence of the degraded component. The occurrence of 25-norhopanes in apparently non-degraded oils has been proposed to signify such mix, although the origin of these compounds is controversial.

#### 1.6.5.2 Thermal maturity

Thermal maturity explains the extent of heat-driven reactions that convert sedimentary organic matter into petroleum. Thermal processes are generally associated with burial, then part of this organic matter is converted into petroleum and, finally, to gas and graphite. Potential source rock can be described by the level of the thermal maturity of the organic matter (content) because it contains an adequate quantity of the proper type of kerogen to generate significant quantities of petroleum yet is not thermally mature. This potential petroleum source rock becomes an effective source rock within the oil-generative window (with appropriate levels of thermal maturity).

In order to effectively describe the thermal maturity of organic matter, various parameters have been developed including Rock-Eval pyrolysis, vitrinite reflectance ($R_o$), thermal alteration index (TAI), which is spore colouration, and a carbon preference index (CPI). However, molecular parameters based on ratios and distributions of specific biomarkers have been increasingly used to study thermal maturity of crude oil.

The organic matter has been described over time as immature, mature or postmature based on their relation to the oil-generative window (Tissot and Welte, 2012). The immature organic matter has undergone alteration caused by biological, physical and chemical processes during diagenesis without a pronounced effect on temperature. With mature organic matter, the thermal process covers the temperature range between diagenesis and metagenesis, which is the oil-generative window equivalent to catagenesis. Thermal maturity of organic matter has been measured for a long time using: (1) generation or conversion parameters used as indices of the stage of petroleum generation and (2) thermal stress used to explain relative effects of temperature/time. Assessing the maturity using vitrinite reflectance has been associated with the threshold of oil generation, where $R_o$ of about 0.6% is accepted widely as indicating the start of oil generation in most source rocks (Peters *et al.*, 2005).

Assessment of oil for thermal maturity in correlation studies has employed biomarkers in the oil to provide important information on the origin, distribution and possible paths of migration of oils. Steranes and pentacyclic tritepanes of the hopane concentration ratio type have attracted much attention as maturity indicators, but they are mostly restricted to low maturation level (Peters *et al*., 2005). However, Hakimi *et al.* (2010) suggested that the concentration ratio of tricyclics/17 (-hopanes, diasteranes/steranes, and Ts/(Ts+Tm)) are useful biomarkers at high thermal maturity (vitrinite reflectance 1.0%).

In this study, the organic matter maturity parameters that will be discussed are biological markers. Various biological markers (biomarkers) ratios have been employed as maturity parameters by geochemists. However, for the purpose of this study, emphasis will be laid on isoprenoid/*n*-alkanes ratios, $C_{29}$ αβ/βα and $C_{30}$ αβ/βα (mortane/hopane), 22 αβS / (22 αβS + 22 αβR) of the $C_{31}$ to $C_{35}$ hopanes (homohopanes) and $C_{27}$ to $C_{29}$ 20 αααS / (20 αααS + 20 αααR) sterane ratios as parameters for biodegradation, source input and maturity parameter. The extent of thermal maturation is calculated by using the peak areas (or height) of the compound isomers in the m/z 71, m/z 191 and m/z 217 mass chromatograms for isoprenoid/*n*-alkanes, hopanes and steranes ratios respectively (Affouri *et al*., 2013).

The hopane $C_{29}$ αβ/βα and $C_{30}$ αβ/βα ratios also fall with increasing thermal maturity from about 0.8 in immature bitumen to a value of less than 0.15 in mature source rocks and 0.05 in crude oils. Both the $C_{31}$ to $C_{35}$ hopanes and $C_{27}$ to $C_{29}$ sterane ratios increase with thermal maturity. The $C_{31}$ to $C_{35}$ ratio increases from 0 to its equilibrium at 0.60 during ripening. Samples showing $C_{31}$ to $C_{35}$ hopane ratios in the range 0.50 to 0.54 have barely entered oil generation, while ratios in the range 0.57 to 0.62 indicate that the main phase of oil generation has been reached or surpassed. The $C_{27}$ to $C_{29}$ steranes ratio also increases from 0 to its equilibrium at 0.50 during maturation (Affouri *et al*., 2013).

#### 1.6.5.3 Biomarkers

Biomarkers are organic compounds whose carbon structure gives an unambiguous link with a known natural or biological precursor. The biomarkers contain an imprint of the depositional environment and information of the thermal history of the oil (Wang *et al*., 2016). They originate from lipid-based cellular constituents of organisms such as bacteria, algae, jellyfish and higher plants. They mostly offer structural support (an architectural role) in living cells, which means they have great strength and stability so that upon the death of an organism, the precursor-products carbon skeleton relationship may persist indefinitely, even after following the processes of diagenesis and thermal maturation in crude oil (Wang *et al*., 2016). For example, cholesterol loses water when deeply buried to become cholestane and finally with the addition of hydrogen from hydrocarbon known as 5α(H) cholestane (Figure 1-3). The cholestane has the same stereochemistry (stereochemistry is the structure connectivity of molecules/atoms and arrangement of molecules/atoms in space) as the original cholesterol, which could be a part of the huge hydrocarbon of a source rock or crude oil.

There are other similar biomarkers that behave like cholesterol, which allows biomarkers to play an exciting role in the developing field of basinal evaluation, reconstruction of paleoenvironments and molecular stratigraphy. The numerous biomarkers in the crude oil and associated source rock are significant, and Figure 1-4 gives an example of biomarkers in crude oil. The product-precursor relationship provides information that has important usefulness for oil-oil and oil-source rock correlation purposes (Peters *et al.*, 2005).

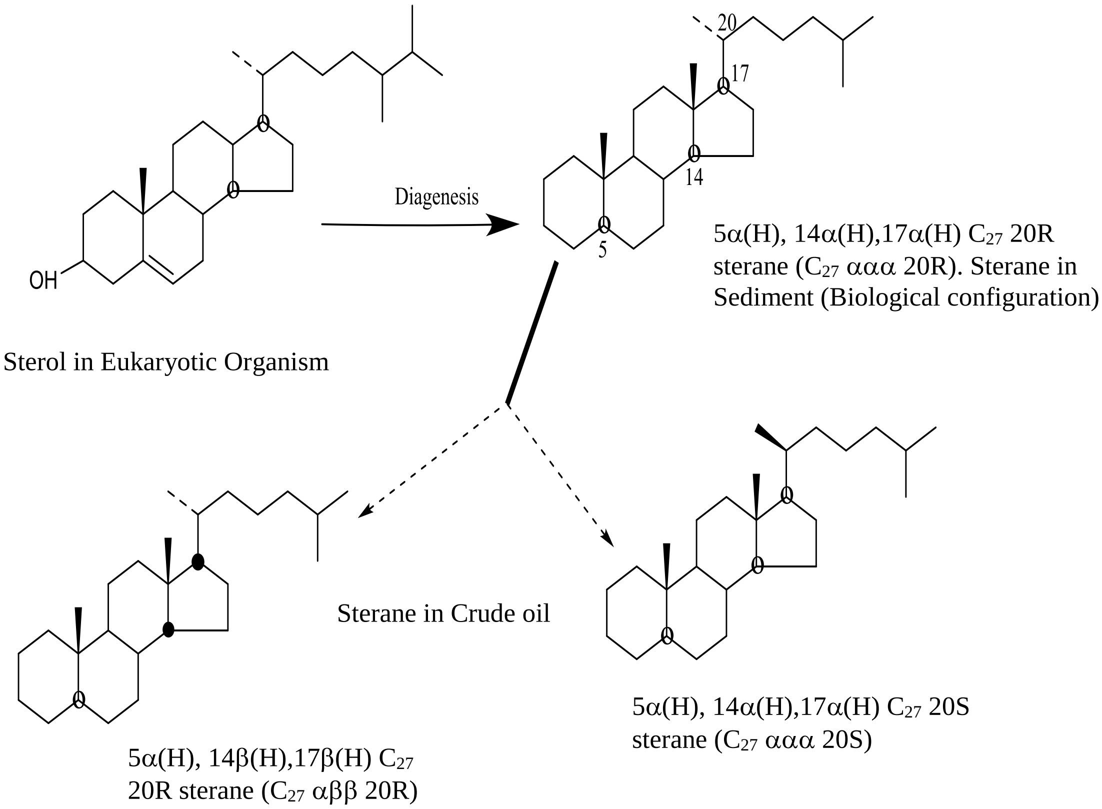

Figure 1-4: Stereochemistry transformation of sterols in the lipid membranes of eukaryotic organism (Peters *et al.,* 2005).

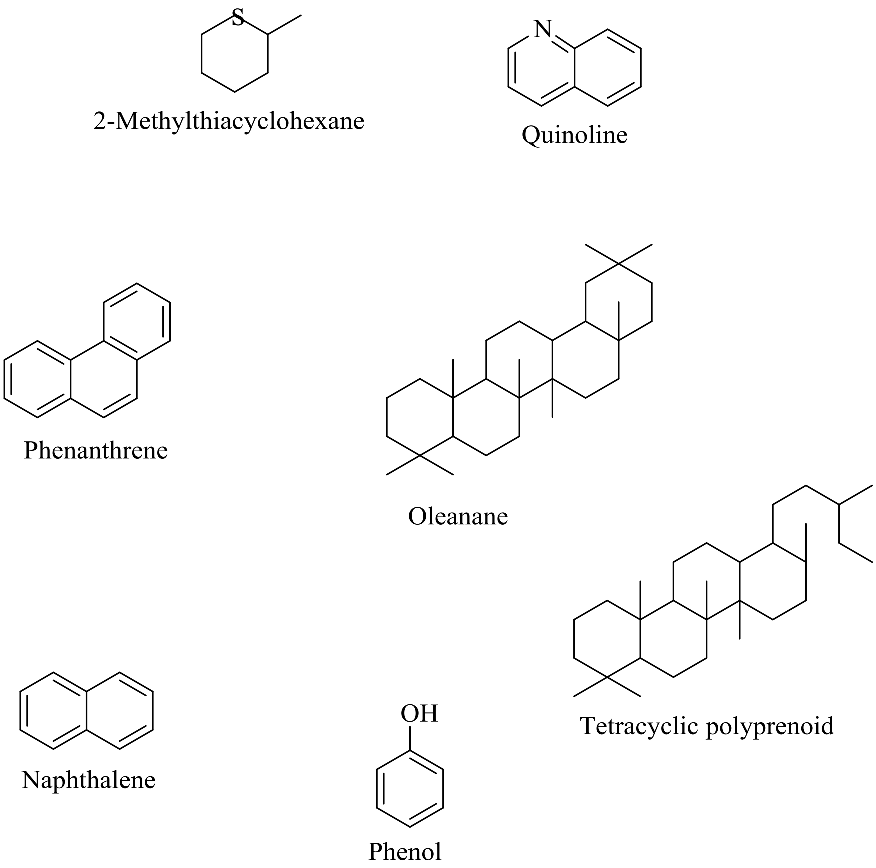

Figure 1-5: Some of the biomarkers in petroleum (Peters *et al.*, 2005)

The biomarker stereochemistry pathway in Figure 1-3 shows the transformation stages of sterol from living things to biomarker in crude oil. Therefore, a detailed understanding of the stereochemistry discussed below is essential to interpret the geochemical data on crude oil removed from the soil in Chapter 5.

i) Stereochemistry and nomenclature of biomarkers

Stereochemistry involves the study of the relative spatial arrangement of atoms that form the structure of molecules. A branch of stereochemistry is the study of chiral molecules which are common in biomarkers. A chiral molecule is a molecule that has another molecule of identical composition arranged in a non-superimposable mirror image, which can be found in biomarkers and influences the recognition and naming of biomarkers. For proper understanding of the stereochemistry of biomarkers, each carbon is labelled systematically (Figure 1-6).

In this dissertation, a subscript number after a capital C refers to the quantity of carbon particles in a biomarker. For example, $C_{35}$ hopane signifies a hopane compound with 35 carbon atoms. But if there is a dash after the C, it signifies the position of the carbon in that compound e.g. C-22 refers to the carbon atom at position 22 in the compounds. Further nomenclatures common in biomarkers are *n*C, which means a normal alkane that consists of specified numbers of carbon atom in the compound. If an alkane is represented as $nC_{19,}$ it means 19 carbon atoms were present in a normal alkane compound (Peters *et al.*, 2005). Other nomenclatures are shown in Table 1-2.

The stereochemical information included in naming a biomarker describes the compound and singles them out of many hydrocarbons in crude oil. Therefore, $C_{29}$ 5α (H), 14α (H), 17α (H)-20S sterane means that the compounds contain 29 carbon atoms, with an asymmetric carbon atom attaching to hydrogen at positions 5, 14, 17 in the ring and they are pointing into the page or down. The spatial orientation of carbon at position 20 obeys the clockwise convention of Peters *et al*. (2005).

Table 1-2: Common modifiers and nomenclature related to biomarkers (Peters *et al.*, 2005).

| Modifier | Nomenclature |
|---|---|
| Homo- | One additional carbon on structure |
| bis-, tris-, (di-, tri-,) | Two, three additional carbon respectively |
| Seco- | Cleaved C-C bond (specified) |
| Benzo- | Fused benzene ring |
| Nor- | One less carbon on structure |
| Des-A (de-A) | Loss of A-ring from structure |
| Iso- | Methyl shifted on structure |
| Neo- | Methyl shifted from C-18 to C-17 on hopanes |
| Spiro | Two rings joined by one carbon |
| α | Asymmetric carbon in ring with functional group (usually H) down or into the page |
| β | Asymmetric carbon in ring with functional group (usually H) up or out of the page |
| R | Asymmetric carbon that obeys clockwise conventions |
| S | Asymmetric carbon that obeys anticlockwise convention |

This working knowledge of the stereochemistry of biomarkers is essential for petroleum geochemists. The range of biomarkers covers many structural types and different functionalities. Therefore, the following section will introduce common biomarkers generally employed for a geochemical description of crude oil relative to degradation and thermal maturity.

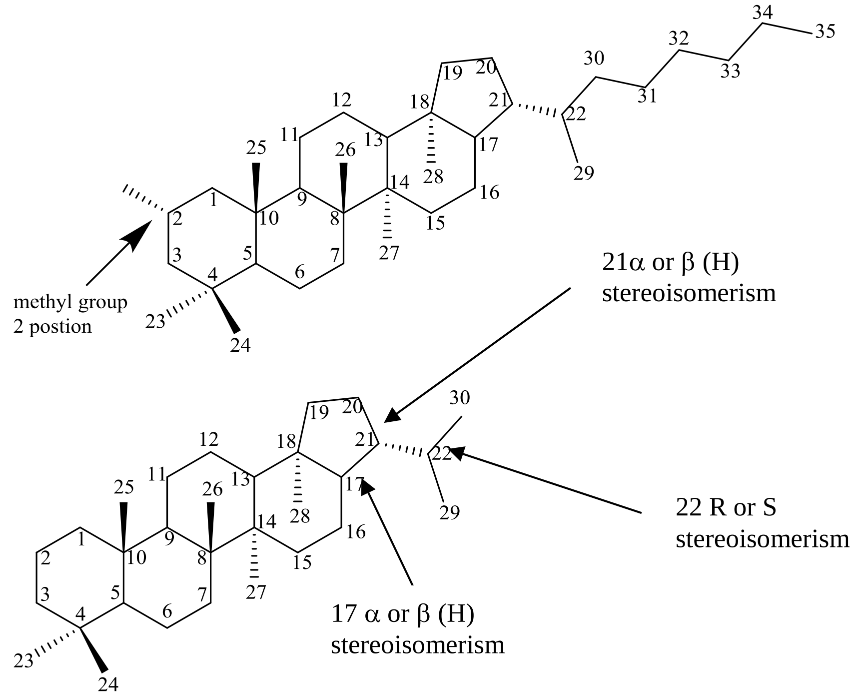

Figure 1-6: $C_{30}$ and $C_{35}$ hopanes structure (modification of hopane structure in Wang *et al.*, 2007).

R and S are used to express the spatial orientation of the carbon structures that are enantiomers i.e. two structures that are mirror images of each other but are non-superimposable (not identical).

ii) Acyclic isoprenoids

They are a series of $C_5$ isoprene units thought to be derived from acyclic isoprenoid squalene ($C_{30}H_{50}$) or related $C_{30}$ precursors (Killops and Killops, 2005). The isoprenoids can have one or more functional groups attached to their carbon skeleton and can be classified into monoterpenes ($C_{10}H_6$), sesquiterpenes ($C_{15}H_{24}$), diterpenes ($C_{20}H_{32}$), triterpenes ($C_{30}H_{48}$), and tetraterpenes ($C_{40}H_{64}$). Some common examples in crude oil are pristane and phytane, lycopene, and methy-heptadecanes. Isoprenoids, especially pristane and phytane ratio, have been widely used to predict depositional environments. The common isoprenoid alkanes normally observed in crude oil are pristane ($C_{19}$) and phytane

($C_{20}$) (Wang *et al*., 2016). Both are thought to arise from the precursor phytol (Figure 1-7), pristane via oxidation and decarboxylation of phytol while phytane is believed to result from dehydration and reduction (Kuhn, 2007).

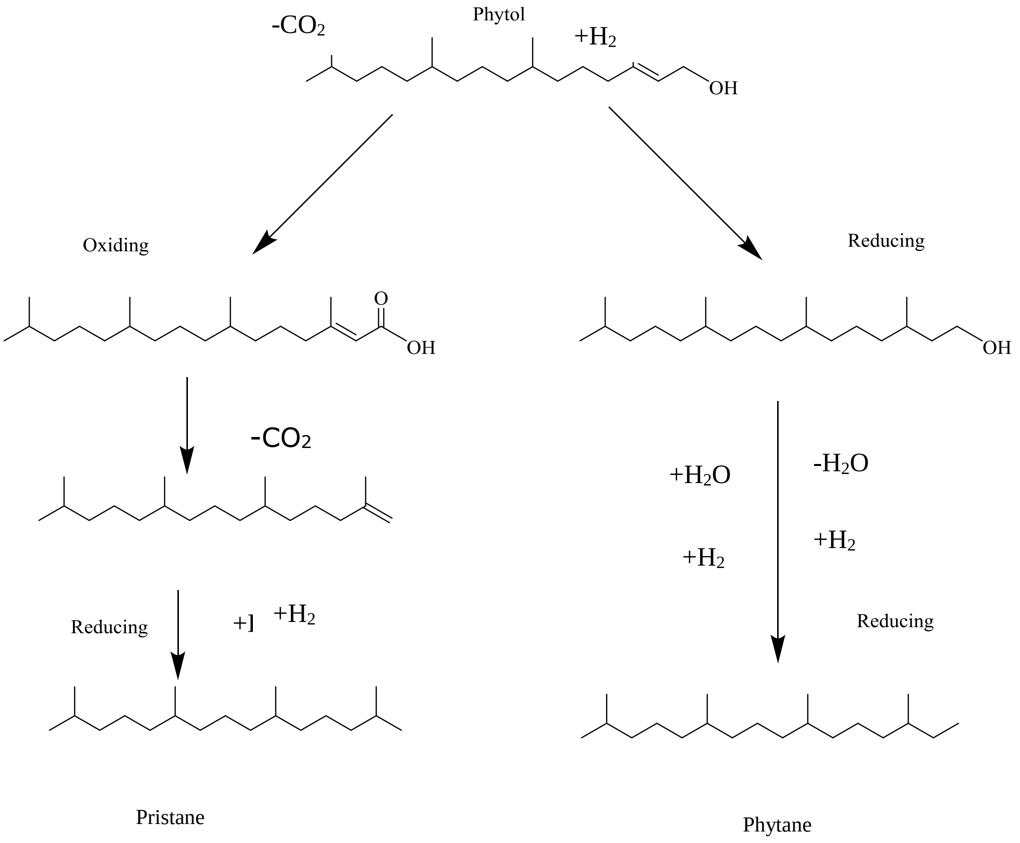

Figure 1-7: Simplified conversic ytol to pristane and phytane (Kuhn, 2007).

Over the years, the ratio of normal to branch alkane (n-C17/pristane and n-C18/Phytane) had been used for measuring biodegradation in oil until research showed that it was not reliable because the rate of biodegradation of the branch alkanes approaching normal alkanes was too rapid. However, caution must be applied in the use of these ratios, especially for oil spill analysis, because it cannot actually be used to correctly determine the rate of biodegradation or distinguish situation where new spills are added to the old spill in an area (Peters et al., 2005).

iii) Hopanes

Hopanes are polycyclic saturated ring pentacyclic triterpanes (Figure 1-6). Most oil samples show the presence of regular hopanes from $C_{27}$ to $C_{35}$. The ratio of $C_{27}$ 17 ((H) -

hopane (Tm), over $C_{27}$ 18 ((H) (Ts)) has been used as a maturity parameter indicator in many crude oil geochemical studies. The diagenesis and maturation process leads to defunctionalisation and a change in the biological 17 β(H), 21 β(H) stereochemistry to a thermodynamically more stable 17 ((H), 21 ((H) configuration. The hopanes with 30 carbon or fewer atoms of carbon skeleton have been thought to have their precursors as diploptene (hop-22(29)-ene) and diplopterol (hopan-22-ol) (Peters *et al*., 2005). Hopanes are of great interest in the crude oil biodegradation analysis because of their innate resistance to biological attack. The hopane hydrocarbons are relatively resistant to biodegradation. The hopane hydrocarbon degradation occurs after the degradation of the regular steranes, in the order $C_{35}<C_{34}<C_{33}<C_{31}<C_{30}<C_{29}$, and the 22R epimer degrades preferentially in relation to the 22S epimer (Wang *et al*., 2016).

### iv) Steranes

Steranes are a class of 4-cyclic compounds derived from steroids or sterols via diagenesis and catagenesis degradation and saturation. Steranes have a skeleton with a side chain at C-17. They are biomarkers used to determine the degree of biodegradation and thermal maturation of crude oil (Wang *et al*., 2016). The alteration and removal of regular steranes and 4α-methlysteranes from petroleum occurs after the complete removal of $C_{15}$–$C_{20}$ isoprenoids (Table 1-1). The methylsteranes have provided significant data as source and depositional environment and serve as useful correlation tools in studies (Wang *et al*., 2016). In general, sterane susceptibility to microbial attack is as follows: ααα20R>> αββ20R ≥ αββ20S≥ ααα20S>> diasteranes and $C_{27}> C_{28} > C_{29} > C_{30}$ (Peters *et al*., 2005).

Steranes are relatively resistant to biodegradation, with regular steranes degrading at a faster rate than diasteranes. The biodegradation decreases as the carbon number increases for each isomeric configuration, but selective depletion of $C_{27} > C_{28} > C_{29}$ steranes occurs in subsurface crude oils (Peters *et al*., 2005); and the biological 20R epimer is more prone to biodegradation than the 20S epimer. The $C_{30}$ steranes appear to be even more bioresistant than lower homologs (Lin *et al*., 1989). The ratio of $C_{30}/(C_{27}\text{-}C_{30})$ steranes has been applied to assess the marine input to crude oil (Peters *et al*., 2005). Source input verification of some selected oil has been carried out by Moldowan *et al.* (1992). When the $C_{30}/(C_{27}\text{-}C_{30})$ steranes ratio was plotted against $C_{35}/(C_{31}\text{-}C_{35})$ 17 α-homohopanes, it was found that oil derived from source rock deposited under restricted saline to hypersaline lagoon conditions show lower $C_{30}/(C_{27}\text{-}C_{30})$ sterane than those from the open marine system. Steranes may be rearranged to diasteranes during diagenesis. Diasteranes are more bioresistant with increasing carbon numbers, and it has been observed that in heavily biodegraded oils where steranes and hopanes are totally removed and there are no 25-norhopanes are present (level 9) (Table 1-1), some diasteranes will still remain (Peters *et al.*, 2005). It has been evidential that the $C_{27}$-$C_{29}$ steranes are destroyed completely before diasteranes alteration (Peters *et al*., 2005).

v) Aromatic biomarker

The aromatic compounds used as biomarkers provide useful information on maturity, source rock and environmental deposition. For instance, the aromatic biomarkers hopanoids originated from bacterial precursors, while tetracyclic and pentacyclic aromatic biomarkers with oleanane, lupine or ursane skeletons indicate higher plant inputs (Bruggeman and De Craen, 2012).

Several aromatic hydrocarbons, such as cadalene derived from sesquiterpenoids, and 1,2,5-TMNr and 1,2,5,6-TeMNr, whose precursors were derived from higher plants, are indicative of general or more specific higher plant sources (Ji *et al*., 2014). Naturally occurring aromatic biomarkers in petroleum are naphthalene and phenanthrene. Often, the higher-plant-derived terpenes are found in association with aromatic biomarkers, for example 1,8-dimethylpicene may be found in association with 1,2,7-trimethylnaphthalene because they both have β-amyrin as their precursor compound. Abundant 1,2,7-trimethylnaphthalene relative to other trimethylnaphthalenes indicates an angiospermous contribution resulting from fragmentation of the carbon ring of β-amyrin during diagenesis (Killops and Killops, 2005).

Relative abundance of naphthalene during catagenesis has been used to determine thermal maturity in hydrocarbon, and it could be used as a source indicator (Killops and Killops, 2005). The pace and extent of aromatisation and cracking can be used as maturity parameters for cyclic aromatic hydrocarbon such as naphthalene and phenanthrene (Peters *et al*., 2005).

## 1.7 Summary

Nigerian crude oil is a light-density and sweet oil, which is a result of its diagenesis process. This attribute of the Nigerian crude oil causes it to have high market value because of the reduced cost of production. The high market value results in high demand in the global market, which has made crude oil an integral part of Nigeria’s economic boost since independence. The high demand for the crude oil has made the principal oil companies expand their exploration processes to different locations at the Nigerian Niger Delta basin. Unfortunately, these activities have given rise to environmental degradation in major parts of the region due to oil spills and other failures during exploration processes on the part of the company and vandalisation of oil pipelines by the oil-producing communities. The continuous unpleasant situation has resulted in a lingering crisis between the communities and the principal players in the oil industries. To address some of the soil pollution problems, remediation work has been contracted out to incompetent hands, which has resulted in no change to the situation.

The government has set up agencies to look into the crisis and provide an answer to the problem, but inadequate data and other indices have been a barrier to finding a solution. To abate the escalating crisis, the government decided to set up the DPR to monitor the activities of the oil companies.

Nevertheless, Nigeria still remains the largest carbon sink in the world with little media attention compared to other parts of the world where similar events occur. The heavy pollution of the environment spurs research to be conducted to restore the arable land of the Niger Delta region. Most of the established remediation techniques will be discussed in detail in the next chapter. These processes require a long period of time and have failed to meet the desire of the local communities to be able to use the land for farming. To address this challenge, the current project seeks to provide technology that could remediate the soil from the Niger Delta region, taking into consideration the resident time, independent of environmental factors, ease of control of the process and evaluation of the technology to achieve the expected outcome. The technology this project intends to employ to achieve the objective is pyrolysis, and the crude oil and soil organic matter will be characterised geochemically before and after remediation. The analysis of the geochemical result will be explained based on the knowledge of the Nigerian petroleum system and petroleum composition to confirm that soil is remediated. The biomarker discussion will be better understood in the correlation study of the crude oil, soil organic matter extract before remediation and liquid pyrolysate after remediation.

This part of the project laid the foundation on the organic properties that will be used to confirm the effects of the remediation technique employed. Details of the available remediation techniques that have been used at laboratory scale, and pilot scales for field study, will be discussed. Furthermore, the discussion will involve current practices in Nigeria used in the oil remediation process (both laboratory and field scale).

# Chapter 2: Overview of remediation techniques

## 2.1 Scope

This chapter covers established remediation techniques that have been used to remediate organic contaminated soil over the years. The chapter further discusses the merit, the demerit and the techno-economic analysis of each technique. The chapter concludes with the justification of pyrolysis as a method of choice for this study.

## 2.2 Introduction

Environmental remediation deals with the removal of pollutants or contaminants from environmental media such as soil, groundwater, sediment or surface water. The term can also refer to rehabilitating areas degraded by pollutants or otherwise damaged through mismanagement of the ecosystem. The purpose of remediation could be divided into three categories:

1. Removal: Removal of pollutants from the soil.
2. Treatment: Contaminants are treated to change them from harmful chemicals to less harmful chemicals.
3. Containment: Contaminants are left in the ground but are confined to a spot through the stabilisation process (later discussed in this chapter) to stop them from escaping into the air or infiltrating groundwater, with the ultimate goal of eliminating any potential threat to human health and the environment.

Many remediation techniques have been used to remediate soil polluted with crude oil, but some of the methods discussed in this chapter have never been used for Nigerian oil-polluted soil as a pilot-scale project. This is partly due to the establishment of many multinational companies before environmental impact assessment was introduced to the Nigerian constitution in 1971 and the prevailing corruption that encouraged negligence from the companies in cleaning up polluted areas. According to Amnesty International (2009), the common practices are burning oil off the spill site, dumping of oil from a spill site in unlined earth pits and use of contractors who simply transport the topsoil from elsewhere to cover the contaminated spill sites.

This research regards remediation of oil-polluted soil as a challenge not only because of the scientific and technical aspects involved but also on a social and economic level. Therefore, a few common remediation techniques are considered in detail to highlight their procedures, efficiency and other factors, as well as techno-economic conditions, to justify the decision to use the pyrolysis process.

## 2.3 Soil washing

Soil washing is a technique that could be a continuous or batch process using physical and chemical techniques to separate contaminants from the soil and sediments (Li, 2007). The process typically does not significantly alter the contaminants but reduces the concentration by particle-size separation, phase transfer and physical removal (Ehsan *et al.*, 2007). Although it is a feasible process for treating heavy metals, radionuclides, polycyclic aromatic compounds, pesticides and polychlorobiphenyl (PCB), it is unlikely to be cost-effective for soil with fine particles (silt/clay) containing under 30% to 50% particles. Soil washing works better with soil containing 50% to 70% particles, and it can separate any solids for safe disposal (Li, 2007).

Soil washing is, however, an extensive commercialised process. The complex nature of the soil and possible complex mixture of contaminants in the soil might require sequential washing using a different wash formulation or different soil-to-wash ratio. This is because a single formulation will not be able to remove all the different contaminants. Also, it has been suggested that laboratory studies must be carried out on land to be treated before pilot-scale work to ensure the effectiveness of the process. The laboratory experiment will be helpful to give an indication as to whether the selected soil-washing agent could satisfy the criteria regarding important factors such as effectiveness; cost; public and regulatory perception; biodegradability and degradation products; toxicity to humans, animals and plants; and the ability to recycle soil-washing agent, prior to field scale (Mulligan *et al.*, 2001).

The primary stages in soil washing are soil preparation, washing, soil and water separation, wastewater treatment and vapour treatment when required. Soil preparation begins with the excavation or moving of contaminated soil to the place of process, where it is normally screened to remove debris and large objects. Depending on the technology and whether the process is semi-batch or continuous, the soil may be made pumpable by the addition of water. The polluted soil is mixed with wash-water and possibly surfactants to remove contaminants from the soil and transfer them to the extraction fluid. Next, the soil and wash-water are separated, and the soil is rinsed with clean water. The clean soil is then removed from the process as a product. Suspended soil particles are recovered, as sludge, directly from the spent wash-water using gravity separation and, when necessary, flocculation with a polymer or other chemical is performed.

Achugasim *et al*. (2011) carried out an experiment on hydrocarbon in crude-oil-polluted Nigerian soil and found that the persulphate used was a good soil-washing agent to remove benzene, toluene, ethylbenzene and xylene (BTEX). The percentage removal for the BTEX was about 97%, 95% and 95% at acidic, neutral and basic pH ranges respectively. However, it was not so effective for polycyclic aromatic hydrocarbons in the crude oil given that their percentage removal was less than 27%, 3% and 41% for the PAH at the acidic, neutral and basic ranges respectively. Thus, the experiment shows that persulphate should not be used as a single soil-washing agent for effective removal of hydrocarbon in crude oil in a polluted soil.

Akpoveta *et al*. (2012) used sodium dodecyl sulphate as surfactant to treat Nigerian soil contaminated with crude oil. It was found that the method was effective, with 88.32% remediation efficiency achieved after seven hours. The physicochemical quality of the soil was also improved, and the mechanism of hydrocarbon removal was solubilisation and the mobilisation of the contaminant. The technique was considered promising because it is capable of reducing both hydrocarbon and heavy metals concentration as well as improving the deteriorated properties of the soil which are essential for soil quality and productivity. Nevertheless, most of the experiments on contaminated land in Nigeria have not been done at field scale. Moon *et al.* (2016) performed a remediation on soil containing heavy metals and low-level petroleum hydrocarbon with various washing solutions, with concentration ranging from 0.1 to 3 M and a liquid-to-solid ratio of 10. The overall result of the treatment showed that tetraacetic acid is a viable washing solution to remove both heavy metals (Pb, Cu Zn) and total petroleum hydrocarbon.

The technique is characterised by high capital costs, which includes equipment rental, start-up, labour, consumables/supplies, health and safety equipment, contingencies, maintenance, utilities, excavation, and water treatment and moblisation costs. These can be unaffordable for developing countries, and the high volume of water required might be in limited supply in some places in the northern part of Nigeria. In addition, there will be a need for extra treatment processes for separation and disposal/destruction of contaminants

(Ehsan *et al*., 2007; Li, 2007). Another factor that might possibly increase the cost of the technology is lack of manufacturing companies in developing countries, which requires purchase from special suppliers of chelating agent recurrently when wash water cannot be recycled (Li, 2007).

## 2.4 Biological remediation

Biological remediation uses microorganisms to degrade hazardous substances or complex organic contaminants into less toxic or non-toxic compounds (Li, 2007). It is more economical and environmentally friendly than incineration, and the pollution generated can be treated on site. The process is divided into *in situ* (biosparging, bioventing and bioaugmentation), *ex situ* (composting and biopiles) and bioreactor (slurry and aqueous reactors).

Bioventing is a method for the treatment of hydrocarbon contamination deep under the surface by supplying air at a rate designed to maximise *in situ* biodegradation and minimise or eliminate the off-gassing of volatilised contaminants into the atmosphere (Khan *et al*., 2004). Bioaugmentation is the addition of microbial cultures (indigenous or exogenous) to contaminated soil to enhance degradation. Two factors limit the use of added microbial cultures in a land treatment unit: either indigenous cultures compete or no indigenous culture compete well enough within an indigenous population to develop and sustain useful population levels. Most soils with long-term exposure to biodegradable waste have indigenous microorganisms that are effective in degrading contaminants if the land treatment unit is well managed (Kumar *et al*., 2011). The most extensive risks involve the introduction of non-native species, both plants and microbial, which could compete with native habitats and alter soil properties (Gerhardt *et al*., 2008). Biopiles are composite cells that provide favourable conditions for indigenous aerobic and anaerobic organisms to attack the contaminant, which produces aerated composted piles above ground. In more integrated designs, soil is amended with nutrients and then piled over a piping system through which air is pumped into the soil. The provision of adequate amounts of oxygen, nutrients and water to hydrocarbon-degrading bacteria in attempts to optimise the bioactivity of microorganisms is another advantage of biopile systems (Chemlal *et al*. 2012).

The effectiveness of the technique depends on the environmental conditions permitting the growth of the microorganisms attacking the pollutant (Mosbech, 2002; Thomassin-Lacroix, 2000). The process is highly specific and limited to biodegradable, organic material, which might yield products that are more toxic or persistent than the parent compound. It takes a longer time to yield the desired result, but it is much cheaper compared to other methods (Vidali, 2001). Gogoi *et al*. (2003) reported bioremediation of petroleum-contaminated soil in the Borholla oilfield. The work examined the effect of aeration, nutrients and inoculation of extraneous microbial consortia, which have a beneficial effect on the laboratory- and pilot-scale test with about 75% degradation over a period of one year. The results from their computer simulation showed that the remediation occurs within the macropores of the system without sufficient penetration into the soil aggregates. The pilot-scale study of petroleum-contaminated soil showed that bioremediation of soil with a consortium of bacteria achieved a 76% reduction of total hydrocarbons. Furthermore, it was noted that it remediated the alkane fractions most effectively but left behind a greater proportion of the aromatic hydrocarbons.

Phytoremediation is another biological remediation technique, which involves the use of plants to remediate contaminated soil (Vidali, 2001). The technique is used for remediation of metals and hydrocarbon from water media or soil. The remediation processes might be the uptake of metals and organic compounds to degrade the organic compounds with subsequent removal of plants from the contaminated site (Vidal, 2001). Cofield *et al*. (2008) studied the use of switchgrass (Panicum virgatum) and fescue (Festuca arundinacea) for phytoremediation of soil contaminated with PAH. Their findings showed that these plants are capable of removing all the PAHs with an average of 40% with the exception of indeno(1,2,3-c,d)pyrene having 1.5% removal efficiency. Ighovie and Ikechukwu (2014) used carpet grass (Axonopus compressus) as a pyhtoremediating agent for soil at Ubeji and Alesa Eleme communities in Niger Delta region of Nigeria. The study revealed that 66% of the hydrocarbons were removed from the oil-polluted land after a period of four months, and the soil pH also improved from acidic pH (4.46 and 4.66 respectively) to almost neutral pH (6.87 and 6.86 respectively).

## 2.5 Thermal desorption

This is fundamentally a thermally induced physical separation process, where contaminants are vaporised from solid matrix (soil, sediment and sludges) and transferred into the gas stream where they can be easily condensed and collected or combusted (the use of thermal energy to vaporise and physically separate volatile and semi-volatile organic compounds from petroleum-contaminated soil) (Li, 2007). It is an *ex situ* remedial technology, which is as well-known as thermal volatilisation, thermal stripping or soil roasting. Thermal desorbers are designed for physical separation of the organic contaminant from the soil. Furthermore, thermal desorption could partially decompose or totally decompose the contaminant, depending on the type of the organic compounds present or temperature of the desorber system.

This highly simple and rapid method does not require sediments to be excavated for clean-up or disposal, thus favouring *in situ* remediation. *In situ* remediation is more economical and viable, as it saves excavation and conveyance costs while avoiding secondary pollution due to transportation of oil-contaminated sediments (Agarwal and Liu, 2015).

Table 2-1: Reactor's advantages and drawback for thermal desorption technology (Marshall, 2013).

| Reactors | Advantages | Drawbacks |
|---|---|---|
| Bubbling fluidised bed (BFB) | Good temperature control and mixing, ease of scale-up, well-established technology, intense heat and mass transfer. | Dilution of products from fluidisation gas, condensation trained and separation challenges, particle size restricted, char traps some sand. |
| Circulating fluidised bed (CFB) | Well-established technology, very large processing capacity, controllable residence time, high heating rate, good heat and mass transfer. | Challenging to operate, condensation, separation challenges, smaller particles required, high gas flow and product dilution, char attrition, char contains some sand, high separation and quenching requirements. |
| Ablative | Large particle sizes can be used, inert gas is not required, controllable residence time, the system is more intensive, good heat transfer. | Reaction rate limited by heat transfer to the reactor, process is surface area controlled, high cost to scale up. |
| Rotating cone | Centrifugal forces move heated sand and biomass, no carrier gas needed, easy quenching. | Complex process, difficult to scale up, high capital cost, small particle size needed. |
| Vacuum | Feed particle size flexibility, fewer aerosols formed (easier quenching), bio-oil free of char, no additional carrier gas/product dilution. | Low bio-oil yield, increased pyrolytic water generation, low heating efficiency, absorption of liquid effluents in the liquid ring compressor pump, high capital cost, maintenance cost and high sealing/gasket requirements. |
| Auger | Low pyrolysis temperature (400°C), compact, flexible design, no carrier gas/dilution, quality biochar produced. | Plugging risk, lower bio-oil yield, moving parts in the hot zone, heat transfer limitations at large scale. |

The vaporised hydrocarbon from either of the units requires secondary treatment such as afterburners or oxidizers (to destroy the organic constituents) or condenser and carbon adsorption beds to trap the organic constituents for disposal or further treatment. The desorber units used for thermal desorption (rotary kiln desorbers, asphalt plant aggregate dryers, thermal screws and conveyor furnaces) depend on some factors such as moisture content, particle size distribution, contaminant concentration, temperature, heat capacity and thermal stability. Details of the advantage of each desorber unit and reactor selection criteria are listed in Table 2-1.

Piña *et al*. (2002) showed that high-temperature thermal desorption was capable of removing gas oil from the soil without appreciable changes in the chemical composition of the gas oil. It was observed that gas oil removal is independent of the soil composition. Also, the study carried out by Falciglia *et al*. (2011) on remediation of diesel-oil-contaminated soil using low-temperature thermal desorption shows that adsorption and desorption efficiency depends on the soil composition, soil texture, temperature and residence time of treatment.

The thermal desorption technology is readily available for on-site and off-site treatment, has very rapid treatment time and is easily combinable with other engineering sciences such as air sparging or groundwater extraction. The soil could be returned to the contaminated site or used for landfill. However, the off-site transportation and the need to de-water before treatment, when the moisture content of the excavated soil is high, add to the total cost of the treatment. On-site treatment will involve a significant area to locate the equipment and to store the processed soil. The soil structure and composition will be affected in the treated soil, which will require the artificial addition of nutrients and nitrogen-fixing bacterial to support plant growth (Nathanail *et al.,* 2001).

## 2.6 Chemical oxidation

This technique employs the use of very reactive chemicals to oxidise the organic contaminant in the soil to generate carbon dioxide or transform the contaminant to more readily degradable organic compounds. The chemical oxidants such as ozone, persulphate, permanganate and hydrogen peroxide have been used to destroy organic contaminants at subsurface levels in contaminated soil (Sutton *et al*., 2014). Fenton’s reagent is a solution of hydrogen peroxide and iron catalyst that has been used for the removal of or to destroy organic contaminants in soil (Sutton *et al*., 2014). Maunakata-Marr (2006) observed that the permanganate ions formed could split double carbon bond in the organic contaminant, and the reaction that follows will lead to the generation of carbon dioxide.

Before application of any chemical oxidant, the oil-contaminated site must be carefully investigated for any ongoing natural reduction processes such as dehalogenation, as these may upset its natural geochemistry (Agarwal and Liu, 2015). Fenton's reagent has been found to be a good chemical oxidant for chlorinated contaminated soil as well as treatments of soil contaminated with pentachlorophenol and trichloroethylene. Although Fenton's reagent\Fenton-like reactions and ozone have been most commonly used for remediation, the modified Fenton's process is more cost-effective than ozonation due to the low amounts added and the chemicals cost (Goi *et al*., 2006b). Moreover, the strong oxidising capabilities of Fenton's process holds promise for the effective remediation of oil-contaminated sediments (Pardo *et al*., 2014). Flotron *et al*. (2005) showed that Fenton's reagent was able to degrade virtually all benzo(a)pyrene in the soil but no significant amount of fluoranthene was degraded. Also, the use of excess Fenton's reagent did not affect the benzo(b)fluoranthene in contaminated soil used for this study. It was likewise noted that some highly toxic by-products were made. Although the efficiency of this technique depends on the point of contact between the contaminant and the oxidative medium, it is useful for highly permeable inorganic soils (Lowe *et al*., 2002).

The iron ion introduced to Fenton's process results in an exothermic reaction with hydrogen peroxide, which could lead to removal of water by evaporation. The addition of the iron ion is achieved in acidic conditions which might cause inhibition of microbial activities and drawback to re-vegetation or greater impact on the biomass of the soil (Sahl and Munakata-Marr, 2006).

## 2.7 Electrokinetic remediation

This technique is the transmission of low-intensity direct current into the subsurface of the soil to remediate contaminated soil. The efficiency depends on the pH, water content and the conductivity of the soil. This method is generally used for inorganic and radionuclides contaminants and a small number organic compounds (Chang and Liao, 2005). Electrokinetic remediation is achieved through electroosmosis (mass flux of fluids under an electric field), electromigration, electrophoresis (charged colloids in fluid moving towards the opposite-charge electrode) and diffusion (transport of chemicals due to concentration differences) in a contaminated soil (Hamberg, 2009). The process mobilises charged species to move towards the ceramic electrodes, which are divided into cathode array and anode array. The removal of contaminants at the electrode may be accomplished by several means, among which are electroplating at the electrode, precipitation or co-precipitation at the electrode, pumping of water near the electrode or complexing with ion-exchange resin (Hamberg, 2009). Negative impact to the environment was observed in the population of the soil bacteria and soil properties; an increase in the soil temperature altered viscosity of water, and the contaminant inhibited revegetation due to increase in the phytotoxicity of Cu and Cd after treatment of soil (Hamberg, 2009).

## 2.8 Stabilisation/solidification

Stabilisation immobilises contaminants by making them less soluble and converting them to less toxic forms through adsorption, precipitation or complex binding with immobilisation agents added to the soil (Kumpiene *et al*., 2007; Hamberg, 2009). Chen *et al*. (2003) used phosphate-based-additive to immobilise lead contaminants in the soil with improvement in the removal efficiency in acidic conditions. Other immobilising agents are limes, peat, manure and synthetics based industrial co-products (Guo *et al*., 2006).

Stabilisation/solidification could be used as a treatment in both asphalt batching and vitrification for organic contaminants and inorganic contaminants by encapsulating the contaminant in a monolithic soil of high structural integrity (Khan *et al*., 2004). The effectiveness of the processes of stabilisation/solidification of organic compounds in cement matrices (with or without additional sorbents) depends significantly on the possibilities of their physical immobilisation. The processes of stabilisation/solidification of contaminated ground can be performed *in situ* – in the place where the pollution occurred – or *ex situ*, e.g. in a waste-neutralising plant. The solidification of waste with hydraulic binders requires mechanical mixing in order to distribute them throughout the whole volume of waste and to dilute them with water. Such a process creates (in the case of processing waste contaminated with aromatic hydrocarbons) a risk of releasing vapours of volatile organic compounds. This especially concerns the stage of material homogenisation, as well as initialising the hydration process through introduction of diluting water (Banaszkiewicz and Marcinkowski, 2014). Some limitations associated with this technique are depth of contaminant and that organic contaminants are not usually immobilised unless destroyed at high temperature (Khan *et al*., 2004). A study by Harbottle *et al*. (2007) shows that future land use and vegetation of the soil may be a hindrance when a solidification technique is used.

## 2.9 Natural attenuation

This is a natural process (physical, chemical and biological) of remediating a contaminated soil under favourable conditions, and it is a low-cost process (Mulligan and Yong, 2004). Naturally occurring processes are allowed to clean up contamination of the soil, and the process is influenced by hydrological changes over the given period of cleaning up. It is totally weather-dependent and the period of remediation may be very long, depending on the toxicity of the soil contaminant and the rate of degradation, sorption, volatilisation, radioactivity decay, diffusion and dilution (Mulligan and Yong, 2004; Ebuehi *et al*., 2005). Microbial metabolism and enzymatic activities target the pollutants in the land and transform them into less toxic compounds over a period of time with some hydrocarbon-degrading microorganisms (Aislabie *et al*., 2004; Smet and Pritchard, 2003). The chief driving power in natural attenuation is the microbial reactions with the synthetic and biogenic organic contaminants and the inorganic (metal) contaminants, which must be monitored to ensure the remediation goal is being achieved (Smet and Pritchard, 2003). The major setbacks are the longer life-cycle potential to reach set goals, that the detailed characterisation of the site to demonstrate the efficiency of the technique might be costly, the changing of hydrological condition, and that it might require other remediation technology to achieve goals.

## 2.10 Pyrolysis

Pyrolysis is the thermal technology for decomposition of organic matter (in the absence of oxygen or inert atmosphere) into liquid, gases and char (Mohan *et al*., 2006; Bridgwater, 2000). Pyrolysis is a technology that could be applied to extract thermally intact organic molecules or to crack large molecules from complex matrices, while cracking of the large organic molecule may form other by-products (White *et al*., 2004).

Pyrolysis technology has been grouped into slow, fast and the flash pyrolysis techniques which depend on the particle size heating rate, temperature and residence time before the innovate technology of microwave heating for the pyrolysis of samples is employed (Robinson *et al*., 2012). Pyrolysis has been used to convert agricultural, food, biofuel and forest residues into valuable products and led to prevention of the production of materials that are potentially harmful to the environment, e.g. surface and groundwater pollution, biohazards, foul odours and greenhouse gases such as methane (Marshall, 2013).

The primary clean-up pyrolytic systems are destruction and removal. Destruction occurs when the organic materials are broken down into lower molecular weight compounds, while removal is desorption of the contaminant from the material  without being destroyed. The pyrolysis system generally brings forth solid, fluid and gaseous products. The solid products include the treated soil and the carbon residue from the hydrocarbon decomposition. The liquid streams are organic materials that are stable liquid from the decomposed parent organic contaminant and possibly streams of processed water. The gas pyrolysates contain light hydrocarbon such as methane, carbon dioxide, carbon monoxide, steam, butane, pentane and other light hydrocarbons that exist as a gas at room temperature. The gas could be used as a feedstock for the production of syngas. Besides, the gas could be used as a source of renewable energy for combined heat and power generation as an alternative to reduce the demand for fossil fuel (Paethanom *et al*., 2013).

Pyrolysis has been used to remove pentachlorophenol (PCP) from a sandy soil in Taiwan, and the experiment shows significant removal of about 90% of PCP (Thuan *et al*., 2013). Shen and Zhang (2003) carried out oil recovery from sewage sludge by low temperature pyrolysis in a fluidised-bed, and the experiment shows that higher temperature and longer residence time will improve the quantity of oil removed from the sewage sludge, which is similar to the earlier observation of Brigdwater *et al*. (1999). Microwave pyrolysis was used to reclaim raw material more economically than conventional pyrolysis (the cost of energy consuming preliminary drying of the organic waste that contains 70–80% moisture was reduced) to give maximum oil yield from the sewage sludge (Bohlmann, 1999).

A pyrolysis process is favoured for this task because it is a thermal technology, which gives a higher efficacy in taking out and degrading organic pollutants in the territory. It provides the advantages of a treatment temperature that is superior to pollutant vaporisation temperature. Accordingly, the crude oil in this case undergoes phase transformation to gas leaving behind the solid matrix of soil (Cocarta *et al*. 2014). The main advantages are that it requires a short time, there is certainty about the uniformity of treatment and the pyrolysis process is an endothermic one; nevertheless, the released hydrocarbon from the soil can be used to generate heat within the process depending on the quantity of hydrocarbon present (Cocarta *et al*. 2014). Previous work on the advantage of scaling-up of the laboratory single-mode microwave pyrolysis process was successful and highlighted the heavy advantage over conventional pyrolysis (Robinson *et al*., 2012). The scale-up batch processes (fixed and stirred) were performed at the same microwave power input with the laboratory single-mode cavity (1.5 kW) but with a longer treatment. The laboratory single-mode system removed 65% of hydrocarbon while the fixed bed removed 30–50%, and 85–95% was removed by the stirred bed system because the penetration depth limitation of the fixed system was overcome. The stirred batch system product yield (95%) was higher than the 70% yield from conventional pyrolysis performed by Bridgwater *et al*. (1999).

## 2.11 Techno-economic analysis of remediation techniques

Techno-economic analysis is an important aspect of the remediation process. It assists in making effective project decisions in order to achieve project objectives. Some of the key aspects of this analysis are:

1.) Identification of project: The project to be embarked on must be clearly defined and the stakeholders with vested interest in the remediation processes must be known. For example, this current research is a project on cleaning crude-oil-polluted soils in the Niger Delta region of Nigeria, which covers many towns, villages and creeks.

2.) Potential demands: The stakeholders will surely have potential demands that the remediation process must satisfy. These demands could be a preference for a solution, based on removing material from the site due to concerns over residual liabilities. Such demands will definitely affect the duration, feasibility or completeness of on-site technology. In addition, the demand may be a quick fix with a very short time frame due to stakeholders' interest in using the land for the construction of social amenities of economic benefit to the society, such as shopping malls.

3.) Selection of optimal technology: Selection of technology is a key factor in an effective remediation solution. Some of the things to consider in selecting effective technology are risk management, technical practicability, feasibility, cost/benefit ratio and the wider environmental, social and economic impacts. Under this heading, the stakeholders' view cannot be overemphasised. Some of the key stakeholders that influence the optimal technology for remediating affected areas are landowners, regulatory authorities, planning authorities, financial community, local pressure groups, site users, contractors, workers and visitors.

    In practical terms, the major stakeholders are the landowners, the sponsors, the regulator and the service providers. Therefore, the stakeholders' perspectives, priorities, concerns and ambitions regarding a site must be well understood and defined before selection of the technology of choice.

In this research, the project of interest is the cleaning of acres of land spreading across many towns, villages, and creeks in the Niger Delta region of Nigeria. In Section 1.2 of this report, highlights on the challenges faced by the community were mentioned as was the demand for a clean-up of the area. Some of the challenges mentioned are loss of farmlands, which is a means of livelihood for those who depend solely on agriculture, and severe ecosystem degradation, which results in various diseases and health disorders. The situations have great influence on the perspective of the stakeholders and their demand. The immediate community may be interested only in the end results of the site rather than the actual process – a cleaner land than was required by the regulator. The regulator's interest may solely be on compliance with acceptable environmental quality standards. The sponsor would be interested in the return on investment and ensuring that the prevailing state of the economy is in a position to absorb the output of the project. The service provider (the company to execute the project) employ their expertise to deliver results that optimally meet the demand of all parties. The technology chosen by the service provider should translate the landowners' need into action that delivers the project on time, within budget, to a specified quality and within regulatory constraints.

This research explores the possible processes considered by service providers making pyrolysis a method of choice for the Niger Delta soil remediation from heavy oil pollution. The initial approach is to obtain information on all the possible technologies. An overview of these technologies is presented in Table 2-2. The selection of the best technology to use would be based on the underlying principles that it will be able to meet the challenges of the ecosystem and the interests of stakeholders. The duration of the possible remediation technology will be considered as shown in Table 2-3 (FRTR, 2007; CIRIA, 2004; Nathanail *et al*., 2007). The next step is the consideration of cost-effectiveness, project risk and lifespan impacts as shown in Table 2-5. The information presented in the tables is the results of a survey by CL:AIRE (2010). The cost-effectiveness of the remediation techniques is based on analysis of the cost from the survey using the cost guide and variability band in Table 2-4.

Table 2-2. Summary of remediation technologies (Bardos *et al*., 2000; Nathanail *et al*., 2001)

| Technology | Description | Type |
|---|---|---|
| Biopiles | Excavated soil is built into a heap within which is a network of perforated pipes to aerate the soil. | Bio |

| | | |
|---|---|---|
| Bioreactors | Soil (dry or slurried) is treated in an enclosed reaction vessel to which nutrients, air water and microbes are added as necessary. Bioreactors are also used to treat groundwater. | Bio |
| Biological treatment beds | Shallow cultivation, where contaminated soil is cultivated in a contained treatment bed on a specially prepared area of a contaminated site. | Bio |
| Chemically enhanced soil washing | Physical processes are integrated with chemical processes such as leaching or extraction. | Chem/Phys |
| Chemical leaching/ Chemical extraction | Transfer of contaminants from the soil into an aqueous solution. The soil is dewatered and the aqueous solution plus contaminants is further processed. | Chem |
| Incineration | High-temperature destruction of contaminants (e.g. in rotary kiln incinerators or fluidised bed systems). Main pre-treatment is to obtain suitable particle size. Thermal desorption occurs during incineration. An *ex situ* process. | Thermal |
| Soil washing | Primarily a physical technique involving size separation and washing of contaminants using aqueous-based solutions. | Phys |
| Solvent extraction | Uses non-aqueous solvent to transfer contaminants from soil into solution. | Chem |
| Stabilisation/Solidification | Mixing of chemical agents into the soil to solidify the ground or otherwise reduce mobility of contaminants. | S/S |
| Thermal desorption by combustion of organics in vapour phase | Two-stage process comprising low-temperature transfer of contaminants from soil to vapour phase via volatilisation followed by destruction or removal of contaminants from gas stream. *Ex situ* process needs extensive pre-treatment e.g. screening, de-watering, neutralisation, blending. Partial combustion often occurs during the process. | Thermal |
| Thermal desorption by condensation | Heating of soil to volatilise volatile metals (so far principally mercury), which is then condensed from exhaust gases downstream. | Thermal |
| Vitrification | Excavation of soil and transportation to a (usually off-site) facility. Soil plus other materials used for glass making (silica, fusing agents) are placed in a smelter, which heats to about 1500ºC. Molten material is continuously removed and cooled to produce granular solids or monolithic mass. | S/S & Thermal |
| Windrow turning | Piles of contaminated soil often mixed with organic materials such as bark are turned on a regular basis to aerate the soil and improve the soil structure. | Bio |
| Bioremediation | Remediation by altering *in situ* conditions, typically by *in situ* flushing (see below) to optimise the biodegradation rate. Examples include the addition of nutrients, oxygen, etc. | Bio |
| Biosparging/Air sparging | Injecting air (or other gases) into the saturated zone to strip volatile contaminants and/or stimulate biodegradation. The latter process is often termed “biosparging”. | Bio/Phys-chem |
| Bioslurping | Multiphase extraction of groundwater, free-phase contamination and soil gas to achieve bulk contaminant removal and supply oxygen for enhanced biodegradation. | Bio-phys |

| | | |
|---|---|---|
| Bioventing | Movement of air or other gases through soil to stimulate biological destruction of contaminants, possibly in combination with their removal in the gas phase (c.f., soil vapour extraction). | Bio-phys |
| Chemical destruction | Use of highly reactive reagents to convert contamination to environmentally acceptable end-products *in situ*. An example is the use of Fenton’s reagent (iron-catalysed hydrogen peroxide). | Chem |
| Electro-remediation | Use of electric fields to move or contain contaminants. | Phys-chem |
| Flushing | Enhanced pump and treat to remove contaminants, for example addition of surfactants or solvents to re-circulated water. | Phys-chem |
| Hydrofracture | Hydraulic or pneumatic techniques to induce fracturing of subsurface zones to increase permeability for other remediation treatments. | Phys |
| *In situ* heating | Use of steam or microwaves (radio-frequency heating) to heat the soil, for example to increase the range of contaminants recoverable by soil vapour extraction. | Thermal |
| Land farming | Cultivation of surface soils (typically the top 50cm) to stimulate biodegradation. Usually includes the addition of various amendments (e.g., fertiliser) - unlikely to easily find regulatory approval under current circumstances. | Bio |
| Natural attenuation | Monitored use of naturally occurring *in situ* processes to remediate contamination without enhancement. Often and more accurately called monitored natural attenuation (MNA). | Bio,<br>Phys & Chem |
| Permeable reactive barriers | A single or combination of biological, chemical or physical process(es) in a specific portion of the subsurface that treats a carrier as it passes through but does not unacceptably impede flow. | Bio/ Chem/Phys |
| Phyto-remediation | Use of plants to recover contaminants and/or stimulate *in situ* biodegradation/stabilisation. | Bio |
| Soil vapour extraction (SVE) | Movement of air or other gas through unsaturated soil to remove contaminants through enhanced volatilisation. Sometimes called “venting “or “stripping”. | Phys |

*Note: Bio – biological process, Chem – checmical process, Phy – physical process, Thermal – exploitation of physical and chemical processes at elevated temperature.*

Table 2-3. Remediation technology and timescale (FRTR, 2007; CIRIA, 2004; Nathanail *et al*., 2007)

| Remedation technology | Timescale |
|---|---|
| 1. Chemical oxidation and reduction | <1 year |
| 2. Electro-remediation | 1–3 years |
| 3. Enhanced bioremediation | 0.5–3 years |
| 4. Flushing | 1–3 years |
| 5. Thermal treatment | <1 year |
| 6. Monitor natural attenuation | 1–30 years (Highly dependent on specific contaminant and remediation design) |
| 7. Phytoremediation | >10 years |
| 8. Sparging | 0.5–3 years |
| 9. Stabilisation/solidification | <1 year |
| 10. Venting | 1–3 years |
| 11. Vitrification | <1 years |

Table 2-4. Cost and variability guide for selection of appropriate remediation technology (CL:AIRE, 2010).

| **Cost band (£/m$^3$)** | **Symbol** | **Variability band** | **Symbol** |
|---|---|---|---|
| 0 – 25 | £ | 0 – 10 (low or well constrained) | V |
| 25 – 60 | ££ | 10 – 40 | VV |
| 60 - 100 | £££ | 40 – 80 | VVV |
| >100 | ££££ | >80 | VVVV |

Table 2-5. Cost, variability, life span, project risk and impact of remediation technology for < $5000m^3$ and >$5000m^3$ polluted soils. (CL:AIRE, 2010)

| Remediation Technique | Cost Guide | Variability Band | Direct Costs | | Life Span / Project Risks | |
|---|---|---|---|---|---|---|
| | | | Definition Criteria | Impacts (Pros/Cons) | Definition Criteria | Impacts (Pros/Cons) |
| ***In Situ* Remediation Techniques** | | | | | | |
| In Situ Chemical Oxidation <$5000m^3$ | ££ | VVVV | Plant/mobilisation + installation costs, Operation & maintenance costs, including sampling, verification and personnel time (duration dependent) | Pro: Low, Con: Timescales strongly dependent on *in situ* application success. Can be difficult to set into a fixed project plan. Consequently, costs coupled to time. | Robustness/ Durability, with respect to changing conditions (i.e. climate change). Outcome success | Pro: Quick reactions for an *in situ* technique, although often a longer requirement to monitor/re-inject/revisit. Cons: - As a contact-dependent remediation technique, proving an effective method of delivery is a significant risk. Frequently used with chlorinated solvents where partial degradation product can be more toxic and is a considerable risk. |
| In Situ Chemical Oxidation >$5000m^3$ | ££ | VV | | | | |
| In Situ Enhanced Bioremediation <$5000m^3$ | ££ | VV | | Pro: Low–Moderate, Con: Timescales strongly dependent on *in situ* application success. Can be difficult to set into a definite project plan. Accordingly, cost of the project depends upon time. | | Con: Relatively slow technique which may involve long-term monitoring and possibly re-injections as required. Cons: - As a contact-dependent remediation technique, significant reliance and risk lies with providing effective contact.<br>- Frequently used with chlorinated solvents where partial degradation products can be more toxic and pose a considerable risk. |
| In Situ Enhanced Bioremediation >$5000m^3$ | ££ | VV | | | | |

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|---|---|---|---|---|
| In Situ Flushing <5000m$^3$ | ££ | VVV | Con: Low–Moderate. Plant and headworks required. Pro: Dependent on whether used as a temporary pathway management solution or a long-term source-removal technique. | Con: Dependent upon expectations, i.e. can be very successful as a management method where complete contaminant removal is not the required outcome. |
| In Situ Flushing >5000m$^3$ | ££ | VV |  |  |
| In Situ Thermal Treatment <5000m$^3$ | £££ | VV | Pro: Moderate–High, Relatively quick with no chemical costs.<br>Con: Significant energy costs. This is traded off against not requiring treatment for as long as a non-heated equivalent (e.g. cold soil vapour extraction). | Pro: Reported potential % organic pollutant removal is very high.<br>Con: The heating effect for some techniques may bypass zones of reduced permeability. Incomplete removal of sources may result in elevated groundwater concentrations. |
| In Situ Thermal Treatment >5000m$^3$ | ££ | VVV |  |  |
| Monitored Natural Attenuation (MNA) <5000m$^3$ | £ | V | Pro: Low. Site investigation and monitoring boreholes required. Low. Monitoring costs, verification. | Con: Subsurface conditions may change, affecting progress and, at worst case, could lead to the release of adsorbed or absorbed contaminants. Risk of contamination reaching receptor before natural attenuation is complete. |
| Monitored Natural Attenuation (MNA) >5000m$^3$ | £ | V |  |  |
| In Situ Sparging <5000m$^3$ | ££ | VV |  | Pro: Within its operational performance range, a relatively |

| | | | | |
|---|---|---|---|---|
| In Situ Sparging >5000m$^3$ | £ | VV | Con: Moderate, but typically a relatively quick technique | robust process with remediation outcomes of extraction, dispersal or destruction.<br>Con: Possible rebound of contamination 6–12 months after system shutdown. |
| In Situ Solidification/Stabilisation <5000m$^3$ | £££ | VVVV | Con: Batching plant required. May require long-term monitoring.<br>Pro: Relatively quick process (weeks to months for curing). | Cons: - Long-term performance concerns have been raised due to the relatively little long-term leachate data available. More extreme climatic conditions brought about by climate change could increase the weathering process and therefore leachability of the final stabilised product. |
| In Situ Solidification/Stabilisation >5000m$^3$ | ££ | VV | | |
| In Situ Venting <5000m$^3$ | ££ | VVV | Con: Low–Moderate,<br>Con: Impacts if using petrol/diesel generator to power pumps/plant | Cons: - Soil venting and SVE actively encourage volatilisation of VOCs. Creation of negative pressure through vacuum pump and vapour treatment mitigation. Off-gassing particularly liable when bioventing through air injection without air extraction. |
| In Situ Venting >5000m$^3$ | ££ | VV | | |
| ***Ex Situ Remediation Technique*** | | | | |

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| *Ex Situ* Biological Treatment <5000m$^3$ | ££ | VV |  | Pro: Low. Tenting is commonly used to control ambient conditions and collect off-gas. Con: Excavation and *ex situ* management costs. Con: Excluding bioreactors, timescales are typically relatively long. Can be difficult to set into a fixed project plan. Consequently, cost might increase with time. | Con: Relatively slow technique which may involve long-term treatment and monitoring. Cons: - Feasibility/pilot trials usually necessary to test conditions on targeted contaminants. - Process may be self-limiting for some contamination problems (see 'Robustness/Durability'), and there is always the likelihood of residual contamination. |
| *Ex Situ* Biological Treatment >5000m$^3$ | £ | VV |  |  |  |
| *Ex Situ* Chemical Oxidation & Reduction <5000m$^3$ | ££ | VV |  | Pro: Timescales likely to be quicker and more dependable than *in situ* equivalent as more thorough control can be exerted. Con: Moderate. Excavation and *ex situ* management costs. | Pro: Quick reactions and as a contact-dependent technique more controllable in an *ex situ* environment than would be the case *in situ*.<br>Con: Frequently used with chlorinated solvents where partial degradation products can be more toxic and is a risk. |
| *Ex Situ* Chemical Oxidation & Reduction >5000m$^3$ | ££ | VVV |  |  |  |
| Soil Washing & Separation Processes <5000m$^3$ | ££ | VVV |  | Pro: Given sufficient volumes, this can work out economically per treated unit volume. Con: Significant. Requires constant monitoring, adjustment and feedstock control. Con: High. Often uneconomic to mobilise | Pro: With sufficient volumes to treat and a pragmatic view on residually contaminated volumes, soil washing can achieve quick and significant throughput of treated soils. Cons: - Efficacy is strongly dependent upon soil type and the nature of the contamination so laboratory treatment trials are usually necessary. |
| Soil Washing & Separation Processes >5000m$^3$ | ££ | VV |  |  |  |

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|---|---|---|---|---|
| | | | for small volumes on site. Excavation and *ex situ* management costs. | - Concentrated material will require secondary treatment or waste disposal. |
| *Ex Situ* Stabilisation/ Solidification (S/S) <5000m$^3$ | ££ | VV | Pro: Relatively quick process (weeks to months for curing). Con: Moderate. Batching plant required. | Cons: - Long-term performance concerns have been raised due to the relatively little long-term leachate data available.<br>- More extreme climatic conditions brought about by climate change could increase the weathering process and therefore leachability of the final stabilised product. |
| *Ex Situ* Stabilisation/ Solidification (S/S) >5000m$^3$ | ££ | VV | | |
| *Ex Situ* Thermal Treatment <5000m$^3$ | ££££ | VVVV | Con: High. Often uneconomic to mobilise for small volumes on site. Excavation and *ex situ* management costs. Con: Very significant energy costs. Also high | Pro: Generally very effective for all organic contaminants.<br>Con: Less effective for fine-grained materials, this may still require further treatment/disposal. Pros: - Can achieve quick and significant throughput of treated soils. Can |

| | | | | |
|---|---|---|---|---|
| *Ex Situ* Thermal Treatment >5000m$^3$ | ££ | V | maintenance in terms of personnel on site. Pro: Given sufficiently high volumes, can work out cost-effectively per treated unit volume – particularly for recalcitrant organic contaminants. | sometimes be the only process available for most challenging and recalcitrant compounds.<br>- Generally a comprehensive option when used with appropriate contaminants.<br>Cons: - Efficacy is strongly dependent upon soil type and the nature of the contamination so pilot trials are usually necessary. May require secondary treatment or waste disposal. |
| *Ex Situ* Venting <5000m$^3$ | ££ | VV | Pro: Regular monitoring required. Cons: - Low – Moderate<br>- Excavation and *ex situ* management costs. | Pro: Within its operational performance range, a relatively robust process with remediation outcomes of extraction, dispersal or destruction. Pro: Within its operational performance range, a relatively robust process with remediation outcomes of extraction, dispersal or destruction.<br>Cons: - Air-flow dependent and a heterogeneous matrix are ideal for even coverage. Can be enhanced through re-working soil (improve effective permeability) or thermal enhancement. |
| *Ex Situ* Venting >5000m$^3$ | £ | VV | | |

The cost and variability band is a guide developed from the analysis of the survey to give cost value range and variation based on standard deviation, calculated for the minimum and maximum values provided for each technique. These costs and variation band ranges, and the mid-point of this range were compared against the four variability bands. The variability band demonstrated how well the cost data is constrained and the degree of confidence in the cost provided. By using the tables above, the service provider would be able to select an optimal technology to meet the requirement of all stakeholders.

Owing to the cost and variability presented in Table 2-5, MNA has the lowest cost (0–25 £/m$^3$) and variability band (0–10) within the range of treatment areas used for comparison. The closest to this technique is *ex situ* thermal treatment (25–60 £/m$^3$) with variability band (0–10) for land mass of > 5000m$^3$. This guide suggests that the best choice of technology to use will be either of these two methods. Further consideration will now be based on the pros and cons of the two methods. The major difference is the timescale to achieve the desired results. MNA was suggested to take 1–30 years to complete, which means that the cost of the project may increase before the end of the agreed deadline, and this may delay the use of the land. In the case of Niger Delta remediation, it would not be an acceptable choice for the pressure groups of Ijaw and Ogoni people, as well as the federal government. Therefore, the technology to be considered for this project would be the *ex situ* thermal remediation technique, with a lifespan of less than 1 year.

In addition, subsurface conditions may change, thereby affecting the progress and, at worst case, it could lead to the release of adsorbed or absorbed contaminants, which would increase the risk of contamination reaching the receptor before natural attenuation is complete. Thermal remediation techniques have been shown to be very effective in removing organic pollutants from the soil within a short timescale. Although the thermal treatment method could be thermal desorption or a pyrolytic process, a decision has to be taken for the best option for the Niger Delta area.

The Niger Delta is a swamp rainforest zone with high annual rainfall; therefore, the moisture content of the soil would be high. This means there would be a need to pre-dry the soil before analysis. This is a huge setback to the conventional thermal treatment because it increases the cost of treatment. Nevertheless, this challenge has been overcome by the microwave pyrolytic remediation techniques. The microwave pyrolysis as mentioned above will make use of the water content to improve on the amount of organic contaminants removed. Therefore, the service provider would carry out laboratory and pilot scale tests of the method. Consequently, this research sets out to conduct a laboratory comparative study of thermal pyrolysis and microwave pyrolysis on soils provided by Shell Petroleum Development Company of Nigeria to examine whether the assumed moisture effect will affect removal efficiency of crude oil in the soil, and also to ascertain whether the resulting products would meet the demands of the stakeholders.

## 2.12 Summary

Remediation technologies have been reviewed with important details that could play a crucial role in decision making on the best technology to remediate contaminated soil. Contaminant source and type, the removal efficiency of technology, potential environmental impact and cost determines the choice of technology to effectively address most contaminated site problems. The techno-economic analysis of the remediation techniques has proven that thermal technology is the best approach to remediate the Niger Delta soil. Li’s (2007) study on remediation techniques for developing countries stated that 99.9% removal of contaminant is achievable with pyrolysis process within a short time compared to bioremediation techniques with a similar cost band (Table 2-5), but a definite project plan might be difficult to set out. Other remediation technologies with a similar cost band with *ex situ* thermal treatment have higher variability, which makes them unsuitable for the Niger Delta soil treatment.

Consequently, a detailed understanding of the pyrolysis process is essential to achieve the objective of this research. The research will elucidate on pyrolysis techniques in Chapter 3, using Gray-King as traditional thermal pyrolysis and microwave pyrolysis.

# Chapter 3: Pyrolysis Technology (principle and theory)

## 3.1 Scope

This chapter discusses in detail the underlining principles of pyrolysis technology, theory of Gray-King pyrolysis, microwave pyrolysis, and it provides a discussion on past soil treatment with pyrolysis technology.

## 3.2 Introduction

The principle of pyrolysis is derived from the Greek word “pyro” meaning fire and “lysis” meaning decomposition or breaking down into constituent parts (Suárez-Abelenda *et al*., 2011). Pyrolysis is the thermal technology for decomposition of organic matter in the absence of oxygen or inert atmosphere into liquid, gases and char (Mohan *et al*., 2006; Bridgwater, 2000). The principle could be described simply as a thermal technology to cleave bonds in the organic macromolecules. When the heat energy applied to the macromolecule is greater than the energy of specific bonds, these bonds will dissociate in a predictable and consistent manner. It is a thermal conversion system similar to gasification and incineration but strictly in the absence of an oxidising agent. It is a complex procedure and it consists of both concurrent and successive reactions when organic matter is heated in an inert atmosphere (Jahirul *et al.*, 2012). The rate of conversion and extent of decomposition of organic matter and product yields depends on the operating parameters of the pyrolysis process, such as operating temperature, heating rate and pressure and residence time (Gai *et al*., 2014; Agarwal *et al*., 2015). The configuration and operating condition of the pyrolysis process determines the reliability, performance, product consistency, product characteristics and scale-up, which requires close attention to obtain optimum or maximum product yield with minimal cost and environmental concerns (Mckendry, 2002). The operating conditions of the pyrolysis process have been used to categorise all conventional pyrolysis as follows: slow, fast and flash pyrolysis.

There are processes that occur during pyrolysis, such as heat transfer from the heat sources to increase the temperature of the target sample, or initiation of the primary reaction pathway to release volatiles and chars, followed by movement of the volatiles to the cooler region of the reactor to condense and react with unpyrolysed samples to increase the char yield and oil yield (an autocatalytic secondary reaction process taking place simultaneously with the primary reaction). An essential parameter is pyrolysis temperature as shown by Gai *et al.* (2014) on biochar adsorption of ammonium and nitrate. The experiment shows that the product yield is temperature dependent because the biochar yield and content of $N_2$, H and $O_2$ decreased, while ash, pH and carbon content increased as pyrolysis temperature increased from 400ºC to 700ºC.

In conclusion, the residence time/temperature/pressure profile of the pyrolysis process regulates the further reactions such as decomposition, reformation, water, gas shift reaction, radical recombination and dehydration (Mohan *et al*., 2006).

Over the years, treatment of organic contaminant in media such as soil, sediment and sewage with convention pyrolysis has been ongoing, but a newer microwave pyrolysis technology was developed to reduce the cost of production (no preliminary drying of soil or sewage prior to the experiment) and reduce residence time (Gomes *et al*., 2013). The microwave pyrolysis was developed to overcome some of the shortcomings of the conventional techniques and to improved product yield (Gomes *et al*., 2013). Microwave pyrolysis has a remarkably high heating rate, temperature distribution, and some interesting behaviours, such as large gas yield and higher syn-gas content (Fernández *et al*., 2010). The exterior of solid materials in conventional pyrolysis must be heated to elevate the temperature in order to initiate heat transfer to the target organic matter inside the material. The heating rate also depends on the nature of the material and the cavity of the microwave heating system, but the conventional heating system is the major influence on radiation, convection or conduction (Robinson *et al*., 2009). Details of the microwave heating technique will be discussed in Section 3.5.

## 3.3 Reviews on pyrolysis for contaminated soil

Conventional pyrolysis has been described as thermal treatment of organic materials in the absence of oxygen, which hinders combustion of organic materials. It is based on heating rate and mass transfer with a long residence time and a slow heating rate (Blackledge, 2006; Robinson *et al*., 2008).

Conventional pyrolysis has been used for the remediation of oil-contaminated soil (*Lee et al*., 1998; Falciglia *et al*., 2011). Advanced technology of combining hydrous pyrolysis oxidation with dynamic underground stripping has been utilised in industry to remediate contaminated soils and soil water. A study on the removal of PAH from soil samples, which involved the comparison of the pyrolysis process with other classical procedures, such as soxhlet and sonication, followed by GC-MS analysis was conducted and the results show that the highest recovery was obtained from the pyrolysis treatment. The pyrolysis treatment of soils contaminated with gas oil prove that the gas oil could be removed from the soil without changing appreciably from the original chemical composition (Buco *et al.*, 2005; Piña *et al.*, 2002).

Pyrolysis has been suggested as an environmentally acceptable method for the decontamination of contaminated soil (Pavel and Gavrilescu, 2008; Singh *et al.*, 2011). An adequate treatment time and temperature provides enough energy to desorb or crack the contaminant, which can be subsequently recovered by condensation. Pyrolysis of pyrene-contaminated soil was performed by Risoul *et al*. (2005) to show a 99% removal efficiency of pyrene from the polluted soil, along with generation of light gases such as $CH_4$, $C_2H_2$, $C_2H_4$, $C_2H_6$, CO and $CO_2$ . Similarly, soil contaminated with pentachlorophenol (PCP) used as wood preservative and herbicides has been pyrolysed by Thuan *et al*. (2013) at low temperature conditions between 250–400°C. The experimental result shows that over 80% of the PCP removal from the soil was achievable. Further work on conventional pyrolysis of organic pollutants such as polychlorinated biphenyls in soil confirms the efficiency of the technique for soil treatment with over 99% removal from experimental work of Corcarta *et al*. (2014).

Further work on contaminated soil with heavy hydrocarbon proves that pyrolysis treatment can reduced the total petroleum hydrocarbon content to a level below regulatory standard (typically <1% by weight) within three hours (Vidonish *et al*., 2015). Bulmău *et al.* (2008) did an evaluation of integrated time-temperature effect in pyrolysis using a rotary kiln reactor to remove cadmium (Cd) and lead (Pb). The pyrolysis process used three process temperatures such as 400°C, 600°C and 800°C with two holding times of 30 and 60 minutes for the experiment. The Cd concentration in the gas phase increased with process temperatures from 400–600°C, while no appreciable increase was observed with Pb until the process time reached 800°C for 60-min retention time when a dramatic change was noticed. At 800°C with a different retention time, only Cd (78% at 30 and 86% at 60 min) had comparable removing efficiencies, while 14% of Pb was removed just after 60-min holding time. The experiment shows that rotary kiln pyrolysis of contaminated soil is possible and treatment of metal-contaminated soil requires a fuel gas cleaning system to recover the contaminant from the gas pyrolysis.

However, the conventional pyrolysis technologies have some disadvantages such as:

1 The technology requires drying of soil to achieve a low soil moisture content (<1%) prior to pyrolysis to reduce cost.

2 There is a temperature gradient that occurs between the outer substrate of the material and the centre of the substrate due to the process of heat transfer (conduction and convention) in the material (Robinson *et al*., 2009).

The steps to overcome some of the challenges faced by conventional pyrolysis were considered in the development of new innovative microwave pyrolysis of soil. Microwave heating has been in use for over 50 years in a variety of applications (Oghbaei and Mirzaee, 2010). The microwave heating system provides a rapid and energy-efficient heating process compared to conventional pyrolysis because it does not require the sample to be dry before processing, and the heating system has properties of rapid, selective and simultaneous (volumetric) heating to overcome the challenge of temperature gradients (Hahn and Ozisik, 2012). Microwave heating depends on the ability of the soil to absorb high-frequency electromagnetic energy and turn it into heat so as to pyrolyse organic contaminated soil (Yuan *et al*., 2006; Chandrasekaran, 2012).

Robinson *et al.* (2009) applied a continuous microwave process to drill cutting for removal of residual oil below the environmental discharge threshold (1%) to show that it is capable of higher levels of remediation. The use of microwave heating as a method of thermal remediation has been employed by Abramovitch *et al.* (1998, 1999) on soil contaminated with polycyclic aromatic hydrocarbon and polychlorobiphenyl with the addition of NaOH in company with $Cu_2O$ (powdered aluminium metal wire, etc.) to serve as microwave absorber and catalyst. George *et al.* (1992) reported removal efficiencies of nearly 100%, with 40wt% carbon particles to enhance the microwave treatment of the simulated API (American Petroleum Institute) separator sludge. Recently, Li *et al.* (2009) reported a similar study with carbon fibre as a strong and microwave absorber to remove oil as a soil contaminant. The outcome of the research showed that 94% recovery of the oil contaminant is possible with no obvious change in soil composition. It suggested that 0.1% carbon fibre could be utilised to enhance microwave treatment within four minutes to achieve 99% oil removal if experimental conditions are corrected.

A microwave generator capacity of 2kw was used as an *in situ* supply of microwaves for field studies at a frequency of 2450MHz. The result established that it is a cost-effective and time-efficient technology to promote volatilisation of contaminants out of the soil directly. The remediation result is reliable, and the personal exposure is minimal (Chien, 2012; Robinson *et al.*, 2012).

Shang *et al*. (2005) experimented on oil-contaminated drill cutting and established that microwave heating was a good technique for removal of oil from the drill cutting to a level below 1% of the environmental discharge limit. It was discovered that the microwave power, treatment time and sample mass govern the quantity of oil removed from the drill cutting. The flow rate of gas helps to improve the mass transfer and create an inert atmosphere. This work further emphasised the influence of water for maximum oil removal. The experiments suggested that the single-mode cavities (details in 3.5.4.3 (A)) are more effective than multimode cavities for achieving low residual oil yield, and this is because it supplies a higher electric field within a short time frame. The single-mode cavity uses lower energy inputs to achieve low residual oil unlike the multimode cavity. This information informed decision to apply a single-mode cavity for this study. The single-mode cavity is also useful for a laboratory scale experiment because it could be utilised to handle small sample sizes as related to this current experiment which is employing a small-size laboratory sample.

It was reported that microwave pyrolysis of soil contaminated with heavy and light hydrocarbon has been successful with 95%+ of the polycyclic aromatic hydrocarbons removed under moderate processing conditions (Robinson *et al*., 2009). Unlike medium to heavy hydrocarbon in contaminated soil that could not be removed by a thermal desorption technique (Khan *et al*., 2004).

## 3.4 Gray-King pyrolysis

Gray-King pyrolysis is a fixed-bed pyrolysis technology that has bene used for coal pyrolysis for many years. According to the operating temperature, it is a destructive technique and could result in the thermal breakdown of the coal composition (Davis and Galloway, 1928; Adeleke *et al.*, 2007; Akpabio *et al*., 2008). Gray-King pyrolysis thermally decomposes coal into coke, liquids and a gaseous state. The yield of the oil and gas depends on the control of heat used in the pyrolysis process (Davis and Galloway, 1928). Like other pyrolysis processes, some of the volatile matter that evolves as a consequence of the thermal decomposition of coal moves towards the coolest part of the rig where it condenses to form tar, while the incondensable fraction that remains forms part of the primary gas flow.

Gray-King pyrolysis has never been used for petroleum-contaminated soil before, but like coal, the hydrocarbon contents will undergo a phase change to liquid and gas, leaving behind the solid residue of the soil (Bulmãu *et al.*, 2014). The gas streams from the pyrolysis process of coal and crude oil is similar, but there might be variations in concentration due to the formation process of the coal and the petroleum. Gas pyrolysate's major constituents are hydrogen, methane, carbon dioxide, carbon monoxide, hydrocarbons, incondensable liquid pyrolysate, water vapours, nitrogen, ammonia and hydrogen sulphide (Adeleke *et al.*, 2007). Uniform heating of the process with a steady rate at the varying temperatures has been demonstrated with coal - both gas flow direction control and heat transfer enhancement. The response of the coal is expected to be similar to crude oil because of their chemical properties, where tar yield was 80.5% to 90.3% from 900 ºC to 1100ºC (Zhang *et al.*, 2014). This suggests that Gray-King pyrolysis has potential to remediate a hydrocarbon-contaminated soil.

The pyrolysis process uses an electric furnace to heat the soil sample in the Gray-King retort tube. The pyrolysis process has accurate mass balance in that all the pyrolysate from the process can be accounted for (solid, liquid and gas products). The pyrolysate gas can be collected with a sample gas bag, while the liquid is condensed with the ice-water condenser at the cold end of the pyrolysis reactor. The solid matrix of the soil can be obtained from the Gray-King tube.

The furnace temperature is applied to describe the operation, whether it is a high-temperature pyrolysis process or low-temperature pyrolysis process. The process was applied to this task because of the easy-to-control sample size, uniform treatment of the contaminated soil, residence time and the accurate mass balance of the pyrolysate. Details of this step-by-step pyrolysis process can be found in Section 4.9.

## 3.5 Microwave pyrolysis

Temperature gradient and thermal diffusivity are phenomens controlled by the conductivity, radiation and convection properties of the materials, which determines the rate of heat transfer in materials from the surface to the internal region (Hahn and Ozisik, 2012). The rate of heat flow from the surface of a material to the internal region is therefore a function of the thermal conductivity, density and specific heat capacity of the material. The rate of heat transfer in a material depends on whether the materials have high thermal diffusivity (heat moves rapidly in materials) or low thermal diffusivity (slow movement). Thus, the conventional process would be slow and high-energy consuming, especially when non-conducting or insulating materials are to be stirred up. Other reported disadvantages of conventional heating are poor product quality, inadequate process control and environmental pollution (Chandra, 2011).

Microwave heating is an energy-efficient method of rapidly heating material (low-energy consumption) and provides the desired short time processing. It has high penetration depth coupled with volumetric heating that generates heat throughout the mass of material rapidly due to complete interaction between microwave absorbers (water molecules) in the soil. The microwave heating technology delivers high efficiency in converting electricity to electromagnetic energy to overcome limitations of conventional heating processes. This is imputable to the high efficiency of magnetrons (86% at 900MHz and 80% at 2450MHz), which generates microwave energy to heat up the matrix. Consequently, the heated matrix serves as the source of heat to the analyte, without the need for conventional or thermodynamic heating of materials (Mehdizadeh, 2010).

Volumetric, selective, rapid, controlled and uniform heating is an important feature of microwave energy enabling it to instantaneously deliver heat to the whole material directly, and this distinguishes microwave heating from conventional heating (Guo *et al.*, 2010; Menezes *et al.*, 2007; Mehdizadeh, 2010). It requires less time to achieve the desired process temperature in solid or semi-solid materials when compared with conventional heating dependence on a slow thermal diffusion process.

### 3.5.1 Microwave heating mechanism

Microwave heating is the utilisation of electromagnetic waves of specific frequencies to generate heat in a material (Metaxas, 1996; Metaxas and Meredith, 1988). Electromagnetic waves can travel through an empty space or matter transversely with an associated velocity equal to the velocity of light (Meredith, 1998). They have all the waves’ properties such as reflection, refraction, interference, diffraction and absorption.

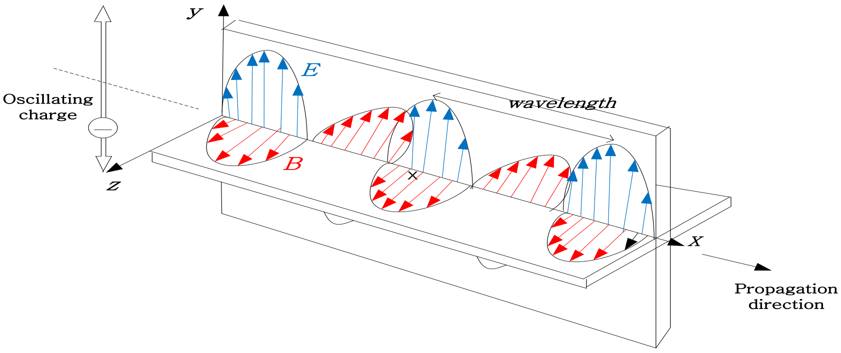


Figure 3-1: Perpendicular oscillations of electric and magnetic fields in electromagnetic waves – E-electric field and B-magnetic field (Chan and Reader, 2000).

$c=\lambda f$ Equation 3-1

Where c= velocity, f= frequency λ= wavelength

Figure 3-1 shows the orthogonal oscillation of magnetic and electric fields during the propagation of electromagnetic waves. They are vectors and aer always perpendicular to each other. The maximum speed that electromagnetic energy can travel (speed of approximately 3.0 x 108m/s) during propagation in free space is associated with the frequency and wavelength in Equation 3-1.

Microwaves are a non-ionising form of electromagnetic energy lying between the radio and infrared region in the electromagnetic spectrum and within the frequency range of 300MHz to 300GHz, with corresponding wavelengths ranging from 1m to 1mm respectively (Thostenson and Chou, 1999). The microwave has the following properties:

1. It can merely be transmitted by photons (particles) which exhibit wave-corpuscle duality.

2. It propagates at the speed of light.

3. It is not affected by empty space when the microwave is propagated.

4. The wavelength is inversely proportional to the frequency.

Though the microwave frequency ranges from 300MHz to 300GHz, the government restricted the frequency range to constricted frequencies for domestic, industrial and medical usage. It is imperative to restrict the microwave heating frequency band for industrial, scientific and medical (ISM) frequencies so as to avoid interference with telecommunications and cellular phone frequencies. These frequencies differ marginally in some states. The regulatory agencies in different countries strictly abide by the international table of frequency allocations designed by the International Telecommunication Union (ITU) for the allocation of certain frequencies for industrial, scientific and medical determinations. For example, 896MHz is used in the United Kingdom while 915MHz is utilised in the United States for industrial heating applications (Metaxas and Meredith, 1983).

Heating with microwaves involves two mechanisms primarily: dielectric and ionic. For dielectric heating of material to take place, water in materials such as mineral, food or clay samples is often the primary component responsible for dielectric heating. The water molecules have a dipolar nature, which follows the electric field associated with the electromagnetic radiation to oscillate at very high frequencies as listed in Table 3-1. The oscillation results in the production of heat employed in the microwave processing of material. The other ionic mechanism requires oscillatory migration of ions in the materials that generate high temperature below the influence of the oscillating electric field. At a particular location in the material, the charge per unit of heat generated per volume can be defined as (Datta and Anantheswaran, 2000):

$$Q = 2\pi f \mathcal{E}_o \mathcal{E}'' E^2 \qquad \text{Equation 3-2}$$

Where $E$ is the strength of the electric field of the wave at that location, f is the frequency of microwave shown in Table 3-1, $\varepsilon_o$ the permittivity of free space (a physical constant), and ε” is the dielectric loss factor which is the dielectric property of the material suggesting the efficiency of conversion of electromagnetic waves to heat in the material. The dielectric loss factor is always positive and usually much smaller than the dielectric constant.

Table 3-1: Frequencies assigned for industrial, scientific and medical use.

| Heating method | Frequency |
|---|---|
| Microwaves | 915MHz ± 13MHz<br>2450MHz ± 50MHz<br>5800MHz ± 75MHz<br>24125MHz ± 125MHz |

### 3.5.2 Dielectric property of materials

A dielectric material is a material that is a poor conductor of electricity but an efficient supporter of electrostatic fields. If the flow of current between opposite electric charge poles is kept to a minimum while the electrostatic lines of flux are not impeded or interrupted, an electrostatic field can store energy. Another important property of a dielectric is its ability to support an electrostatic field, though dissipating minimal energy in the form of heat.

Dielectric properties centre on the manner of interaction between a material and electromagnetic radiation (Metaxas and Meredith, 1983). The interaction of material with the electromagnetic radiation could be grouped into three, depending on the formulation of the material. The interaction might result in microwaves passing through with slight or no attenuation (technical language for its description is transparent material). Another interaction might result in reflection of the microwave without penetration (opaque material), and lastly an absorber, which implies a material that absorbs the microwave because of its dielectric properties. Nevertheless, a heterogeneous combination of materials such as soil having dielectric material like water as part of the component might be responsible for their interaction during microwave heating (Clark *et al.*, 2000).

Microwave heating technology follows the principle of assimilation of microwave energy by materials in an electromagnetic field distribution region within a reflective cavity. Materials that respond to microwave treatment by transforming the absorbed microwave energy to heat are generally called dielectric material. The dielectric material is branded by the small electrical conducting properties which affect their interaction with electric fields. This characteristic influences the total energy absorbed and rate of heat propagation in an electric field at varying alternating frequencies (Nelson and Trabelsi, 2012).

The dielectric interaction of material with the microwave depends uniquely on two key parameters: absorbed power (P) and microwave penetration depth (D), and they also cause the microwave volumetric heating of the material. The dielectric properties are therefore employed to infer whether a material can be stirred up by microwave energy and besides for the simulation and engineering design of the microwave heating cavity, waveguide and choke system.

The property that determines the behaviour of a dielectric under the influence of an electric field is known as the complex permittivity ($\varepsilon^*$), which is expressed as a function of a real component, the real permittivity or dielectric constant ($\varepsilon'$), and an imaginary component, the dielectric loss factor ($\varepsilon''$).

$\varepsilon=\varepsilon'-j\varepsilon''$ Equation 3-3

Where ε is the relative complex permittivity, ε’ is the dielectric constant, ε” is the loss factor and j is an imaginary component.

The ratio between the dielectric loss factor and the dielectric constant is the loss tangent (tan $\delta$), which provides a measure as to how well a material absorbs the electromagnetic energy and dissipates it as heat throughout the material:

$$tan\delta=\frac{\varepsilon''}{\varepsilon'}$$ Equation 3-4

The dielectric constant is another dielectric property of the material that affects the intensity of the electric field in the material. The dielectric constant serves as an indicator of the amount of electromagnetic energy that could be stored in a material and the extent of its polarity. The dielectric properties of materials depend on the arrangement of the material and the water content in the material (Mudgett, 1995; Fernandez *et al.*, 2011). Dielectric properties describe the ability of a material to absorb, transmit and reflect electromagnetic energy.

The heating mechanism of microwaves is complex, and its propagation is governed by Maxwell’s equations for electromagnetic waves, the interactions between microwaves and dielectric properties of materials, while heat dissipation is governed by heat absorption and heat transfer. The combination of the ionic heating and dielectric heating can be related to power (P) per total volume of a dielectric material (Clark *et al.*, 2000; Robinson *et al.*, 2012) in a wave field as shown in the following equation:

$$P=2\pi f\varepsilon_o\varepsilon''|E|^2$$ Equation 3-5

P = power density.

$f$ = frequency of the electromagnetic wave (Hz).

$\varepsilon_o$ = permittivity of free space ($8.85\ \text{x}10^{-12}$F/m).

ε” = loss factor (ability to transfer microwave energy into heat).

$\varepsilon'_r$ = relative dielectric constant (ability of material to be polarised).

tanδ = loss tangent (ability of material to be polarised and heated in a microwave equipment).

E= strength of the electric field within a material which depends on the power of the microwave applied.

In a good loss material, the loss factor determines the temperature increase of the material when the microwave field is applied (Clark *et al.*, 2000):

$$\frac{\Delta T}{\Delta t} = \frac{2\pi f \varepsilon_0 \varepsilon'' |E|^2}{\rho C_p} = \frac{P\Delta t}{\rho C_p}$$ Equation 3-6

Penetration depth (D) is another crucial parameter in microwave heating of materials. The depth of penetration depends on the dielectric properties of the material. The penetration depth can be set as the point in the material where the power flux in the material has fallen to 1/e (approximately 37%) from the initial surface value (Thostenson and Chou, 1999; Risman, 1991a; Peng *et al.*, 2010; Peng *et al.*, 2012) and the 97% to 100% correct value can be calculated from Equation 3-7 based on the dielectric properties of the material (relative dielectric constant and loss factor), if the tan δ is less than 0.5:

$$D_p = \frac{\lambda_o \sqrt{\varepsilon'}}{2\pi\varepsilon''}$$ Equation 3-7

If the tan δ is greater than 0.5, the correct formula to use should be (Risman, 1991a):

$$D_p = \frac{\lambda_o}{2\pi\left(2\varepsilon_r'\right)^{1/2}} \left\{ \left[ 1 + \left( \varepsilon_r'' / \varepsilon_r' \right)^2 \right] - 1 \right\}^{-1/2}$$ Equation 3-8

The equation indicates that the depth of penetration or the rate of disintegration of the power of dissipation totally depends on the dielectric constant and the loss factor. The equation shows that the higher the loss factor (ε”), the lower the penetration depth, while a low loss factor (ε”) will result in a higher level of penetration. In the microwave, a transparent material exhibits remarkably little or no loss factor (ε”), which means that they do not respond positively in the microwave analysis because there is little or no energy dissipation as heat.

Clark et al. (2000) suggested that (high frequency) low wavelength (~1/$f$) and large values of the dielectric properties will result in surface heating, and turning back the setting to (low frequency) high wavelength and low dielectric properties leads to more volumetric heating. Thus, the penetration depth is extremely valuable in defining the high temperature distribution in the material under microwave treatment.

### 3.5.3 Measurement techniques

A measurement of dielectric properties of materials is important for exploring the material response to microwave treatment. There are many measurement techniques for dielectric properties of materials: coaxial probes, cavity perturbation, waveguide, free space, resistivity cell, time domain reflectometry, parallel plate, lumped circuit, and waveguide transmission line. Numerous review papers on the characterisation of the dielectric properties of materials have been published (Gregory and Clarke, 2006; Hasar, 2010; Sheen *et al.*, 2007; Lester *et al.*, 2006).

The measurement of the propagation of electromagnetic waves and parameters has been used to group the various measurement techniques into resonant and non-resonant methods. Each of these techniques has specific advantages and disadvantages, and the choice of a particular technique for dielectric description of a material depends upon the physical properties of the material, the required frequency and temperature ranges, accuracy, cost and availability of the necessary equipment. The dielectric properties measurement technique used in this project is cavity perturbation (Figure 3-2).

Although it is regarded as the most suitable method for measuring material dielectric properties at frequencies above 100MHz, it is likewise considered a more accurate and simpler technique for measurements above 600MHz. It is generally designed for high-temperature measurements of dielectric materials (Chen *et al.*, 2004). The resonant mode of the cavity governs the range of frequencies that could be measured (Chen *et al.*, 2004). The technique is generally used for measuring the dielectric properties of low-loss solid materials in powder form as well as low-loss liquid material (Metaxas and Meredith, 1983; Komarov *et al.*, 2005a). This technique was employed to determine the dielectric properties of contaminated soil samples, the crude oil and extraction residue of the soil in the project.

The principle of this technique is based on the perturbation of a resonant cavity, when a small volume of a sample is introduced into it, followed by the relative analysis of the electromagnetic characteristics of the empty and partially loaded resonance cavity. Thus, the difference in the response from the network analyser when material is inserted into the cavity and when it is empty serves as a premise to predict the dielectric property of the material in the cavity (Raju, 2003; Venkatesh and Raghavan, 2005). Figure 3-2 shows the basic components of the cavity perturbation technique for dielectric property measurement of materials. The system consists of an insulated cylindrical copper cavity placed underneath a conventional furnace that is capable of supporting the heating to temperatures up to 1800°C (Tinga and Xi, 1993).

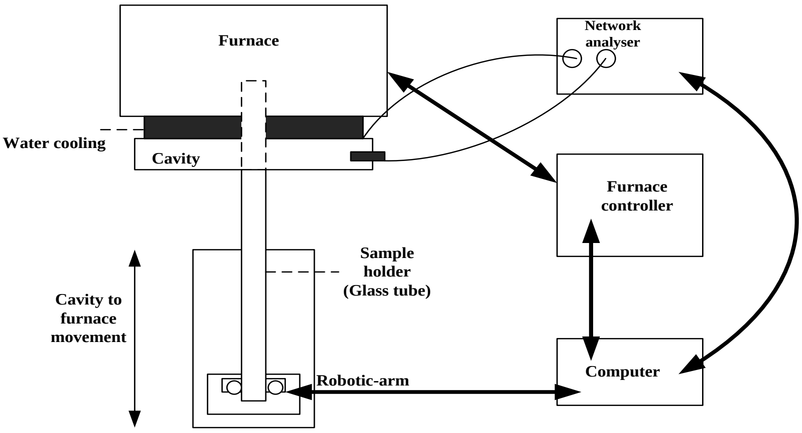


Figure 3-2: Basic components of the cavity perturbation technique for measurements of dielectric properties.

A microwave-transparent quartz tube and low-loss fibre glass act as the sample holder, and both are attached to a computer-controlled robotic arm, which moves the measured sample vertically upward and downward into the furnace and cavity respectively. A vector network analyser (VNA) is used for transmitting energy to the system and for detection and determination of frequency shift and quality factor when the dielectric material is inserted into the quartz tube.

The dielectric constant and loss factor are computed from the solution of Maxwell's equations, derived from perturbation theory using an appropriate boundary condition corresponding to the cavity dimensions (Venkatesh and Raghavan, 2005).

$$\varepsilon'' = J_1^2\left(x_{1,m}\right)\left(\frac{1}{Q_1} - \frac{1}{Q_2}\right)\frac{V_c}{V_s}$$ Equation 3-9

$$\varepsilon' = 1 + 2J_1^2\left(x_{1,m}\right)\frac{f_0 - f_1}{f_0}\frac{V_c}{V_s}$$ Equation 3-10

Where $V_c$ = cavity volume ($m^3$), Vs = volume of sample ($m^3$), $f_0$ = resonant frequency of the empty cavity (Hz), $f_1$ = resonant frequency of the cavity with sample (Hz), $J_1$ = first order Bessel function, $Q_1$= quality factor of the empty cavity, the $Q_2$= quality factor of the cavity with dielectric material and $x_{1,m}$ = function of the air-filled cavity.

### 3.5.4 Microwave processing equipment

The microwave-generating device produces the electromagnetic energy directly incident on the sample in the applicator as shown in Figure 3-3 (Das *et al.*, 2008). The waveguide is a transmission device which conveys the propagated microwave energy from the source to the applicator, where the energy is absorbed by the material (Das *et al.*, 2008; Thostenson and Chou, 1999). The use of these three main components is governed by complex Maxwell's equations using approximate boundary conditions (Venkatesh and Raghavan, 2005; Metaxas and Meredith, 1988; Zhang and Li, 2007).

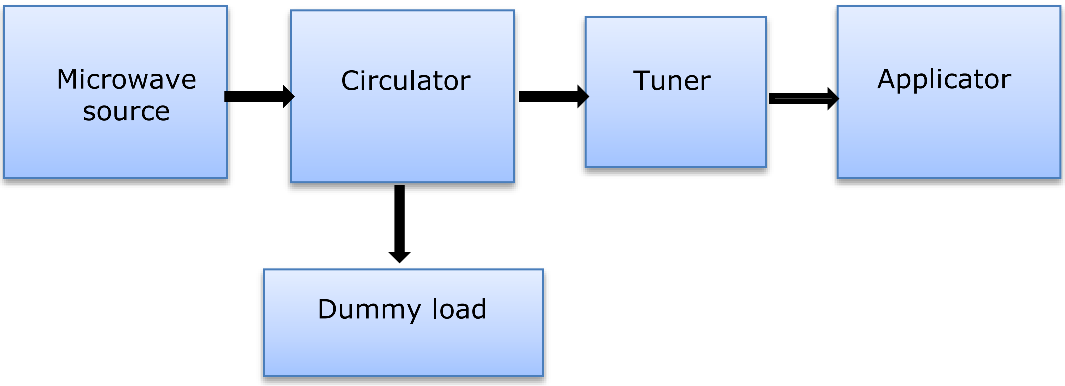


Figure 3-3: Block diagram of the microwave processing system.

In between the applicator and the microwave-generating source are the automated adjustable tuner and circulator. The circulator safeguards the magnetron by redirecting the excess microwave energy reflected back from the load. The excess microwave energy may be redirected to a dummy load, which is usually water because of its high microwave-absorbing capacity. The purpose of the tuner is to match the impedance (resistance) of the microwave source and the transmission line to that of the load, thereby maximising the microwaves absorbed by the sample and minimising the power reflected.

### 3.5.4.1 Devices for generating microwaves

Microwaves are made as a consequence of the motion of electrons accelerating along a big potential difference in an orthogonal magnetic field. This magnetic field effects the oscillation of these electrons in a helical path (Sobby and Chaouki, 2010). Some of the vacuum tubes used for microwave generation are magnetron, klystron, extended interaction oscillator (EIO), permanent magnet gyrotron and travelling wave tubes (TWT). The selection of microwave sources is a function of the cost, efficiency, frequency stability and power (Metaxas and Meredith, 1988). Most domestic, industrial and commercial microwave processing systems use magnetrons as the generating device because of its high power output, higher efficiency, frequency stability and relatively low cost (Metaxas and Meredith, 1988), therefore its operational principle is discussed below.

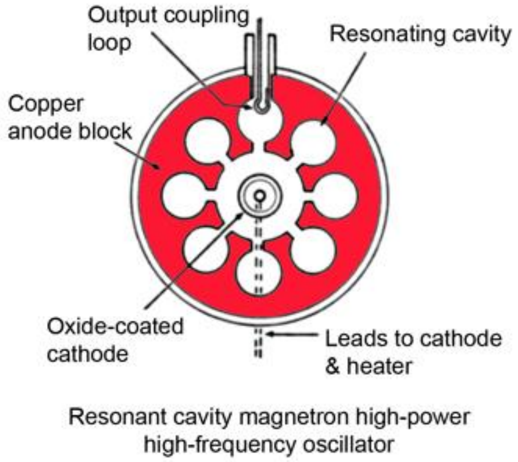


Figure 3-4. Travelling wave resonant cavity magnetron (Metaxas, 1996).

Magnetrons (Figure 3-4) are high-powered tubes with a high vacuum of approximately 6-10mm Hg and an electronic valve consisting of electron-emitting cathodes surrounded by hollow copper anodes. It is the most commonly used microwave source for domestic and industrial microwave heating, and its usage is close to 98% of all installations (Metaxas, 1996).

The anode has a set of vanes that project radially inward to form slots, which are approximately λ/4 between them and therefore resonate at the microwave frequency (Metaxas and Meredith, 1983; Schubert and Regier, 2005). It can produce either continuous or pulsed power up to a megawatt and an operating frequency between 1–40 GHz. The power efficiency is approximately 85% with a lifetime close to 5000 hours (Chandra, 2011). Two large pole pieces of magnets produce a magnetic field normal to the cavity plane, and the anode is at higher potential relative to the cathode.

The interaction in the magnetron depends on the motion of electrons in an orthogonal electric and magnetic field. The trajectory and velocity of these electrons are found out by the direct current, electric field strength and magnetic field intensity level in the distance between the anode and the cathode. The magnetic field strength or the tube’s current controls the power output of the magnetron, and the maximum power is limited by the anode temperature. The 2.45GHz frequency can achieve a maximum power of 1.5kW and 25kW for air- or water-cooled anodes respectively (Schubert and Regier, 2005; Metaxas, 1996; Thostenson and Chou, 1999).

#### 3.5.4.2 Microwave transmission devices

Transmission lines guide the microwave energy generated by the microwave source to the microwave applicator, where the interaction of electromagnetic waves with the materials to be processed takes place. The type of transmission line used depends on the power of propagated microwave. A coaxial transmission line can be used to broadcast a low power microwave, but it produces significant losses at high power and frequency. Thus, at high microwave power and frequency, the waveguide is used for transmission owing to its low losses at high frequency (Thostenson and Chou, 1999; Chan and Reader, 2000). Only the waveguide, which is utilised in this project for transmitting microwave energy into the cavity, is talked about.

The waveguide consists of hollow metallic tubes of constant cross section, which are either rectangular or circular in shape. Transverse electric (TE) and transverse magnetic (TM) are the two possible modes of microwave propagation in waveguides (Chan and Reader, 2000; Metaxas and Meredith, 1983). Figure 3-5 shows the TE and TM modes in a waveguide system.

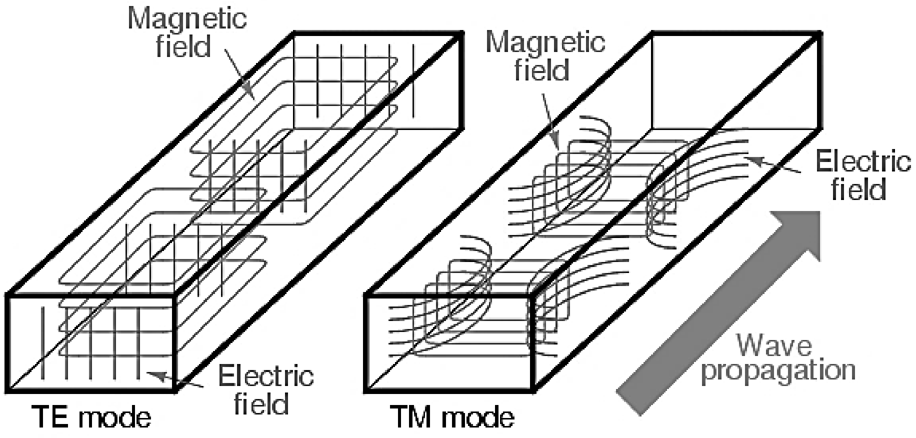


Figure 3-5: Transverse electric (TE) and transverse magnetic (TM) waveguide (Kuphaldt, 2007).

For the TE mode, the electric line of force is perpendicular to the axis of the waveguide, and the electric field component in the direction of propagation is zero ($E_z = 0$) whereas for the TM mode, the magnetic line of force is perpendicular to the axis of the waveguide and the magnetic field component in the direction of propagation is zero ($H_z = 0$) (Meredith, 1998; Chan and Reader, 2000). Energy is conveyed by the electric and magnetic fields associated with the wave, and there is a possibility of having several modes of propagation (Chan and Reader, 2000; Thostenson and Chou, 1999).

#### 3.5.4.3 Microwave heating applicators

Microwave applicators are metallic enclosures where microwave interaction with dielectric materials takes place. The applicator enables coupling of the microwave energy into the workload volume to a degree sufficient to make a temporary or permanent change in the workload property (Mehdizadeh, 2010). The temperature distribution within the material is inherently related to the distribution of the electric field and the power density within the cavity where the material is positioned for processing (Thostenson and Chou, 1999; Metaxas and Meredith, 1983). Single-mode and multimode microwave heating cavities are commonly used for domestic, laboratory research and industrial heating applications, but the focus of discussion shall be based primarily on the single mode used in this research. The type of applicator used for materials processing depends on the processing requirement and the electromagnetic properties of materials to be processed (Tadmor and Scachter, 1999; Chan and Reader, 2000; Bradshaw *et al*., 1998).

A. Single-mode cavities

The single-mode cavity electromagnetic field pattern is well defined and can be easily determined by solving Maxwell's equations using suitable boundary conditions either by applying an analytical or numerical method. This type of cavity supports only one resonant mode, i.e. one standing wave with maximum field intensity created by resonance (superposition of forward and reflected waves) with a size that gives the order of approximately one wavelength. To maintain this single resonant mode requires a microwave source that has little frequency variation, and the size of this type of cavity needs to be within the vicinity of the operating wavelength or a slightly higher wavelength. The areas of high and low electromagnetic distributions are well known from the electromagnetic field configuration of the cavity. The electromagnetic field configuration of the single-mode cavity causes it to have only one hot spot where electric field intensity is highest, and the processed material is placed in this region for optimum heating. An example of a single-mode cavity made of waveguide that is shorted by a short tuner at one end and with the microwave fed from the other end is presented in Figure 3-6 (Chan and Reader, 2000; Metaxas and Meredith, 1983; Mehdizadeh, 2010).

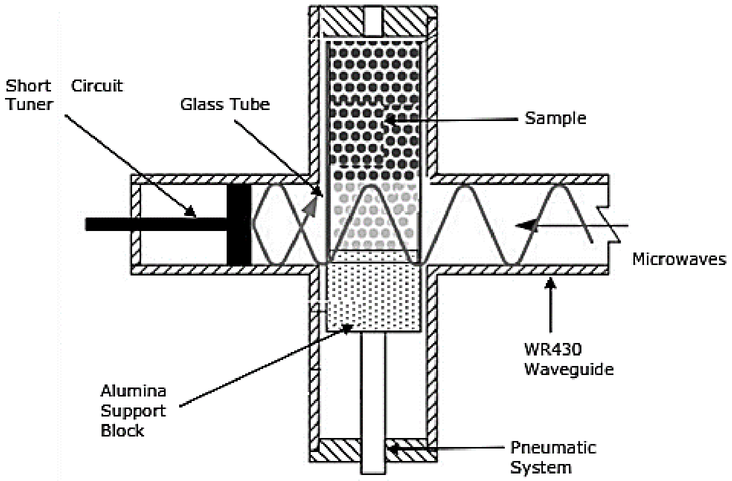


Figure 3-6: Schematic diagram of microwave single-mode cavity (Kobusheshe, 2010).

The magnetic field with its maximum located at a position different from that of the electric field is achievable with this type of cavity, which makes it a suitable cavity for processing magnetic materials. Applying the same microwave power, a single-mode cavity will generate higher electric field strengths than other forms of cavity, which makes it useful for processing low loss materials that are difficult to heat to high temperatures (Metaxas and Meredith, 1983; Huanga *et al*., 2009; Sutton, 1992).

Some of the advantages of using single-mode cavities are ease of design and construction, homogeneity of the electromagnetic field in a targeted zone of the applicator, sensitivity and predictable high field zone. It is advantageous for metal sintering because one of its features is that it can produce separate locations for the electric and magnetic fields within the cavity (Gupta and Eugene, 2007; Leonelli *et al*., 2008; Demirskyi *et al*., 2010). Due to the small size and geometry, only smaller sizes of material can be processed, and the cavity requires continuous tuning (Chan and Reader, 2000; Mehdizadeh, 2010). Other limitations of this type of cavity include high cost per load volume and ease of arcing due to the creation of high field zones.

### B. Other components in industrial microwave systems

Circulators and directional couplers are important elements of microwave systems. Hypothetically, zero reflection of microwave energy from the load occurs when the losses of the load and the cavity walls are equal to the impedance of the waveguide. Remarkably, this may not be possible in practice because the impedance of the heating system may be affected by a slight variation in the characteristics of the heating cavity due to temperature, chemical or phase change (Chan and Reader, 2000). Therefore, a circulator is used to redirect the reflected waves into a dummy load, which is ordinarily water. Normally, the circulator is installed in a microwave system to preclude the magnetron from being damaged as a result of reflecting waves. A three-port circulator is the most common type in use. One port of the circulator is connected to the applicator, another to the microwave source while the third port is linked to a dummy water load to adsorb reflected wave. The circulator is a very important component of the microwave system, especially if the material is a very poor microwave absorber. A directional coupler is used to measure the forward and reflected power during microwave heating to help researchers investigate the coupling capability of the workload with microwave energy (Thostenson and Chou, 1999; Chan and Reader, 2000; Schubert and Regier, 2005).

# Chapter 4: Research methodology

## 4.1 Scope

The objective of this research is to remediate Nigerian crude-oil-contaminated soil with the best technology that will meet the demands of the oil-producing community and government. To this end, detailed breakdown and discussion of all materials, methods and techniques involved in this research are incorporated within this chapter. The methodologies described in this chapter refer to works carried out on the reference crude oil and the soil sample provided by SPDC, Nigeria.

This section will outline the methods and techniques that form the pedestal from which the remediation process was achieved, and detailed geochemical interpretation of results will follow:

1. Sample collection and experimental preparation.
2. Sequential extraction of soil sample; fractionation of the crude oil, extractable organic matter of the soil and oil pyrolysate from Gray-King; and microwave heating pyrolysis.
3. Analysis of fractioned extracts/pyrolysates via GC-MS.
4. Application, operation and procedure of pyrolytic analytical technique: hydropyrolysis.
5. Elemental analysis for total organic carbon (TOC), which serves as indicator of the amount of biodegradable carbon in the soil.

A summary of each stage of the processes carried out in this work is shown in Figures 4-1 and 4-2.

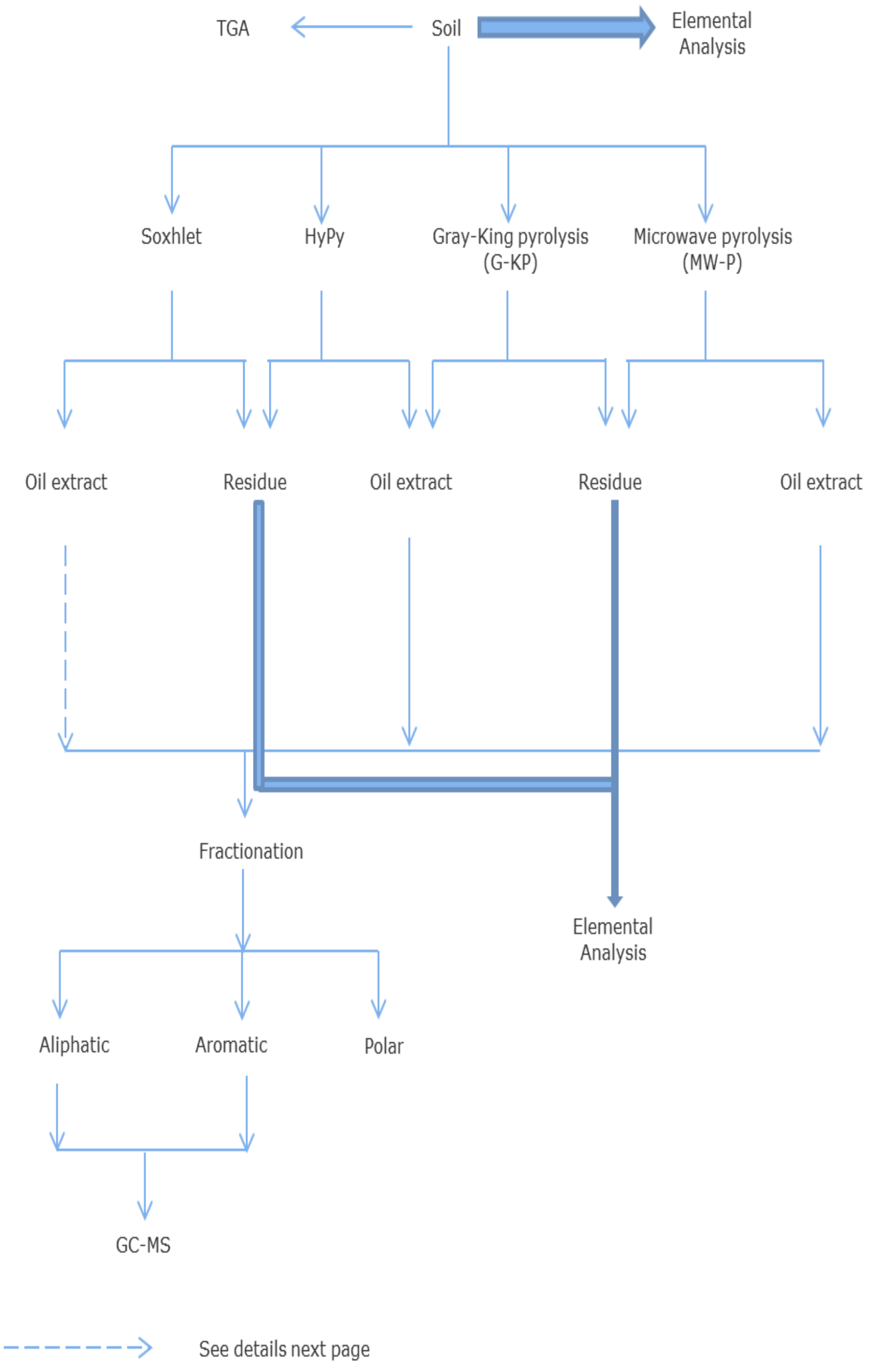


Figure 4-1: Showing the summary of each stage of the processes employed in the thesis to analyse the organic component of the soil sample and the remediation techniques used.

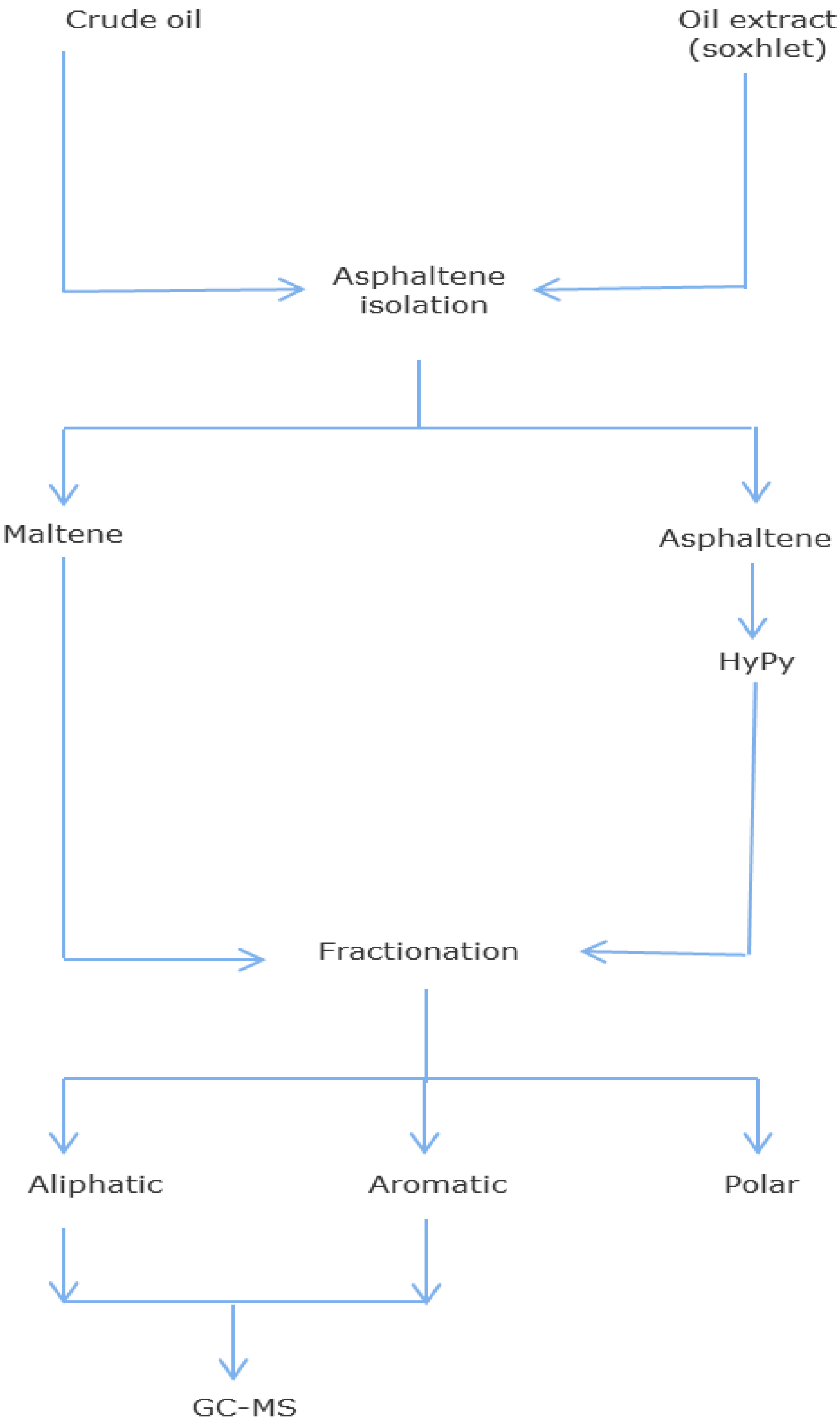


Figure 4-2: Asphaltene isolation from the crude oil and the oil extract from soxhlet extraction; fractionation of the hydropyrolysate product and maltene prior to GC-MS.

## 4.2 Sample collection and preparation

The crude-oil-contaminated soil used for this study was collected by the remediation team of SPDC, Nigeria, and supplied on 17th of August 2011. The crude oil was received in a specialised jar with a Teflon-lined cap on the same day from the same SDPC Port Harcourt office, Rivers State, Nigeria. A total of 4kg of the polluted soil sample was received and transferred into a dark glass with minimal headspace. The specialised jar containing the crude oil was stored in a Haier Thermocool freezer at -21± 2°C in a semi-solid form before being sent by air cargo freight to the UK.

The soil sample was stored in same freezer at -21± 2°C before being sent by air cargo freight to the UK in a specialised sealed parcel for hazardous material. On receipt, the soil sample was stored in the Whirlpool freezer as the crude oil at -21± 2 °C.

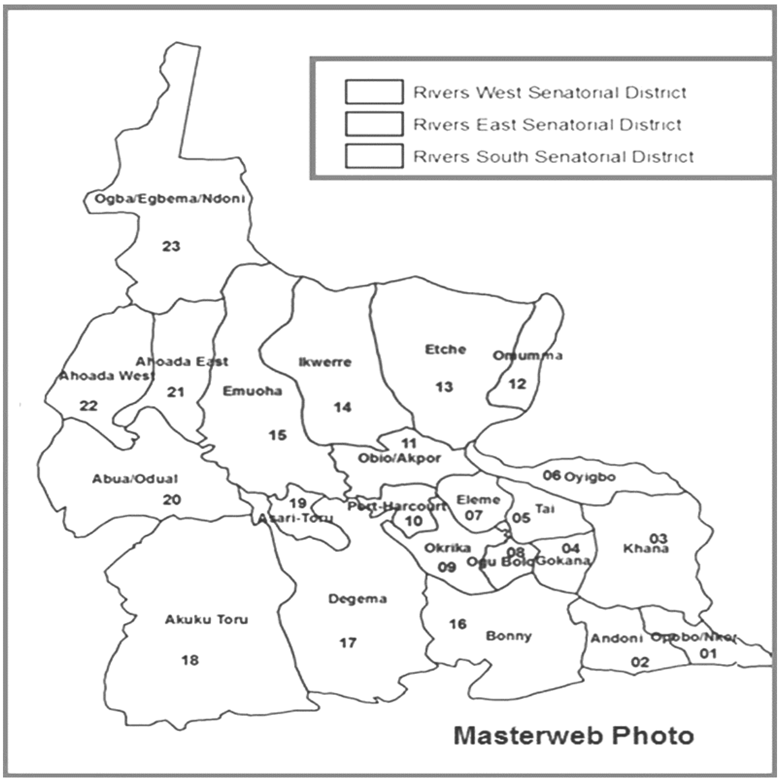


Figure 4-3: Map of Rivers State of Nigeria showing the Bonny, where the sample was collected (from Nigeria masterweb.com).

The sampling procedure was implemented on the polluted soil to obtain a representative laboratory-size sample from the bulk soil received. The representative laboratory-size sample was achieved by the quartering method, and the process was repeated several times to ensure proper mixing of the soil. The representative soil was transferred into a Teflon laboratory bag and labelled. Then the samples were placed in the freezer (-21± 2$^{o}$C) prior to analysis.

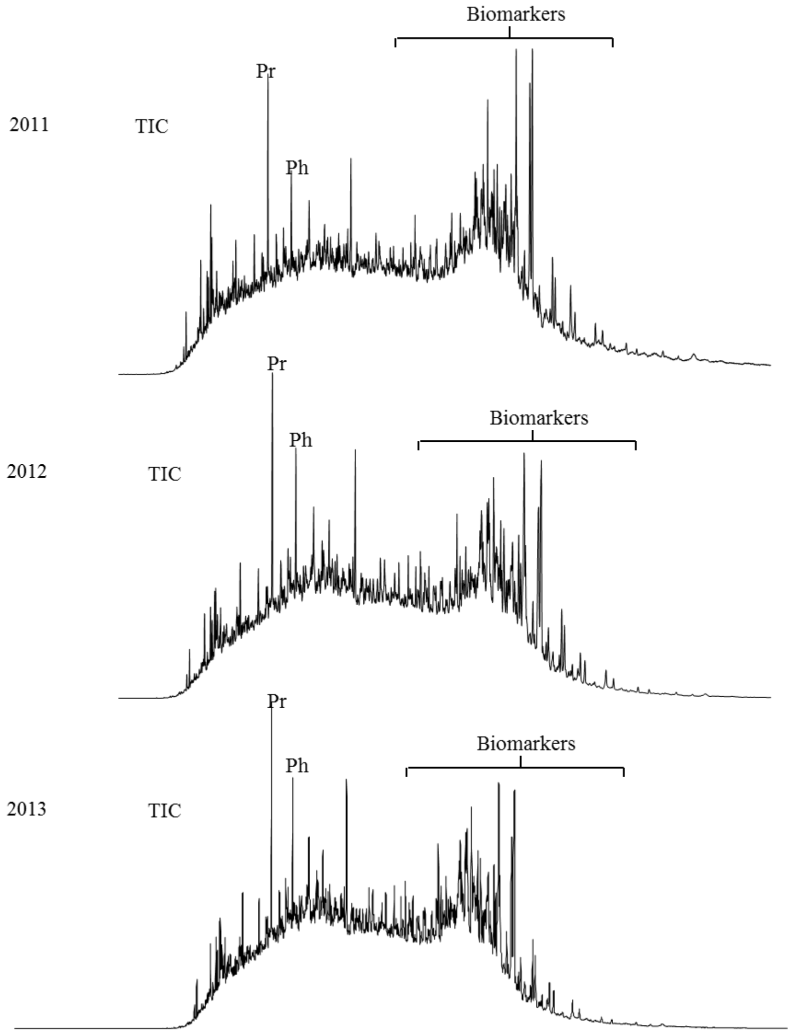


Figure 4-4. Chromatogram plot of total ion chromatograms (TIC) for the extract from the soil sampled annually from the freezer (-21± 2$^{o}$C).

Throughout this study all extracted organic matter samples were kept in the freezer (-21± 2$^{o}$C). Prior to experimental work, all glassware and related equipment was thoroughly cleaned with detergent, rinsed in distilled water and dried in an oven. In addition, the pyrolysis rigs (Gray-King and microwave heating rig) for remediation were thoroughly cleaned before each run. The hydropyrolysis rig was subjected to sonification in dichloromethane for a period of five mins after a thorough cleaning of the rig. Alumina and silica used in chromatography or hydropyrolysis were thoroughly cleaned in order to prevent contamination.

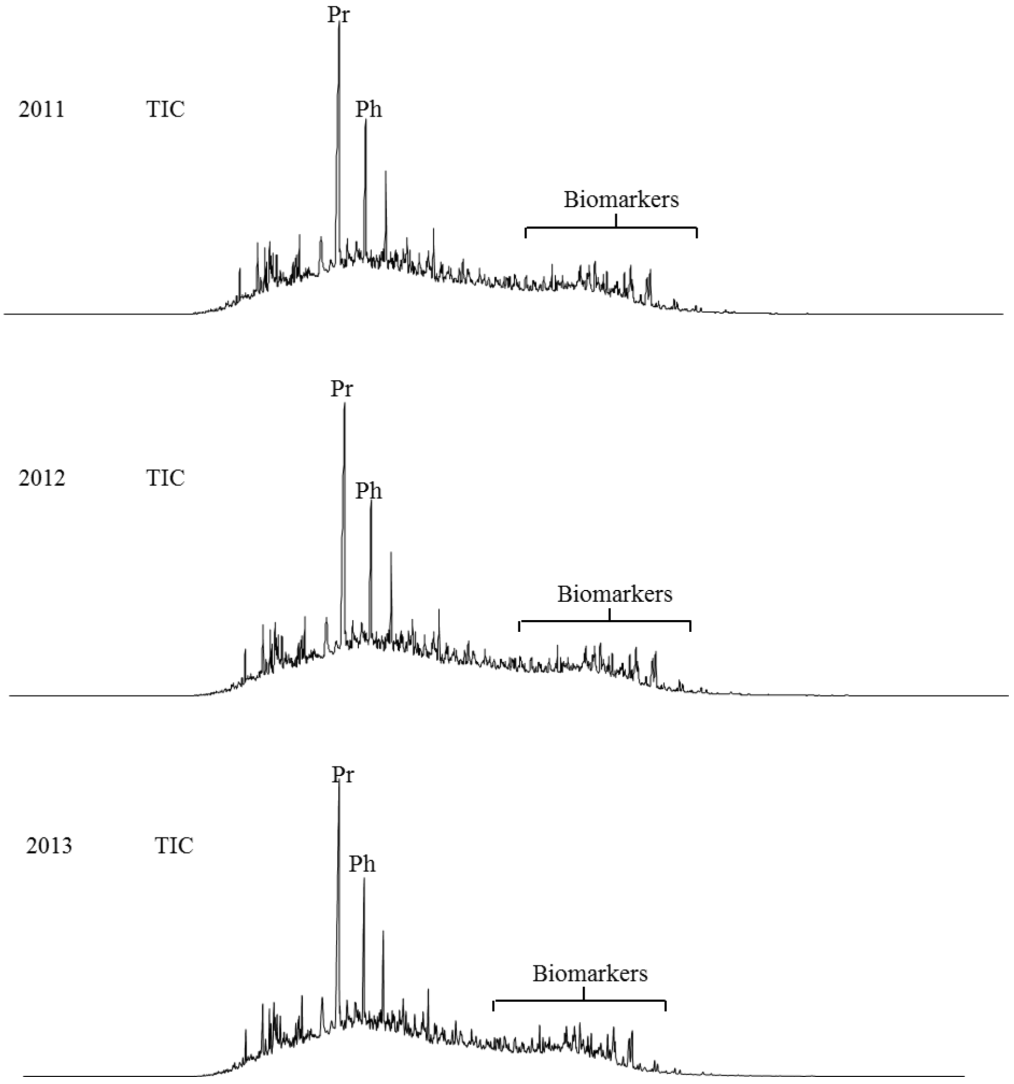


Figure 4-5. Chromatogram plot of total ion chromatograms (TIC) for the crude oil sampled annually from the freezer (-21± 2$^{o}$C).

To examine the stability of the soil and crude oil samples over the period of this project, annual samples were taken and analysed to check that their geochemical characteristics had not changed. In both cases, no significant changes were evident in the total ion chromatograms as shown in Figures 4-4 and 4-5. The Pr/Ph ratio range over the three years of sampling is remarkably consistent with values of 2.98, 2.99 and 2.99 for the crude oil and 1.85, 1.86 and 1.86 for the soil organic matter providing evidence that no significant changes in composition have occurred. The lower Pr/Ph ratio for the soil arises from the oil having been biodegraded to a greater extent as also indicated by the more pronounced unresolved broad bands evident in the chromatograms for the soil organic matter.

For effective remediation of the soil sample, total organic carbon was the parameter employed to decide the best remediation techniques between the two pyrolysis techniques used in this research. The experimental procedures used to achieve the objectives set out are discussed in this chapter of this study.

## 4.3 Elemental analysis

Organic carbon is one of the major components of crude oil expected to be present in soil as a consequence of oil spillage. It is an indispensable factor of interest in comprehending the effectiveness of remediation techniques based on the TOC values of char left after treatment. To achieve this objective of expressing the inital TOC of the contaminated soil and the final TOC of the remediation techniques, an elemental analyser (Thermo Finnigan EA 1112 Series Flash Elemental analyser) is required for proper quantification. The elemental analyser is used to determine qualitative and quantitative of each element, such as carbon, hydrogen, nitrogen and sulphur present in the organic samples.

The analyser has the following major components: auto-sampler, reactor, furnace, chromatography column, thermal conductivity detector (TCD) and adsorption filter. The samples (~6mg) were analysed with a Thermo Finnigan EA 1112 Series Flash Elemental analyser in an oxygen-rich atmosphere, using Eager 300 operational software (Thermo Electron, Milan, Italy). The instrument uses a quartz reactor tube, containing sequential beds of copper oxide (oxidising reactant) and copper (reductant) wire, which are encased within a furnace held at 900°C.

The introduction of the weighed sample wrapped in a tin capsule from an auto-sampler into the reactor was accompanied by an injection of an aliquot of pure oxygen, to aid flash combustion of the organic matter. During operation, a continuous stream of helium gas was passed through the reactor at 140ml/min, where any by-products ($CO_2$, $H_2O$ and $NO_2$) of this combustion were swept from the system during the oxidation stage by the gas flow. The generated gases were removed to the reductant bed by the carrier gas and reduced to $CO_2$, $H_2O$, $N_2$ and $SO_2$. The generated gases were separated on a chromatographic column (stainless steel packed column, 2m x 0.5mm, Porapak Q) immediately then quantified by comparing them with known combustion products from a standard (4-amino benzene sulfonamide-$C_6H_8N_2O_2S$- 68% carbon), using TCD.

## 4.4 Thermogravimetic analysis

It is essential that the characteristics of the fresh contaminated soil are ascertained before taking out further analysis of the contaminated land. This is especially crucial to determine the possible response of the polluted soil sample to microwave treatment, which depends on the moisture content as one of the key parameters. Full details have been provided in Section 3.5.1. To this end, the moisture content of the soil was analysed with the use of a thermogravimetric analyser because it has been established as an instrument for proximate analysis of material such as soil. Consequently, it is essential to understand the underlying principle and operation of the instrument regarding how to obtain information about aspects such as oxidative/thermal stability of the material, moisture content, volatile organic matter, fixed carbon and residue. With this in mind, the thermogravimetric analysis (TGA) principle is based on monitoring the mass of a substance as a function of temperature or time in a controlled temperature programme in a controlled atmosphere, which is sample percentage weight change with time or temperature. Nevertheless, the major focus of this section is information on the moisture content of the soil before analysis.

The controlled atmosphere for the analysis of the soil moisture content and volatile organic carbon section uses nitrogen gas, which creates an inert atmosphere. After this section, the fixed carbon in the soil was combusted in the air to form gas in the controlled atmosphere, leaving behind the residue. The whole experiment was performed under a controlled temperature programme stated as follows.

The soil samples were placed in sample pans of TGA SDT Q500 for analysis. The soil in the pan was automatedly moved to the heating chamber, where the soil was ramped at 5°C/min from room temperature to 110°C and kept isothermal for 60 minutes to remove all the moisture content. Then, the temperature was increased to 700°C (ramp 5°C/min) and kept isothermal for 20 minutes to ensure removal of all the labile volatile compounds. The nitrogen gas was changed to air for combustion of the fixed carbon as the temperature increased to 850°C (ramp 5°C/min) from 700°C to leave behind residues. The process was isothermal for 60 minutes at 850°C.

After the moisture content of the soil was determined, the crude oil content was the next crucial parameter to be considered before analysis. This was vital because the initial extracted organic content of the soil will be the platform to investigate the efficiency of the two remediation techniques considered in this current work. The two analytical techniques employed for the removal of the crude oil discussed in details in Sections 4.6 and 4.8 are soxhlet extraction and hydropyrolysis.

## 4.5 Soxhlet extraction

Crude oil spilled over time gets into the soil by gravity and capillary action, a disintegration that is primarily determined by soil, topography, porosity and mineralogy (Peters *et al.*, 2005). Therefore, the solvation property of the crude oil encourages the use of a soxhlet extraction process to examine the quantity of solvent extractable organic matter in the soil.

The soxhlet extraction principle uses the advantage of forming emulsion with crude oil fractions in the soil sample through more rigorous mixing and removes the crude oil from the soil for further analysis. The soxhlet extraction procedure is as stated stepwisely:

The contaminated soil (5.5g) is weighed into a pre-cleaned thimble and loaded into the main chamber of the soxhlet extractor. An azeotropic mixture of dichloromethane ($CH_2Cl_2$) and methanol ($CH_3OH$) (93:7% v/v) of close to 250ml is placed in a 500ml distillation flask. The flask, which is linked to a reflux condenser, is put on the heating element while the soxhlet extractor is located atop it. The solvent is heated to reflux. The solvent vapour travels up a distillation arm and floods into the chamber housing the thimble of solid matter. The condenser ensures that any solvent vapour cools and drips back down into the chamber housing the contaminated soil (5.5g). The chamber containing the contaminated soil slowly fills with warm solvent. Some of the desired compound dissolves in the warm solvent. When the soxhlet chamber is nearly full, the chamber is emptied with the siphon. The solvent is returned to the distillation flask. The thimble ensures that the rapid movement of the solvent does not transport any soil to the distillation flask. This cycle may be allowed to repeat continuously for 24 hours to achieve considerable extraction efficiencies (Khan, 2005).

During each round, a lot of the non-volatile compound dissolves in the solvent. After many cycles, the oil is concentrated in the distillation flask. The advantage of this system is that instead of many portions of warm solvent being passed through the sample, just one batch of solvent is recycled. After extraction, the solvent is removed, typically by means of a rotary evaporator, yielding the extracted oil. The non-soluble portion of the extracted soil remains in the thimble, which is dried and weighed. The weight of organic extract is equivalent to the maximum solvent-extractable organic matter of the soil.

## 4.6 Separation of crude oil into maltene and asphaltene

It has been established from past studies that crude oil components contain maltene and asphaltene (Russell *et al*., 2004; Shi *et al*., 2010; Akmaz *et al*., 2011). The maltene and asphaltene content of the crude oil has been studied, and past work suggests that the maltene is attacked before asphaltene by microbial action during degradation. This means that original composition or markers of the crude oil can be determined from the preserved content of asphaltene. Therefore, it was essential to be able to separate the maltene from asphaltene to determine the extent of biodegradation of the maltene and the preserved content of the asplhatene. Furthermore, a similar separation of the maltene from the asphaltene in the extracted organic matter from the soil was performed. Then, the correlation of the resulting maltene and asphaltene from the reference crude oil with that of the extracted organic matter from the soil was established. The information will be used to examine if the crude oil provided for this research, or another crude oil, is the possible contaminant in the soil. To achieve this intended objective, evidence from past work has arguably proven that *n*-heptane can be used because asphaltene is precipitated out of the solvent (Omole *et al*., 1999; Bozzano *et al*., 2005; Bowden *et al*., 2006). Therefore, *n*-heptane was used to separate the crude oil into maltene and asphaltene using the process described in this section.

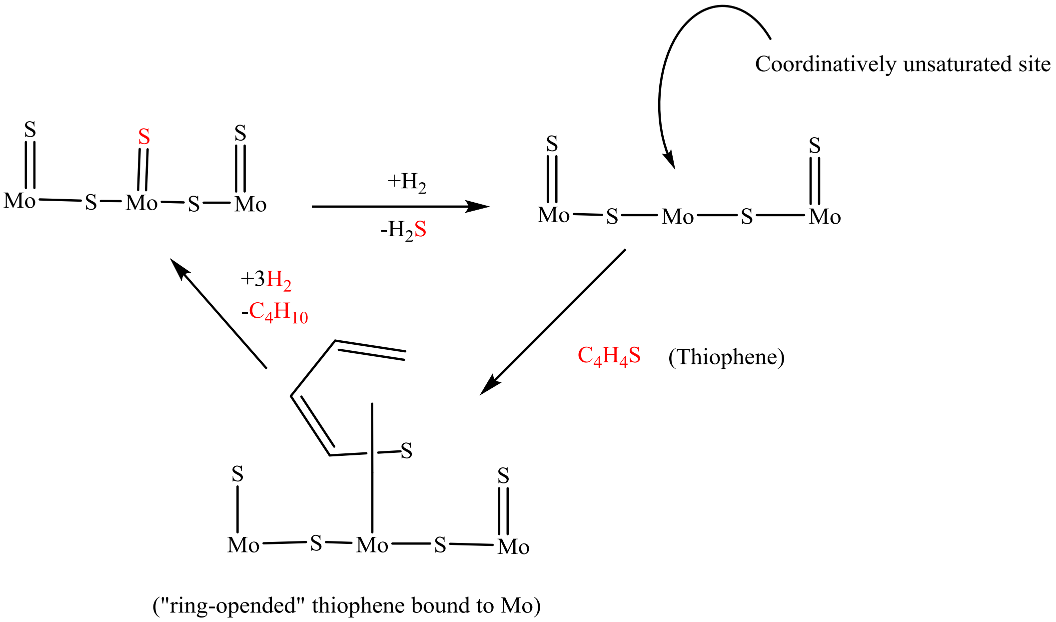
The dry extractable organic matter from the soxhlet extraction in Section 4.6 was dissolved in a minimal amount of dichloromethane (DCM) in a conical flask (250ml). With this solution, a 40-fold excess of chilled *n*-heptane was added and mixed for approximately 20 minutes using a magnetic stirrer. The solution was then transferred to centrifuge tubes where the suspension was spun for five minutes at 2500rpm. The *n*-heptane supernatant, containing the dissolved maltene fraction, was removed, leaving a solid asphaltene precipitate on the bottom of the centrifuge tubes.

The precipitate was then re-dissolved and transferred to the conical flask. The process was repeated till clear *n*-heptane supernatant was obtained, suggesting that all the maltene should have been removed. The maltene fractions were combined and rotary evaporated. The asphaltene and maltene fractions were then transferred to clean pre-weighed glass vials and the dried weight of each fraction was obtained.

## 4.7 Hydropyrolysis

The aim of this research, as has been stated earlier, is remediation of the polluted soil using two remediation techniques. Therefore, it is essential to determine the baseline for the extraction of pollutant from the soil, which is the maximum extractable organic (includes solvent extractable and thermally labile components of the crude oil) component of the soil. This value is expected to be higher than the normal values from normal pyrolysis, leaving behind only black carbon (Ascough *et al*., 2009). Thenceforth, the values obtained will be converted to percentage TOC removed, and it will be applied to find out the efficiency of the two remediation techniques as fully discussed in Chapters 5 and 6 of this thesis. The the baseline for the extraction of pollutant from the soil was achieved by applying an analytical technique called hydropyrolysis (HyPy).

HyPy data is basically used for comparative study with data from the remediation technique because HyPy can remove all the thermally labile and solvent soluble contents of crude. Likewise, HyPy preserves the structural integrity (stereochemistry) of organic compounds release for better understanding of their geochemical properties through sensitive and rapid characterisation with GC-MS (Ascough *et al*. 2009). The HyPy process is a catalytic process similar to hydrogendesulphurisation or hydrogenolysis reaction during the refinery process. Hydrogenolysis (addition of hydrogen) during HyPy is achieved with the use of active $MoS_2$ catalyst with minimal structural rearrangement to reflect a structure close to the parent kerogen (Meredith *et al*., 2004). Equation 4-1 is an example of hydrogendesulphurisation of thiophene, which results in C-S scission and C=C hydrogenation. The hydrogen serves multiple roles such as generation of anion vacancy by removal of sulphide, hydrogenation and hydrogenolysis, thus showing a simple cycle of possible reaction during HyPy to generate products similar to the parent biomarker. The HyPy stepwise process to achieve the ultimate objective is stated in this section.



Equation 4-1. Hydrogendesulphurisation mechanism for thiophene (Wikipedia).

Prior to analysis of the samples, the rig was meticulously cleaned with DCM. The spherical metallic wool sample supports, which are located below the sample in the reactor and beneath the silica in the cold trap, were prepared by extraction in DCM:methanol solution, followed by drying under controlled atmospheric conditions, then heating in a muffle furnace at >300°C to ensure all contamination was eliminated. Furthermore, the Incoloy reactor tube with fittings was also heated to exterminate possible sources of contamination.

The catalyst was prepared by the slow addition of ammonium heptamolybdate (4g) to 16%v/v ammonium sulphide solution (22ml) in small portions at a time. The heptamolybdate salt was dissolved using a magnetic stirrer, and the solution stirred until precipitate of ammonium dioxydithiomolybdate formed. The precipitate was collected using a Büchner funnel and dried in a vacuum oven.

The residue, soil and the solvent-extracted samples were loaded with catalyst by impregnation with an aqueous/methanol solution (20% v/v) of ammonium dioxydithiomolybdate [(NH4) $_2MoO_2S_2$] to give a nominal Mo loading of 3 weight % sample. This catalyst precursor decomposes upon heating to yield catalytically active oxysulphide Mo species ($MoS_2$ at approximately 400°C). The impregnated soil sample was quantitatively transferred into a 25cm length of incoloy stainless steel tubing (5/16 inch internal diameter, 9/16 inch outside diameter) with fittings to undergo resistive heating from 50 to 250ºC at 300ºC/min, followed by heating from 250 to 520°C for 8°C/min$^{-1}$, under a hydrogen pressure of 15MPa (Figure 4-5). The volatile products were quickly swept from the reactor to a cold trap with dry ice containing grade silica to absorb the generated oil under hydrogen with a gas flow rate of 5L/mins.

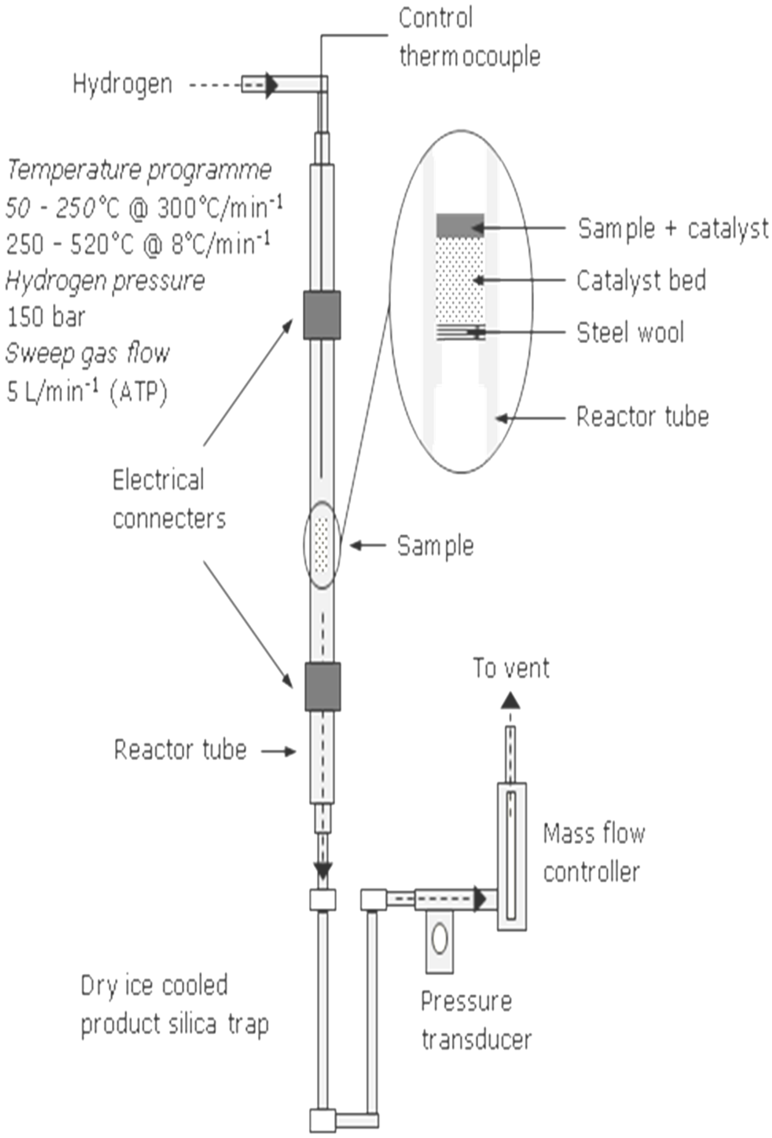


Figure 4-6: Schematic diagram of the hydropyrolysis rig.

The organic products collected in the cooled trap were recovered with DCM and fractionated into aliphatic, aromatic and polar using open column chromatography before analysis with gas chromatography/mass spectrometry.

## 4.8 Gray-King pyrolysis

It has been repeatedly stated that the focus of this work is remediation of polluted soil. Therefore, choice of remediation technology is essential after Sections 4.6 and 4.8 discussed the analytical method for extraction of the soil contaminant. This section discusses one type of remediation technology called Gray-King pyrolysis. Although it is a batch technique, it has revealed the usefulness of the geotechnical engineering process. It is a process that gives accurate results of the pyrolysis product and can easily be scaled up to the pilot process as detailed in Section 7.2.

The Gray-King pyrolysis consists of a quartz tube reactor placed in an electric furnace that protrudes out of the electric furnace. The protruding end has a side outlet to transfer the oil product into a receiving coolant as shown in Figure 4-2. The gas content from the reactor passes though the coolant into a gas bag for gas chromatographic analysis. The procedure of the Gray-King process requires the dry soil to be placed in a quartz reactor tube that is 25cm long and 2cm in diameter, before inserting it in the electric furnace. The electric furnace is heated at 5°C/min from room temperature to 300°C prior to insertion of the dry soil. After insertion of the soil, the reactor temperature was raised by the same heating rate (5°C/min) (the uniform rate for all experiments) to various peak temperatures investigated which were 450°C, 550°C, 650°C, 750°C and 850°C respectively. The remediation treatment was repeated twice for all the peak temperatures investigated at treatment times of 30 and 60 minutes respectively.

The significant departure from the Gray-King pyrolysis process was the introduction of nitrogen gas as the sweep gas. The nitrogen gas flow rate was at 2L/min before passing it into the pyrolysis chamber steadily for five minutes prior to commencement of pyrolysis of the soil to establish an inert atmosphere. The nitrogen gas flow rate was set at the prescribed rate above in order to have a similar rate with the microwave process. And so, the furnace was heated up to 300°C before the sample was introduced. Afterwards, the furnace temperature was brought up to the peak temperatures as discussed above at the same heating rate (5°C/min) and was sustained at the peak temperature for a full 60 minutes residence time respectively for each run. The pyrolysis products were char, oil/water mixture and gas.

The char products were quantified to consider the efficiency of the technique as a thermal decontamination technology for the polluted soil. Quantitative analysis of the gas was carried out using Perkin Elmer Clarus 580N gas chromatograph fitted with flame ionisation detector (FID) by comparing the gas yield with known standards.

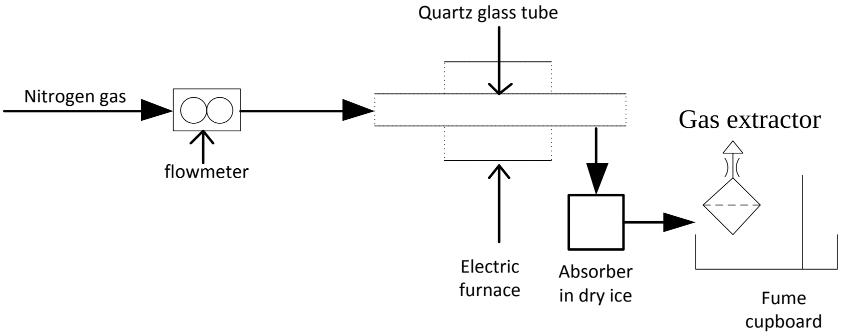


Figure 4-7: Schematic diagram of the modified Gray-King pyrolysis equipment for the remediation of the crude-oil-contaminated soil.

The oil/water mixture generated from Gray-King pyrolysis was later separated by means of Dean-Stark apparatus. The flask containing toluene solvent was heated using a heating mantle at 110°C for seven hours. After reflux, the set-up was allowed to cool, and the mass of water generated from the reaction was recorded. The solvent was distilled off and the oil was weighed. The oil products were subsequently analysed by gas chromatography-mass spectrometry as discussed in Section 4.15 to determine the geochemical properties of the oil yields and to compare it with the reference oil geochemical properties provided.

## 4.9 Dielectric properties measurement of the soil

Microwave heating depends on the response of a material to electromagnetic energy. The interaction of material with an electric field has been used to classify into material that is transparent, reflective and absorbs electromagnetic energy. The material that absorbs electromagnetic energy is called dielectric material. Thus, the dielectric properties of the material are determined before microwave treatment. There are various dielectric property measurement techniques (coaxial probes, cavity perturbation, waveguide and waveguide transmission line) used for material dielectric property characterisation (Gregory and Clarke, 2006; Hasar, 2010; Sheen *et al.*,;2007, Sheen, 2009; Komarov *et al.*; 2005a).

In this current study, a cylindrical cavity of diameter 570mm and height 50mm was mounted below a KANTHAl electrical furnace capable of controlled heating up to 1400˚C (Figure 4-6). A Hewlett Packard 8753C vector network coupled with a Hewlett Packard 85047 S-parameter test set were connected to the cavity. Both resonant frequencies and Q factors of the cavities were measured in turn by the network analyser and computer software. The principle of this technique is based on the perturbation of a resonant cavity, when a small volume of sample is introduced into it, followed by the relative analysis of the electromagnetic characteristics of the empty and partially loaded resonance cavity. Thus, the difference in the response from the network analyser when material is inserted into the cavity and when it is empty serve as premises to predict the dielectric property of the material in the cavity.

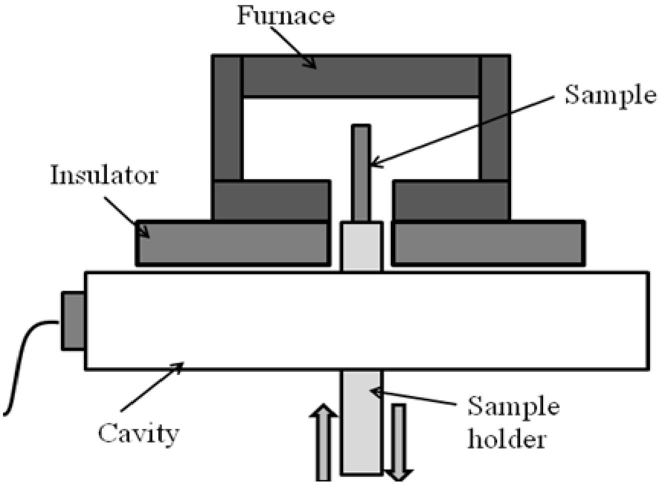


Figure 4-8: Schematic of a resonant cylindrical cavity (Meredith, 1998).

A quartz tube of internal diameter 2.8mm containing a thin layer of glass wool was introduced into the cavity at room temperature. The resonant frequencies and Q factor were measured. Approximately 0.2g of soil sample was then placed above the glass wool layer in the quartz tube. The height of the sample was recorded to calculate the dielectric properties of the material by using Equations 5.6 and 5.7. The soil sample was packed tightly to minimise the gaps, and the packing density was approximately 1.6g/ml. The differences between the bulk densities will affect the dielectric properties because the calculation was based on volume, and a higher bulk density means that more mass of soil was present in the same volume. However, these differences will not affect the trend of dielectric property change against temperature, which is of primary interest in this project. The soil sample within the tube was inserted into the cavity until a maximum perturbation was achieved (indicated by the VNA as the maximum shifting of the resonant frequency peak) before the sample was introduced into the furnace above the cavity to heat it to the desired set temperature. At the target temperature the heated soil samples were immediately introduced into the cavity and the resonant frequency and Q factor were measured.

$$\varepsilon'' = J_1^2\left(x_{1,m}\right)\left(\frac{1}{Q_1} - \frac{1}{Q_2}\right)\frac{V_c}{V_s}$$

Equation 4-1

$$\varepsilon' = 1 + 2J_1^2\left(x_{1,m}\right)\frac{f_0 - f_1}{f_0}\frac{V_c}{V_s}$$

Equation 4-2

Where $V_c$ = cavity volume ($m^3$), Vs = volume of sample ($m^3$), $f_0$ = resonant frequency of the empty cavity (Hz), $f_1$ = resonant frequency of the cavity with sample (Hz), $J_1$ = first order Bessel function, $Q_1$= quality factor of the empty cavity, the $Q_2$= quality factor of the cavity with dielectric material, and $x_{1,m}$ = function of the air-filled cavity.

## 4.10 X-ray diffraction (XRD) analysis

Mineralogy is a scientific study of chemistry, crystal structure and physical properties of minerals and the rapid analytical technique employed is X-ray power diffraction (XRD), which determines the atomic arrangements of minerals to identify and classify them and defines the crystal structures of the minerals. The principle of XRD relies on the fact that crystalline materials do have their own atomic arrangement and compositions, which result in a specific physical structure that scatters X-ray irradiation at certain angles of incidence (Moore and Reynold, 1998). It can be generated by rapid deceleration of fast-moving electrons as they strike the metal target in a vacuum X-ray tube. Though X-ray diffraction gives high spectral resolution, its intensity is lower for a specific beam of current compared to energy dispersive X-ray (EDX). As the name implies, EDX is used for the elemental analysis or chemical characterisation of samples. The space between two successive planes is known as the inter-atomic spacing or interplanar spacing (d-spacing). A concept known as Bragg’s law (Equation 6-2) gives the relationship between this inter-atomic spacing, the angle of diffraction (θ) and the wavelength of the incident radiation (Brown, 1961; Dinnebier and Billinge, 2008).

$$n\lambda = 2d\sin\theta$$

Equation 6-2

Where n = integer (order of diffracted beam); λ = wavelength (Å); d = inter-atomic or d-spacing; θ = diffraction angle or Bragg's angle (degrees).

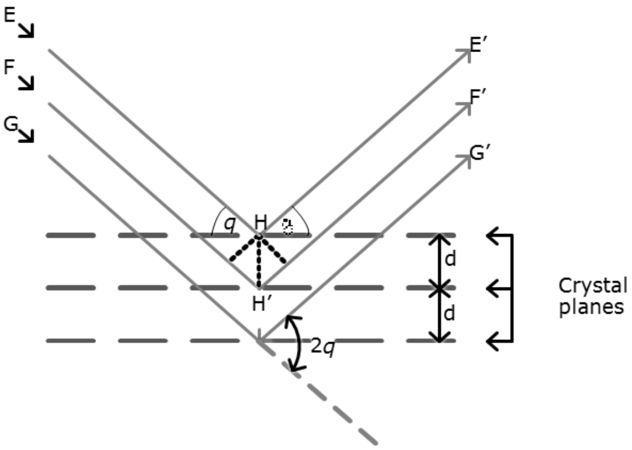


Figure 4-9: Bragg reflection of coherent X-ray from uniformly spaced atomic planes within the crystal.

When a focused monochromatic X-ray beam interacts with a single crystal, mineral or mixture of minerals in powder form, diffraction occurs from the atomic planes in the crystal materials. This takes place when the optical path difference between rays EHE and FHF (Figure 3-7) is an integral multiple of the wavelength, leading to the constrictive interference and formations of XRD peaks. The movable detector in the X-ray diffractometer measures the intensity and diffraction pattern, which yield information about the morphological details of the measured minerals.

## 4.11 Microwave pyrolysis

Microwave power and heating time were investigated as key operational variables. The effect of energy input can then also be determined. The main components of the experimental apparatus are shown in Figure 4-7.

They include a 2.45GHz microwave generator with a maximum power input of 6kW, a microwave power reading to detect the reflected power, a manual E-H tuner to improve the impedance matching, a TE10 single-mode cavity, a series of WR340 waveguides to connect the microwave generator with the cavity, a nitrogen cylinder to supply nitrogen gas, a flow meter to control the nitrogen flow, a gas extractor to extract off the gas, and a reactor with an internal diameter of 35mm (Figure 4-5).

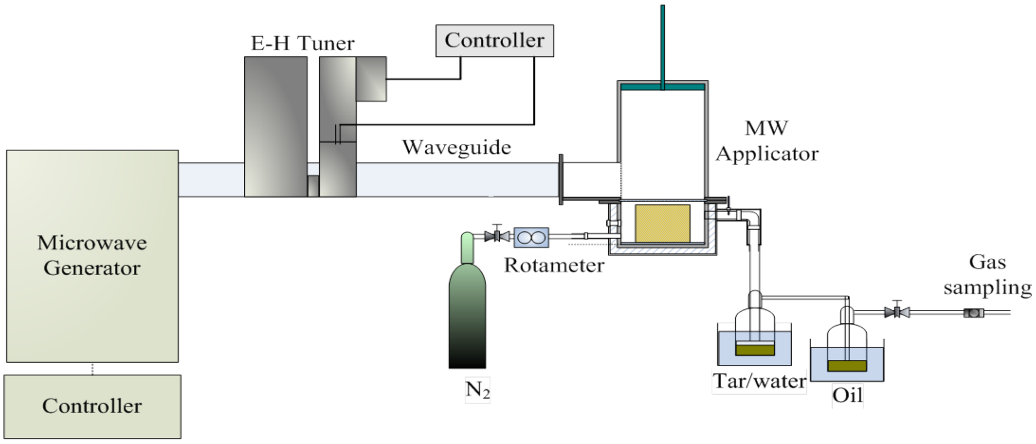


Figure 4-10: Illustration of equipment used to perform microwave treatment of contaminated soils.

The underlying principles of functioning of a TE10n single-mode cavity were introduced in Chapter 3. The microwave exposure was monitored using the HOMER software to log both forward and reflected power. The gas flow rate was set using a gas regulator and maintained throughout the exposure period. Pressure is monitored on the pressure gauge attached.

Soil residue was collected inside the applicator post exposure. Crude oils generated were collected from within the applicator by solvent washing and recovery. The remaining oil was collected from the traps for analysis. A proportional valve was used for collecting a gas sample within a gas chromatography bag, and the remaining gas was vented into the extraction system. The equipment was operated at elevated pressures and temperatures, therefore a temperature and pressure drop was required to stop the reaction. This was done by a collection of the product stream into a condensing vapour trap using a coolant; the coolants used were dry ice/acetone. The temperature of the treatment was calculated using the equation below:

$$\Delta T = \frac{P\Delta t}{\rho C\rho}$$

Where P = operating power of the microwave system, $\Delta t$ = treatment time (Sec), $\rho$ = soil density, $C\rho$ = specific heat capacity of the soil.

## 4.13 Open column chromatography

Chromatography is the general term for the physical and/or chemical separation technique which depends on the interaction of the sample with the stationary phase, which is subdivided according to the physical state of the two separating phases (mobile phase and stationary phase). The theory behind the column chromatography is similar to other forms such as Thin-Layer chromatography. A mixture of substances of interest is swept by a carrier liquid through the column containing media or a medium (stationary phase) to which they have some physical or chemical affinity (e.g. size, solubility or polarity). Thus, each component of the mixture will travel at different speeds due to different affinities to the stationary (alumina and silica) phase and hence become separated.

Separation of oil fractions (extracts, free oils and hydropyrolysate products) into compound classes was performed on the basis of molecular polarity, retention to the alumina/silica stationary phase (pre-extracted as described previously) and solubilities in different solvents. A small plug of pre-extracted cotton wool was placed at the base of the column, which was then pre-rinsed with $CH_2Cl_2$ to remove all organic contamination, and then washed with n-hexane and silica. The stationary phase was added to the chromatographic column by the “tap and fill” method to ensure consistent column density with no trapped air and consistent eluent received into a conical flask. The alumina/silica (2:3) was then flushed with n-hexane. The sample was then added to the top of the wet column (Figure 4 -10.

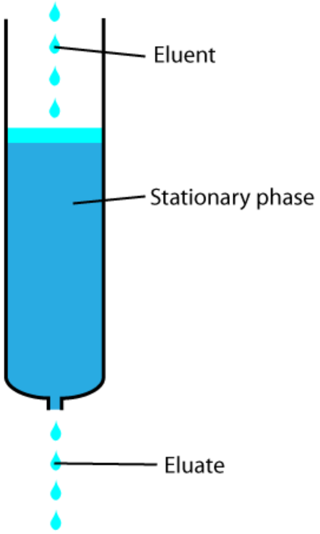


Figure 4-11. Diagram of a column chromatography (Wikipedia).

Separation of the aliphatic hydrocarbons was attained by elution with 15ml n-hexane. The aromatic hydrocarbon was obtained by elution with a mixture of DCM and n-hexane (40:60). Lastly, the polar species were obtained by elution with 1:1 mixture of DCM and methanol. Product yields were collected in cleaned, pre-weighed glass vials where they were evaporated to dryness.

## 4.14 Gas chromatography

The gases generated during the experiments were collected from the pyrolysis reactor with a gas bag, and transferred for gas chromatography and GC analysis (Figure 4-8) with a gas-tight syringe. Gas in the syringe was injected into a Perkin Elmer Clarus 580N gas chromatograph equipped with capillary columns for analysis. A Flame-Ionisation Detector (FID) and a Thermal Conductivity Detector (TCD) were used for the GC chromatograph with the temperature set at 200°C respectively. Samples were injected in split mode (split ratio 10:1) with a sampling rate of 12.5 pts/s. The injector temperature for the FID and TCD was 250ºC and 165ºC respectively. The oven temperature was held at 60ºC for 13 minutes before being raised from 60–180ºC at a heating rate of10ºC/min$^{-1}$, then isothermally held for 10 minutes.

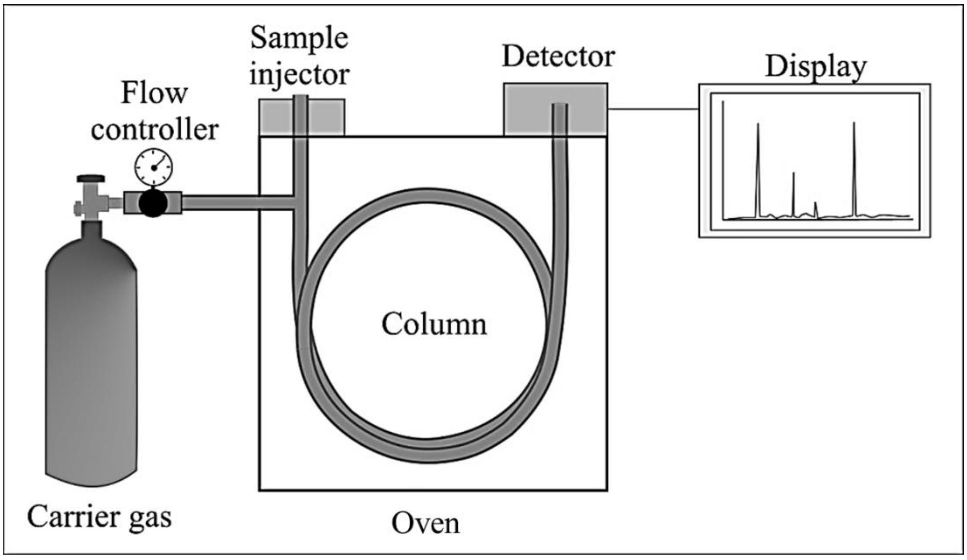


Figure 4-12: Schematic diagram of a gas chromatography (adapted from Eötvös University webpage).

For hydrocarbon analysis, helium with a flow rate of 2mLmin$^{-1}$ as carrier gas while argon was used as carrier gas for non-hydrocarbon at a flow rate of 41.7mLmin$^{-1}$ respectively. The gas constituents were identified and quantified by comparison to standard mixed calibration gas components: hydrogen 10%, carbon monoxide 40%, carbon dioxide 10%, hydrogen sulphide 20% for the TCD detector, and ethene 0.2%, propylene 0.2%, 1-butene 0.2%, 1-pentene 0.2%, methane 20%, ethane 10%, propane 5%, n-butane 2%, n-pentane 1% for the FID detector.

The GC is used to measure the gas by drawing a small amount of the sample to be analysed up into a gas-tight syringe. The syringe needle is placed into a hot injector port of the gas chromatograph, and the sample is injected. The injector is set to a temperature higher than the components' boiling points, so the components of the mixture evaporate into the gas phase inside the injector. A carrier gas, such as helium, flows through the injector and pushes the gaseous components of the sample onto the GC column. It is within the column that separation of the components takes place. Molecules partition between the carrier gas (the mobile phase) and the high boiling liquid (the stationary phase) within the GC column. After components of the mixture move through the GC column, they reach a detector. Ideally, components of the mixture will reach the detector at varying times due to differences in the partitioning between mobile and stationary phases. The detector sends a signal to the chart recorder, which results in a peak on the chart paper. The area of the peak is proportional to the number of molecules generating the signal.

## 4.15 Gas chromatography-mass spectrometry (GC-MS)

The analytical technique combines the resolving power of capillary GC with the sensitivity of mass spectrometry, and enables separation, quantification and identification of many complex organic mixtures like crude oil fractions, and is one of the most widely used analytical techniques in organic geochemistry. GC-MS is particularly adept at resolving higher cyclic alkanes and aromatic hydrocarbons (Miles, 1994). This has allowed for the positive identification of volatile or low-molecular-weight hydrocarbons, but these are not suitable methods for the analysis of heavy-molecular-weight hydrocarbons with low volatility. Traditionally the analysis of extracting hydrocarbon fractions has been done by gas chromatography (GC) (Behar and Albrecht, 1984; Mackenzie *et al.*, 1983), mass spectrometry (MS) (Seifert and Teeter, 1970a; Dzidic *et al.*, 1988) and GC-MS (Seifert and Teeter, 1970a; Jaffé & Gallardo, 1993).

GC-MS (Figure 4-9) is an analytical instrument used to measure the level of degradation and maturity of the oils. Analysis of hydrocarbon fractions in the present work was carried out on a Varian 1200 Quadrupole MS (ionising energy 70eV, source temperature 250$^o$C, transfer line 300$^o$C) coupled with a CP3800GC. Separation was achieved on a VF-1MS-low-bleed 100% dimethylpolysiloxane column (50m length, 0.25mm internal diameter, and 0.25µm film thickness), with helium as a carrier gas (100KPa) at 1.5ml/min, and an oven temperature program of 50$^o$C (two minutes) to 300$^o$C (33 minutes) at 5$^o$C/min.

The oil sample was injected into the GC chamber by syringe through a self-sealing septum and separated into fractions based on partitioning of sample fractions between the mobile carrier gas flow (helium) and the stationary phase (a thin dimethylpolysiloxane film lining). The oil fractions were separated into their components before leaving the GC column based on their retention on the stationary phase (McMaster, 2008).

The gas chromatograph separates the components of the mixture and are directly fed via heated interface into the ion sources of the mass spectrometer; they are bombarded with a high-energy beam of electrons. This results in ionisation of the separated fraction of the oil sample to create molecular ions and cause the unstable compounds to fragment into lower mass species according to their molecular structure. The ionised molecules are subsequently focused into a concentrated beam and transported into the mass analyser, where only positive ions of a given mass-to-charge ratio (m/z) contact the detector at any moment through a quadrupole (consisting of four cylindrical rods, orientated in a square arrangement) generated electric field because of their fast scanning rate and cost-effectiveness (Masucci and Caldwell, 2004; McMaster, 2008). When radio frequency and direct current are applied it enables the ions with a specific m/z to have a stable trajectory and pass through the detector. By increasing the RF and DC potential simultaneously, ions of increased m/z pass through the analyser into the detector (Masucci and Caldwell, 2004). On reaching the detector after leaving the mass anaylser, where the detector is an electron multiplier, owing to their fast response and large gain, the initial small ion current that arrived to produce a recordable signal is amplified. The signal is then processed as an ion current m/z versus time – effectively recording results in three dimensions (Masucci and Caldwell, 2004; McMaster, 2008). These provide information to aid structural identification of the GC effluents.

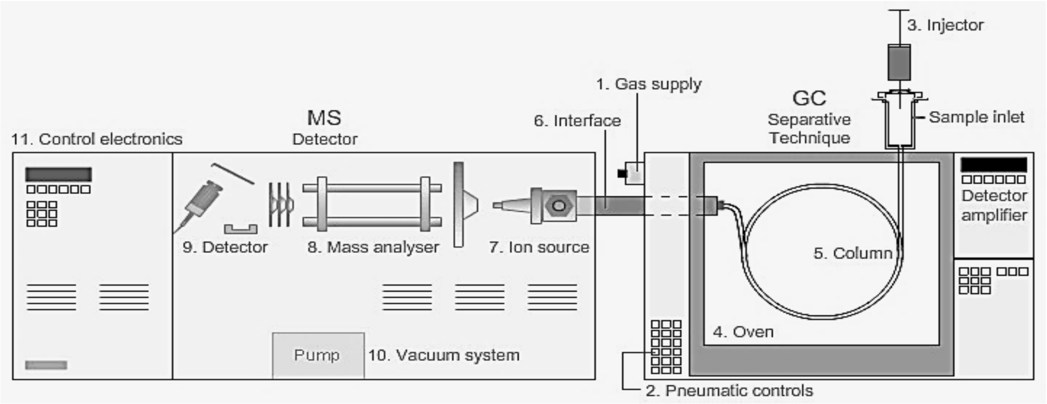


Figure 4-13: Schematic diagram of gas chromatography-mass spectrometry (adapted from CHROMacademy).

The raw signal summed all ions and the representative relative abundance of all eluted compounds, and it can be plotted against retention time as total ion chromatogram (TIC). The saturated aliphatic fractions were detected by selective ion chromatogram (SIC) mode, which involves monitoring the ion current for a selected mass fragment (m/z) value characteristic of a particular compound or group. The aromatic fractions were detected by full scan mode, which is the sum of the currents generated by all the fragment ions of a particular compound that is proportional to the instantaneous concentration of that compound in the ionising chamber of the mass spectrometer. SIC mode is mostly used for trace analysis because it is more selective and often more specific than full scan. It results in better signal-to-noise ratios.

In this current research, full scan analysis was performed on the oil and soil organic extract to provide mass spectra for structural elucidation and chromatograms of all ions. However, SIC mode was used to identify some selected biomarkers such as saturated hydrocarbon (m/z 71), hopanes (m/z 191), steranes (m/z 217), and aromatic fraction such as naphthalene and phenanthrene as diagnostic ions to provide better results in the signal-to-noise ratio correlation study of the oil and soil organic extract. A brief description of the procedure for the oil products from the remediation process is provided below:

The pyrolysis oil or crude oil in DCM solution is injected into the GC inlet where it is vaporised and swept onto a chromatographic column by the carrier gas (usually helium). The sample flows through the column, and the compounds comprising the mixture of interest are separated by virtue of their relative interaction with the coating of the column (stationary phase) and the carrier gas (mobile phase). The latter part of the column passes through a heated transfer line and ends at the entrance to the ion source, where compounds eluting from the column are converted into ions. As the chemicals exit the GC column they enter the high vacuum chamber of the MS where the chemical is exposed to an ionisation source that breaks apart the chemical into a number of ionised fragments. By controlling the ionisation energy and “tuning” the MS, a reproducible fragmentation pattern (spectrum) is created and compared to a reference database (library) of over 150,000 chemicals.

# Chapter 5: Organic matter distribution and geochemical analysis of the polluted soil

## 5.1 Scope

This chapter discusses the distribution of carbon in the soil as solvent-extractable, insoluble but thermally labile and black carbon. The proportion of the carbon distribution will determine the proportion of contaminants in the soil that is removable by the remediation techniques. Therefore, the amount of black carbon or recalcitrant will consequently be used to suggest how effective and efficient the remediation techniques used in this study are. This will be followed by a description ofthe yields of the components of solvent-extractable oil contaminant that was removed by the soxhlet extraction process, along with the yield of components of insoluble but labile oil extract released by HyPy from the asphaltene present in the soil residue obtained from the soxhlet extraction process. The oil extract from the soxhlet extraction and the HyPy was further fractionated to yield aliphatic, aromatic and polar fractions.

In addition, the chapter shows a comparison between the oil extract from the soxhlet extract with both the crude oil provided for this research and oil extract isolated from HyPy. The comparison was based on the biomarker's nature of aliphatic hydrocarbon in the oil extracts from the asphaltene and the maltene from the soxhlet extraction process. The major areas of interest in this study on the biomarker's nature are the depositions environment, the degree of the biodegradation and thermal maturity of the crude oil and the oil extracts respectively.

## 5.2 Nature of the organic carbon in the soil

Soil organic carbon is the component of organic matter in the soil resulting from the decomposition of organic materials such as crude oil in the soil. The distribution of the soil organic carbon gives insight into the proportion of organic carbon that potentially comes from the crude oil contamination and those from pyrogenic organic carbon in the soil.

The elemental analyser was used to determine the total organic carbon (TOC) present in the fresh contaminated soil, the soil residue from soxhlet extraction. The HyPy was used to separate effectively insoluble thermally labile from the soil, leaving behind residue composed of resistant carbon fraction (black carbon) (Ascough *et al.*, 2009) . The TOC distribution of the three samples gave the proportion of carbon that is solvent extractable, thermally labile and black carbon or recalcitrant carbon (Ascough *et al.*, 2009). The pie chart in Figure 5-1 clearly shows that the majority of the soil TOC (78%) is solvent extractable in methanol/dichloromethane mixture, with most of the insoluble remainder (17%) being thermally labile under HyPy conditions, while the residual 5% of the soil TOC is composed of insoluble recalcitrant (black carbon) material. Therefore, the overall 95% of the original TOC in the soil could potentially be removed when thermal remediation techniques are employed, while 5% will remain as black carbon in the soil. The observed result will be used to determine the effectiveness and efficiency of the remediation technology employed in this research.

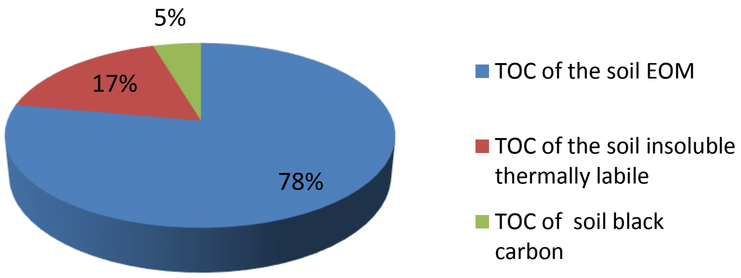


Figure 5-1: Shows distribution of organic carbon in the soil matrix.

## 5.3 Distribution of the soil organic matter

The soil was soxhlet extracted and the extractable organic matter was then separated into maltene and asphaltene. The asphaltene fraction was isolated from the extractable organic matter using n-pentane and that of the crude oil was subjected to HyPy. The HyPy products and the maltenes from the crude oil and the soil-extractable organic matter were fractionated. The yield of the crude oil separation yielded 95.2% maltene and 4.8% asphaltene respectively. Likewise, the soil-extractable organic matter yielded 88.3% maltene and 11.7% asphaltene respectively. The reduction in the maltene content and increased asphaltene content may have resulted from the biodegradation of the crude oil within the soil sample, which will be verified by the biomarker analysis. The yields obtained from the fractionation of the maltenes (free phase) and the HyPy oil extract from the asphaltene (bound phase) into aliphatic, aromatic and polar components are shown in Table 5-1. There was an increasing trend apparent in the aromatic and polar fraction values in the asphaltene of the crude oil and soil-extractable organic matter. Furthermore, the aliphatic fractions in the maltene and asphaltene of the crude oil were greater than the soil-extractable organic matter respectively.

Table 5-1: Yields of products obtained from column fraction of crude oil and oil extract maltenes and asphaltene hydropyrolysates.

| Sample | Maltene (%) | | | Asphaltene (%) | | |
|---|---|---|---|---|---|---|
| | Aliphatic | Aromatic | Polar | Aliphatic | Aromatic | Polar |
| Crude oil | 87 | 9 | 4 | 51 | 12 | 37 |
| Oil extract (Sox. Ext.) | 85 | 10 | 6 | 44 | 21 | 35 |

The reduction might have been as a result of degradation of the oil in the contaminated soil, and Section 5.4 describes the nature of the biomarker in the soil to show if there is degradation of the oil in the soil sample.

## 5.4 Geochemical analysis of the maltene fractions of crude oil and the extractable organic matter (EOM) from soil using soxhlet extraction procedure

The most widely useful applications for biomarkers are dispositional environment, biodegradation and the thermal maturity of organic matter in the organic materials (Peters *et al.*, 2005). It has found usefulness in correlation studies of oil correlation studies (Curiale, 2008; Eneogwe and Ekundayo, 2003; Wang *et al.*, 2011; Onyema and Manilla, 2010).

The current study has provided information on the source of the organic input, depositional conditions, biodegradation, thermal maturity and correlation between the maltene fraction of the crude oil and EOM from the soil as well as the bound phase biomarkers released by HyPy from the soil residue obtained from the soxhlet extraction process. The geochemical characteristics of the samples were examined based on saturated and aromatic hydrocarbon in the samples, and the geochemical parameters used are the following molecular ratio pristane/phytane (Pr/Ph), pristane/$n$-$C_{17}$, phytane/$n$-$C_{18}$, homohopane index and $C_{29}$ sterane index. The molecular ratios used in this study were quantified by integration of peak areas in the m/z 71, m/z 191 and m/z 217 chromatogram respectively.

### 5.4.1 Source input and depositional conditions of the crude oil and oil extract from soil

Some specific biomarkers are apparently restricted to certain environmental settings, presumably owing to the limited occurrence of their source organism(s). Furthermore, the environmental conditions may influence the biomarker's composition obtained after diagenetic transformation of the precursor biochemical in sediments (Didyl *et al.*, 1978).

The pristane/phytane (Pr/Ph) ratio and oleanane have been interpreted to describe the source input and depositional condition of samples in correlation studies. Peters *et al.* (2005) suggested that high Pr/Ph indicates terrigenous input under oxic conditions and low Pr/Ph indicates anoxic/hypersaline or carbonate environments. Table 5-2 and Figure 5-2 showing high values of the Pr/Ph ratio in both crude oil and EOM suggest terrigenous input. Table 5-2 is a list of diagnostic ratios calculated from semi-quantitative data (peak area) from their chromatograms. The CPI, Pr/n-$C_{17}$ and Ph/n-$C_{18}$ in Table 5-2 are used for examination of biodegradation of organic matter, while $C_{29}$ to $C_{30}$ hopanes, Ts/Tm, Oleanane and $C_{29}$ steranes are used for source input, depositional environment and thermal maturity of the crude oil and EOM. The $C_{29}$ $\alpha\beta\beta/(\alpha\beta\beta + \alpha\alpha\alpha)$, $C_{29}$ 20S/(20S + 20R), $C_{31}$-hopane, $C_{32}$-hopane and oleanane index are used for the thermal maturity of organic matter.

Table 5-2: Geochemical parameters computed from the biomarkers distributions in oil samples.

| Parameters | Crude Oil | EOM |
|---|---|---|
| CPI | NM | NM |
| Pr/n-$C_{17}$ | 5.99 | 4.51 |
| Ph/n-$C_{18}$ | 9.11 | 4.44 |
| Pr/Ph | 2.99 | 1.86 |
| Ts/Tm | 0.96 | 0.95 |
| $29\alpha\beta/29\beta\alpha$ | 0.73 | 0.49 |
| $29\alpha\beta/30\alpha\beta$ | 0.80 | 0.69 |
| $Ol/30\alpha\beta$ | 0.91 | 0.82 |
| $30\beta\alpha/30\alpha\beta$ | 0.15 | 0.16 |
| 31(S/S+R) | 0.60 | 0.59 |
| 32(S/S+R) | 0.59 | 0.59 |
| $29\alpha\alpha\alpha$(S/S+R) | 0.36 | 0.36 |
| 29 $(\alpha\beta\beta/(\alpha\alpha\alpha+\alpha\beta\beta)$ | 0.51 | 0.45 |
| MPI-1 | 0.80 | 0.73 |

Oleanane arises mainly in late Cretaceous or younger rocks, and oleanane content suggests a deltaic source rock with strong terrigenous input (Ekweozor *et al.*, 1979). The oleanane index is the ratio of oleanane to $C_{30}$. Peters *et al.* (2005) suggested that a value of oil greater than 0.2 for the oleanane index implies a tertiary source rock, which means that the two samples are similar and likely to be from a tertiary source rock.

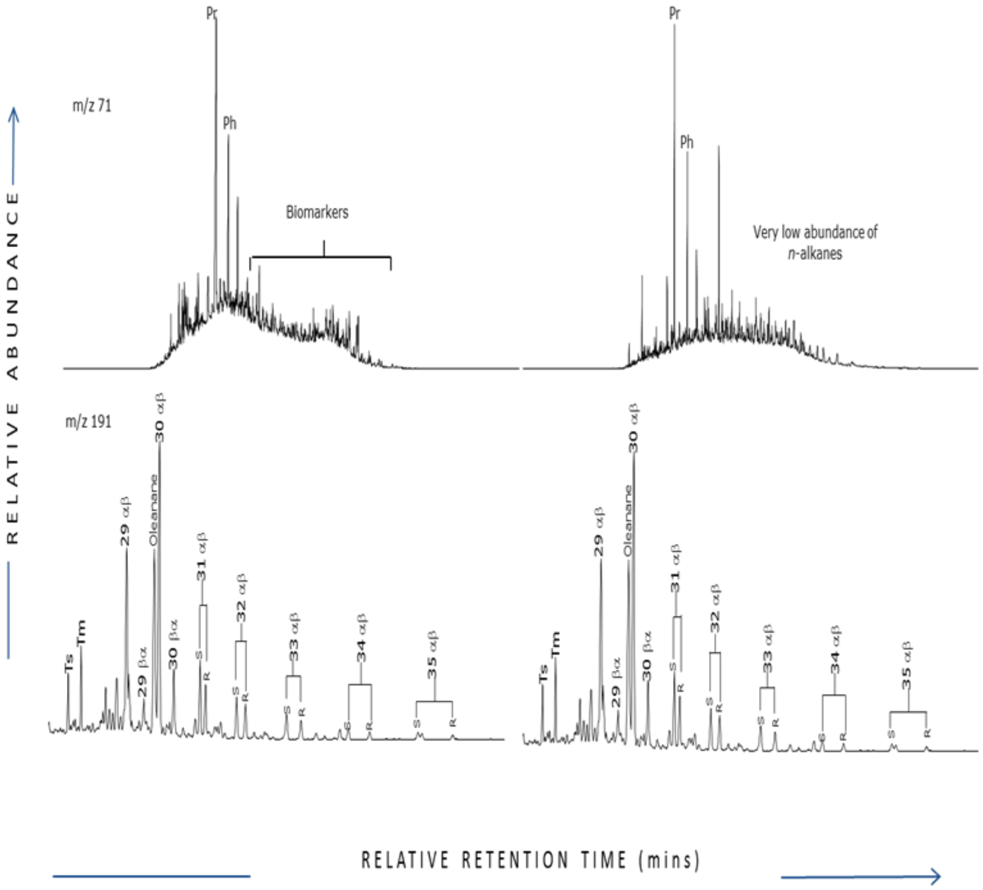


Figure 5-2: Chromatogram plot of aliphatic (m/z 71) and hopane (m/z 191) hydrocarbons of crude oil and oil extract from soil sample.

Since Ekweozor *et al*. (1979a) suggested that oleanane is common to oil from the Niger Delta basin, it could be inferred that the oil extract is similar to the crude oil provided for this work from the SPDC based in Nigeria. The overall assumption from the molecular ratio of the Pr/Ph and the oleanane is that the crude oil and the EOM from the soil have the same source input and depositional environment.

### 5.4.2 Biodegradation of the crude oil and EOM from soil

The sequence of increasing resistance to biodegradation of biomarkers is: *n*-alkanes, isoprenoids, steranes, hopanes/diasteranes and aromatic steroids and porphyrins (Peters *et al.*, 2005). The differential resistant to biodegradation has been used to rank oils' extent of biodegradation. Peters and Moldowan's (1993) scale of degree of biodegradation has been used over the years to classify organic sediments and oil based on the relative amount of biomarker types present.

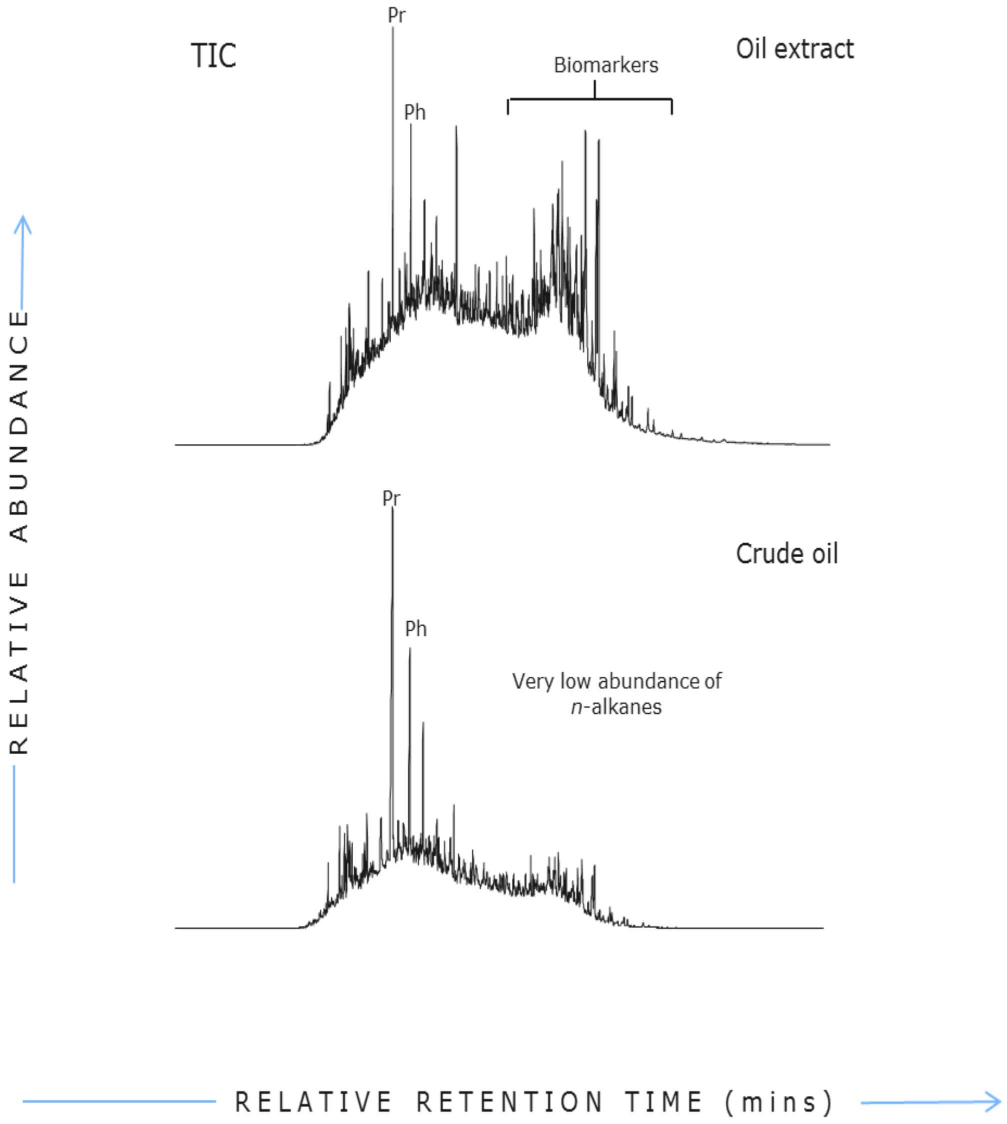


Figure 5-3: TIC of the oil extract and the crude oil.

The pristane/*n*-$C_{17}$ and phytane/*n*-$C_{18}$ ratios are largely dependent on the degree of biodegradation as the isoprenoids are more resistant than the corresponding *n*-alkanes, and these ratios increase as biodegradation progresses (Peters *et al.*, 2005). The value for pristane/*n*-$C_{17}$ and phytane/*n*-$C_{18}$ were quantified by integration of peak areas in the m/z 71 chromatogram, and it was a high value of 5.99 and 9.11 respectively. This indicates that the crude oil and the oil extracts were biodegraded.

The TIC (total ion current) chromatogram (Figure 5-3), which represents the total intensity across the entire range being detected at every point, revealed an unresolved complex mixture (UCM) of *n*-alkane and the presence of pristane and phytane in both crude oil and oil extract respectively. The Peters and Moldowan (1993) scale ranks such observation as level 4. These observations suggested that both the crude oil and oil extract from the soil are biodegraded to the same degree.

### 5.4.3 Thermal maturity of the crude oil and the oil extract from the soil

Hopanes and steranes are mostly used for thermal maturity assessment because their biologically inherited configuration of the precursors is thermodynamically unstable, which leads to progressive configuration isomerisation at a certain defined chiral (C-20 for sterane, C-22 for hopane) as maturation progresses in crude oil (Ascough *et al.*, 2009, Peters *et al.*, 2005). The homohopane isomerisation ratio measures hopane side chain isomerisation at the C-22 chiral centre within the $C_{31\text{-}35}$ 17$\alpha$-hopanes. The biologically dominant 22R configuration is gradually converted to 22R and 22S (diastereomers) with increasing thermal maturity (Peters *et al.*, 2005).

This relationship is commonly measured for the abundant $C_{31}$ and $C_{32}$ homohopanes using the 22S/(22S+22R) ratio, rising from approximately 0 to 0.6, where equilibrium was suggested to be between 0.57–0.62 during maturation. After this equilibrium, no further reliable information on maturation could be obtained, and approximately 0.5 signifies the beginning of the oil generation window (Peters *et al.*, 2005). The Ts/Tm of hopane is expected to increase from 0 to 1 with increasing maturity (Peters *et al.*, 2005).

In this current study, the hopane chromatogram in Figure 5-4 revealed many hopane series with 17$\alpha$, 21$\beta$(H) isomers being the dominant stereochemistry. The hopane profile is dominated by 29$\alpha\beta$, oleanane, 30$\alpha\beta$ hopane and Ts (18$\alpha$-22, 29, 30-trisnorneohopane) and Tm (17$\alpha$-22, 29, 30-trisnorhopane).

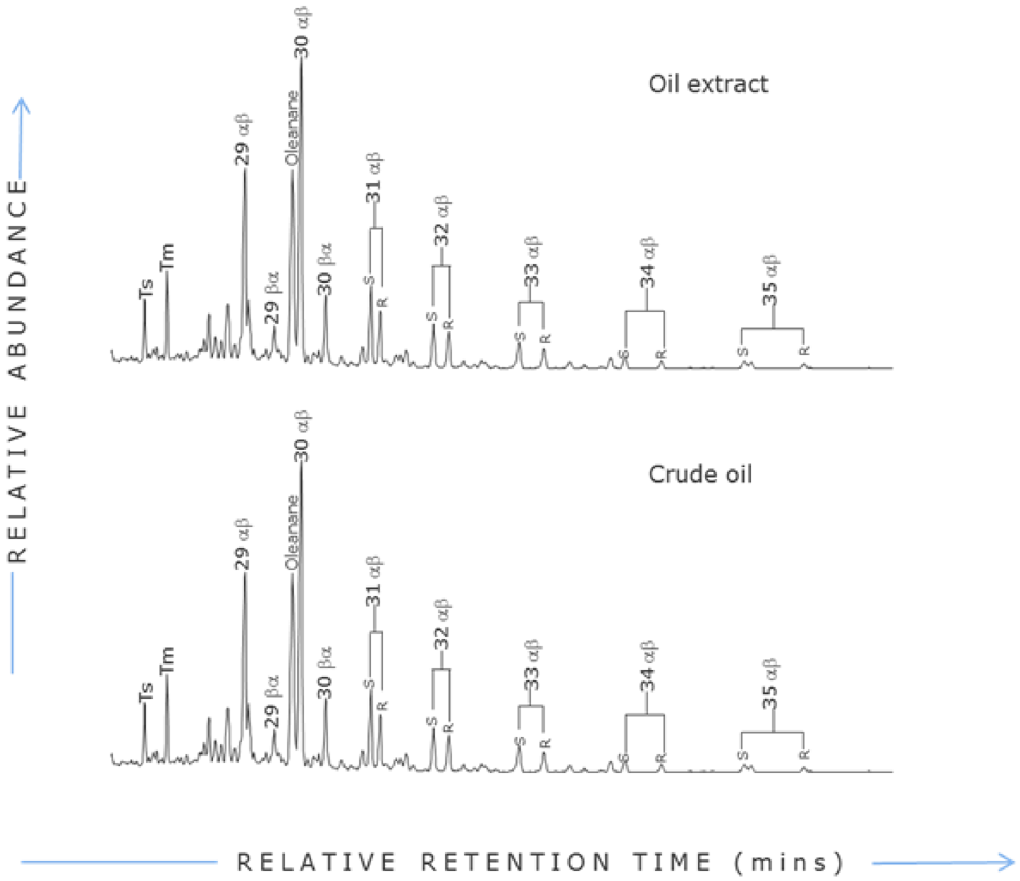


Figure 5-4: Showing the chromatogram plot m/z 191 hopane fractions of the crude oil and the oil extract from the soil.

From Table 5-2, the value of the Ts/Tm ratio (crude oil = 0.96 and oil extract = 0.95) signifies that they (oil extract and crude oil) are both moderately matured oil. $C_{29}/C_{30}$ hopane ratio is low (<1), which means the oil and the oil extract were not generated from sources rich in carbonaceous organic matter (Peters *et al.*, 2005). The 31S/S+R ratio for both crude oil and the oil extract is the same (0.59), which indicates that crude oil is quite mature and has reached the equilibrium maturation, which is the main phase of oil generation (Peters *et al.*, 2005). Sterane biomarker in crude oil and the oil extract from the soil can be assessed with m/z 217 (Figure 5-5). Steranes undergo degradation in the following order: ααα 20R > ααα 20S > αββ 20R > αββ 20S > diasteranes (Hegazi and El-Gayar, 2009).

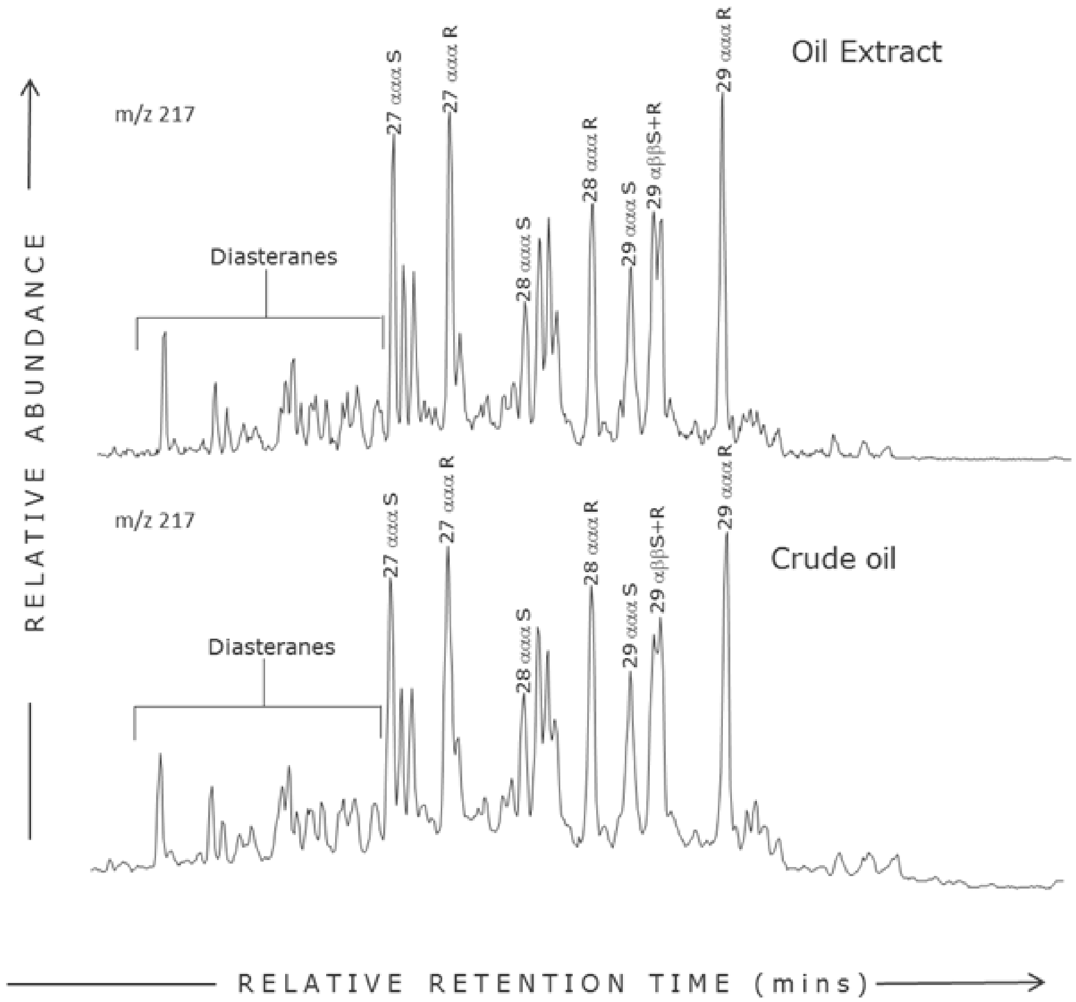


Figure 5-5: Chromatogram plot of m/z 217 for the crude oil and the oil extract from the soil.

The sterane maturity parameter mostly makes use of $C_{29}$ sterane because it offers the least interference from co-eluting peaks, but $C_{27}$ and $C_{28}$ are also used if they are separated from unwanted compounds and properly isolated from parent ions (Peters *et al.*, 2005). During thermal maturation, 20R configuration at C-20 of $C_{29}$ 5α, 14α, 17α H steranes is progressively altered into 20R and 20S epimers. The ratio of 20S/(20S+20R) is to measure the thermal maturity from immature stage to peak thermal maturity, and the value increases from 0 to 0.5 as the maturation progresses (Peters *et al.*, 2005). For steranes maturity, isomerisation measurement that occurred at $C_{14}$, $C_{17}$ are considered for $C_{29}$ sterane. As thermal maturity progresses, it results in an increase in the 5α, 14β, 17β (H) (20R+20S) in relation to the 5$\alpha$, 14$\alpha$, 17$\alpha$ (H) counterpart. Therefore, the isomerisation ratio for C29-steranes ($\alpha\beta\beta$ /($\alpha\alpha\alpha$+$\alpha\beta\beta$)) can be used to express thermal maturity changes with values lower than 0.7, while 0.7 is the equilibrium ratio for steranes (Peters *et al.*, 2005).

The current partial gas chromatogram presented in Figure 5-5 for this study shows a dominant sterane distribution range from $C_{27}$ to $C_{29}$ 5$\alpha$, 14$\alpha$, 17$\alpha$ H of both R and S. The $C_{29}$ 5$\alpha$, 14$\beta$, 17$\beta$ (H) (20R+20S) was also present in a good amount. The distribution of $C_{27}$ to $C_{29}$ steranes indicates that the soil extract is derived from a source rock of terrestrial organic matter (Peters and Moldowan, 1993). The chromatograph of steranes (Figure 5-5) consists predominantly of $C_{27}$, $C_{28}$, $C_{29}$ (20S and 20R) and the presence of diasteranes. Figure 5-5 shows that the steranes show no sign of changes in the distribution, which suggests a moderate degree of degradation of the oil and the oil extract because it is only the *n*-alkanes that are severely affected. The $\alpha\alpha\alpha$/$\alpha\beta\beta$ and 29 S/S+R ratio are expected to increase with maturity.

The maturity parameters for $C_{29}$ steranes 20S/(20S+20R) for both samples (crude oil and oil extract) are 0.36, while the $C_{29}$-steranes $\alpha\beta\beta$ /($\alpha\alpha\alpha$+$\alpha\beta\beta$) are 0.51 and 0.45 respectively (Table 5-3). The parameters confirmed that the crude oil and the oil extract are generated near the peak of the oil window indicating moderate maturity (Peters *et al.*, 2005).

In summary, the biomarker distributions in the crude oil and oil extract from the soil have been examined. The correlation observed based on the source input, deposition environment, biodegradation and thermal maturity parameters suggest that the crude oil is similar to the source of the crude oil in the contaminated soil sample used for this study.

During traditional soxhlet extraction, both maltene and asphaltene content of crude oil are extracted. The procedure was followed by asphaltene isolation as fully discussed in Chapter 4. The asphaltene is an insoluble constituent of crude oil in *n*-heptane. The asphaltene is a large structure in crude oil containing biomarkers that are preserved from biodegradation. It reflects the possible state of the aliphatic hydrocarbon components of the crude oil before degradation. Hydropyrolysis as an analytical tool was used for opening up the asphaltene hydrocarbons to release the saturated hydrocarbon covalently bound to the aromatic constituent, and they were compared with the free phase (maltene) counterpart.

## 5.5 Comparison of the maltene and asphaltene in the oil extract from the soil

### 5.5.1 Comparison of the maltene and asphaltene *n*-alkanes in the oil extract from the soil

In terms of *n*-alkane distribution, the maltene fraction showed that most *n*-alkanes have been severely depleted with only pristane and phytane dominating the partial gas chromatogram.

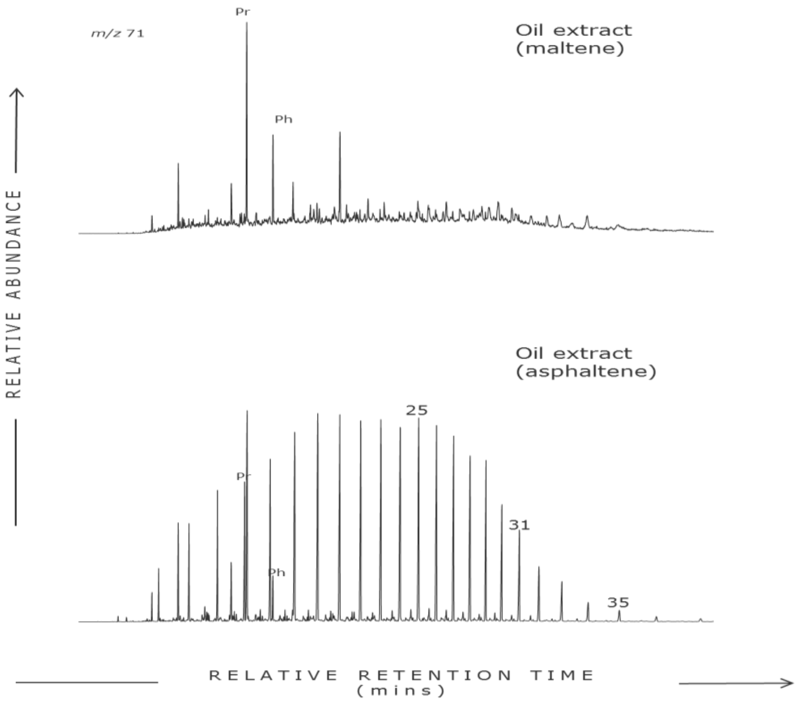


Figure 5-6: m/z 71 partial gas chromatogram of *n*-alkanes distribution release from EOM asphaltene using hydropyrolysis.

However, *n*-alkanes distribution in hydropyrolysate was generated from the asphaltene, and the *n*-alkane distribution was enormous compared to the *n*-alkane in the partial gas chromatogram obtained from maltene (Figure 5-6). Hydropyrolysate shows significant distributions having a strong presence of surviving *n*-alkane ($<C_{17}$) within the bound phase of the oil extract with an extension of *n*-alkanes up to $C_{35}$.

Consequently, the *n*-alkanes in the asphaltene were preserved and are not affected by the biodegradation process experienced by maltene fraction.

### 5.5.2 Comparison of the maltene and asphaltene hopanes in the oil extract from the soil

The hopane parameters are used mostly for thermal maturity and degree of biodegradation, but they can also be used for the source rock depositional environment in the case of oleanane (Peters *et al.*, 2005). In this section, the hopane chromatogram will be used to determine the thermal maturity of the oil extract (Figure 5-7).

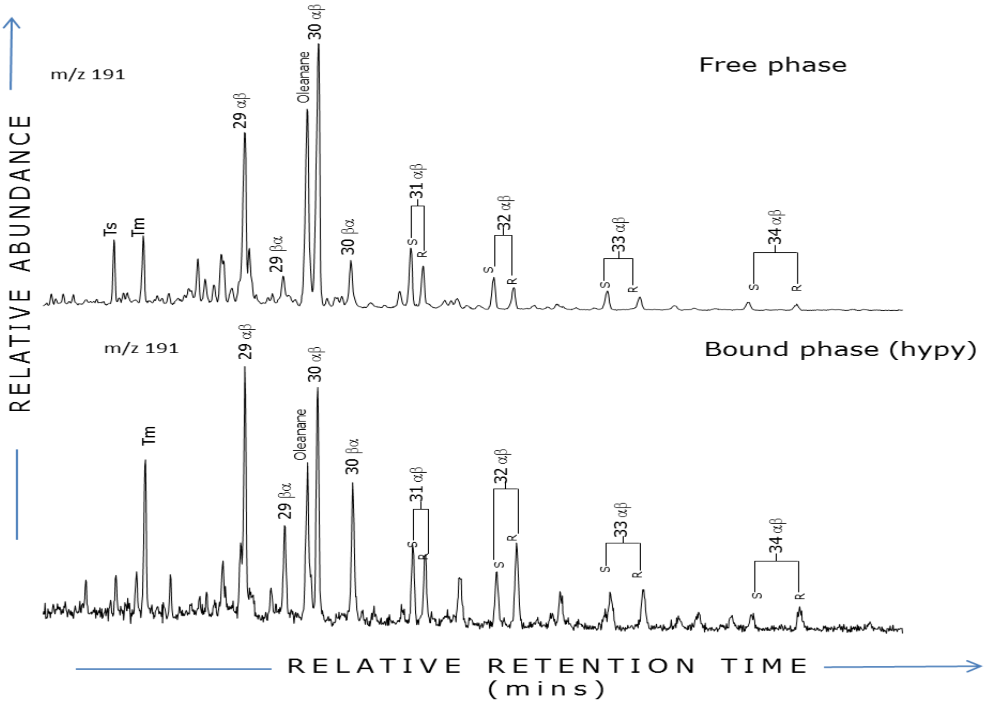


Figure 5-7: m/z 191 partial gas chromatogram of hopanes distribution in the maltene and the asphaltene.

Figure 5-7 revealed the hopane series of the oil extract from the maltene and the asphaltene, with 17α, 21β(H) isomers being the dominant stereochemistry. The hopane profile is dominated by 29αβ, oleanane, 30αβ hopane and Ts (18α-22, 29, 30-trisnorneohopane) and Tm (17α-22, 29, 30-trisnorhopane) for the free phase. The asphaltene hopane profile is similar to the maltene except for the absence of Ts (18α-22, 29, 30-trisnorneohopane) in the profile.

The $C_{29}$ and $C_{30}$ moretanes are βα-isomers that are highly specific for immature to early oil generation. The moretanes are thermally less stable than the αβ-hopanes, and abundances of the $C_{29}$ and $C_{30}$ moretanes decrease relatively to the corresponding hopanes with thermal maturity. The ratio of βα-moretanes to their corresponding αβ-hopanes decrease with thermal maturity from ca. 0.8 to 0.15. (Peters *et al.*, 2005). The visual observation of the chromatogram shows that the $C_{29}$ and $C_{30}$ in the maltene appeared too small in abundance. Thus, it shows that the crude oil is mature.

On the other hand, the hydropyrolysis process of breaking down the asphaltene to produce hopanes series showed a high abundance of $C_{29}$ and $C_{30}$ moretanes (0.87 and 1.39 respectively) in comparison with the maltene value (0.68 and 0.99) (Figure 5-7). This observation suggested that the hydrocarbon was preserved inside the asphaltene structure and was not seriously affected by degradation. The asphaltene contains a hopane series that has high values of Tm, which signifh low maturity. However, the molecular ratio of $C_{29}/C_{30}$ of the free phase and the bound phase were 0.68 and 0.42, which was an indication of terrestrial influence that agrees with past work on Nigeria crude oil by Osuji *et al*. (2015). The values obtained were less than 1, which illustrates that the samples are sourced from hypersaline rock (Peters *et al.*, 2005).

Table 5-3: The biomarker index in maltene and asphaltene of oil extract from the soil.

| Parameters | Maltene | Asphaltene |
|---|---|---|
| CPI | ND | 1.76 |
| Pr/n-C17 | 4.51 | 2.86 |
| Ph/n-C18 | 4.44 | 5.83 |
| Pr/Ph | 1.86 | 0.76 |
| Ts/Tm | 0.95 | ND |
| 29αβ/29βα | 0.49 | 0.20 |
| 29αβ/30αβ | 0.69 | 0.40 |
| Ol/30αβ | 0.82 | 0.86 |
| 30βα/30αβ | 0.16 | 0.67 |
| 31(S/S+R) | 0.59 | 0.51 |
| 32(S/S+R) | 0.59 | 0.37 |
| 29ααα(S/S+R) | 0.36 | 0.10 |
| 29 (αββ/(ααα+αββ) | 0.45 | 0.21 |
| MPI-1 | 0.73 | 0.87 |

The presence of the oleanane in the apshaltene confirmed that the oil extract has terrestrial input from the oil-prone source rocks deposited in a deltaic environment (Ekweozor *et al.*, 1979; Philip and Gilbert, 1986). It has been shown in various studies that oleananes may be considered to be reasonably reliable indicators of higher plant source material (Peters *et al.,* 2005). The value of the oleanane index in both the maltene and asphaltene fractions suggested that it is derived from rock of tertiary age because the values are higher than 0.78 used for classifying oil into the age group (Moldowan *et al.*, 1993).

The observation from the hopane distribution shows that asphaltene fraction has low maturity and hinders rearrangement process to form Ts. Likewise, the $C_{29}$ and $C_{30}$ moretanes in the asphaltene is in higher value than the maltene fraction, which shows that the hopane series was not as matured as the maltene because $C_{29}$ and $C_{30}$ moretanes are expected to decrease with maturity. Consequently, the maltene fractions are more matured than the asphaltene. This was further examined with the sterane distribution discussed in Section 5.5.3.

### 5.5.3 Comparison of the maltene and asphaltene steranes in the oil extract from the soil

The asphaltene showed a full suite of steranes with $C_{27}$ – $C_{29}$ of R configurations dominating the distribution. $C_{29}\alpha\beta\beta$ (R+S) isomers are also present in good amounts. The molecular data derived from the sterane distributions in the bound phase are listed in Table 5-3. The domination of the $C_{29}\alpha\alpha\alpha$R steranes over the $C_{27}$ and $C_{28}$ homologoues suggesst greater contributions of high terrestrial organic matter to the oil source rock (Peters *et al.*, 2005).

The values of the $C_{29}$ $(\alpha\beta\beta/(\alpha\beta\beta+\alpha\alpha\alpha)$ was 0.21, which corroborated the fact that the oil was a low thermally mature sample (Seifert and Moldowan, 1986) as indicated by the hopanes distribution. The isomerisation of the components of the asphaltene were significantly retarded relative to the maltene. The steric protection of the covalent bond biomarkers species by the macromolecular structure of the asphaltene makes the oil less susceptible to isomerisation/rearrangement reaction (Sonibare *et al.*, 2009). Diasteranes are found to be absent in the hydropyrolysates of the aspalthene, which agreed with early investigations that suggested that diasteranes cannot be formed from regular steranes that are bound in asphaltene fractions due to the hindered site of their double bond (Wang *et al.*, 2007). This suggested that the diasteranes in the free phase were results of the oxidative cross-linking/diagenetic rearrangement (C-27 to C-30 rearrangement at C-18 and C-19, no R at C-24) probably catalysed by clay minerals (Figure 5-9). The rearrangement regularly leads to elevation of the concentration of diasteranes in petroleum as thermal maturity increases in derived clay-rich source rocks as shown in the maltene (Peters *et al.*, 2005).

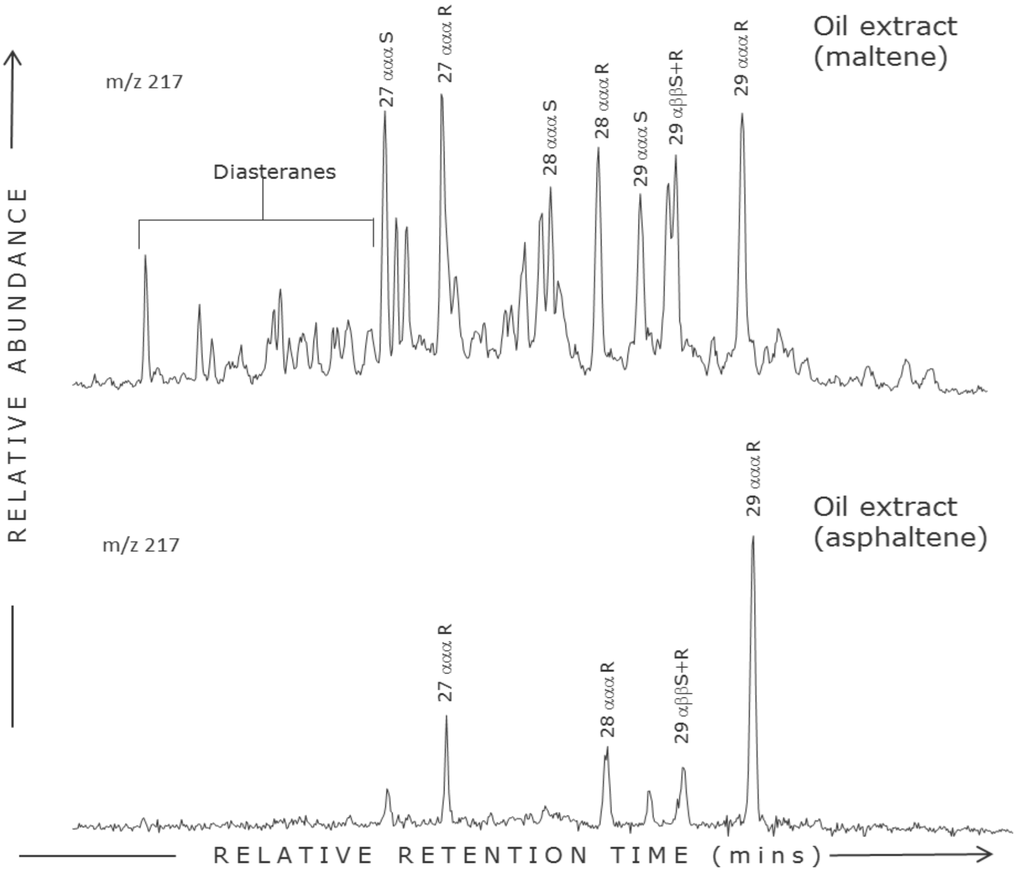


Figure 5-8: m/z 217 partial gas chromatogram of sterane distribution of the oil extract in maltene and sphaltene in the soil.

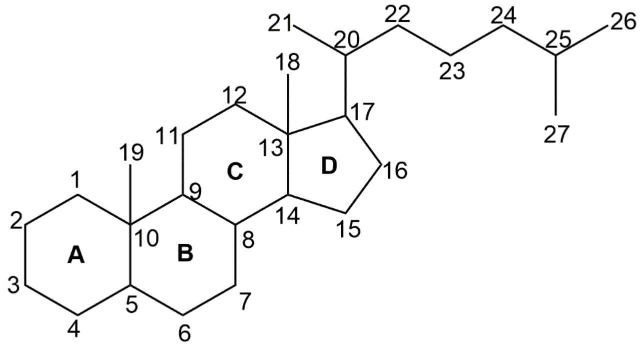


Figure 5-9: The carbon position in sterane where rearrangement will occur to form diasterane.

### 5.5.4 Other biomarker distribution from the soil

The bound phase of the soil from HyPy treatment releases another set of ββ– ($C_{31}$, $C_{32}$, $C_{33}$, $C_{34}$, $C_{35}$) hopanes series as shown in Figure 5-10. The distribution suggests low maturity indicative of the diagnostic contribution from some microaerophilic proteobacteria (Zundel and Rohmer, 1985a, b; 1985c; Summons and Jahnke, 1992). The absence of oleanane in the distribution suggests that it is not from terrigenous source rock and not from Nigerian crude oil because Ekweozor *et al.*'s (1979) past work has confirmed its presence in Niger Delta crude oil.

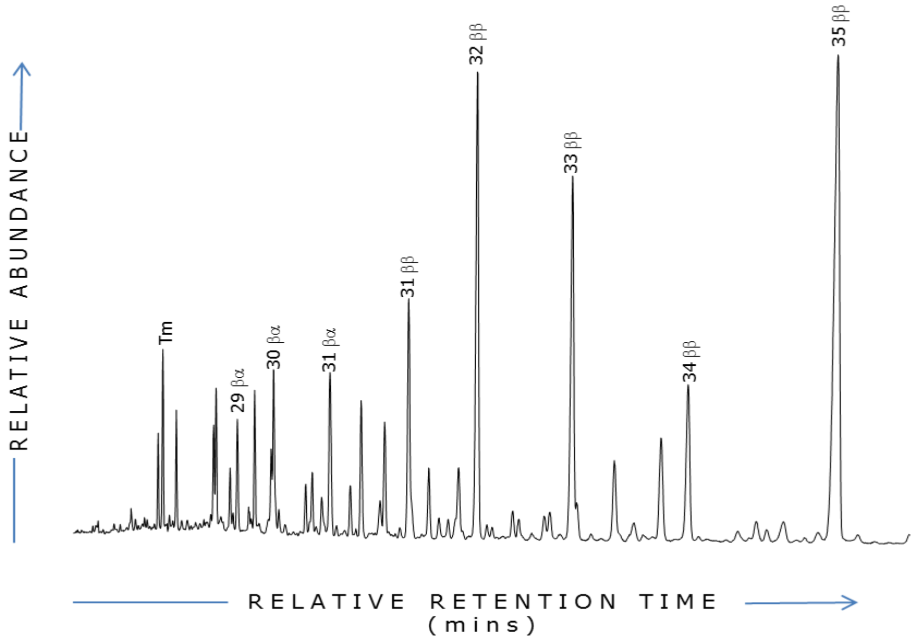


Figure 5-10: m/z 191 partial gas chromatogram of ββ− ($C_{31}$, $C_{32}$, $C_{33}$, $C_{34}$, $C_{35}$) hopanes distribution release from soil using hydropyrolysis.

Overall, the biomarker profile of the maltene experienced biodegradation and thermal maturity to a large extent. The *n*-alkanes of the maltene have been greatly depleted, while the *n*-alkanes of the asphaltene are well preserved. The Ts and diasteranes are absent in the biomarker profile of the asphaltene but present in the maltene fraction of the oil extract from the soil. This further suggests that the hopane and sterane distributions in the maltene have undergone rearrangement in their profiles to form the Ts and the diateranes as the thermal maturity and biodegradation increases, while such events were hindered in the asphaltene fraction. Therefore, it could be said that the maltene fraction showed a significant biodegradation and thermal maturity compared with the biomarker fractions in the asphaltene of the oil extract from the soil.

# Chapter 6: Effectiveness of pyrolysis technologies for remediation of the crude-oil-contaminated soil

## 6.1 Scope

This chapter describes the effectiveness of static Gray-King pyrolysis and microwave pyrolysis as remediation technologies for the polluted soil. The TOC of the char remaining in the soil was used to assess the removal of the extractable organic matter by the two remediation techniques. The techniques are compared to draw conclusions on the most effective approach for the removal of crude oil from the contaminated soil.

## 6.2 Gray-King pyrolysis

### 6.2.1 Precision

#### 6.2.1.1 Solid residue statistical analysis

The full description of the Gray-King pyrolysis can be found in Section 4.7. The repeatability was assessed using a peak temperature of 550°C, which was held for 60 mins treatment time by replicating analysis of the polluted soil 10 times with three different starting masses of approximately 76, 68 and 65g giving 30 tests in total. The repeatability was determined by statistical analysis of the soil residues from the 10 replicates for each mass to determine the precision of the pyrolysis in terms of overall mass loss.

The results of the statistical analysis gave 0.02, 0.02 and 0.02 as the standard deviations for the three different masses used. The relative standard deviation (RSD) is 0.02 for the residues (Table 6-1) indicating that the data obtained are extremely precise.

To affirm the precision of the results, F-test statistics was performed. F-test is a comparison of the spread of sets of data to test if the precisions are similar or dissimilar. This precision is determined by comparing the calculated F value with the applicable F value in the F-table. The calculated F values are obtained by the ratio of variances of the data set ($F= S^2_1/ S^2_{2,}$ where S is the standard deviation of the data set), while the F values are obtained based on the degree of freedom for $S_1$ and $S_2$. If the calculated F value is higher than the F value from the F-table, it means there are significant differences in the precision of the data set, while if the the values are reversed and the F value from the F-table is higher, it means there is no significant difference in the precision.

In the current study, the calculated F value is lower than the F value from the F-table [$F_{cal}$ (1.01) < $F_{tab}$ (1.59)], for an F-table with critical value ($\alpha$) = 0.025. Clearly, no significant differences are evident for the three sample masses used. This clearly confirms that any of the starting sample masses can be used and their precisions are similar.

Table 6-1: Statistical analysis of 30 residues of polluted soil with initial masses of approximately 76g, 68g and 65g at 550 °C at 60 mins (no nitrogen carrier gas).

| Exp | IS (g) | R1 (g) | % | IS (g) | R2 (g) | % | IS (g) | R3 | % |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 76.01 | 69.34 | 91.23 | 68.01 | 62.05 | 91.23 | 65.04 | 59.24 | 91.1 |
| 2 | 76.06 | 69.36 | 91.20 | 68.07 | 62.04 | 91.13 | 65.08 | 59.25 | 91.0 |
| 3 | 76.03 | 69.37 | 91.24 | 68.08 | 62.06 | 91.15 | 65.03 | 59.24 | 91.1 |
| 4 | 76.05 | 69.35 | 91.18 | 68.03 | 62.04 | 91.21 | 65.06 | 59.26 | 91.1 |
| 5 | 76.03 | 69.37 | 91.25 | 68.10 | 62.05 | 91.12 | 65.10 | 59.23 | 91.0 |
| 6 | 76.01 | 69.35 | 91.24 | 68.09 | 62.04 | 91.12 | 65.09 | 59.23 | 91.0 |
| 7 | 76.03 | 69.34 | 91.21 | 68.04 | 62.07 | 91.17 | 65.03 | 59.23 | 91.1 |
| 8 | 76.08 | 69.36 | 91.17 | 68.06 | 62.09 | 91.22 | 65.07 | 59.24 | 91.0 |
| 9 | 76.02 | 69.34 | 91.21 | 68.10 | 62.05 | 91.11 | 65.07 | 59.24 | 91.0 |
| 10 | 76.08 | 69.34 | 91.14 | 68.07 | 62.05 | 91.14 | 65.12 | 59.29 | 91.0 |
| Mean |  | 69.35 |  |  | 62.05 |  | 65.04 | 59.24 | 91.0 |
| Std. dev |  | 0.02 |  |  | 0.02 |  |  | 0.02 |  |

IS = Initial soil , R = Residue of soil after treatment

#### 6.2.1.2 Statistical analysis of oil/water mixture

The statistical analyses of the recovered oil and water yields are presented in Table 6-2 and 6-3 respectively. The results were obtained after separation of the oil/water mixture using the Dean-Stark method.

Table 6-2 show the masses of oil recovered by subtracting the masses of moisture separated in the Dean-Stark apparatus from the total masses of the oil/water mixtures. Table 6-2 shows, in addition, that the standard deviation (76g – 0.2; 68g – 0.2 and 65g – 0.1), standard error (76g – 0.15; 68g – 0.13 and 6g – 0.13) and the % RSD (76g – 8.4; 68g – 6.7 and 65g – 6.8) for oil recovered were extremely high compared to those obtained for the soil residue, which resulted from inconsistencies in the loss of low masses of hydrocarbon during the Dean-Stark method and evaporation of solvent from the oil.

Table 6-2: Statistical analysis of masses of 30 recovered oils (O) obtained by difference from polluted soil (S) with initial masses of approximately 76g, 68g and 65g at 550°C at 60 mins (no nitrogen carrier gas).

| | S (g) | O (g) | O (%) | S (g) | O (g) | O (%) | S (g) | O (g) | O (%) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 76.0 | 2.0 | 2.6 | 68.0 | 1.6 | 2.4 | 65.0 | 1.4 | 2.2 |
| 2 | 76.1 | 1.9 | 2.5 | 68.1 | 1.4 | 2.1 | 65.1 | 1.6 | 2.5 |
| 3 | 76.0 | 2.0 | 2.6 | 68.1 | 1.6 | 2.4 | 65.0 | 1.4 | 2.2 |
| 4 | 76.1 | 1.8 | 2.4 | 68.0 | 1.2 | 1.8 | 65.1 | 1.4 | 2.2 |
| 5 | 76.0 | 1.8 | 2.4 | 68.1 | 1.4 | 2.1 | 65.1 | 1.6 | 2.5 |
| 6 | 76.0 | 1.5 | 2.0 | 68.1 | 1.5 | 2.2 | 65.1 | 1.5 | 2.3 |
| 7 | 76.0 | 1.6 | 2.1 | 68.0 | 1.6 | 2.4 | 65.0 | 1.2 | 1.8 |
| 8 | 76.1 | 2.0 | 2.6 | 68.1 | 1.6 | 2.4 | 65.1 | 1.4 | 2.2 |
| 9 | 76.0 | 1.9 | 2.5 | 68.1 | 1.2 | 1.8 | 65.1 | 1.2 | 1.8 |
| 10 | 76.1 | 2.2 | 2.9 | 68.1 | 1.5 | 2.2 | 65.1 | 1.6 | 2.5 |
| Mean | 76.0 | 1.9 | 2.5 | 68.1 | 1.6 | 2.4 | 65.1 | 1.3 | 2.2 |
| Std. dev | | 0.2 | | | 0.15 | | | 0.15 | |
| % RSD | | | 8.4 | | | 6.7 | | | 6.8 |

A similar observation was noticed during statistical analysis of the water generated as listed in Table 6-3, where the standard deviation (76g – 0.19; 68g – 0.19 and 65g – 0.11), standard error (76g – 0.11; 68g – 0.11 and 65g – 0.06) and the % RSD (76g – 4.6; 68g – 4.1 and 65g – 2.5) for oil recovered were extremely high compared to those obtained from the soil residue in Table 6-1. The high values of the % RSD for the oil compared to the solid residue are consistent with measuring error for the volume of water, i.e. about 0.1 ml.

Table 6-3: Statistical analysis of water (W) generated from polluted soil with initial masses of approximately 76g, 68g and 65g at 550°C at 60 minutes (no nitrogen carrier gas).

| | Exp. 1 | | | Exp. 2 | | | Exp. 3 | | |
|---|---|---|---|---|---|---|---|---|---|
| | Soil (g) | W (g) | W (%) | Soil (g) | W (g) | W (%) | Soil(g ) | W (g) | W (%) |
| 1 | 76.0 | 3.2 | 4.2 | 68.0 | 3.2 | 4.7 | 65.0 | 3.0 | 4.6 |
| 2 | 76.1 | 3.0 | 3.9 | 68.1 | 3.0 | 4.4 | 65.1 | 3.0 | 4.6 |
| 3 | 76.0 | 3.4 | 4.5 | 68.1 | 3.4 | 5.0 | 65.0 | 2.9 | 4.5 |
| 4 | 76.1 | 3.2 | 4.2 | 68.0 | 3.2 | 4.7 | 65.1 | 2.8 | 4.3 |
| 5 | 76.0 | 3.0 | 3.9 | 68.1 | 3.0 | 4.4 | 65.1 | 3.0 | 4.6 |
| 6 | 76.0 | 3.0 | 3.9 | 68.1 | 3.0 | 4.4 | 65.1 | 2.9 | 4.5 |
| 7 | 76.0 | 2.9 | 3.8 | 68.0 | 2.9 | 4.3 | 65.0 | 3.0 | 4.6 |
| 8 | 76.1 | 2.9 | 3.8 | 68.1 | 2.9 | 4.3 | 65.1 | 3.0 | 4.6 |
| 9 | 76.0 | 3.4 | 4.5 | 68.1 | 3.4 | 5.0 | 65.1 | 2.7 | 4.1 |
| 10 | 76.1 | 3.3 | 4.3 | 68.1 | 3.3 | 4.8 | 65.1 | 2.8 | 4.3 |
| Mean | 76.0 | 3.2 | 4.2 | 68.1 | 3.2 | 4.7 | 65.1 | 3.2 | 4.5 |
| Std. dev | | 0.19 | | | 0.19 | | | 0.11 | |

After the experimental precision was established, all the experiments were performed in duplicate at 30 and 60 minutes treatment time without carrier gas to produce soil char, water/oil mixture and gas as mentioned earlier. This duplicate analysis of the polluted soil was carried out with a starting mass of approximately 65g so as not to run out of sample. Further, using 65g gave the lowest standard deviation for both oil and water generated as well as having the lowest standard error and %RSD value for water in this study.

Meanwhile, the water yield obtained from the 30 tests performed showed that the percentage mean values of water generated (Exp. 1 = 4.2 %, Exp. 2 = 4.7% and Exp. 3 = 4.5%) were significantly higher than the initial moisture content of the soil (1.3%). The high value suggested that much of the water might have been generated from the clay minerals present in the soil (see details in Section 6.2.3).

#### 6.2.1.3 The void volume

The void volume was calculated for each starting sample mass in the retort reactor tube of Gray-King pyrolysis to examine if the gas generated is from the soil sample. Table 6-4 listed the % void volume for each approximately initial soil masses. The void volume occupied by air is insignificant compared to all the total gas volume for each peak temperature investigated. This suggested that void volume makes an insignificant contribution to the total gas generated from the remediation process of the clay crude-oil-polluted soil from Nigeria.

Table 6-4: The void volume in the retort of Gray-King pyrolysis used for the polluted soil treatment.

| Initial soil (g) | %OSR | R vol. (ml) | S vol. (ml) | V vol. (ml) |
|---|---|---|---|---|
| 65 | 80.0 | 44.2 | 35.3 | 8.8 |
| 68 | 82.4 | 44.2 | 36.4 | 7.8 |
| 76 | 90.0 | 44.2 | 39.8 | 4.4 |

OSR = occupied by sample in the reactor; Retort = R; Sample = S; Void = V

### 6.2.2 Gas yields

The gas yields of $CH_4$, $C_2H_4$, $C_2H_6$, $C_3H_6$, $C_3H_8$, $C_4H_8$, $C_4H_{10}$, $C_5H_{10}$, $C_5H_{12}$ , CO and $CO_2$ from the Gray-King pyrolysis are listed in Table 6-5 and 6-6 respectively for the 30- and 60-minute treatment times without nitrogen gas. The gas yields for 60-minute treatment time with nitrogen gas as the carrier gas could not be presented because the gas sampling bags (1 litre) were not large enough to collect all the gas.

Figure 6-1 shows the gas volumes obtained at 30- and 60-minute treatment time without carrier gas across all the peak temperature investigated. The total gas volumes were calculated from multiplication of volume of gas components with volume collected divided by volume of gas injected (Equ. 6-1).

Total gas generated (ml) (TGC) = (GC*V)/GI Equation. 6-1

Where GC = volume of gas components identified; GI = volume of gas injected and V = volume collected in gas bag.

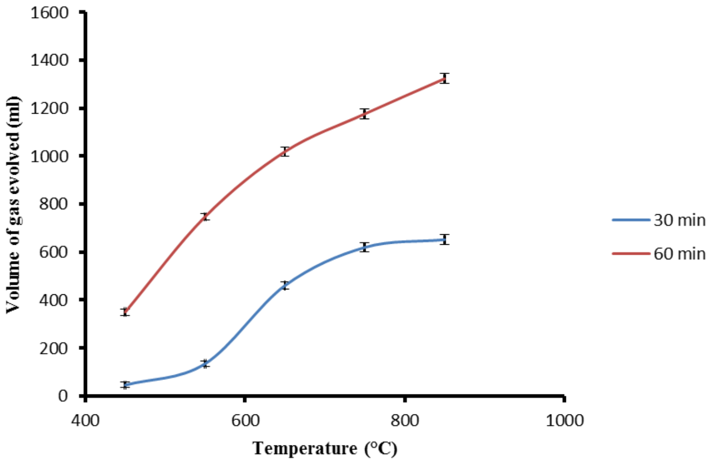


Figure 6-1: Gas yield (mls) from Gray-King pyrolysis of polluted soil at 30- and 60-minute holding time without carrier gas.

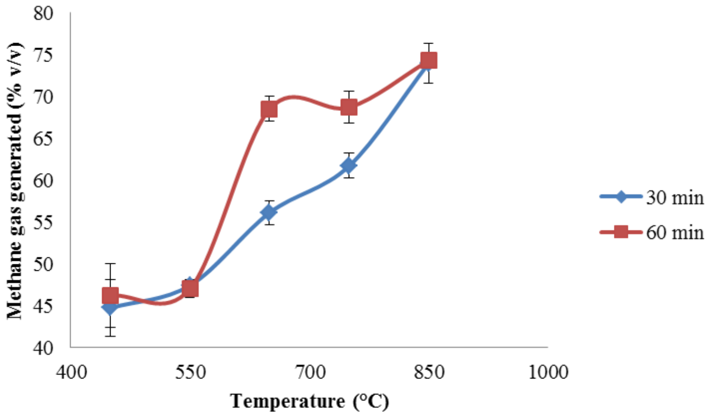


Figure 6-2: Methane yield (%v/v) from Gray-King pyrolysis of polluted soil at 30- and 60-minute holding time without carrier gas.

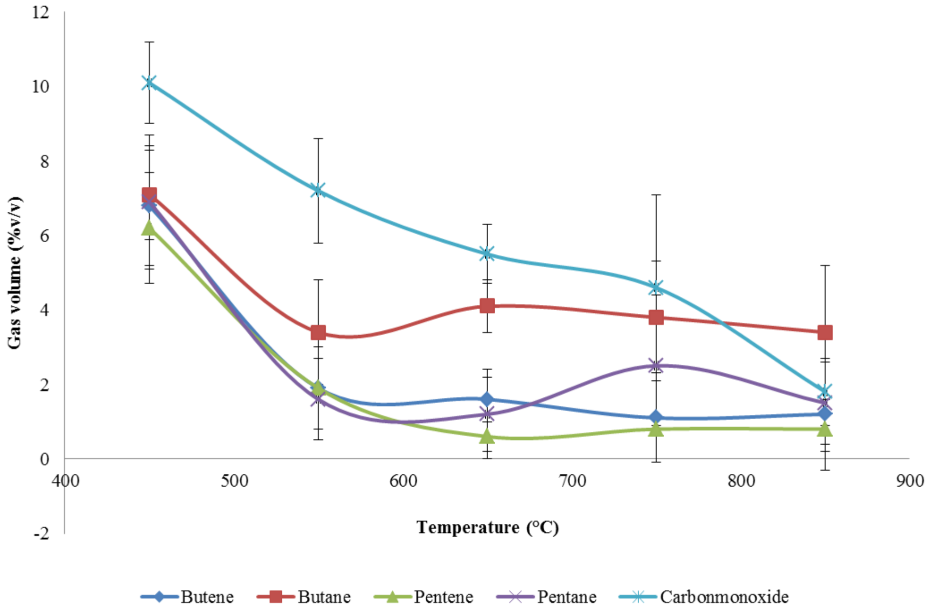


Figure 6-3: Selected gas yield (%v/v) from Gray-King pyrolysis of polluted soil at 30 minutes holding time without carrier gas to show the decrease in volume with increased peak temperatures.

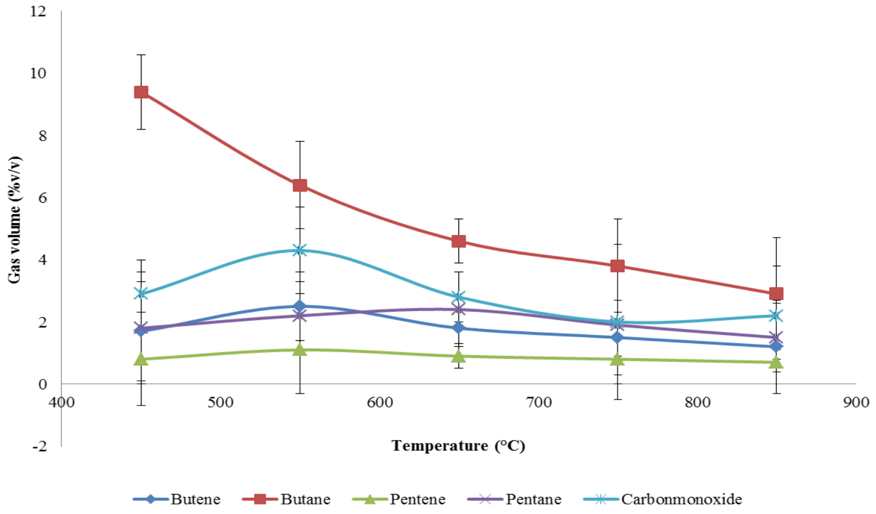


Figure 6-4: Selected gas yield (%v/v) from Gray-King pyrolysis of polluted soil at 60 minutes holding time without carrier gas to show the decrease in volume with increased peak temperatures.

The TGC values at 30 minutes were generally small compared to those for 60-minute treatment time due to slow evolution of gases. Figure 6-1 indicates the two variables of peak temperatures and treatment times as major influential parameters that determine the gas yield from the Gray-King pyrolysis. The figure shows an increase in gas yields with increasing peak temperatures as well as evolution of low volume of gases at 30 minutes holding times compared to the 60 minutes. The total volume of gas generated at 60 minutes holding time (Figure 6-1) for peak temperatures at $550^{o}$C and below are approximately ratio 8:1 and 6:1 to 30 minutes holding time. However, the trend changed to ratio 2:1 above $550^{o}$C. The gaps between the gas yields at the two treatment times (30 and 60 minutes without carrier gas) were greatly reduced to ratio 2:1 above 550°C due to slow gas evolution. This clearly shows that temperature has more influence on gas yield at higher temperatures apart from the short treatment time. From the Figure 6-2, it could be seen that the % (v/v) of methane increases with increasing peak temperatures. This suggests that higher components of gas yields are released from the oil and possibly crack to yield more methane. The cracking suggestion could explain the results from Figure 6-3 and 6-4 which show a decrease in the volume of the gas yield instead of the increase observed for methane (Figure 6-2). Also, the m/z 71 chromatogram of the pyrolysed oil from Gray-King in Section 6.4 confirms the formation of lighter *n*-alkanes ($C_{10}$ $C_{14}$) that are not present in the EOM of the oil extracted from the same soil. This suggests a cracking of the heavier *n*-alkanes to form a lighter *n*-alkane series.

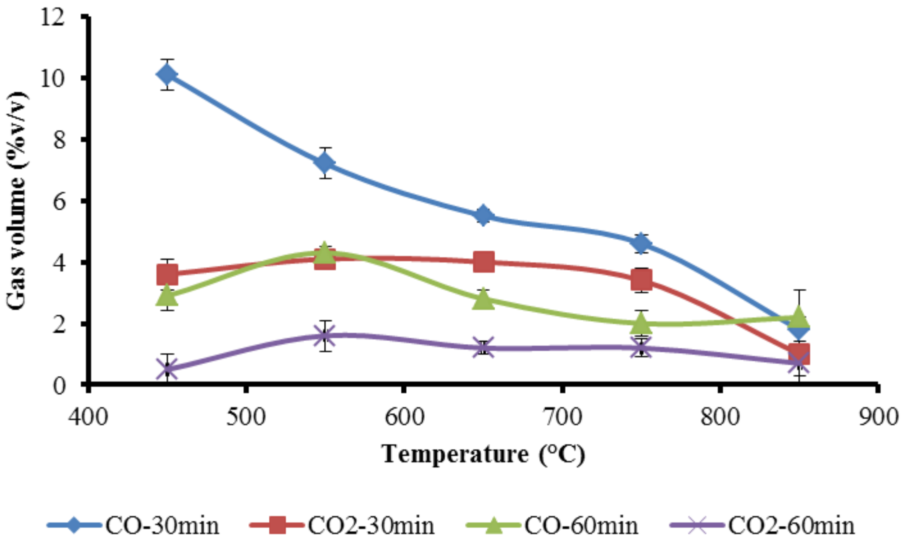


Figure 6-5: Yield (%v/v) of carbon monoxide (CO) and carbon dioxide ($CO_2$) from Gray-King pyrolysis of polluted soil at 30 and 60 minutes holding time without carrier gas to show decrease in volume with increased peak temperatures.

The values of carbon monoxide generated (Figure 6-5) at 30 and 60 minutes holding time were higher than that of carbon dioxide across all the peak temperatures, which indicates that the source of the carbon monodixe might be the crude oil in the soil with minimal contribution from any other source (e.g. air).

These observations imply that the volume injected might seem consistent, but the precision is lower than the precision of the GC in the collection process. To correct this anomaly, online GC analysis of the gas yield from Gray-King might be considered.

In addition, the values of carbon monoxide were higher than carbon dioxide across all the peak temperatures for both 30 and 60 minutes treatment time, suggesting that it might have resulted from pyrolysis of the crude oil in the soil.

The % TOC of the gas (Table 6-5 and 6-6) increased across all the peak temperatures for both the 30 and 60 minutes treatment times without nitrogen gas. The trends are the same with the gas yield for each peak temperature as discussed above. The high temperature and long treatment time favours high gas, while the short treatment time favours low gas yield and high liquid yield as listed with the % TOC results.

The % TOC of gases at 450°C for both 30 and 60 minutes treatment time were 0.64 and 5.47, which indicates the slow evolution of gases at a low peak temperature, but it gradually increases with an increase in the peak temperatures. There is an approximately equal wide margin between peak temperature at 550°C and 650°C for both 30 (4.77%) and 60 (4.38%) minutes treatment with no carrier gas, suggested a slowing of evolution gas and dissolution of heavier components in the oil with thermal cracking of the heavier hydrocarbon gas such as *n*-pentane (hydrogenation and free radical formation from homolytic fission of C-C bond) to form more methane content in the gas yield (Reeve and Long, 1963; Bridgwater and Peacocke, 2000).

The highest gas % TOC was obtained at 60 minutes treatment time with 850°C peak temperature due to slow evolution of gas that caused low % TOC of gas yields at 30 minutes treatment time with no carrier gas.

Table 6-5: The % TOC in gases from Gray-King pyrolysis of polluted soil at 30 minutes treatment time without carrier gas.

| Temp (°C) | Parameters | $CH_4$ | $C_2H_4$ | $C_2H_6$ | $C_3H_6$ | $C_3H_8$ | $C_4H_8$ | $C_4H_{10}$ | $C_5H_{10}$ | $C_5H_{12}$ | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 450 | Gas (mg) | 14.69 | 1.86 | 2.72 | 2.87 | 3.29 | 7.83 | 8.44 | 8.89 | 10.28 | |
| | mg/g TOC | 4.43 | 0.56 | 0.82 | 0.87 | 0.99 | 2.36 | 2.55 | 2.68 | 3.10 | |
| | C in TOC (mg/g) | 3.32 | 0.24 | 0.33 | 0.25 | 0.27 | 0.51 | 0.53 | 0.46 | 0.52 | |
| | % TOC of C | 0.33 | 0.02 | 0.03 | 0.02 | 0.03 | 0.05 | 0.05 | 0.05 | 0.05 | 0.64 |
| 550 | Gas (mg) | 42.58 | 24.41 | 8.71 | 19.61 | 22.60 | 7.77 | 14.55 | 6.74 | 7.14 | |
| | mg/g TOC | 12.97 | 7.43 | 2.65 | 5.97 | 6.88 | 2.37 | 4.43 | 2.05 | 2.17 | |
| | C in TOC (mg/g) | 9.73 | 3.19 | 1.06 | 1.71 | 1.88 | 0.51 | 0.92 | 0.35 | 0.36 | |
| | % TOC of C | 0.97 | 0.32 | 0.11 | 0.17 | 0.19 | 0.05 | 0.09 | 0.04 | 0.04 | 1.97 |
| 650 | Gas (mg) | 184.28 | 61.88 | 27.56 | 42.00 | 60.34 | 18.56 | 48.78 | 8.73 | 18.11 | |
| | mg/g TOC | 55.79 | 18.73 | 8.34 | 12.71 | 18.27 | 5.62 | 14.77 | 2.64 | 5.48 | |
| | C in TOC (mg/g) | 41.84 | 8.03 | 3.34 | 3.63 | 4.98 | 1.20 | 3.06 | 0.45 | 0.91 | |
| | % TOC of C | 4.18 | 0.80 | 0.33 | 0.36 | 0.50 | 0.12 | 0.31 | 0.05 | 0.09 | 6.74 |
| 750 | Gas (mg) | 273.18 | 69.84 | 30.13 | 45.94 | 67.18 | 16.83 | 61.42 | 15.22 | 49.61 | |
| | mg/g TOC | 82.41 | 21.07 | 9.09 | 13.86 | 20.27 | 5.08 | 18.53 | 4.59 | 14.97 | |
| | C in TOC (mg/g) | 61.81 | 9.03 | 3.64 | 3.96 | 5.53 | 1.09 | 3.83 | 0.79 | 2.49 | |
| | % TOC of C | 6.18 | 0.90 | 0.36 | 0.40 | 0.55 | 0.11 | 0.38 | 0.08 | 0.25 | 9.22 |
| 850 | Gas (mg) | 344.52 | 55.42 | 24.22 | 36.05 | 50.05 | 18.76 | 58.04 | 13.32 | 31.01 | |
| | mg/g TOC | 103.92 | 16.72 | 7.31 | 10.87 | 15.10 | 5.66 | 17.51 | 4.02 | 9.35 | |
| | C in TOC (mg/g) | 77.94 | 7.16 | 2.92 | 3.11 | 4.12 | 1.21 | 3.62 | 0.69 | 1.56 | |
| | % TOC of C | 7.79 | 0.72 | 0.29 | 0.31 | 0.41 | 0.12 | 0.36 | 0.07 | 0.16 | 10.23 |

Initial soil TOC = 3.31 at 450°C; 3.28 at 550°C; 3.30 at 650°C; 3.31 at 750°C; 3.32 at 850°C

Table 6-6: The % TOC in gases from Gray-King pyrolysis of polluted soil at 60 minutes treatment time without carrier gas.

| Temp (°C) | Parameters | $CH_4$ | $C_2H_4$ | $C_2H_6$ | $C_3H_6$ | $C_3H_8$ | $C_4H_8$ | $C_4H_{10}$ | $C_5H_{10}$ | $C_5H_{12}$ | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 450 | Gas (mg) | 115.7 | 46.7 | 20.4 | 32.6 | 45.5 | 15.3 | 175.9 | 9.3 | 19.8 | |
| | mg/g TOC | 34.92 | 14.11 | 6.17 | 9.84 | 13.73 | 4.61 | 53.11 | 2.80 | 5.98 | |
| | C in TOC (mg/g) | 26.19 | 6.05 | 2.47 | 2.81 | 3.75 | 0.99 | 10.99 | 0.48 | 1.00 | |
| | % TOC of C | 2.62 | 0.60 | 0.25 | 0.28 | 0.37 | 0.10 | 1.10 | 0.05 | 0.10 | 5.47 |
| 550 | Gas (mg) | 251.21 | 124.01 | 56.20 | 96.17 | 133.65 | 46.24 | 124.53 | 25.89 | 51.70 | |
| | mg/g TOC | 76.49 | 37.76 | 17.11 | 29.28 | 40.70 | 14.08 | 37.92 | 7.88 | 15.74 | |
| | C in TOC (mg/g) | 57.37 | 16.18 | 6.85 | 8.37 | 11.10 | 3.02 | 7.85 | 1.35 | 2.62 | |
| | % TOC of C | 5.74 | 1.62 | 0.68 | 0.84 | 1.11 | 0.30 | 0.78 | 0.14 | 0.26 | 11.47 |
| 650 | Gas (mg) | 498.34 | 42.46 | 52.63 | 87.88 | 120.18 | 46.45 | 120.69 | 29.53 | 76.98 | |
| | mg/g TOC | 150.87 | 12.85 | 15.93 | 26.61 | 36.38 | 14.06 | 36.54 | 8.94 | 23.30 | |
| | C in TOC (mg/g) | 113.15 | 5.51 | 6.37 | 7.60 | 9.92 | 3.01 | 7.56 | 1.53 | 3.88 | |
| | % TOC of C | 11.31 | 0.55 | 0.64 | 0.76 | 0.99 | 0.30 | 0.76 | 0.15 | 0.39 | 15.85 |
| 750 | Gas (mg) | 568.66 | 124.35 | 55.24 | 83.40 | 122.07 | 42.76 | 117.04 | 30.29 | 72.97 | |
| | mg/g TOC | 171.55 | 37.51 | 16.66 | 25.16 | 36.83 | 12.90 | 35.31 | 9.14 | 22.01 | |
| | C in TOC (mg/g) | 128.66 | 16.08 | 6.67 | 7.19 | 10.04 | 2.76 | 7.31 | 1.57 | 3.67 | |
| | % TOC of C | 12.87 | 1.61 | 0.67 | 0.72 | 1.00 | 0.28 | 0.73 | 0.16 | 0.37 | 18.39 |
| 850 | Gas (mg) | 702.00 | 112.92 | 49.35 | 73.45 | 101.98 | 38.22 | 98.88 | 27.15 | 63.19 | |
| | mg/g TOC | 211.75 | 34.06 | 14.89 | 22.16 | 30.76 | 11.53 | 29.82 | 8.19 | 19.06 | |
| | C in TOC (mg/g) | 158.81 | 14.60 | 5.95 | 6.33 | 8.39 | 2.47 | 6.17 | 1.40 | 3.18 | |
| | % TOC of C | 15.88 | 1.46 | 0.60 | 0.63 | 0.84 | 0.25 | 0.62 | 0.14 | 0.32 | 20.73 |

Initial soil TOC = 3.31 at 450°C; 3.28 at 550°C; 3.30 at 650°C; 3.31 at 750°C; 3.32 at 850°C

### 6.2.3 Water content

The soil sample used for this experiment was air-dried to a constant weight. This was achieved to give the moisture content of 1.3% before the commencement of the experiment. The water content of the soil was reduced prior to analysis in order to reduce loss of energy to drying of the soil before actual pyrolysis. However, it has been suggested that the water in the feed should be discounted in the final pyrolysis products with only the water of pyrolysis being quoted and the product yields expressed on a dry-feed basis (Bridgwater, 1999).

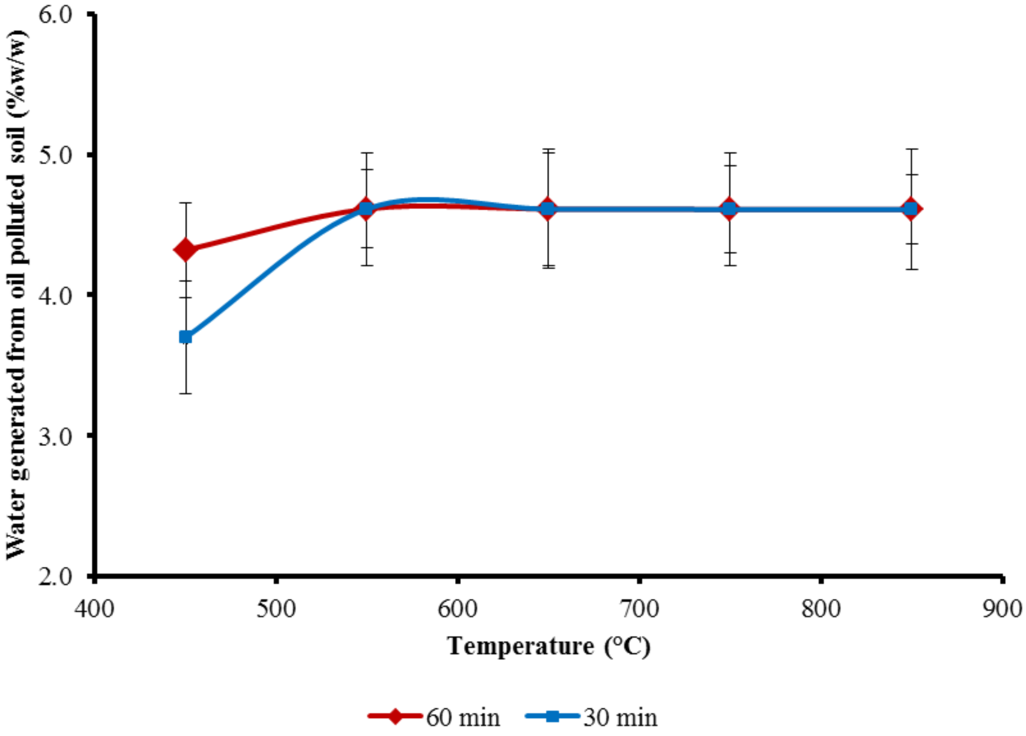


Figure 6-6: The % (w/w) of water separated from pyrolysis products of polluted soil on a dry basis (n = 3).

Figure 6-6 shows that the variation of triplicate wt. % of water generated on a dry basis with increasing peak temperatures for both 30 and 60 minutes with no carrier gas. The 60-minute treatment time with carrier gas was not presented in the figure because of poor recovery from the nitrogen gas stream. At 450°C, water is 3.7% (w/w) at 30 minutes and 4.3% (w/w) at 60 minutes treatment time with no carrier gas, but both reached their maximum value of 4.6% (w/w) beyond 450°C for all the peak temperatures.

It is interesting to note that the weight percentage of the water separated from the water/oil mixture is higher than the initial moisture content of the soil (1.3% w/w). This suggests that there is a possible contribution from the clay mineral due to dehydration and a two-step homogenous dehydroxylation process (Frost and Vassallo, 1996) at higher temperatures, as previous work by Akinyemi *et al.* (2014) stated that kaolinites are abundant in the soil from tropical rainforests in Nigeria. Kaolinite is a layered silicate mineral (clay mineral), with one tetrahedral sheet linked through oxygen atoms (ionic bond) to one alumina octahedral sheet characterised by 1:1 layers and 1nm with a sorbed interlayer water (Newman and Brown, 1987; Deer, Howie and Zussman, 1992). It is expected that kaolinite will contribute to the water products based on the XRD results (Figure 6-7). The XRD shows that the intensity (counts) of the quartz and kaolinite decreased after Gray-King treatment compared to the fresh soil.

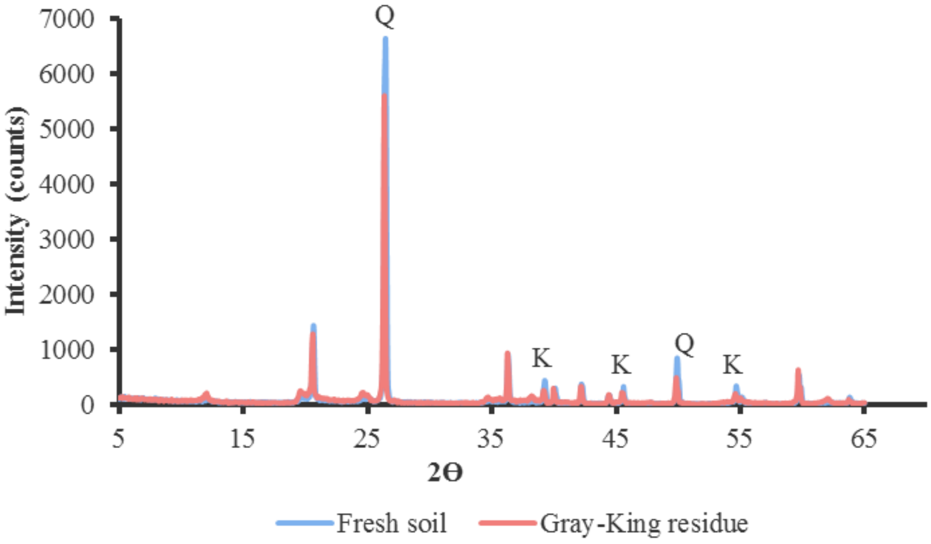


Figure 6-7: The XRD results of the fresh soil and Gray-King pyrolysis residue showing the changes in the intensity of quartz and kaolinite (Q = quartz; K= kaolinite), which suggested structural changes with temperature.

$$Al_2O_2.2SiO_2.2H_2O \xrightarrow{400\text{- }600\ °C} Al_2O_2.2SiO_2 + 2H_2O \text{ (dehydrogenation)}$$

$$OH^- \longrightarrow H^+ + O^{2-} \quad \text{(Step 1 dehydroxylation)} \qquad \text{Equation 6-2}$$

$$2OH^- + 2H^+ \longrightarrow 2H_2O \quad \text{(Step 2 dehydroxylation)}$$

These suggested structural changes that led to a release of interlayer water content of the mineral (kaolinite) at the peak temperatures agreed with the past work of Newman and Brown (1987) that interlayer water in kaolinite will be released at temperatures between 400 to 600°C. This process of release of interlayer water has been described as dehydration and a two-step homogenous dehydroxylation process, which is depicted by Equation 6-2.

### 6.2.4 Char

#### 6.2.4.1 The conversion of TOC for the contaminated soil at 30 minutes (no sweep gas)

The char as measured comprises the residues of the oil that stick to the soil after pyrolysis of the soil sample. Table 6-7 highlights the conversion of total organic carbon (TOC) for the contaminated soil at 30 minutes with no nitrogen gas as carrier gas by the static Gray-King pyrolysis, which is directly related to the TOC of the chars in the residue generated from the remediation technique. Figure 6-8 shows the average value of the two experiments in Table 6-7.

Table 6-7: The conversion of TOC for the contaminated soil at 30 minutes (no sweep gas).

| Parameter | Experimental 1 (Exp. 1) | | | | | Experimental 2 (Exp. 2) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Temp. (°C) | 450 | 550 | 650 | 750 | 850 | 450 | 550 | 650 | 750 | 850 |
| IS (g) | 65.7 | 65.2 | 65.5 | 65.8 | 65.8 | 65.7 | 65.2 | 65.5 | 65.8 | 65.8 |
| EOM in IS (g) | 5.26 | 5.21 | 5.24 | 5.26 | 5.26 | 5.26 | 5.21 | 5.24 | 5.26 | 5.26 |
| IS TOC (g) | 3.31 | 3.28 | 3.30 | 3.31 | 3.32 | 3.31 | 3.28 | 3.30 | 3.31 | 3.32 |
| TOC of char (g) | 1.07 | 1.05 | 0.66 | 0.66 | 0.65 | 1.03 | 0.93 | 0.64 | 0.63 | 0.63 |
| % TOC char | 34.4 | 31.9 | 20.0 | 20.0 | 19.7 | 31.2 | 28.2 | 19.5 | 19.1 | 19.1 |
| % TOC removed | 67.6 | 68.1 | 80.0 | 80.0 | 80.3 | 68.8 | 71.8 | 80.5 | 80.9 | 80.9 |
| % TOC (HyPy) | 71.1 | 71.7 | 84.2 | 84.2 | 84.6 | 72.4 | 75.6 | 84.7 | 85.1 | 85.2 |
| % TOC (EOM) | 86.7 | 87.4 | 100 | 100 | 100 | 88.2 | 92.1 | 100 | 100 | 100 |

Footnote: % TOC removed by HyPy = 95 %; % TOC removed by EOM = 78 %, Measure carbon in starting soil (g) =5.04, % TOC (HyPy) = % TOC removed with respect to HyPy, % TOC (EOM) = % TOC removed with respect to EOM, IS = initial soil

Table 6-7 shows the two experiments (Exp. 1 and 2) carried out on the polluted soil, the initial TOC of the soils, the % TOC of char in the residue and % TOC removed by Gray-King pyrolysis for all the peak temperatures. The tables emphasise the % TOC removed from Gray-King pyrolysis with respect to the % TOC of extractable organic matter (EOM) removed and hydropyrolysis (HyPy) discussed in Section 5.2. Table 6-7 shows the % TOC removed by the Gray-King remediation technique across all the peak temperatures investigated. The char yield in all pyrolysis conditions is unequivocally affected by the peak temperature, which means the controlling variable of pyrolysis reaction kinetics is temperature (Antal and Grønli, 2003). In Exp. 1, the lowest % TOC removed by the static Gray-King pyrolysis corresponds to the lowest temperature at 450°C, and the highest % TOC removed corresponds to the highest temperature at 850°C, with values of 67.6 and 80.3 respectively. Similarly, Exp. 2 % TOC removal at the lowest temperature was 68.8 % TOC at 450°C and the highest % TOC removed was 80.9% TOC at 850°C.

There is a sharp increase of 11.9% at Exp. 1 and 8.7% at Exp. 2 between the % TOC removed at 550 and 650°C, followed by an almost constant value of 80.1% TOC above 650°C due to devolatilation that is reflected in the gas yield’s sudden leap at 650°C as discussed in Section 6.2.1. The maximum % TOC removed below 650°C is 87.4 % for Exp. 1 and 92.1% for Exp. 2 respectively, while the entire % TOC with respect to EOM was removed at peak temperature above 550°C. However, the maximum % TOC removed by Gray-King by the two duplicate analyses with respect to HyPy and EOM are 84.6 % and 85.2 % respectively.

Figure 6-8 shows the average % TOC removed by Gray-King with respect to EOM and HyPy for both experiments in Table 6-3 at 30 minutes with no nitrogen gases as carrier gas. The average % TOC removed ranges from 68.2% at 450°C to 80.6 % at 850°C respectively. The average % TOC removed increases steadily with an increase in peak temperatures to an approximately constant value above 650°C, when devolatilisation is almost complete (Scott *et al.*, 1988).

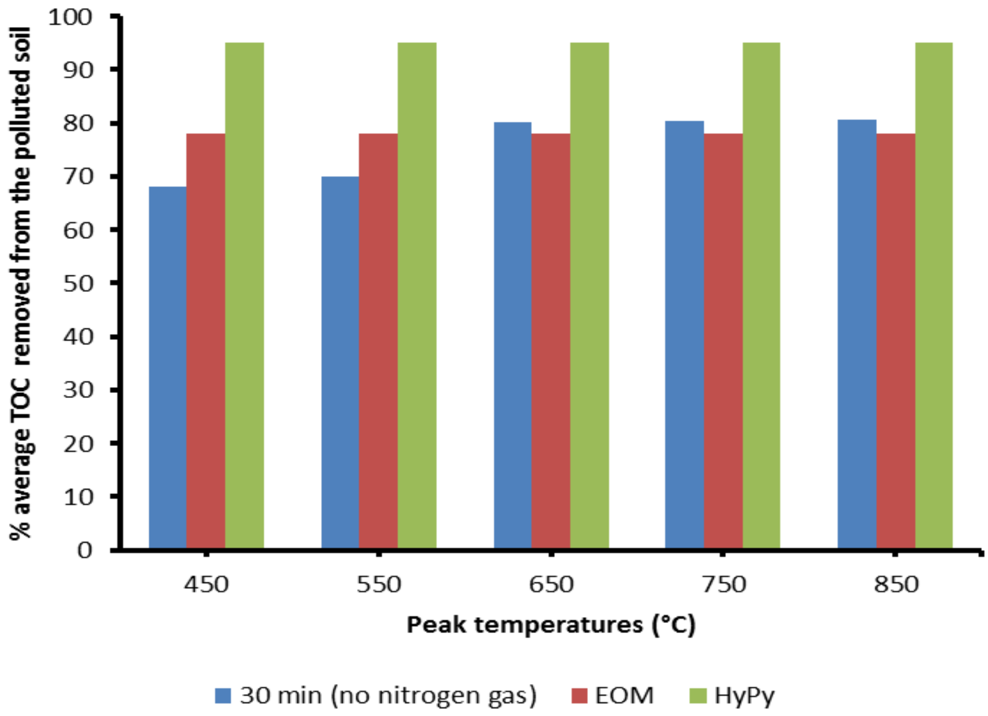


Figure 6-8: Average conversions of TOC for the contaminated soil at 30 minutes (no sweep gas) with respect to EOM (78%) and HyPy (95 %) (n = 2).

In comparison with the % TOC removal of HyPy and EOM mentioned above, the % TOC removed at 650°C and below is lower than the % TOC removed by both HyPy and EOM as shown in Figure 6-8, which are 73.4% and 89.7% with respect to both HyPy and EOM. At the highest peak temperature (850°C) investigated, 84.6% with respect to HyPy was removed, while peak temperature beyond 650°C removed all the % TOC with respect to EOM.

### 6.2.4.2 Percentage products recovery

The % TOC recovered oil from the static Gray-King pyrolysis process at 30 minutes treatment time increased with an increase in the peak temperatures and remained almost the same beyond 650°C peak temperature as revealed in Table 6-8. The high value of recovered oil agrees with the slow evolution of gas to encourage more liquid yield. The % TOC removed is expected to increase or decrease with any change in the experimental conditions. However, the results show that temperature is the major condition that determines the products' yields because the recovered oil increases with constant treatment time. There is variation in the % TOC recovery from the Gray-King experiments due to loss of differing amounts of lighter constituents in recovered oil with toluene during rotary evaporation after Dean-Stack analysis.

Table 6-8: Average % TOC recovery for the contaminated soil at 30 minutes (no sweep gas) (n = 2)

| Temperature (°C) | 450 | 550 | 650 | 750 | 850 |
|---|---|---|---|---|---|
| % TOC of gas by Gray-King | 0.6 | 2.0 | 6.8 | 9.2 | 10.2 |
| % TOC of char by Gray-King | 31.8 | 30.0 | 19.8 | 19.6 | 19.4 |
| % TOC of recovered oil by Gray-King | 65.8 | 67.4 | 70.7 | 69.4 | 69.3 |
| % TOC recovery from Gray-King | 98.3 | 99.4 | 97.2 | 98.2 | 98.9 |
| % TOC Loss from Gray-King | 1.7 | 0.6 | 2.8 | 1.8 | 1.1 |

#### 6.2.4.3 The conversion of TOC for the contaminated soil at 60 minutes (no sweep gas)

The treatment time of the static Gray-King pyrolysis was increased from 30 to 60 minutes with no carrier gas to investigate the impact it will have on the pyrolysis yield with a similar peak temperature investigated at 30 minutes treatment time with no nitrogen gas as carrier gas. The static Gray-King pyrolysis technique was set up in a similar mode as described in Section 4.7.

Duplicate analysis with a treatment time of 60 minutes was performed on the contaminated soil as shown in Table 6-8. The product yields show an increasing trend for the % TOC removed from the polluted soil with increase in the peak temperature investigated, which agreed to some extent with previous work.

The lowest % TOC removed is 68.7% at 450°C and 81.2% at 850°C for Exp. 1 and 77.6 % TOC which is higher than the average % TOC removed in Table 6-6 for the peak temperature investigated at 30 minutes treatment time. Above 650°C, the % TOC removed gave approximately constant values.

Consequently, a second repeat was carried out with no change in the experimental conditions. The % char removed improved significantly to give the lowest value of 77.6 % at 450°C and 82.4% at 850°C. The effective average % TOC removed at peak temperature at 450 and 850°C by 30 minutes treatment time was approximately the same with the %

TOC removed at the peak temperatures below 650°C for 60 minutes treatment time in Table 6-8.

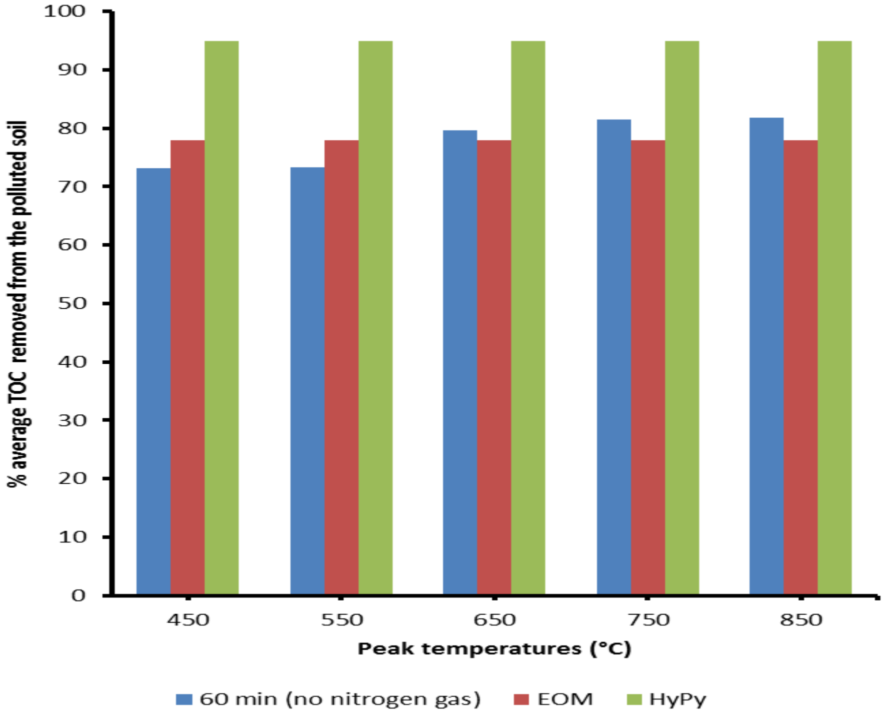


Figure 6-9: Average % TOC removed by Gray-King pyrolysis at 60 minutes treatment time with no nitrogen carrier gas compared to the % TOC removed with respect to EOM (78%) and HyPy (95%) (n = 2).

Table 6-9: The conversion of TOC for the contaminated soil at 60 minutes (no sweep gas).

| Parameter | Experimental 1 (Exp. 1) | | | | | Experimental 2 (Exp. 2) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Temperature (°C) | 450 | 550 | 650 | 750 | 850 | 450 | 550 | 650 | 750 | 850 |
| IS (g) | 65.6 | 65.0 | 65.1 | 65.6 | 65.7 | 65.6 | 65.0 | 65.1 | 65.6 | 65.7 |
| EOM in IS (g) | 5.24 | 5.20 | 5.21 | 5.25 | 5.26 | 5.2 | 5.2 | 5.2 | 5.2 | 5.3 |
| IS TOC (g) | 3.30 | 3.28 | 3.28 | 3.31 | 3.31 | 3.3 | 3.3 | 3.3 | 3.3 | 3.3 |
| TOC of char (g) | 1.04 | 1.02 | 0.62 | 0.62 | 0.62 | 0.7 | 0.7 | 0.7 | 0.6 | 0.6 |
| % TOC char | 31.3 | 31.1 | 19.0 | 18.8 | 18.8 | 22.4 | 22.3 | 21.5 | 18.2 | 17.6 |
| % TOC removed | 76.4 | 76.8 | 81.0 | 81.2 | 81.2 | 77.6 | 77.7 | 78.5 | 81.8 | 82.4 |
| % TOC (HyPy) | 72.3 | 72.6 | 85.2 | 85.5 | 85.5 | 81.7 | 81.8 | 82.6 | 86.1 | 86.7 |
| % TOC (EOM) | 88.0 | 88.4 | 100 | 100 | 100 | 99.5 | 99.6 | 100 | 100 | 100 |

Footnote: % TOC removed by HyPy = 95 %; % TOC removed by EOM = 78 %, Measure carbon in starting soil (g) = 5.04, % TOC (HyPy) = % TOC removed with respect to HyPy, % TOC (EOM) = % TOC removed with respect to EOM, IS = initial soil.

The repeat of the experiment at 60 minutes treatment time with no nitrogen carrier gas yield was controlled mainly by the peak temperatures (Table 6-9). The % TOC removed increased from the 77.6% TOC at 450°C to 82.4 % TOC at 850°C which is an increase of 3.9% TOC.

Subsequently, Figure 6-4 shows the comparison of the averaged % TOC removed during the two experiments performed at 60 minutes treatment time (no nitrogen gas) with % TOC removed in respect to HyPy and EOM.

The average % TOC removed by static Gray-King shows that all the % TOC with respect to EOM cannot be removed below 650°C peak temperature at 60 minutes with no nitrogen gases (93.7% and 94.0% ) as seen in Figure 6-9, while the % TOC removed by Gray-King with respect to HyPy at the same peak temperature wasis 77%. Beyond 650°C peak temperatures, all the % TOC with respect to EOM were removed.

Above 650°C, static Gray-King technique was able to remove the entire % TOC removable with respect to EOM in order to leave behind only TOC with respect to HyPy as shown in Figure 6-4.

#### 6.2.4.4 Percentage products recovery

The % TOC of recovered oil in Table 6-10 fluctuates between 54.3 and 65.4% across all the peak temperatures with the highest hydrocarbon gas yield of 20.8% at 850°C. The % non-recoverable TOC from Gray-king pyrolysis across all the peak temperatures ranges between 5.4 and 9.6%. The variation in the % TOC recovery from the Gray-King experiments is due to loss of differing amounts of lighter constituents in recovered oil with toluene during rotary evaporation after Dean-Stack analysis.

Table 6-10: The average % TOC of products from Gray-King pyrolysis of the contaminated soil at 60 minutes (no sweep gas) (n = 2).

| Temperature (°C) | 450 | 550 | 650 | 750 | 850 |
|---|---|---|---|---|---|
| % TOC of gas by Gray-King | 5.4 | 11.6 | 15.8 | 18.4 | 20.8 |
| % TOC of char by Gray-King | 23 | 22.8 | 20.3 | 18.5 | 18.2 |
| % TOC of recovered oil by Gray-King | 65.4 | 60.3 | 54.3 | 56.3 | 54.4 |
| % TOC recovery from Gray-King | 93.8 | 94.6 | 90.4 | 93.2 | 93.4 |
| % TOC Loss from Gray-King | 6.2 | 5.4 | 9.6 | 6.8 | 6.6 |

### 6.2.4.5 The conversion of TOC for the contaminated soil at 60 minutes (sweep gas)

The introduction of carrier gas caused a significant departure from the static Gray-King pyrolysis technique, which is reflected in the pyrolysis products yield. Table 6-11 describes the % TOC of char removed during the Gray-King pyrolysis for all the peak temperatures investigated. The duplicate analysis shown in the table shows that the lowest average % TOC removed at 450°C is 77.2 % and the highest average % TOC removed at 850 °C is 85.3%. The introduction of the nitrogen gas as carrier gas results in significant improvement in the % TOC removed with respect to EOM even at low peak temperature.

The average TOC conversion for the duplicate experiments is presented in Figure 6-11, to illustrate the treatment process performance with respect to the HyPy and EOM. The average TOC conversion of TOC at 60 minutes treatment time with nitrogen gas shows that all the % TOC with respect to EOM was removed even at low peak temperature (450°C). At 850°C, 89.5% with respect to HyPy was removed, which is the highest % TOC removed (85.3 %).

Table 6-11: The conversion of TOC for the contaminated soil at 60 minutes (sweep gas).

| Parameter | Experimental 1 (Exp. 1) | | | | | Experimental 2 (Exp. 2) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Temp. (°C) | 450 | 550 | 650 | 750 | 850 | 450 | 550 | 650 | 750 | 850 |
| IS (g) | 65.7 | 65.5 | 65.3 | 65.5 | 65.4 | 65.74 | 65.48 | 65.33 | 65.47 | 65.37 |
| EOM in IS (g) | 5.26 | 5.24 | 5.23 | 5.24 | 5.23 | 5.26 | 5.24 | 5.23 | 5.24 | 5.23 |
| IS TOC (g) | 3.31 | 3.30 | 3.29 | 3.30 | 3.29 | 3.31 | 3.30 | 3.29 | 3.30 | 3.29 |
| TOC char (g) | 0.75 | 0.77 | 0.68 | 0.66 | 0.51 | 0.76 | 0.68 | 0.61 | 0.59 | 0.46 |
| % TOC char | 22.5 | 23.3 | 20.5 | 20.1 | 15.5 | 23.1 | 20.7 | 18.6 | 17.9 | 14.0 |
| % TOC removed | 77.5 | 76.7 | 79.5 | 79.9 | 84.5 | 76.9 | 79.3 | 81.4 | 82.1 | 86.0 |
| % TOC (HyPy) | 81.6 | 80.7 | 83.7 | 84.1 | 89.0 | 81.0 | 83.5 | 85.7 | 86.4 | 90.6 |
| % TOC (EOM) | 99.3 | 98.3 | 100 | 100 | 100 | 98.6 | 100 | 100 | 100 | 100 |

Footnote: % TOC removed by HyPy = 95%; % TOC removed by EOM = 78%, Measure carbon in starting soil (g) =5.04, % TOC (HyPy) = % TOC removed with respect to HyPy, % TOC (EOM) = % TOC removed with respect to EOM, IS = initial soil.

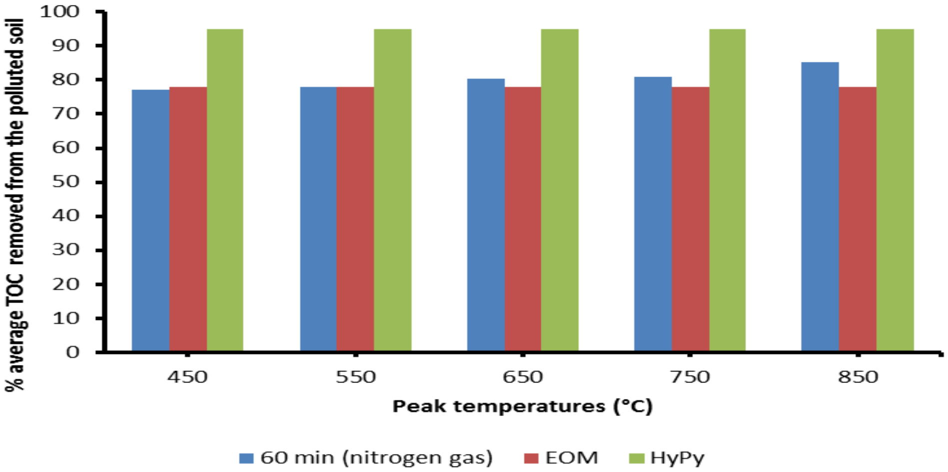


Figure 6-10: Average % TOC removed in the Gray-King retort at 60 minutes treatment time with carrier gas with respect to EOM and HyPy (n = 2).

### 6.2.5 Comparing the % TOC removed by Gray-King pyrolysis for all treatment conditions

The effective average % TOC removed from all the conditions was compared to assess the best method for the soil remediation. Table 6-12 presents the % TOC removed from 30 and 60 minutes treatment time without nitrogen gas. Likewise, the 60-minute treatment with nitrogen gas was also considered in the table (Table 6-13). The effective average % TOC removed increases with the increase in treatment time for each peak temperature when 30 and 60 minutes treatment times without carrier gas are compared.

Table 6-12: Comparing % TOC of products from Gray-King pyrolysis at 30 and 60 minutes treatment time without carrier gas.

| | 30 min (no carrier gas) | | | | | 60 min (no carrier gas) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Temp (°C) | 450 | 550 | 650 | 750 | 850 | 450 | 550 | 650 | 750 | 850 |
| % TOC of gas | 0.6 | 2.0 | 6.8 | 9.2 | 10.2 | 5.4 | 11.6 | 15.8 | 18.4 | 20.8 |
| % TOC of char | 31.8 | 30.0 | 19.8 | 19.6 | 19.4 | 23 | 22.8 | 20.3 | 18.5 | 18.2 |
| % TOC of oil | 65.8 | 67.4 | 70.7 | 69.4 | 69.3 | 65.4 | 60.3 | 54.3 | 56.3 | 54.4 |
| % TOC recovered | 98.3 | 99.4 | 97.2 | 98.2 | 98.9 | 93.8 | 94.6 | 90.4 | 93.2 | 93.4 |
| % TOC loss | 1.7 | 0.6 | 2.8 | 1.8 | 1.1 | 6.2 | 5.4 | 9.6 | 6.8 | 6.6 |

For 30 minutes (no carrier gas), % TOC removed are 68.2 % at lowest peak temperature of 450°C and 80.6 % at highest peak temperature of 850°C, while 60 minutes (no carrier gas) are 73.1% at 450°C and 82% TOC at 850°C. However, 60 minutes treatment time with nitrogen gas removed the highest possible amount of TOC from the soil, which is 77.2% at

450°C and 85.3% TOC at 850°C. This implies that carrier gas and treatment times are the two major factors determining the remediation of the soil.

Table 6-13: The average % TOC removed for all the experimental conditions of the Gray-King pyrolysis to remediate the polluted soil.

| Temperature (°C) | 450 | 550 | 650 | 750 | 850 |
|---|---|---|---|---|---|
| 30 min (no carrier gas) | 68.2 | 70.0 | 80.2 | 80.4 | 80.6 |
| 60 min (no carrier gas) | 77.0 | 77.3 | 80.0 | 81.5 | 81.8 |
| 60 min (carrier gas) | 77.2 | 78.0 | 80.4 | 81.0 | 85.3 |

Subsequently, the % TOC of products recovered from the Gray-King pyrolysis at 30 and 60 minutes treatment time with no nitrogen gas as carrier gas are presented in Table 6-12. The % TOC of products recovered from Gray-King at 30 minutes treatment time is higher than at 60 minutes treatment time with no nitrogen gas. The 30 minutes treatment time has higher % TOC recovered oil than the 60 minutes treatment time with no nitrogen gas. % TOC gas generated at 60 minutes treatment time with no nitrogen gas is higher than 30 minutes treatment time because of the slow evolution of the gas. Therefore, the highest oil recovered and gas yield are 70.7 % and 20.8 % to give 91.5 % TOC recovery. The loss observed may be as a result of the separation process of the oil from the water using the Dean-Stark method, followed by evaporation of solvent from the oil.

The 30 minutes treatment time has a good TOC balance because of high recovery of oil and loss of fewer gas components. However, the % TOC recovered products for 60 minutes treatment time was lower compared to 30 minutes because there is a loss of more light hydrocarbon gas.

### 6.2.6 Conclusions

1. The lowest % TOC char yield was obtained with 60 minutes treatment time with the nitrogen gas at 850°C (14.7% TOC), while the highest % TOC recovered oil was 70.7% TOC at 30 minutes residence time (no carrier gas) with 650°C peak temperature and the highest gas generated was 20.8% TOC at 850°C.

2. The amount of water generated was 4.6%, which is higher than the 1.3% initial moisture content of the soil. The XRD results show that there is a

structural change due to reduction in the quartz and kaolinite in the soil mineral to suggest the release of interlayer water.

3. The slow evolution of gas was observed at both 30 and 60 minutes with no carrier gas, which is reflected in the total volume of gas yields below 650°C peak temperatures.

4. The yield of methane gas increased with the increasing peak temperatures due to cracking of the heavier gas (such as pentane) as they were released from the solution.

5. The remediation techniques show that a critical peak temperature of 650°C is crucial to the process because there is a sudden leap in mass of products for treatment times of 30 and 60 minutes without carrier gas investigated. Above 650°C, cracking of the oil pollutant in the soil is suspected; and it is more evident with the % TOC removed values for all the conditions.

6. Finally, the most efficient conditions to remediate the soil were 60 minutes treatment time with nitrogen carrier gas because the % TOC char removed with respect to EOM at 550°C recorded 100% and 89% with respect to HyPy. These results are higher than the values obtained by the treatment of the polluted soil at both 30 and 60 minutes treatment time without nitrogen gas treatment.

## 6.3 Microwave pyrolysis technology for remediation of crude-oil-contaminated soil

The microwave is a new innovation to overcome the challenges faced by conventional thermal processing such as slow heat transfer, giving long heating-up periods due to the temperature gradient from the surface to the core of the material. It also reduces energy losses to the environment and has the added advantage of direct delivery of energy to materials with high conversion efficiency of electrical energy into volumetric heating (80%–85%) of samples (Osepchuk, 2002; Mutyala *et al.*, 2010). These attributes of microwave energy have made it very attractive for industrial applications as an alternative thermal processing technique (Chen, 2012; Horikoshi *et al.*, 2011)

This was demonstrated by earlier works to show the properties of the microwave as a heating system that has the potency as volumetric heating system for material, which has been applied for the treatment of drill cuttings and potential applications in pyrolysis of heavy- and light-oil-contaminated soils and domestic wastes (Robinson *et al.*, 2008; 2012; 2014). Li *et al.* (2009) reported that 99% oil removal was possible with the use of carbon fibres as microwave absorber during remediation of crude-oil-contaminated soil. This agreed with further work by Dawei *et al.* (2009) that crude-oil-contaminated soil clean-up can enhance carbon fibre with a short treatment time and high oil recovery without causing significant secondary pollution.

Further work reports that the penetration depth of a microwave in soil determines the heating performance, which removes 95% of hydrocarbon contaminant in soil in a stirred bed system (where a mechanical stirrer at the base of the reactor is used to stir the sample) and 30-50% in a fixed bed system (use of flowing nitrogen to remove evolving vapours in the fixed bed instead of a mechanical stirrer). The same report suggested that water impacts the high dielectric properties of the soil to generate enough heat to remove the hydrocarbon in the soil (Robinson *et al.*, 2012).

This observation agrees with the report of Hakala *et al.* (2011) that water saturation and wettability affects the dielectric properties of soil samples. Likewise, some earlier reports state that the higher the moisture content of a material, the larger the value of its dielectric properties of materials and coupling with microwave (Metaxas and Meredith, 1983; Meredith, 1998; Komarov *et al.*, 2005a). Further work by Robinson *et al.* (2014) and Shang *et al.* (2006) established the fact that the water content of the hydrocarbon-contaminated soil influences their response to microwave treatment. It was concluded in the report that microwave-transparent materials could respond to microwave treatment if there is presence of a microwave absorber such as water in the soil.

Mudgett (1995) and Fernandez *et al.* (2011) further reported that the dielectric properties of materials depends on the interlayer structure of the component of material that will make it absorbent or transparent to microwave radiation and the water content.

Therefore, this study investigates the dielectric properties of the soil based on the low moisture content of 1.3% prior to microwave treatment. The result of the microwave treatment of the soil after examination of the dielectric properties is compared to the Gray-King pyrolysis of the soil.

### 6.3.1 Dielectric property of the dry crude-oil-contaminated soil

The structure of the clay mineral of the soil has been discussed in Section 6.2.3. The clay minerals in the soil are quartz and kaolinite. The kaolinite contains interlayer water that increase the percentage of water generated from Gray-King pyrolysis compared to the starting moisture content of the dry soil.

There are two parameters of interest during dielectric measurement of soil, namely the dielectric loss factor (ε") and the dielectric constant (ε'), and these were fully discussed in Section 3.5.2. The two parameters are measured with the cavity perturbation technique (Section 4. 10). The dielectric loss factor (ε") (amount of microwave converted to heat the material) and the dielectric constant (amount of microwave absorbed by the material) (ε') values computed from Equations 4-3 and 4-4 is the dielectric property of the soil are measured against temperature increase. The ratio of the dielectric loss factor (ε") with the dielectric constant (ε') gives the loss tangent. The loss tangent (tanδ) provides a measure as to how well a material absorbs the electromagnetic energy and dissipates it as heat throughout the material. The value of loss tangent measured relative to temperature changes, determines whether a material can be regarded as a microwave absorber or not. If the loss tangent recorded for a material is very low, the response to microwave treatment will be poor. They might cause low dissipation of heat within the material and the occurrence of the phenomenon called thermal runaway (see Section 6.2.3) (Meredith, 1998).

In this current study, the soil moisture content is 1.3% and the loss tangent at room temperature is 0.03 (Figure 6-11). The loss tangent values decreased as the temperature increased to 100°C due to removal of moisture content. This occurred because water is the major microwave absorber in the soil at this temperature range. Above the 115°C mark, the carbonaceous content and bound water released from the clay minerals continue to absorb electromagnetive waves and dissipate less heat within the material (Robinson *et al.*, 2008; Cosenza and Tabbagh, 2004; Robinson *et al.*, 2014). This makes an area warmer than other cold areas, and heat exchange between the hot spot and the rest of the material is slow.

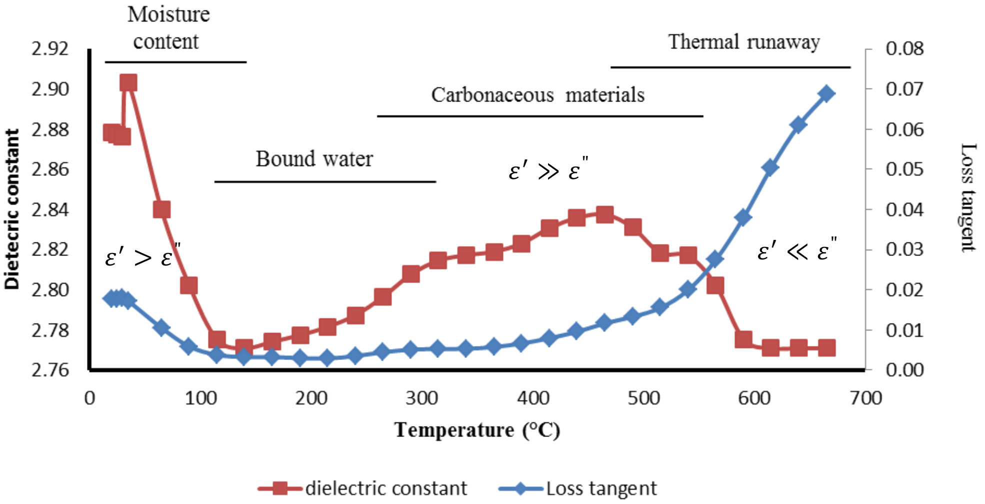


Figure 6-11: Loss tangent of the dry soil with frequency at 2.5GHz at varying temperature by cavity perturbation technique.

Then, a point is reached where an increase in temperature changes the condition in a way that causes a further increase in temperature, which often leads to a destructive result as shown in Figures 6-12 and 6-13. Therefore, the current study ensured that the temperature used for this experiment did not exceed 115 °C with the aid of parameters such as time (s), power input (kW), soil density ($\rho$) and specific heat capacity of the soil ($C\rho$) as shown in Equation 6-3. This procedure is called microwave steam stripping technique.

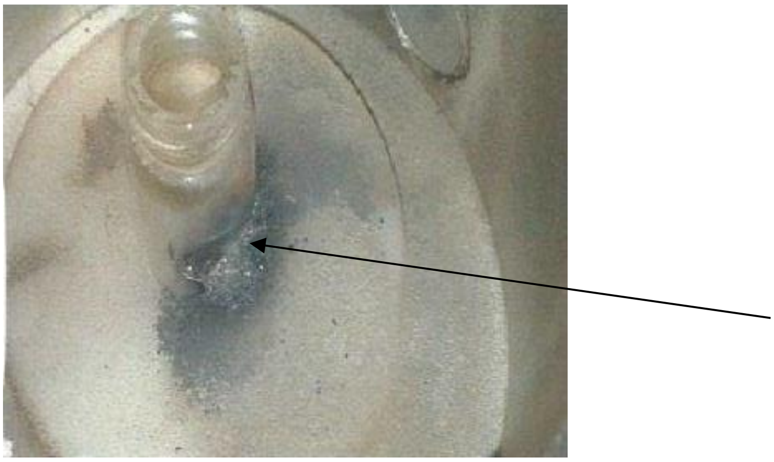
$$\Delta T = \frac{P\Delta t}{\rho C\rho} \qquad \text{Equation 6-3}$$

Where $\Delta T$ = temperature change, P = power input, Cp = specific heat capacity, $p$ = density (mass/volume).

Since the loss tangent at 2.5GHz was calculated from the measured loss factor and dielectric constant instead of direct measurement by cavity perturbation, the propagation error of the calculated loss tangent was determined using Equation 6-4.

$$\Delta Tan\delta = Tan\delta \times \sqrt{\left(\frac{\Delta\varepsilon''}{\varepsilon''}\right)^2 + \left(\frac{\Delta\varepsilon'}{\varepsilon'}\right)^2} \qquad \text{Equation 6-4}$$

Where ΔTanδ is the uncertainty in the calculated loss tangent and Δε’ and Δε’’ are the standard deviations of measured dielectric constant and loss factor. The calculated propagation errors are from 0.001 to 0.008 for the soil sample. This result of the propagation error shows that the loss tangent obtained is a true reflection of how the sample will respond to a microwave.



Combustion as a result of thermal runaway

Figure 6-12: Effect of thermal runaway on the reactor in the applicator during microwave pyrolysis of dried polluted soil during preliminary test beyond the timescale used for this experiment.

Figure 6-13: Combustion of reactor as a result of thermal runaway in the applicator during microwave pyrolysis of dried polluted soil during preliminary test beyond the timescale used for this experiment.

### 6.3.2 Microwave remediation of the dry contaminated soil

The experimental procedure as described in Chapter 4 stated that 20g of the dry soils was placed in a single-mode cavity and irradiated with the microwave power input of 1kW for varied periods of time at 30-second intervals with the lowest treatment time of 60 seconds and a maximum treatment time of 120 seconds in an inert atmosphere by passing nitrogen gas as a sweeping gas at a flow rate of 2L/min for 5 minutes prior to the beginning of the experiment, which was left running till the completion of each run.

The microwave pyrolysis parameters were then changed by increasing the microwave power input to 2kW at varying time ranges from 30 seconds to 90 seconds, though the time interval was changed to 15 seconds. The time range of the experiment was calculated using Equation 6-3, and the result is presented in Table 6-14. This time range was adopted for this experiment because free water has been regarded as a good microwave absorber due to its high dielectric properties (ε'=76.7 and ε'' =12.2 at 25°C) to create selective heating of the interlayer water to generate the steam-stripping process for the removal of contaminant (Hakala *et al.*, 2011). This causes remediation of the soil with the potential to reduce the energy requirement compared to conventional heating whereby 100% of the material is heated to the required temperature. Similarly, the presence of a vapour stream leads to an increase of vapour pressure, resulting in a reduction of the temperature needed for the contaminant desorption and consequently in an increase in removal efficiency.

Table 6-14: The calculated temperature of the microwave steam-strippng heating process to remove oil pollutant from the soil.

| Power | Time | Density | SHC | Temp (°C) |
|---|---|---|---|---|
| 1000 | 60 | 1.3 | 1480 | 31.19 |
| 1000 | 90 | 1.3 | 1480 | 46.78 |
| 1000 | 120 | 1.3 | 1480 | 62.37 |
| 2000 | 30 | 1.3 | 1480 | 31.19 |
| 2000 | 45 | 1.3 | 1480 | 46.78 |
| 2000 | 60 | 1.3 | 1480 | 62.37 |
| 2000 | 75 | 1.3 | 1480 | 77.96 |
| 2000 | 90 | 1.3 | 1480 | 93.56 |

Therefore, the preliminary experiments performed on the dried polluted soil sample were repeated six times at 60 seconds, 90 seconds and 120 seconds respectively at 1kW microwave power to determine the precision of the experimental protocol as shown in Table 6-15.

Table 6-15: Preliminary experiments to examine the precision of mass loss based on the soil residues after microwave treatment of approximately 20g of the polluted soil at 1kW microwave power, using different treatment times.

| Time(s) | 60 | 90 | 120 |
|---|---|---|---|
| 1 | 0.99 | 1.15 | 1.20 |
| 2 | 0.89 | 1.10 | 1.50 |
| 3 | 0.94 | 1.15 | 1.25 |
| 4 | 0.78 | 1.24 | 1.15 |
| 5 | 0.98 | 1.09 | 1.15 |
| 6 | 0.89 | 1.24 | 1.10 |
| mean | 0.89 | 1.19 | 1.13 |
| STD | 0.10 | 0.08 | 0.03 |

The values presented are the masses (g) lost after treatment of an initial 20g of soil with 1kW microwave power, which were obtained by subtracting the values of sample mass (g) after treatment from the initial mass (g) to examine the precision of the process. 20g of dried soil was weighed into the reactor and placed in the microwave applicator to receive incident microwave power of 1kW for the length of treatment time mentioned above. The mean value and standard deviation (STD) were calculated. The mean value increased with increasing treatment times. The standard deviation was very low for the preliminary test, which suggested that the experimental result that will be measured from the microwave treatment process is reliable and should be repeatable over recurrent trials for each treatment time. Subsequently, the main experiments were performed at the same treatment time and microwave power in triplicate to determine the % TOC of the char after each treatment time. The % TOC of the char from the microwave was used to determine the % TOC removed. The % TOC removed from the microwave treatments is presented in the next set of sections. The standard deviation of the triplicates is determined to examine the repeatability and reliability of the results for both the 1 and 2kW microwave power input.

In addition, the effectiveness of the process will be based on the comparison of % TOC removed from the soil with an average value from the Gray-King pyrolysis at 60 minutes with nitrogen gas, since it gave the highest % TOC removed. As for Gray-King pyrolysis, the efficiency of the process will also be based in relation to the % TOC removed by HyPy and EOM from the original soil.

#### 6.3.2.1 The TOC conversion for 1 and 2kW microwave power input

##### 6.3.2.1.1 Microwave 1kW power for polluted dry soil treatment

The results from the triplicate microwave treatment tests of the soil with 1kW power are presented in Table 6-16. The average % TOC of the analysis is presented in Table 6-18. The initial soil TOC for all the triplicate analysis is between 1.01 and 1.02g respectively.

Exp. 1 indicates that more TOC is removed from the soil by increasing the treatment time, as 12.3% TOC was removed after 60 seconds and 21.5 % TOC after 120 seconds. The % TOC removed was very low compared to all the Gray-King pyrolysis treatment investigated and, therefore, also very poor with respect to % TOC removed by HyPy and EOM.

Table 6-16: The conversion of TOC for the dry, polluted soil after 1kW microwave treatment.

| | Exp. 1 | | | Exp. 2 | | | Exp. 3 | | |
|---|---|---|---|---|---|---|---|---|---|
| Time (s) | 60 | 90 | 120 | 60 | 90 | 120 | 60 | 90 | 120 |
| IS (g) | 20.16 | 20.02 | 20.02 | 20.16 | 20.02 | 20.02 | 20.16 | 20.02 | 20.02 |
| EOM IS (g) | 1.61 | 1.60 | 1.60 | 1.61 | 1.60 | 1.60 | 1.61 | 1.60 | 1.60 |
| TOC IS (g) | 1.02 | 1.01 | 1.01 | 1.02 | 1.01 | 1.01 | 1.02 | 1.01 | 1.01 |
| TOC of char (g) | 0.89 | 0.86 | 0.79 | 0.87 | 0.86 | 0.79 | 0.87 | 0.87 | 0.86 |
| % TOC removed | 12.3 | 14.7 | 21.5 | 14.29 | 14.68 | 21.48 | 14.33 | 13.41 | 15.12 |

Measure C in starting soil (g) =5.04, IS = initial soil.

Exp. 2 and Exp. 3 highlighted similar observations as discussed earlier. The triplicate analysis shows that the microwave treatment of the dry soil at 1kW microwave power input does not have a sufficient volumetric heating effect on the soil to remove a large percentage of the oil. This observation is due to the low moisture content of the soil and it was not enough to create a localised temperature to desorb large % TOC from the soil compared to the Gray-King pyrolysis discussed in Section 6.2.4.

Table 6-17:. The average conversion of TOC for the polluted dry soil after 1 and 2kW microwave treatment.

| Time (s) | 60 | 90 | 120 |
|---|---|---|---|
| Exp. 1 | 12.3 | 14.7 | 21.5 |
| Exp. 2 | 14.3 | 14.7 | 21.5 |
| Exp. 3 | 14.3 | 13.4 | 15.1 |
| Mean value | 13.7 | 14.3 | 19.4 |
| STD | 1.15 | 0.73 | 3.68 |
| % TOC removed with respect to HyPy | 14.3 | 15.0 | 20.3 |
| % TOC removed with respect to EOM | 17.5 | 18.3 | 24.8 |

% TOC removed by HyPy = 95 %; % TOC removed by EOM = 78%; measure of C in starting soil (g) =5.04.

The repeatability of the 120 seconds treatment time is not as good as for 60 and 90 minutes. The average results of the triplicate analysis are presented in Table 6-17 with statistical analysis to examine the precision of the results. The mean standard deviation of the 120 seconds was very high compared to 60 and 90 seconds. The overall average % TOC removed were 13.7% TOC at 60 seconds, 14.3% TOC at 90 seconds and 19.4% TOC at 120 seconds respectively. The highest % TOC removed with respect to HyPy and EOM were 20.3 and 24.8% respectively.

###### 6.3.2.1.2 Microwave 2kW power for polluted dry soil treatment

The microwave power was increased to 2kW and reduced the treatment time to investigate whether the same energy input and a little increase will improve the % TOC removed. The treatment times used for the 2kW microwave power input were 30, 45, 60, 75 and 90 seconds. Table 6-18 presents the % TOC removed from the three replicate experiments performed on the dried polluted soil at 2kW microwave power input. The additional treatment time shows a significant improvement in the amount of TOC removed between 60 and 75 seconds with the % TOC removed at 75 seconds and 90 seconds being almost the same. Comparing the % TOC removed at 1kW with the 2kW, there is no significant increase as represented in Figure 6-14. This suggests that a further increase in the microwave power input might result in no significant increase.

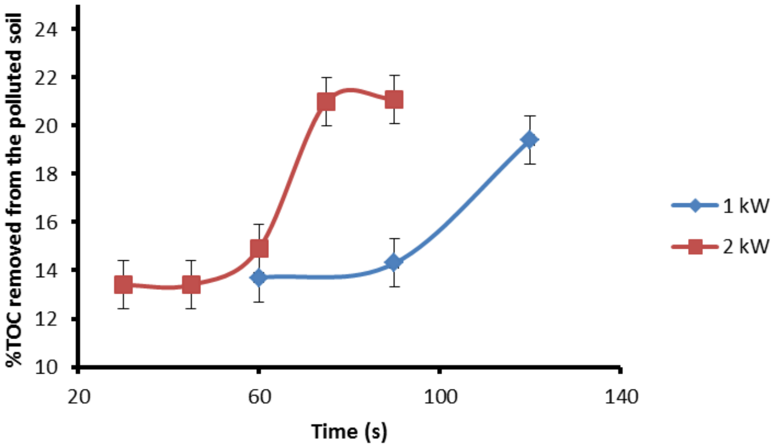


Figure 6-14. The average conversion of TOC for the polluted dry soil after 1 and 2kW microwave treatment.

Figure 6-14 shows the average % TOC removed after triplicate microwave treatment of the polluted dry soil at 2kW microwave power input (error bar = standard deviation). The overall average of the % TOC removed at 2kW power input efficiency was compared with % TOC removed with HyPy and EOM. The % TOC removed was similar with the % TOC removed with 1kW microwave power input as indicated in Table 6-18.

Table 6-18: The % removal of TOC for the polluted dry soil after 2kW microwave treatment.

| Time (s) | 30 | 45 | 60 | 75 | 90 |
|---|---|---|---|---|---|
| Exp. 1 | 12.3 | 12.6 | 14.9 | 21.6 | 21.1 |
| Exp. 2 | 14.0 | 13.7 | 15.0 | 21.7 | 20.7 |
| Exp. 3 | 13.8 | 13.7 | 14.9 | 19.8 | 21.5 |
| Mean | 13.4 | 13.4 | 14.9 | 21.0 | 21.1 |
| STD | 0.9 | 0.6 | 0.1 | 1.1 | 0.4 |
| % RSD | 6.8 | 4.8 | 0.6 | 5.0 | 1.8 |

Measure of carbon in starting soil (g) = 5.04; initial TOC range in soil = 1.01-1.02.

The highest values of removal efficiency of % TOC from the polluted dry soil after 2kW microwave pyrolysis with respect to HyPy and EOM were 22 and 27% TOC at 90 seconds as shown in Table 6-19. These % TOC results obtained from the dry soil initiated the idea of artificially increasing the moisture content of the dry soil to investigate if there will be an improvement in the % TOC removed from the soil.

To achieve this objective, distilled, de-ionized water was added to the soil to improve the soil moisture content, and the same experimental conditions were performed on the soil to enable the researcher to compare the results confidently. The soil moisture content was examined with TGAQ500 after the addition of distilled, de-ionized water, and was found to be 8.6% compared to the initial value of 1.3%. This sample is now referred to as wet soil.

Table 6-19: Overall conversion of % TOC removed from the polluted dry soil after 2kW microwave treatment.

| Time (s) | 30 | 45 | 60 | 75 | 90 |
|---|---|---|---|---|---|
| Initial soil (g) | 20.4 | 20.1 | 20.2 | 20.1 | 20.2 |
| EOM in initial soil (g) | 1.63 | 1.61 | 1.61 | 1.61 | 1.61 |
| Initial TOC of soil (g) | 1.02 | 1.01 | 1.02 | 1.01 | 1.02 |
| TOC of residue (g) | 0.88 | 0.87 | 0.87 | 0.80 | 0.80 |
| % TOC removed by Microwave | 13.4 | 13.4 | 14.9 | 21.0 | 21.1 |
| % TOC removed with respect to HyPy | 14.0 | 14.0 | 15.7 | 22.1 | 22.1 |
| % TOC removed with respect to EOM | 17.1 | 17.1 | 19.2 | 27.0 | 27.0 |

% TOC removed by HyPy = 95%; % TOC removed by EOM = 78 %; measure of C in starting soil (g) = 5.04.

#### 6.3.2.2 The TOC conversion after 1 and 2kW microwave power input on the wet contaminated soil

##### 6.3.2.2.1 Microwave 1kW power for polluted wet soil treatment

The wet soil was treated with a microwave input of 1kW with the same treatment time as performed on the dry soil for basis of comparison. The triplicate pyrolysis results of the wet soil are presented in Table 6-20.

Table 6-20 shows a massive increase in the % TOC removed from the soil compared to the dry soil at the same treatment time. Experiment 1 shows % TOC removed ranging from 61.2% at 60 seconsd to 69.0% at 120 seconds, instead of 13.7% TOC removed at 60 seconds and 19.4% TOC removed at 120 seconds for the dry soil at 1kW treatment. Experiments 2 and 3 equally show a vast increase in the % TOC removed, although the yields are different with 71.7 % TOC at 60 seconds and 74.2 % TOC at 120 seconds for Experiment 2 and 61.8 % TOC at 60 seconds and 72.7 % TOC at 120 seconds for Experiment 3 as shown in Table 6-21. The % TOC removed results obtained from Experiment 3 as shown in Table 6-21 were not a significant departure from Experiment 1 because their values at 60 sedonds treatment time are almost the same and the result for 120 seconds is not too far from the result of Experiment 2. The % TOC removed at 120 seconds with respect to Experiments 2 and 3 are relatively close to the average 73.3 % TOC removed by Gray-King pyrolysis at 550 °C with 60 minutes residence time with no carrier gas. This suggests that a further increase in treatment time might produce similar results with the Gray-King treatment if arcing of the sample can be controlled.

Table 6-20: The conversion of TOC for the dry polluted soil after 1kW microwave treatment.

| | Exp. 1 | | | Exp. 2 | | | Exp. 3 | | |
|---|---|---|---|---|---|---|---|---|---|
| Time (s) | 60 | 90 | 120 | 60 | 90 | 120 | 60 | 90 | 120 |
| IS (g) | 20.16 | 20.02 | 20.02 | 20.16 | 20.02 | 20.02 | 20.38 | 20.19 | 20.12 |
| EOM in IS (g) | 1.61 | 1.60 | 1.60 | 1.64 | 1.61 | 1.61 | 1.63 | 1.62 | 1.61 |
| IS TOC (g) | 1.02 | 1.01 | 1.01 | 1.03 | 1.01 | 1.02 | 1.03 | 1.02 | 1.01 |
| TOC of char (g) | 0.4 | 0.4 | 0.3 | 0.29 | 0.28 | 0.26 | 0.4 | 0.4 | 0.3 |
| % TOC removed | 61.2 | 65.3 | 69.0 | 71.69 | 72.31 | 74.22 | 61.8 | 62.6 | 72.7 |

% TOC removed by HyPy = 95 %; % TOC removed by EOM = 78 %, measure C in starting soil (g) = 5.04, IS = initial soil.

The overall average % TOC removed for the triplicate experiments was found to be 64.9% at 60 seconds and 72% at 120 seconds as shown in Table 6-21. Comparing the result with % TOC removed by HyPy and EOM, the treatment was able to remove 75.5% with respect to HyPy and 92.3% with respect to EOM. The mean standard deviation and the % RSD from the table show that the result for 120 seconds is more precise than for 60 and 90 minutes treatment time unlike dry soil at the same treatment time.

Table 6-21: The average conversion of TOC from the polluted wet soil after 1kW microwave treatment.

| Time (s) | 60 | 90 | 120 |
|---|---|---|---|
| Exp. 1 | 61.2 | 65.3 | 69.0 |
| Exp. 2 | 71.7 | 72.3 | 74.2 |
| Exp. 3 | 61.8 | 62.6 | 72.7 |
| Mean | 64.9 | 66.8 | 72.0 |
| STD | 5.9 | 5.0 | 2.7 |
| % RSD | 9.1 | 7.5 | 3.7 |
| % TOC removed with respect to HyPy | 68.10 | 70.04 | 75.52 |
| % TOC removed with respect to EOM | 83.20 | 85.58 | 92.27 |

% TOC removed by HyPy = 95%; % TOC removed by EOM = 78%; measure of C in starting soil (g) = 5.04.

#### 6.3.2.2.2 Microwave 2kW power for polluted wet soil treatment

The wet soil was later treated with 2kW microwave power input and same treatment time with the dry soil. The experiment was performed in triplicate as was done with polluted dry soil to give a good comparison as shown in Table 6-22.

Table 6-22: The average % TOC removed from the crude polluted wet soil after 2kW microwave treatment.

| Time (s) | 30 | 45 | 60 | 75 | 90 |
|---|---|---|---|---|---|
| Exp. 1 | 63.5 | 66.7 | 68.5 | 75.4 | 77.0 |
| Exp. 2 | 71.7 | 72.3 | 74.2 | 75.9 | 76.6 |
| Exp. 3 | 62.0 | 63.6 | 72.9 | 75.4 | 77.0 |
| Mean | 65.7 | 67.5 | 71.9 | 75.6 | 76.9 |
| STD | 5.2 | 4.4 | 3.0 | 0.3 | 0.2 |
| % RSD | 7.9 | 6.6 | 4.2 | 0.4 | 0.3 |
| % TOC with respect to HyPy | 69.2 | 71.0 | 75.7 | 79.6 | 80.9 |
| % TOC with respect to EOM | 84.2 | 86.5 | 92.2 | 96.9 | 98.6 |

% TOC removed by HyPy = 95%; % TOC removed by EOM = 78%; measure of C in starting soil (g) = 5.04.

The % TOC removed across all repeated experiments increased with treatment time. The average % TOC removed at 30 seconds for the triplicate test was 65.7 % while 90 seconds was found to be 76.9 %. This suggested that longer treatment times will increase the % TOC removed. The % TOC removed was found to be a minimum of four times higher than the mean value TOC removed from dry soil. At higher treatment times, the % TOC removed was fairly constant showing that there is equal distribution of a volumetric heating effect of microwave in the soil. The mean standard deviation and the % RSD of the wet soil decreased with increasing treatment times, and the lowest values were found to be 0.2 and 0.3 % after 90 seconds, which suggested a better repeatability of experiments or better precision at higher treatment times. Compared to the Gray-King pyrolysis, the mean % TOC removed at 90 seconds was approximately equal to the 77.2% TOC removed at 450°C, using 60 minutes with nitrogen gas as the carrier gas. Furthermore, the 76.9% TOC removed at 90 seconds was higher than the average % TOC removed by 30 minutes and 60 minutes with no carrier gas at 550°C peak temperatures (69.0% at 30 minutes and 73.3% at 60 minutes).

The average % TOC removed with respect to EOM was 84.2% after 30 seconds and 98.6% after 90 seconds, while it was 69.2% after 30 seconds and 80.9% after 90 seconds with respect to HyPy. These results suggest that microwave is a good treatment technique for polluted soil with the potential of surpassing the Gray-King pyrolysis at longer treatment times.

The average conversion of the TOC removed from the wet soil was compared with the dry soil. The % TOC removed at 2kW in the wet soil was found to increase to 73.8% after 30 seconds and approximately 96.1% after 90 seconds compared to dry soil. Hopefully in future work on redesigning the microwave pyrolysis applicator, the problem of thermal runaways can be controlled and the treatment time increased to reduce the % TOC in the soil to <1 %.

### 6.3.3 Conclusion

The dry crude-oil-contaminated soil with moisture content of 1.3% had a low loss tangent and responded poorly to microwave treatment. The highest % TOC removed was 21.1% at 2kW, which is very low compared to the lowest peak temperature (450°C) of Gray-King pyrolysis with 30 minutes treatment time without sweep gas (68.2%). This confirms that moisture is a major key parameter for dielectric properties of the soil that will encourage coupling with a microwave to create a localised temperature adequate enough to desorb the crude oil thermally from the soil. This was further established when water was added to the soil to increase the moisture content to 8.6%. The % TOC removed at 90 seconds for 2kW treatments of the wet soil was very high (76.9% TOC), and close to the Gray-King pyrolysis at 60 minutes treatment time with nitrogen sweep gas. The result of the soil with 1.3% moisture content with microwave pyrolysis agreed with Falciglia *et al.* (2011) that it is not cost-effective to treat very low moisture content soil with a microwave system.

The microwave treatment results of the wet soil further affirmed the findings established by Robinson *et al.* (2008) that crude oil can be removed from soil without the aid of any additional microwave absorbers. In this current work, the wet soil treatment time was not varied because it was carried out as a measure of comparison with the dry soil to understand how the soil will behave in a microwave field with sufficient water content. However, the result of % TOC removed at 90 seconds (76%) was higher than the 65% removal from previous work on the use of a single-mode applicator but less than the 95% organic removal of the stirred bed system of Robinson *et al.* (2012). The results of the experiment might improve yield to 95% with a further increase of water and treatment time with the same heating rate with the challenge of overcoming thermal runaway. Falciglia *et al.* (2013) suggested that soil texture affects the responses to microwave treatment. Their report stated that fine soils have a poor response to microwave treatment unless a high operating power source is used, which will increase the energy cost of remediation. This perspective could be a contribution to the result observed in the study because the soil samples were grounded into powdered form before anaylsis. This means the major response of the soil was possibly based on the increase in the moisture content of the soil (Falciglia and Vagliasindi, 2016). Therefore, care will be taken in future work to attain 99 % TOC removal while ensuring that the soil is not grounded to fine powder and dried before analysis.

## 6.4 Geochemical properties of the EOM after thermal remediation

The thermal remediation of the oil-polluted soil was successfully performed by the two thermal remediation processes. However, the conventional treatment was carried out at very high temperatures between 450°C and 850°C, while the microwave steam-stripping pyrolysis technique was operated at temperature not more than the boiling point of water. Therefore, the geochemical properties of the oil products were examined to consider the effect of the operating temperature of the two methods. The oil products from Gray-King and microwave treatment were analysed by GC-MS using SIC mode at m/z 71, 191, 217, 178 and 192 for a comparative study of the effect of operational temperatures of the two methods shown in Figures 6-15, 6-16, 6-17 and 6-18.. The aromatic hydrocarbons such as phenanthrene were also considered since they are expected to be in abundance in crude oil and less easily biodegraded as the aliphatic hydrocarbons.

Table 6-23. Source and thermal maturity parameters derived from the biomarkers distributions in oil samples.

| Parameters | Crude Oil | Gray-King | Microwave |
|---|---|---|---|
| Ts/Tm | 0.96 | 0.94 | 0.96 |
| Ol/30αβ | 0.91 | 0.84 | 0.83 |
| 31(S/S+R) | 0.59 | 0.57 | 0.54 |
| 29ααα(S/S+R) | 0.36 | 0.44 | 0.49 |
| 29 (αββ/(ααα+αββ) | 0.51 | 0.56 | 0.58 |
| MPI-1 | 0.80 | 0.85 | 0.83 |

The results obtained from the GC-MS analysis confirm that the Gray-King (850°C) and the microwave pyrolysis oils (94°C) are derived from the Nigerian crude oil in the soil. The

GC-MS analysis parameters presented in Table 6-24 show a resemblance in source and thermal maturity across the crude oil, Gray-King and microwave pyrolysis oil. according to Table 6-22, 31 (S/S+R) hopane ratios (0.59 and 0.57) of the crude oil and Gray-King have reached equilibrium values, while the microwave oil is less matured compared to the crude oil. C29 sterane SS/S+R (0.36, 0.44 and 0.49) shows that the oils are moderately thermally matured. The Ts/Tm ratios of the crude oil and the oil removed from the microwave are the same (0.96), which suggests that they were in a similar thermal maturity state and that the geochemistry of the microwave pyrolysis oil was not significantly affected because of the use of a low temperature for the experiment. These observations that the oils were similar was further confirmed by the MPI-1 index for the three oils, which were quite close (0.80, 0.85 and 0.83). The high values of the MPI-1 and the Ts/Tm ratio mentioned above suggested that they are matured oils, deposited under oxic conditions with a substantial terrigenous input.

The SICs for m/z 71, 191 and 217 in Figures 6-15, 6-16 and 6-17 show that they all contain pristane, phytane, *n*-alkanes, hopanes and steranes. In addition, the aromatic hydrocarbons investigated as shown in Figure 6-18 show similar resemblance due to the presence of the phenanthrene and the methylphenanthrene present in the GC-MS trace.

Figure 6-15 shows the presence of pristane and phytane in all the three oil products, namely microwave oil, Gray-King oil and solvent-extracted crude oil from soil. The m/z 71 of the crude oil shows the presence of few *n*-alkanes due to its complex composition, but the Gray-King oil has more *n*-alkanes due to the cracking of the heavier hydrocarbons to form light hydrocarbons. The microwave oil has a cleaner chromatogram because of the selective removal due to the steam-stripping process employed. The pyrolysis temperature (<100$^{o}$C) does not encourage cracking of hydrocarbon, but only desorbs the oil from the soil sample. The dominant features present in the three oil products are oleanane, 30$\alpha\beta$ and 29$\alpha\beta$. Ts (18$\alpha$-22, 29, 30-trisnorneohopane) and Tm (17$\alpha$-22, 29, 30-trisnorhopane) werre likewise present in all the oil products considered (Figure 6-11).

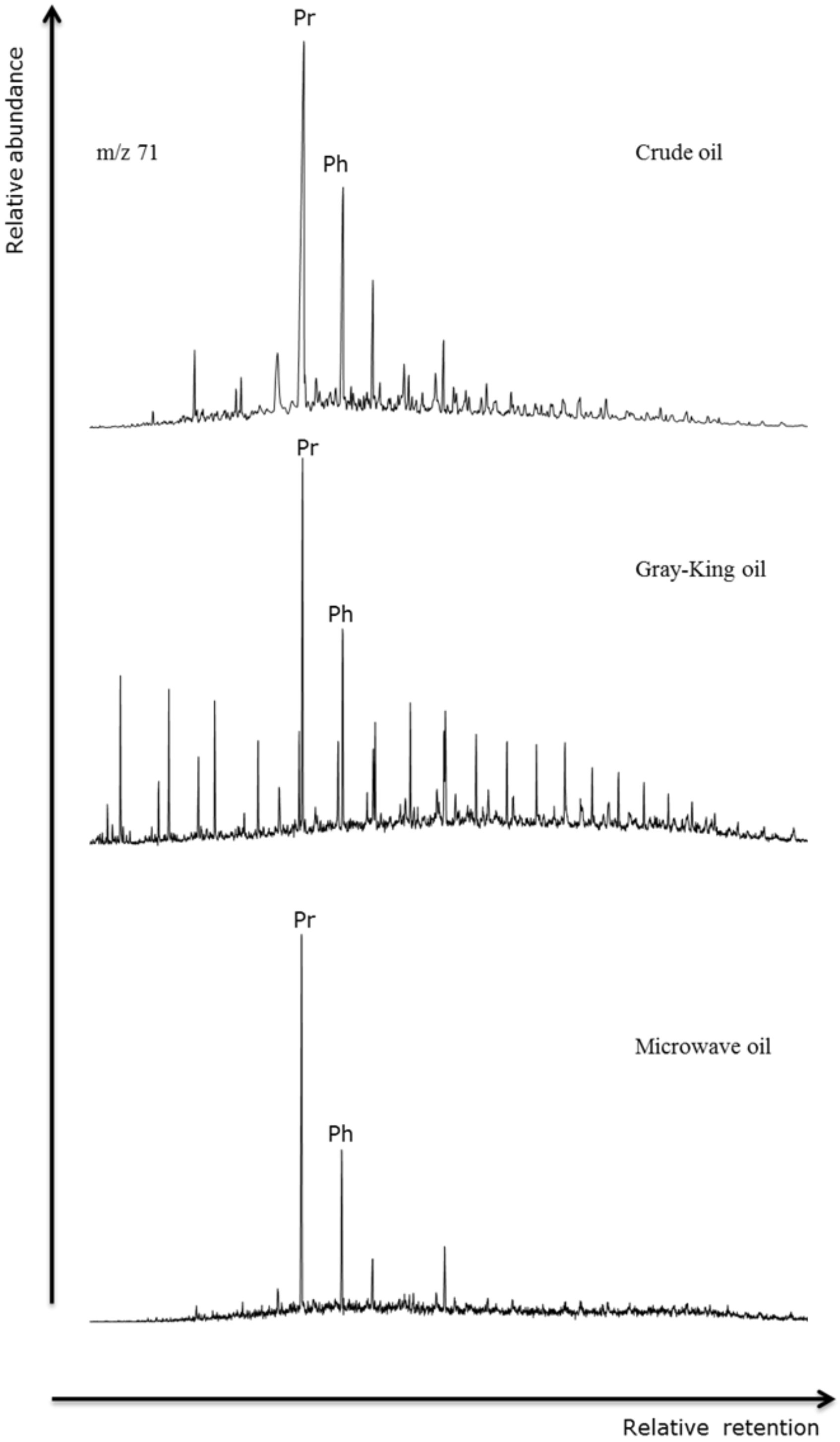


Figure 6-15: SIC chromatogram for m/z 71 showing isoprenoids and aliphatic fractions of crude oil in the soil, Gray-King oil after 850°C treatment held at 60 minutes with nitrogen gas and microwave oil of wet soil at 90 seconds treatment time.

Oleanane has been associated with crude oil in the previous work of Ekweozor *et al.* (1979a) which examined biomarkers present (e.g. oleanane) in crude oil from Niger Delta. It suggests terrigenous input from deltaic settings in the later Upper Cretaceous period. The oleanane ratio index clearly shows that they are all from the same sources because their values are very close and are greater than 0.2.

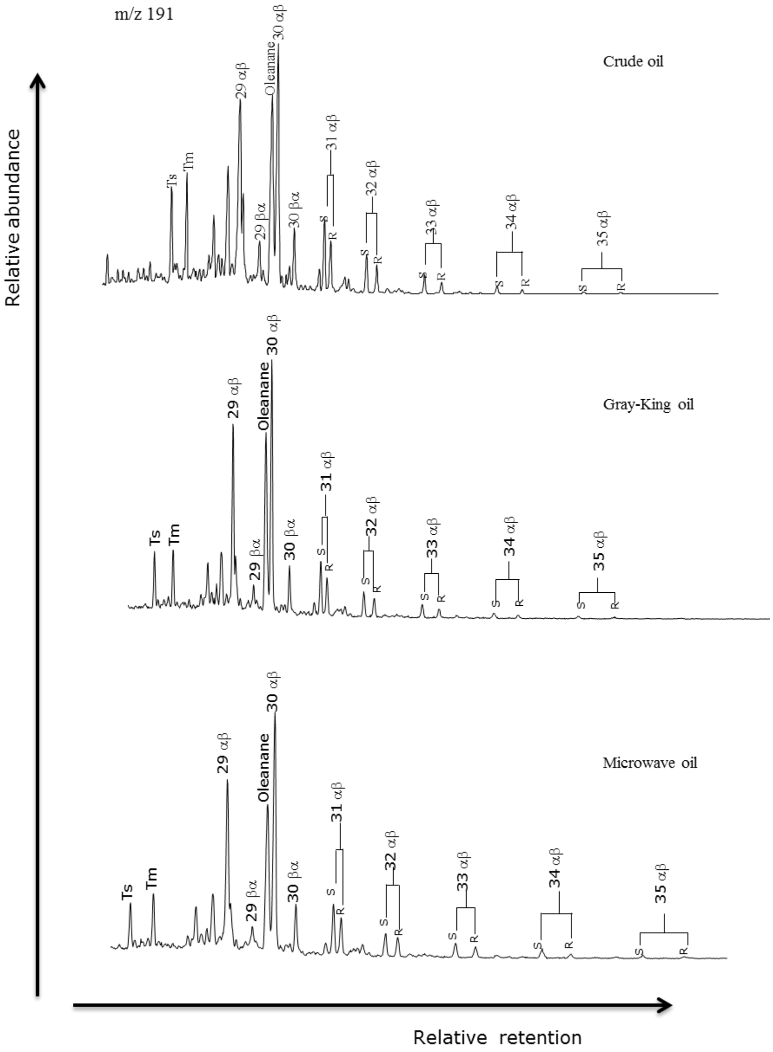


Figure 6-16: SIC chromatogram for m/z 191 showing hopanes and aliphatic fractions of crude oil in soil, Gray-King oil after 850°C treatment held at 60 minutes with nitrogen gas and microwave oil of wet soil at 90 seconds treatment time.

Figure 6-17 shows that the sterane distribution is intact and not affected in any way. This suggests a moderate degree of degradation of oil products because the *n*-alkanes are mostly affected by biodegradation. The dominant sterane distribution range from $C_{27}$ to $C_{29}$ 5α, 14α, 17α H for both R and S, with C29 5α, 14β, 17β (H) (20R+20S) is present in a good amount. The distribution of $C_{27}$ to $C_{29}$ steranes indicates that the soil extract is derived from a source rock of terrestrial organic matter (Peters and Moldowan, 1993).

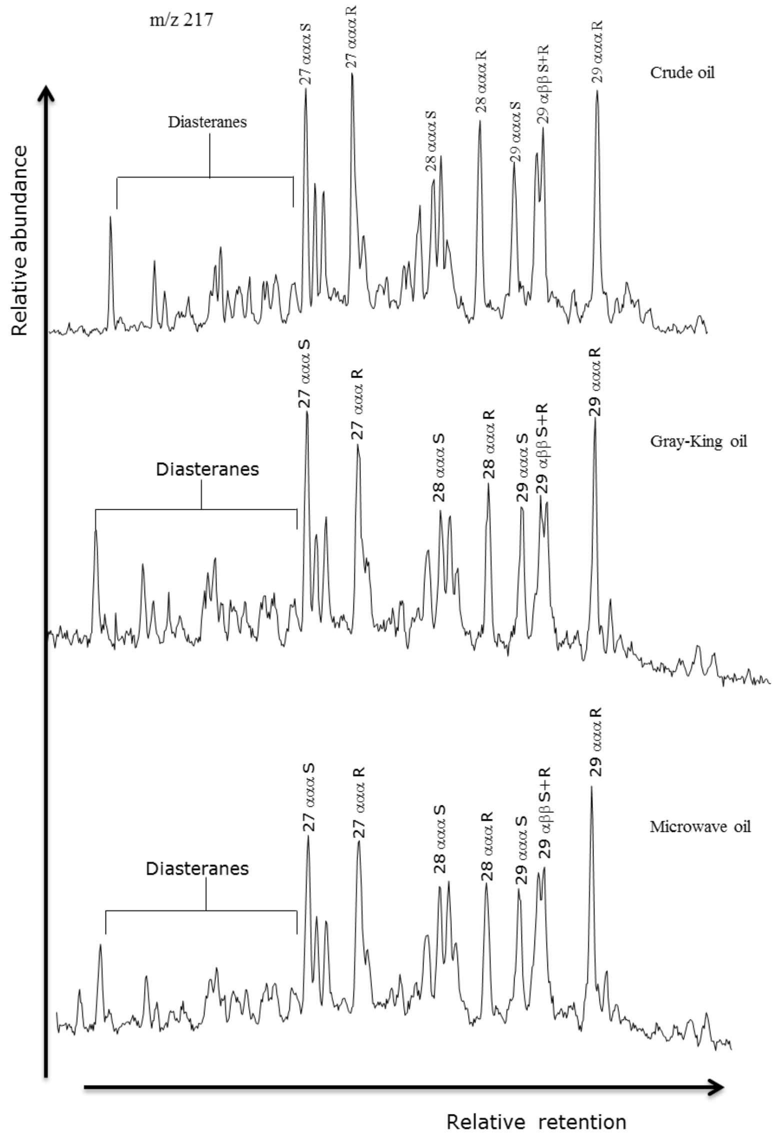


Figure 6-17: SIC chromatogram for m/z 217 showing steranes and aliphatic fractions of crude oil in soil, Gray-King oil after 850°C treatment held at 60 minutes with nitrogen gas and microwave oil of wet soil at 90 seconds treatment time.

Figure 6-18 shows the chromatogram plot of phenanthrene (m/z 178) and methylphenanthrene (m/z 192) for the three oils: crude oil, Gray-King oil and microwave oil. The oils' methylphenanthrene has its methyl group position at 1, 2, 3 and 9 on the aromatic rings of phenanthrene. The maturities of the oils were calculated using the methylphenanthrene index (MPI-1= 1.89 (2-MP + 3-MP/[P + 1.26(1-MP + 9-MP)]). The MPI-1 is expected to increase with the rise in the thermal maturity of the oil. The values of the MPI-1 for all the oils show that they are all moderately matured. However, the relative abundance of the 1-MP to 9-MP varies in the chromatogram of Gray-King and microwave oil.

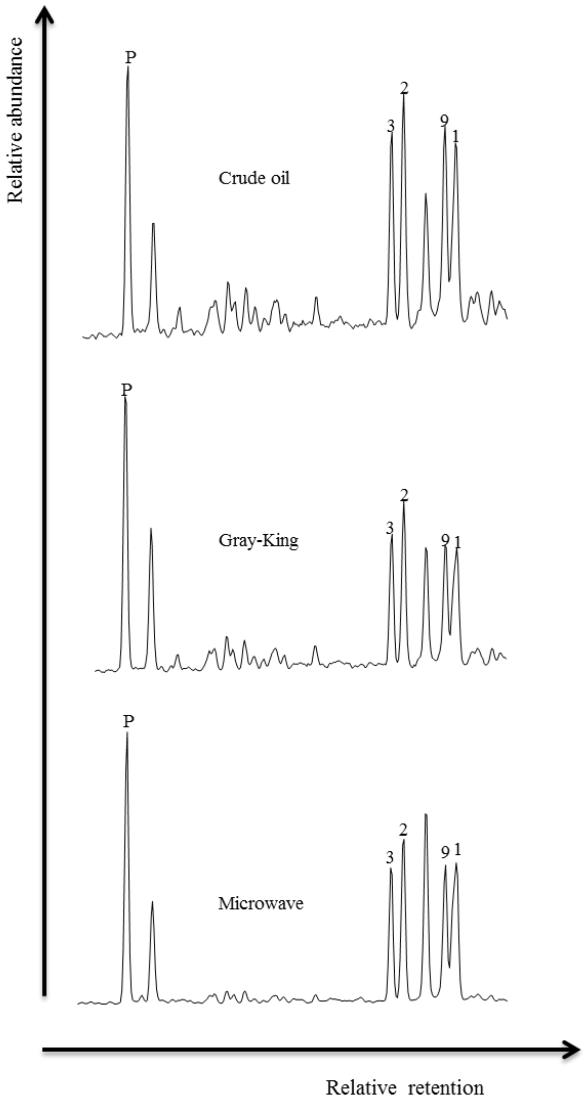


Figure 6-18: SIC chromatogram for m/z 178 and 192 phenanthrene and 1-methyl phenanthrene, 9-methylphenanthrene, 2-methylphenanthrene, 3-methylphenanthrene fractions of crude oil in soil, Gray-King oil after 850°C treatment held at 60 minutes with nitrogen gas and microwave oil of wet soil at 90 seconds treatment time.

In conclusion, the geochemical data and the graph show that the temperature used for the remediation does not affect the oil property to a great degree. They are not different from the starting crude oil, which suggests that they can be re-used to power the energy supply to the remediation equipment or they can be sold to petrochemical companies, thus adding to return on investment for the stakeholders.

### 6.4.1 Conclusions

1. The geochemical analysis of the oil products from the soxhlet extraction, Gray-King and the microwave pyrolysis was examined by GC-MS and presented in Figures 6-10 to 6-13. They show the presence of aliphatics such as isoprenoids, hopanes, steranes and phenanthrenes as aromatic distribution in the soil.

2. The m/z 71 traces of the three oil products were very similar as shown in the chromatogram in Figure 6-10 to depict the extent of biodegradation. The traces show biodegradation of the *n*-alkanes with the abundance of *n*-alkanes shown in the Gray-King trace due to cracking. The hopanes and the steranes at m/z 191 and 217 were intact while m/z 71 were greatly affected by biodegradation. This clearly shows that the oils were moderately biodegraded.

3. The hopanes, steranes and phenanthrene were very intact, which suggested that the oils were not fully matured. Likewise, the traces were very similar to each other e.g. the phenanthrene was intact. Ts/Tm ratio tends to be close 1, which confirms the maturity state of the oil. The hopanes series calculation from Figure 6-11 was found to be above 0.5, signalling the beginning of the oil generation window.

4. The sterane distribution contained diasteranes due to cross-linking. The steranes' dominance with $C_{29}$, $C_{28}$ and $C_{27}$ showed moderate maturity. The $C_{29}$ sterane was used as a maturity parameter in Table 6-22 because it offered the least interference from co-eluting peaks.

5. The Phenanthrene MPI-1 value is comparable for the three oils with the Gray-King oil having the highest value of 0.85, suggesting a slight thermal rearrangement of the methylphenanthrene. This was supported by the reduction of the 1-methlyphenanthrene relative abundance in the Gray-King oil compared to the starting crude oil trace. Moreover, the results of the MPI-1 supported the maturity state indicated by the aliphatic hydrocarbons.

## 6.5 Overall conclusion

1. The % moisture content of the dry soil after Gray-King pyrolysis was 4.6 %, which is far higher than the initial 1.3 % because the soil minerals were able to release the water in their interlayer structure. This was confirmed with the XRD that showed depletion in the count intensity of the mineral content of the soil following the Gray-King pyrolysis of the soil.

2. Slow evolution of gas was observed in the experimental process of the Gray-King pyrolysis at 30 and 60 minutes with no carrier gas used across all the peak temperatures investigated. This slow evolution was noticed evidently in the total gas volume yield below 650°C with over 8% between the yield at 30 minutes and 60 minutes. However, the gas volume using Gray-King and microwave pyrolysis with nitrogen gas was not collected because the gas sampling bag was not large enough to collect all the gas.

3. The Nigeria crude-oil-contaminated soil was remediated using Gray-King and microwave pyrolysis technology. The highest % TOC removed from the soil at 850°C with 60 minutes treatment time with nitrogen was 85.3%, which is 8.4% higher than the maximum % TOC removed by microwave after 90 seconds of treatment of the wet soil with 2kW microwave power.

This study recommends that Gray-King pyrolysis at 850°C for 60 minutes treatment time with nitrogen gas is the most effective methodology for polluted soil remediation. Moreover, it is suggested that a longer treatment beyond 90 seconds could provide an equal or better performance than Gray-King with 60 minutes treatment time with nitrogen.

4. The oil products from the Gray-King and microwave treatment were compared with the starting oil structure, using the GC-MS SIC mode to identify aliphatics (m/z 71), hopanes (m/z 191), steranes (m/z 217), phenanthrenes (m/z 178) and methylphenanthrenes (m/z 192). The three oil products were similar based on the chromatogram plots. The dominant hydrocarbons in the m/z 71 were the pristanes and the phytanes, while the *n*-alkanes were mostly biodegraded except the Gray-King chromatogram that showed higher abundance than the original oil due to cracking of higher hydrocarbon to generated light hydrocarbons that appeared in Figure 6-15.

5. The chromatogram plots show maturity parameters which are hopanes and steranes as mentioned above. The Ts/Tm ratios 0.96, 0.94 and 0.96 signifies the thermal maturity of the three oil products and the 31 (S/S+R) lend support to the interpretation of the Ts/Tm ratio that they are thermally maturing. The sterane ratio shows close correlation among the three oil products to suggest that they are predominantly terrestrial source inputs deposited in oxic conditions. The presence of the oleanane in all the three oil products further confirms the similarities among them and that the possible sources of the oil are the same. This further confirms that the oil products from the remediation process are the same with the starting oil from Nigeria because previous work has associated oleanane with Nigeria crude oil from the Late Upper Cretaceous and deltaic settings (Ekweozor *et al.*, 1979a; Ekweozor and Udo, 1988).

**6.** Based on the above considerations, it is clear that MW technology is a potential economic and powerful remediation technique with high contaminant removals and short remediation times, representing a suitable alternative to conventional thermal or physical-chemical treatments for the remediation of hydrocarbon-polluted soils.

# Chapter 7 General discussion

## 7.1 Scope

This chapter discusses how the results of this study relate to previous work, and how the thermal and microwave heating remediation technologies used in this study could be scaled up to remediate polluted soil sites in the Niger Delta.

### 7.1.1 Geochemical analysis of the polluted soil

Geochemical analysis of petroleum-contaminated soil is of great importance to environmental forensic investigations in terms of examining the source of spilled oil, differentiating and correlating oils and degradation (Wang *et al.*, 2006; Stout *et al.*, 2007).

Regarding other relevant work on the effect of degradation of oils similar to the one studied here, a 22-year-old spilled Arrow oil sample from the north shore of Chedabucto Bay, Nova Scotia, Canada, was characterised to determine the extent of degradation in comparison to the original oil (Wang *et al.*, 1997). The percentage of the aliphatic hydrocarbons in the original oil was 21% higher than in the 22-year-old spilled sample. The lower aliphatic hydrocarbon content was accompanied by an increment of 14.7% in the asphaltene content. Thus, the extent of degradation of the oil was directly relative to the asphaltene content (Wang *et al.*, 1997). A similar trend was found in the current study, where the EOM contained 6.9% asphaltenes compared to 4.8% of the reference Niger Delta crude oil. This is consistent with the study by Adebiyi and Thoss (2014), who reported the asphaltene contents of oils from various fields in the Niger Delta area, with the Belema field containing 3.8%, the Eket field 3.8% and the Imo field 3.3% asphaltenes. This too confirms that significant asphaltene deposition does not occur during crude oil production and transportation (Idris and Okoro, 2013). Noticeably, other crudes worldwide can have lower asphaltene content compared to Nigerian crude oil, such as Russian, Kaluga and North Sea (0.5%) and Brazilian, Campos (2.80%) crude oils. The crude oil with lower asphaltene contains a high resin content, unlike the Nigerian crude oil which has little or no resins present (Nwadingwe and Alumona, 2014; Adebiyi and Thoss, 2014).

This work indicated that the reference crude oil has organic geochemical characteristics similar to those of other oils from the Niger Delta. For example, the crude oil pristane/phytane ratio (2.99) in Table 5-2 is close to those reported by Akinlua and Ajayi, (2009) having values ranging from 2.67 to 3.30. The distribution of patterns of the methylnaphthalenes and methylphenanthrenes of oils from northwest and central Niger Delta (Akinlua *et al.*, 2007; 2009) are closely related to the patterns found here in the reference crude oil and the EOM. The high MPI-1 index in Table 5-2 for the reference crude oils and the EOM are 0.80 and 0.73, which is the expected value for mature oils with an abundance of phenanthrene (Seifert and Moldowan, 1986). Although Seifert and Moldowan (1986) predicted that the high mature oil should have 29ααα(S/S+R) and 29 (αββ/(ααα+αββ) values are 0.5 and 0.7 respectively, the crude oil from central Niger Delta sterane ratios ranges from 0.39 to 0.57 and 0.37 to 0.44, respectively (Akinlua *et al*., 2009) which are similar to 0.36 for 29ααα (S/S+R) as reported for both the reference crude oil and EOM, alongside 0.51 and 0.45 (29 (αββ/(ααα+αββ) as reported for both the reference crude oil and EOM in Table 5-2. They are relatively low mature oils, which is not surprising since it has been reported that sterane isomerisation ratios of such are common to oils like Niger Delta oils (Grantham, 1986). Thus, it was also not a surprise that the moretane/hopane ratios are generally higher in the crude oil and the EOM as seen in Table 5-2 (Grantham, 1986). It is therefore clear that the EOM and the crude oil have oxic depositional environments with a strong terrestrial organic matter input that was further substantiated by the presence of oleanane arising from angiosperms (Ekweozor *et al.*, 1979; Philip and Gilbert, 1986).

The biomarker profiles of the EOM provided significant information on the extent of the biodegradation based on the Peters and Moldowan (1993) scale. The total ion current (TIC) chromatograms of the aliphatic hydrocarbon fractions (*n*-alkanes) are useful to distinguish unaltered or mildly biodegraded oils from biodegraded oils (Akinlua *et al.*, 2006). The free *n*-alkanes in the EOM are still present, unlike the Nigerian oil seep characterised by Sonibare *et al.* (2009), where *n*-alkanes are completely absent due to high biodegradation. The TIC of the EOM shows that it is moderately biodegraded because it contains an unresolved complex mixture (UCM) and pristane with phytane as well as the fact that the hopanes and steranes are intact, which is between level 3 and 4 on the Peters and Moldowan scale (1993). The asphaltene hydropyrolysate bound phase of the EOM shows lower homologues of *n*-alkanes and high abundance of Tm with the absence of Ts (Figure 5-7), which is a rearrangement of products not expected to be present in the bound phase. The hopane αβ-configuration is more abundant than the βα-configuration, which is consistent with previous work (Sonibare *et al.*, 2009) with bound biomarkers being less mature than their free phase counterparts. However, there is an aberration observed that is different from most of the previous work in the hydropyrolysis of the soil from Nigerian contaminated soil. ββ–distributions were evident in the chromatogram of the insoluble organic matter from the soil with high abundance of 35ββ to indicate diagnostic contribution from soil microbes (microaerophilic proteobacterial) that are not related to crude oil (Zundel and Rohmer, 1985a, b; 1985c; Summons and Jahnke, 1992).

### 7.1.2 Remediation of the polluted soil

#### 7.1.2.1 Conventional pyrolysis

Identifying means for the thermal remediation of the polluted soil from Nigeria is one of the main aims of this work, which has been accomplished by both conventional (Gray-King static retort) and microwave pyrolysis.

Gray-King pyrolysis remediation of the oil-polluted soil produced a maximum gas yield of approximately 20 wt. %, similar in yield and composition with previous work (Risoul *et al.,* 2005; Domínguez *et al.*, 2007; Amutio e*t al.*, 2012). Previous work on conventional thermal remediation treatment of contaminated soil gave hydrocarbon removal efficiencies between 95–99%, which is comparable to the Gray-King pyrolysis removal efficiency in this study (Khan *et al.*, 2004; Cocarta *et al.*, 2014; Risoul *et al.*, 2005; Thuan *et al.*, 2013). Although the Gray-King retort works well at a laboratory scale technique, there is a need to scale up to industrial scale. The widely developed commercial-scale technology used for years by various companies has been rotary kiln technology to treat organic contaminated soils, hazardous waste slag, spent potlining used in electrolytic smelting of alumina, scrap tyres, plastic waste, coal gasification and calorific industrial waste (Pershing *et al.*, 1993; Hittner *et al.*, 1998; Li *et al.*, 1999; Behzadi and Farid, 2006; Chun *et al.*, 2011; Hatzilyberis, 2011; Vandecasteele and Vermeulen, 2011).

Two possible industrial-scale rotary kiln pyrolysis technologies useful for polluted soil were developed by SoilTech Inc. USA and Deutsche Babcock Anlagen AG, Germany. SoilTech Inc. developed an anaerobic thermal processor (ATP) as a mobile *in situ* indirect heating rotary kiln pyrolysis technology to clean up organic contaminated soil, while

Deutsche Babcock Anlagen AG developed off-site or *ex situ* technology (Schneider and Beckstrom, 1990; US EPA, 1993).

Deutsche Babcock Anlagen AG, a German company, employed an indirect heated rotary kiln to clean up the organic contaminated soil. The industrial application of the developed unit in 1988 with a designing rate of 7 tons/hour for organic contaminated soil with 21 % moisture and 5% volatile compounds gave 99.9% decontamination efficiency at 650°C. This technology is an *ex situ* process that requires excavation of contaminated soil from the site to the pyrolysis system operating at a temperature range between 550 and 650°C. The volatile and semi-volatile organic present in the soil will be desorbed to generate gases that entered into the afterburner where combustion takes place at higher temperatures between 982 and 1315°C. The effluent gases from the process pass to a scrubber before discharge. The operational cost of the pyrolysis system is \$65–\$80 per ton of soil (Schneider and Beckstrom, 1990).

On the other hand, technology marketed by SoilTech, Inc. (ATP) had a throughput of 10 tons/hour with a treatment cost of \$280/ton during the clean-up of Wide Beach contaminated soil in USA (US EPA, 1993). The ATP unit consisted of four chambers for preheat, reaction, combustion and cooling. The contaminated soil fed into the preheating chamber underwent desorption to remove water, volatile and some semi-volatile organics, leaving behind heavy oil in the soil. The retort or pyrolysis chamber received the heated soil to vaporise the heavy oils and thermal cracking of the hydrocarbons to form coke and decontaminated soil. These were further heated and combusted in the combustion chamber to achieve 99% decontamination efficiency. Some of the decontaminated soil from the combustion chamber would be recycled through a cycling channel to the pyrolysis zone to maintain the elevated temperature in the zone, while the remaining decontaminated soil would be transferred to the cooling zone and would exit at the appropriate temperature (Figure 7-1). The cooling and the preheating can act as a heat exchanger to transfer heat from the combustion residue to the feed (Ritcey and Schwartz, 1990; US EPA, 1993). The ATP process was used industrially to remediate the Wide Beach Superfund site, New York in conjunction with chemical dehalogenation (alkaline polyethylene glycol (APEG)). The polychlorinated biphenyl (PCB) in the soil was reduced from over 5000 ppm to less than 2 ppm with \$80/ton for off-site disposal of treated soil (Vorum, 1991; US EPA, 1993).

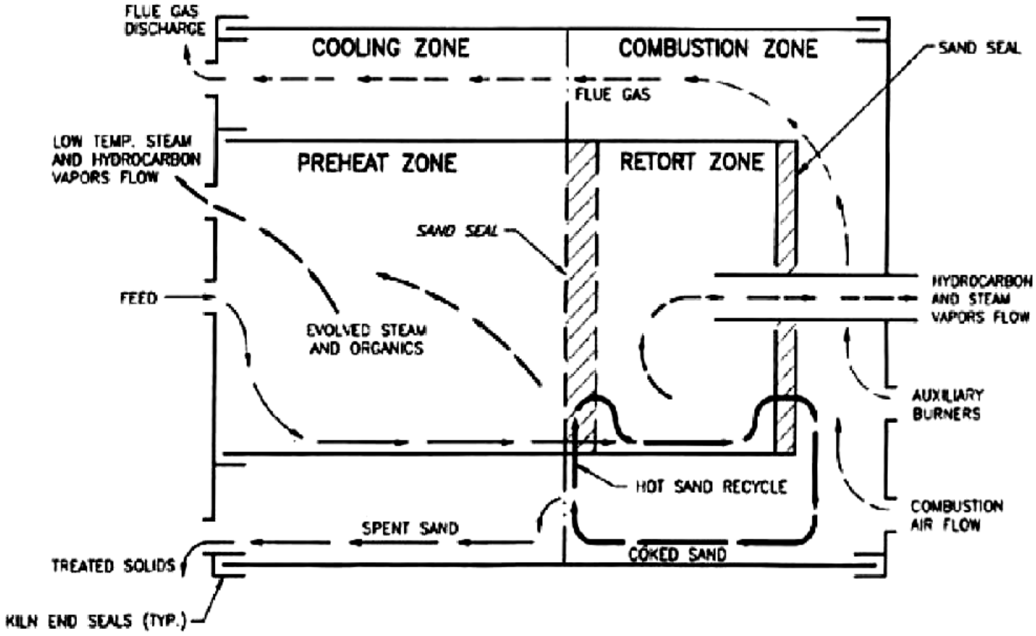


Figure 7-1: Schematic diagram showing the four internal zones of ATP (adapted from US EPA, 1993). The retort zone is the pyrolysis zone seal with clean sand to prevent oxidation of hydrocarbons and coke.

An advantage of this conventional pyrolysis process is the low-carbon content of the soil, which could be useful as biochar, which improved the plant productivity at a low rate (Kimetu *et al.*, 2008). The biochar further impacts the soil’s performance by increasing the ground water-retention capability. This in turn may have a direct impact on soil texture at the macroscale due to its particle size distribution, which gives a positive effect on sandy soil that is ordinarily dominated by much larger pores than biochar (Glaser *et al.*, 2002; Brodowski *et al.*, 2007). In the case of soil fertility, biochar decreases the potential for nutrient leaching in the soil. Although the biochar produced might hold the nutrient from leaching, it can also sorb toxic organic by-products from the wastewater treatment process (Yu *et al.*, 2006; Sohi *et al.*, 2010).

#### 7.1.2.2 Microwave pyrolysis

The conventional laboratory-scale pyrolysis discussed in Section 7.1.4.1 was able to effectively remove 85% TOC, which is 8% higher than microwave pyrolysis as shown in Table 6-23 but microwave treatment has better operability and throughput. Despite the low percentage of 8.6% moisture content compared to 14.05–16.42% moisture content of contaminated soil previously performed by Robinson *et al.* (2012), the decontamination efficiency of this study is 12% higher. Apart from the advantages mentioned earlier, the material handling of the microwave pyrolysis system makes it a better technology for the Niger Delta zone prone to high precipitation because there is no need for pre-drying of soil before treatment unlike in conventional processes. Furthermore, there is ease of equipment control, size, treatment time and selective heating of the material.

Although the stirred bed system with higher throughput than the single-mode cavity removed 85–95% at a longer treatment time of 400 seconds maximum, the treatment time is still short compared to the time it will require for the same quantity of contaminated soil in a conventional process due to the delay that will be caused by temperature gradients.

Microwave treatment of contaminated soil can be scaled up to a commercial mobile *in situ* or *ex situ* treatment plant. However, some of the challenges observed in this study must be considered in the development of the pilot scale design before the commercial scale is developed. The effectiveness of mobile *in situ* microwave treatment depends on the depth of the water layer. However, the problem of arcing will not occur since the microwave will dissipate down into the soil matrix. Other issues that need to be considered will now be discussed.

The material handling before the treatment is essential because the presence of a sufficient quantity of microwave absorber (between 14–16 % moisture) is required for effective treatment as shown in this study. Since the Nigeria Delta has a high precipitation rate, it suggests that water content will be high enough for effective microwave treatment.

The penetration depth of microwaves must be considered at an industrial scale to ensure that all the microwave absorbent materials are well exposed to incident microwave power to initiate the remediation the polluted soil. The penetration depth as discussed in Section 3.5.1 affected the results of the scale-up of a single-mode cavity to a large fixed-bed cavity in previous work to give 30–50% hydrocarbon removal from the treated soil (Robinson *et al.,* 2012). The penetration depth problem in a fixed bed causes the top soil to get hotter while the bed or bottom remains untreated, sometimes resulting in arcing and damage of equipment. Therefore, it has lower power absorbed per unit volume or power density compared to the single mode. This was overcome by the introduction of a stirrer. This provided vertical movement of the soil in the cavity to enhance even and equal exposure of the soil to the microwave power input, whereby the microwave was able to penetrate deeper into the material with time to give up to 95% removal of hydrocarbon (Robinson *et al.*, 2012).

The stirring bed system may give good results for pilot scale, but at the industrial stage, the bed height in the cavity will affect the penetration depth, leading to some part of the soil experiencing a significantly lower microwave power than the others. The second disadvantage will be the quantities of sample per time, which in a heavily polluted region like Niger Delta will be low. It will require more carrier gas to compensate for the height above the soil to avoid the pressure drop in the cavity. The suggested option to tackle some of the challenges facing the stirring bed system is a continuous system.

A continuous microwave pyrolysis process is shown in Figure 7-2. The conveyor belt receives the excavated polluted soil from the spill site at a controlled speed from the screening and mixing section, where the designated particle size (grain size) will be selected. The conveyor speed will be regulated for adequate exposure of the soil to the microwave power input. The microwave chamber will have adequate width to encourage the greatest throughput of soil possible with even distribution of microwave power density to treat all the soil equally.

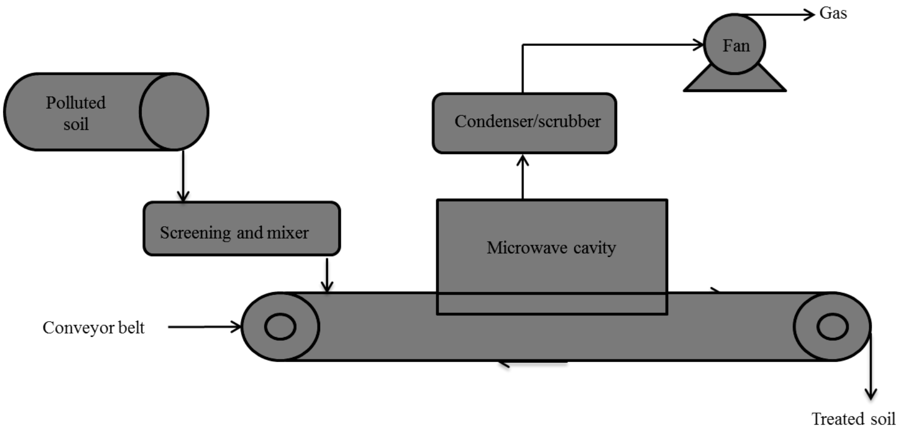


Figure 7-2: Schematic diagram of an *ex situ* continuous microwave system for remediation of polluted soil in Niger Delta (adapted from Robinson *et al.*, 2009).

To ensure uniform distribution of the microwave power and effective remediation of the soil, consideration needs to be given to the width of the microwave applicator, the taper height for transmission of the microwave from the waveguide to the cavity, the height above the load in the cavity to give adequate space to remove the oil/water mixture and minimised pressure drop throughout the cavity, and the depth of the bed because it affects both the electromagnetic efficiency and the power density ratio. The velocity of the carrier gas will be regulated to avoid combustion taking place instead of pyrolysis of the soil in the heating chamber. The sole aim of considering the parameters will be to ensure that the % TOC left in the soil will be <1%, which is the current environmental discharge threshold in the UK (Robinson *et al.*, 2010).

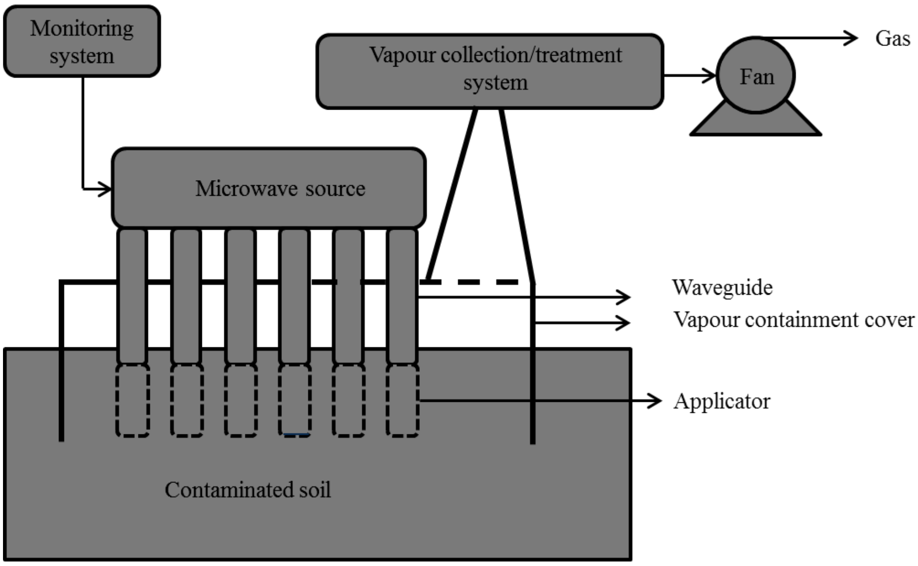


Figure 7-3: *In situ* application of microwave on contaminated soil.

On the other hand, on-site or *in situ* treatment of the contaminated soil can be designed as suggested in Figure 7-3. The applicator system is arranged in series with microwave sources with acceptable frequency, a monitor control system, vapour collection with a treatment system, removal of the screening and a mixing section. The monitor system is used to monitor the water level, crude oil quantity remains in the soil, vapour analyser and the reflected wave. The applicators are lowered into the soil to the appropriate depth and the heating will be commenced to reach the desired temperature for a specified period of treatment time. It will be of interest to note that the depth of the inserted rod into the soil will be the extent of the microwave treatment of the soil. The capillary water in the soil will be converted into steam, which then acts as mass transfer media to remove the organic pollutant. The collected vapour will be passed through a condenser and the gas scrubber system before venting non-hazardous gas.

The electrode array is placed in bore holes drilled through the soil, and the frequency of the applied power will be selected from the industrial, scientific and medical (ISM) band. The frequency used depends on factors such as dielectric properties of the soil, the depth of treatment and the size of the heated volume. A recent study demonstrated that this is a feasible technique for soil remediation. Chien's (2012) *in situ* field study with microwaves to remediate petroleum-hydrocarbon-contaminated soil was achieved without disturbance or evacuation of the contaminated soil. The study showed that microwave heating is a cost-effective and time-efficient technology for the remediation of soil contaminated with volatile organic compounds and petroleum hydrocarbons. The remediation is permanent and there is minimal exposure of the public and personnel to the affected contamination site. The microwave heating system is relatively simple and can be developed easily. This technique involves introducing microwaves into the site to encourage volatilisation of contaminants out of the soil directly. The results suggest the contaminated soils can be remediated safely by microwave energy, even if the soils are going to be used for agricultural purposes. The organic contaminants present in the soil will either be destroyed *in situ* or volatilised in a short remediation time without excavating soil.

## 7.2 Techno-economic analysis of the two methods

The techno-economic analysis in Section 2.10 shows that *ex situ* thermal remediation is the best option for the soil treatment. *Ex situ* thermal treatment can achieve a quick and significant output of treated soil. However, the running costs of microwaves and Gray-King pyrolysis are different based on soil moisture content and operating temperatures. The Gray-King process requires drying of the soil before analysis, which adds to the overall cost of soil treatment. The Gray-King test as the conventional thermal method is a traditional carbonisation process to remove soil pollutants, which limits the benefit of the treated soil. In the case of soil fertility, pyrolysis char from the polluted soil that has been treated decreases the potential for nutrient leaching in the soil. Although the char produced might hold the nutrients from leaching, it can also sorb toxic organic by-products from the wastewater treatment process (Sohi *et al.*, 2010). However, the process can only be performed by excavation of the polluted soil, which will lead to high operational cost and risk of air pollution (Li, 2007). Although the char products can have usefulness for road construction, they cannot support plant life alone unless it is used as an amendment with fresh soil. The oil products described in Section 6.4 show that they can be re-used as fuel or production of petrochemicals. However, it takes a longer time to treat soil samples compared to microwave treatment. If the Gray-King procedure requires a 30-minute treatment to treat 20g of soil, the microwave will treat 400g of soil with the same treatment time at the rate of 20g per 90 seconds. This means that 100 tons/hour for conventional treatment of soil is equivalent to 4,000 tons/hour treatment of soil with the aid of microwave treatment. Considering the temperature of the soil during microwave treatment is less down 100°C, this means the soil structure is not seriously affected and it can easily regain its natural existence to support plant life. Low temperature remediation has been demonstrated by Chien (2012) where the soil temperature was about 28–30°C when the field study of *in situ* remediation of petroleum-hydrocarbon-contaminated soil was performed. Chien (2012) further emphasised that it is a robust and cost-effective cleaning-up technology for petroleum hydrocarbon polluted soil. Falciglia and Vagliasindi (2016) reported that thermal treatment of diesel-polluted soil cost £387 per ton, while a continuous microwave processing system reported an average operating cost of about £15 per ton to reach a maximum contaminant removal of 75% because the treatment time is shorter and the process is quicker. The maximum cost of microwave heating is £121 per ton, which is lower than the conventional thermal treatment of £480 per ton (Falciglia and Vagliasindi, 2016).

Economically, the microwave treatment is better than the conventional thermal treatment because the microwave heating system with low power generators is very flexible, is low cost and imposes no restrictions on the number and arrangement of the antennas if *in situ* treatment is considered (Chien, 2012).

# Chapter 8 Conclusion and future work

## 8.1 Overall conclusions

This study has provided insight into thermal remediation of crude-oil-polluted soil. The study compared conventional carbonisation (Gray-King pyrolysis) with the microwave pyrolysis of the polluted soil. In addition, this thesis has explored the variables controlling the treatment of the oil-polluted soil. The study further discussed the effectiveness and cost-efficiency of the two methods.

### 8.1.1 Geochemical analysis

The diagnostic ratios are semi-quantitative data calculated from the peak area of chromatograms of crude oil provided for the research, extractable organic matter from the soxhlet extraction and HyPy treatment of the soil. In addition, similar calculation was done for oil generated from the two pyrolysis methods. The interpretation of the diagnostic ratio for all the samples shows that the oil pollutant in the soil is similar in every respect to the crude oil provided by SPDC, Nigeria. This conclusion was reached because their diagnostic ratios show a similar source input and depositional environment, and the same level of degradation and thermal maturity.

### 8.1.2 Gray-King soil treatment

The oil-polluted soil was extracted using the soxhlet extraction process to remove 78% TOC, while HyPy removed 95%. The HyPy result is the baseline for the maximum % TOC that can be removed from the polluted soil because it covers the total amount that is solvent extractable and the thermal labile component of the soil. The results of the soxhlet and the HyPy was used to justify the effectiveness of the remediation techniques. The Gray-King treatment was performed on the soil with 1.3% moisture content and the 85% TOC was removed at a maximum temperature of 850$^{o}$C. This percentage is greater than the soxhlet extraction result, which means all solvent-extractable hydrocarbon content of the oil-polluted soil was removed while leaving behind 10% of the thermal labile hydrocarbon content. The result obtained is within the range of 80–88% hydrocarbon removal by thermal treatment reported by Merino and Bucalá (2007). Therefore, Gray-King treatment of the oil-polluted soil is proven to be a useful method for dried soil samples or oil-polluted soil with very low moisture content.

### 8.1.3 Microwave treatment of the oil polluted soil

The microwave is a new thermal innovation technique for remediation of petroleum or hydrocarbon-polluted soils. The study performed microwave treatment of the soil with a low operating power and temperatures below 100ºC. The technique used is called steam-stripping technique. The moisture in the soil-absorbed microwave energy was turned to steam. The steam vaporised carrying the contaminants with it, thus removing the contaminants from the soil. In this study, the microwave's effectiveness is limited to the oil-polluted soil (low water content and fine texture) remediation, and this was attributed to the drastic electric field drop and low penetration depth (Falciglia and Vagliasindi, 2016). Therefore, in order to achieve a cost-effective remedial intervention, the treatment of soils with low moisture or fine-grain size should be avoided, as demonstrated in this study. The oil-polluted soil with 1.3% moisture content was irradiated with microwaves at varied treatment times. The maximum temperature of the experiment was about 93ºC. The experimental result was 21% TOC removal, which shows that microwave treatment is ineffective for very low moisture content and fine-grain sizes as earlier stated.

The moisture content of the oil-polluted soil was increased to 8%, and the microwave treatment was repeated with the same condition with 1.3% moisture content treatment. The 8% moisture in the polluted soil has demonstrated the already-established fact that water is a good absorber of microwaves, and the cost-effectiveness was observed at low treatment temperatures and short treatment times. The % TOC removed suddenly increased from 21% to 77% TOC caused by pollutants being co-evaporated from the soil without decomposition. The moisture may have played an important role in the absorption of microwaves and in the distribution of heat within the system. Roland *et al.* (2010) also stated that the formation of steam from soil moisture is actually related to a volume increase by about three orders of magnitude, resulting in an additional gas stream directed outward from the soil. It is the proficient transport medium for the hydrocarbons in the microwave pyrolysis system.

### 8.1.4 Comparative study based on data from the Gray-King and microwave pyrolysis of the oil polluted soil

1. The Gray-King pyrolysis process could treat dry soil or soil with very low moisture content as shown in this study, but it is not economically viable using microwave pyrolysis. Therefore, it will be a useful method for petroleum-polluted soil with low moisture content, for locations with low precipitation per annum. Moreover, the Niger Delta region has a high precipitation rate annually, which means that the operational costs of the conventional thermal treatment will increase. There will be costs associated with soil excavation and drying, and fuel costs for transportation, which is separate from the energy costs of running the equipment. Hence, the return on investment for investors will be marginal.

2. The microwave pyrolysis will be the method of choice for Niger Delta region because the process can be carried out either *in situ* or *ex situ* without the extra costs associated with soil of drying before treatment. Also, throughput will be higher than the Gray-King pyrolysis because of the short treatment time, and no restrictions on the number and arrangement of the antennas for *in situ* treatment process. If an *in situ* treatment method is employed, treated soil can be re-used immediately for other purposes as there are no disturbances to the soil structure. The low temperature treatment only removed the contaminants by the steam-stripping desorption process. The microwave pyrolysis process serves as a promising technology that will satisfy the demands of the stakeholders as the environmental impact on humans and the immediate community is minimal, as suggested by Chien (2012). The treated soil can be reused for agriculture, which is the major source of livelihood of the community. Also, the treated soil can be used to construct good roads to provide access routes for farmers to transport their produce from farmland to marketplaces around the nation, thereby enhancing food distribution nationally.

## 8.2 Future work

The knowledge gained from this study has proven that pyrolysis is suitable for the remediation of oil-polluted soil of the Niger Delta region. Therefore, it will be important to analyse more soils from various parts of the Niger Delta region as previous reviews on soils revealed a wide variation in soil composition from location to location. This is mainly due to the varying extent of the degradation effect of petroleum on soils from constant spillages and leakages during exploration and transportation (Mutyala *et al*., 2010; Mukherjee and Bordoloi, 2011; Das and Chandran, 2010; Hunt *et al.*, 2002).

Furthermore, a pilot-scale study of the microwave pyrolysis processes discussed in Section 7.1.2.2 would be encouraged to ensure that the expected throughput from this study can be achieved. Finally, a study on the different polluted soil grades would be encouraged as this would explore the effects of microwave remediation on the different soil grades.

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