REMEDIATION OF TYPICAL NIGERIAN CRUDE OIL CONTAMINATED SOILS USING MICROWAVE HEATING

Uwem Bassey

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ABSTRACT

The Nigerian economy has received a boost from crude oil production since independence in 1960, with a daily crude oil production capacity of 2.5 million barrels per day and a reserve of 28.2 billion barrels. Over the years, exploration and transportation of raw and refined products have significantly impacted negatively on the environment. Most striking causes oil leakage and spillage is due to pipeline faults and sabotage. Over 11 million barriers of crude oil have been split into the environment. Oil spillage in Nigeria is a major issue, especially in the Niger Delta region, covering land mass of over 70,000 km^2. This research work aims to apply microwave heating as a remediation technique for the treatment of different crude-oil-polluted soils (clay, loamy and sand). Conventional pyrolysis using a Gray-King (GK) retort provided a basis for comparison.

Batch scale microwave heating was carried out using different cavity power (0.8, 1, 2, and 3 kW), the results revealed that soil properties strongly influence oil removal. At various microwave power and optimum time, the percentage of oil removal is least for sand soil and similar levels for loamy A and loamy B soils contaminated soils. Results are consistent with the microwave properties of loamy A and loamy B soils. It has been shown that water in soil generally increases the dielectric constant and loss factor, which indicates that higher water content in soil is beneficial for microwave heating. Clay soil with higher water content gave best removal at all optimum treatment conditions. Percentage oil removal in soils increased with increasing MW power for 0.8, 1, 2 and 3 kW at equivalent treatment time and energy input. These results reveal that the remediation of crude oil contaminated soil by MW heating can be enhanced using higher microwave power inputs.

It was found that steam velocity increases when microwave power increases, improving the oil mass transfer rate out of the sample. This phenomenon is steam stripping and provides a more robust explanation of the power density and increasing soil water content effect on oil removal than has been previously suggested. The mass transfer correlation shows that steam velocity contributes to oil removal from clay and sandy soils than loamy soil. Oil removal through steam mechanism investigated in this work account for up to 20-40 % for clay, 2-7 % for loamy B and 4-26 % for sand soil. Oil removal increased with the steam velocity within the soil pores. Mass transfer models for clay and sand soils reveals that pore steam velocities impacts on the mass transfer coefficient

Conventional pyrolysis using a Gray-king (GK) retort provided a basis for comparison where complete oil removal was achieved at 500 ^{o}C with slow heating. For microwave heating, using 0.8 kW power and a treatment time of 400 seconds, close to 100 % oil removal was achieved for the clay soil, 80 to 90 % for the loamy soils, and less than 50 % for the sandy soil. The composition of recovered oil after microwave heating remains essentially unchanged, indicating thermal desorption is the primary mechanism for oil removal, compared to extensive cracking occur during conventional pyrolysis using a Gray-King furnace.

In conclusion, based on the findings, microwave heating can treat clay and loamy soil polluted by crude oil and can reduce treatment times compared to conventional pyrolysis.

CONFERENCE PRESENTATION

1. American Chemical Society National Meeting and Expo 2020, Philadelphia, United State

Title of presentation: Remediation of crude oil polluted soil: comparison of Gray-King and microwave pyrolysis

2. American Chemical Society National Meeting, theme: Resilience of Chemistry, 2021, Atlanta, United State

Title of presentation: Removal of petroleum oil from soils during microwave heating: Understanding mechanism and mass transfer

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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 any other University.

Uwem Bassey

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CHAPTER ONE. Introduction

1.1. Scope

This chapter introduces the oil pollution environmental issues faced by the people of the Niger Delta in Nigeria. Also, the need for quick and efficient technology response is discussed in this chapter. The aim and objectives of this study are highlighted.

1.2. Background to this study

Crude oil and gas exploration in Nigeria started in 1956 upon discoveries in the Niger Delta region. Presently, Nigeria is one of the major oil-producers in Sub-Saharan Africa, accounting for approximately 32 and 34 % of Africa's oil and gas reserves, respectively (Umar et al., 2021).Nigeria is recognized by the Organization of Petroleum Exporting Countries (OPEC) as the 11 largest exporting country globally(Jack et al., 2016). Daily crude oil production capacity is estimated to be 2.5 million barrels per day with proven reserves of 28.2 billion barrels (Giwa et al., 2017. Natural gas reserves are estimated to be 165 trillion standard cubic feet. Oil production activities in Nigeria takes place in the Niger Delta region, covering land mass of over 70,000 km^2, which is 7.5 % of total Nigeria land mass (Uwem, 2004). The region encompasses 800 oil-producing communities with more than 900 oil wells and 100 flow stations (Collin & Jürgen, 2008).

Crude oil exploration in the Niger delta region has led to spillages due to several factors including corrosion of pipelines and tankers sabotage, oil production operations, and inadequate production equipment.(Anyanwu & Ejem, 2020). Amongst these, a significant contributor to the oil spill total is the corrosion of pipes and tanks. This is due largely to poor routine maintenance infrastructure and replacement of worn-out machine parts and also leaks arising from flow-lines accounts. In onshore areas, most pipelines and flow-line are twenty to twenty-five years old against the standard practice of fifteen years (Adegboye et al., 2019). Another contributing factor is pipeline sabotage, whereby crude oil infrastructures are destroyed due to economic and political issues. The National Oil Spill Detection & Response Agency (NOSDRA) recorded more than 900 sabotage incidents in 2014 across the 12,700 km of pipes belonging to local and international companies (the Guardian newspapers, November 10, 2015). Broken lines may go unnoticed for days, and repair of the damaged pipes takes even longer. According to the Department of Petroleum Resources (DPR), from 1976 to 1996, the country lost 2,369,470 barrels of crude oil to the environment from 4647 spills incidents (NNPC Bulletin, 2003). They reported that 77 % of the total volume lost (1,820,411) barrels could not be remediated from the environment with the spilled crude oil sinks being both aquatic and terrestrial environments (Nuhu et al., 2021). The United Nations Development Programme (UNDP) (2006) also reported a loss of 3,000,000 barrels of crude oil between 1976 to 2001, with a 70 % loss to the environment representing a volume of 2,700 000 barrels. Most striking is the Oyakama oil spillage that occurred in 1980, which destroyed over 836 acres of mangrove forest (Kadafa, 2012). The increasing oil spills incident has resulted to 13 million barrels of oil loss to the environment, causing considerable contamination of the region's land and coastal environments (Osuagwu & Olaifa, 2018). The National Oil Spill Detection Agency reported that over 1million barrels of oil is spilt between 2015 to March, 2021 (https://nextierspd.com/). Recently in November 2021, an oil leak of 2 million barrels occurred in the south of Niger Delta and lasted for over 25 days (https://www.aljazeera.com/news/2021/12/7/niger-delta-youths-protest-against-month-long-oil-spill).

It is observed that there is a continuous release of oil into the environment. Regarding the prompt response to restoring the contaminated soil, the Government of Nigeria has mandated several agencies, such as Federal Environmental Protection Agency and the Clean Nigeria Associates (C.N.A), and Oil Spill Detection and Response Agency to control oil pollution and manage oil spill incidents in the Niger Delta (Egberongbe et al, 2006). The case of oil exploration in Ogoni in the Niger Delta over the years by Shell petroleum, has caused several oil spillage into the environment. Shell applied bioremediation through microbial degradation. The technology applied seems not plausible. UNEP (2014), in their publication, faulted the method adopted by Shell Petroleum Development Company of Nigeria in their clean-up of polluted soil not been effective. Hydrocarbons below 1m of soil are not destroyed over the years with contamination from 8 spills site migrating into ground water. (UNEP, 2014).UNDP has proposed a thirty-year plan to restore highly contaminated soil in Ogoni-land, a suburb in the Niger Delta region. However, economic activities are still on hold, especially since the occupants of these regions practice commercial and subsistence farming. However, oil production has been put on the hold due to the crisis between various communities in Ogoni and Shell Petroleum.

1.3. Environmental effects of oil spillage

Transportation of crude oil from the drilling site to various usage points has incurred the risk of spilling into the environment. Cases have been reported of land degradation and harm to marine habitat. The adverse effects of oil spills on the environment are enormous. The estuarine zone is significantly impacted by oil as plants and animals struggle for survival. Typical instance is the oil well blowout that occurred in 1980, leading to pollution of 836 acres of mangroves and mangroves plant species (Nuhu et al., 2021). Products from the mangrove forest, such as wood for fuel and habitat, are depleted due to the inability to survive toxic pollutants from oil spillage. Living organisms on beaches and ocean floors are poisoned by oil. Recently, December 2021 the east of Niger Delta experienced oil spillage (https://guardian.ng/news/buhari-laments-oil-spill-in-bayelsa-promises-quick solution) and is described as the biggest oil spill disaster in the history of petroleum exploration in the region. A total volume of two million barrels oil was reportedly spilled though the amount has been contended (https://guardian.ng/news/expert-faults-report-on-bayelsa-oil-leak/). Hydrocarbons from oil spills affect the physical and chemical properties of soil. The concentration of hydrocarbon is vital in causing damage to soil particles. Small spills evaporate faster from the soil. Clay with suitable liquid retaining characteristics is affected by oil spills for quite a long time. Since most soils such as sand form conglomerates with clay, they become associated with pollutants. Organisms domicile within the habitat tends not to be spared since they depend on soil for support and other forms of nutrients (Ihunwo et al., 2021). Overtime, these, if not treated migrate into the water aquifer.

Underground water is susceptible to pollution caused by oil, especially shallow aquifers. Lindén & Pålsson, (2013) investigated underground water's suitability in a community prolonged to constant oil spillage. Their outcome is quite appalling as water from shallow aquifer had extractable petroleum hydrocarbon (C_{10}-C_{40}) content of 42 200 µg/l and benzene of 900 0 µg/l. This value is 900 times the limit reported by the World Health Organisation (2003).

1. Oil spills from a wellhead contaminating water leading to loss of aquatic animals

2. Oil spill from pipeline contaminating farmland

Figure 1.1. Effect of crude oil pollution on water and soil

Source 1 (https://www.vanguardngr.com/2021/12/comparing-nembe-oil-spill-to-gulf-of-mexico-is-in-bad-faith-ndyc/):

Source 2 (https://newscentral.africa/2021/01/29/dutch-court-finally-rules-shell-guilty-for-oil-spills-in-nigerias-nNger-Delta-region/

Dissolved or emulsified oil in the water column leads to the contamination of plankton, algae, fish eggs, and invertebrate larvae (Kampa, 2008). Sediments in water bodies become sinks for the heavier hydrocarbon groups. Ingestion of these hydrocarbons by crustaceans such as crab, shrimp, and lobster bio accumulates their internal anatomy in parts of the world like the Gulf of Mexico, marine invertebrate under threat of becoming extinct (Michele et al., 2014).

1.4. Soil treatment methods

The major challenge is immediate response in remediating affected land. Though thermal methods of soil treatment have been applied and have gained recognition globally. Thermal remediation of hydrocarbon contaminated soil is well established and has been deployed extensively. An example is the former coking plant site near Chesterfield, UK, where major pollutants included PAHs, acids and hydrocarbons. Excavated soils in 50 m^3 batches were heated at temperatures between 450-650 ºC, leading to over 70 % hydrocarbon removal (Claire, 2006|). Song et al (2019) applied a continous kiln reactor in pilot scale treatment of heavy crude oil contaminated soil. However, the energy investment seems to be so high while contributing to high carbon dioxide emissions especially incinerating the soils. This research involves applying microwave technology to treat crude oil-contaminated soils and compare them with conventional thermal treatment technology.

Much work has been undertaken to investigate the use of microwaves to process a wide range of materials, including ceramics, polymers, composites (ceramic and polymer matrix), powders, and minerals (Raveendran et al., 2019). Microwaves have also been investigated in a broad range of plasma processes (surface modification, chemical vapour infiltration, powder processing), chemical synthesis and processing, and waste remediation (Sun et al., 2019). The first report of this technology for the remediation a typical Nigerian contaminated soil was reported by Ogunkeyede (2016). The author investigated how microwave could remove oil from soil. One of the drawbacks was that his samples was limited to a single sampling site and other soil types was not investigated conclusion from this studies cannot be generalize for the entire Niger Delta State area as suggested by the author. It is based on this premises this research is prompted.

1.5. Aim and objectives

This research work aims to apply conventional pyrolysis using a Gray-King retort and microwave heating as remediation techniques for treatment of crude-oil-polluted soils. To accomplish this purpose, the following objectives would be considered.

1. This work addresses the response of different crude oil contaminated soils to microwave and how absorbed water will influence oil removal. Different sample textures tend to arise from differences in sample mineralogy and initial oil and water content. The difference in texture can have a significant impact in oil and water

removal as it affects the structure of the material. This study will be a panacea for further scale-up process in the quest to provide economical and cost-effective technology for the treatment of oil polluted soils in Niger Delta region of Nigeria.

2. The energy implication involved in the removal of crude oil from soils will be investigated. Finally, several mechanisms such as steam distillation, physical entrainment and steam stripping have been suggested in the past as competeting mechanisms of oil removal from soils during microwave heating. Over the years, there is no conclusive evidence to support such claim. Hence, this research will examine and quantify the contribution of steam stripping mechanism which is produced as it is heated by the microwaves for oil removal in typical Nigerian soils.

3. Comparing conventional and microwave heating technology for oil removal from different soils. Information from both technologies will be important in understanding their influence on oil removal and distribution of pyrolysis products

The remaining chapters are:

Chapter two Literature review on different soil treatment technologies, with emphasis on thermal and microwave heating methods.

Chapter three Experimental methods and materials used in the research as described. These sections also give details of each analytical equipment used

Chapter four Describes the impact of soil properties and microwave power on oil removal from

Chapter five Addresses the energy requirements for removal of oil from soils and discusses the mechanisms involved.

Chapter six Provides comparison of microwave heating to conventional thermal heating method

Chapter seven Conclusions and recommendations for further work

CHAPTER TWO. LITERATURE REVIEW

2.1. Scope

This chapter highlights the various soil remediation techniques and their limitations. It also highlights the economic effect in terms of operational cost. The theory, principles and application of microwave heating is then considered in detail.

The need for other technology in the sequestration of contaminants from the soil is undoubted, especially in the application of environmentally friendly technologies. Thermal technologies such as incinerators have been applied before this time but negate the environment. The choice of microwave pyrolysis looks promising as it has been proven feasible in lab-scale and pilot scale in removing a substantial quantity of hydrocarbons from the soil (Song et al., 2019: Kang et al., 2020). As mentioned earlier, the bioremediation method of soil treatment has been applied in restoring the polluted soil in the Niger Delta region of Nigeria (UNEP, 2011). However, the major threat inherent in the method is the inability to degrade high molecular weight aliphatic and aromatic compounds present in saturates, resins, and asphaltene in the soil, which source is from crude oil. The intricate structure and boiling points of these compounds are contributing factors. An increase in their weight contributes to an overall increase in the weight of oil pollution in soil. Legislation for Environmental Policies and Standards for the Nigerian oil industry was developed by DPR in 1992 and updated in 2002. The laws are applicable for use in the oil and gas industry (UNEP, 2011). This was based on a report on corrective actions applied at oil sites prepared by the American Society for Testing and Materials. The department of petroleum resources in Nigeria has set up appropriate limits and standards, for crude oil waste. The essence is to determine the extent to which oil spills in the environment can be toxic and dangerous. The limits are used to indicate soil quality required for sustainability and for the possibility of restoration of the soil's functionality for human, animal and, plant life" (EGASPIN, 2002; UNEP, 2011). Thus, tolerance values indicate desirable soil quality and action, or restoration is not mandatory. The level of oil weight concentration of in soil or sediment that is considered not contaminated is 0.5 % w/w and at this level, soil function is not impaired (EGASPIN, 2002; UNEP, 2011). A conclusion in the use of the limits was drawn after Risk-Based Corrective Action (RBCA) was applied to see the impact of the pollution on sensitive receptors such as workers, residents, water bodies, and potentially significant transport pathways (such as groundwater flow, atmospheric dispersion). To achieve an oil weight of less than 0.5 % (DPR, 2002) weight/weight, it is imperative to break down various non-biodegradable hydrocarbon chains within a short treatment time.

2.2. Review of soil remediation techniques

Soil pollution is among the significant threat to its sustainability; this was identified during 2015 World's Soil Resources (Intergovernmental Technical Panel on soils, 2015). The degradation of soil arises from the release of harmful waste from industries and households into the environment in an amount above the recommended level. These pollutants affect the natural soil system and organisms in the soil. The development of techniques for remediation of polluted soil contamination is gaining global attention. Different remediation technologies can be applied to solve the problem of contaminated soil. The treatments are divided into three groups: biological, physical, and chemical. Biological treatments involve the pollutant biodegradation by living organisms; physical treatments are based on the removal of the pollutant through physical means, and chemical treatments refer to the application of agents to promote the pollutant extraction. Moreover, these methods can be in situ when they are carried out without removing the soil or ex-situ when the contaminated soil is treated in other places.

2.3 Biological remediation

Biological remediation is considered as a useful and environmentally friendly technology for restoring polluted soils to near it natural form using living organisms (Villaverde et al., 2019). Some of the biological remediation includes biostimulation, bioaugumentation and phytoremediation.

2.3.1. Biostimulation

Biostimulation utilizes the metabolic versatility of microorganisms to degrade hazardous pollutants. The process aims to transform organic pollutants into harmless metabolites or mineralize the pollutants into carbon dioxide and water. It is commonly implemented both in situ and ex-situ. The principle of this technique is to optimize soil parameters that govern the rate of biodegradation, namely, soil temperature, moisture, porosity, pH, available nutrients, redox potential, and microbial populations, diversity, and activity (Essabiri et al, 2019). These parameters may be optimized for an indigenous microbial community. It is achieved by optimizing various limiting nutrients like phosphorus, nitrogen, oxygen, electron donors and electron acceptors to polluted soil to stimulate the existing bacteria to degrade the petroleum hydrocarbon and toxic contaminants. Biostimulation is a viable technology and has long be used to degrade environmental pollutants in various matrices and environments. Research conducted by Li et al (2021) in clay rich crude oil contaminated soil reveals that biostimulation of the soil by adding petroleum degrading bacteria such as *pseudomonas* and *acinetobacter* led to 76.9% total petroleum hydrocarbon removal after 53 days. A field trail was conducted by

(Venosa, 2004) to treat 17.5 tons of oil contaminated soil with an initial value of 0.61 % w/w using combination of fertilizer and foreign microorganism.

2.3.2. Bioaugumentation

Bioaugmentation involves adding exogenous microbial cultures to enhance the existing populations with the soil matrix and increase the rate of biodegradation process. This technology has been successfully applied this technique autochthonous fungi from a petroleum hydrocarbon contaminated soil to remediate clay soil contaminated with petroleum hydrocarbons (Ossai et al., 2022). After 60 days of remediation, 79.7 % removal of the contaminating oil was achieved (Ossai et al., 2022).

2.3.3. Phytoremediation

Phytoremediation is employed in bioremediation techniques in which plant sequestration or detoxification of organic contaminants in soil (Azubuike et al., 2016). In phytoremediation organic pollutants (hydrocarbons and chlorinated compounds) are removed mainly by degradation, rhizoremediation, stabilization, and volatilization (Azubuike et al., 2016). Factors considered in using plants for remediation are root system, a pollutant to plant toxicity, plant survival, adaptability to prevailing environmental conditions, plant growth rate, site monitoring, and time for pollutants sequestration above. According to San et al. (2013), decontamination process involves uptake, mainly by the passive process, translocation from roots to shoots, which is carried out by xylem flow, and accumulation in the shoot. Further, translocation and accumulation depend on transpiration and partitioning between xylem sap and adjacent tissues, respectively. Alongside identifying the diverse soil-remediating abilities of different plant species, the mechanisms of phytoremediation also raised much research interest. Some stages of the mechanisms have been identified.

The first is phytoextraction, also known as phytoaccumulation, wherein contaminants are absorbed by plant roots and translocated to other parts of the plant (Rascio & Navari-Izzo, 2011). Phytoextraction can be achieved by extracting high concentrations of contaminants from the soil as for the hyperaccumulators (Tang & Angela, 2019). Secondly, phytostabilization reduces the leaching of contaminants from soil by binding the contaminants to the roots of plants, thus immobilizing them (Sarma, 2011). Thirdly, phytodegradation depends on microorganisms attached to and enzymes secreted by the roots to break down contaminants which are then removed via uptake and transpiration. Phytodegradation is well-suited for the removal of herbicides, methyl tert-butyl ether, and trichloroethylene (Limmer & Joel, 2016).

On the other hand, phytostimulation involves stimulating soil microbial activity at the rhizosphere for the breakdown of organic contaminants. It effectively degrades petroleum hydrocarbons and polyaromatic hydrocarbons (Tang & Angela, 2019). Phytovolatilization removes contaminants from soil by volatilization, often transforming the contaminants into a less toxic and more volatile forms (Limmer & Burken, 2016; Tang & Angela, 2019). The problem with this technology is post-treatment of the plants. However, several methods such as burning and desorbing the pollutants from the plants have been investigated.

Generally, bioremediation requires less resource input than other techniques, and it is perceived as an environmentally friendly approach. Different organisms have been applied for the remediation of soil. However, bioremediation is often slow, and thresholds of toxicity to microorganisms may preclude its use in any circumstance

(Dvořák et al., 2017). It may be argued that also bioremediation leads to the release of CO_2 by bacteria (Ali et al., 2020).

2.4. Chemical remediation

Chemical approaches to remediate petroleum hydrocarbons-contaminated soil include the use of chemical oxidation, soil washing and solidification and stabilization**.**

2.4.1. Chemical oxidation

Decontamination of contaminated soil via chemical oxidants uses oxygenated compounds such as hydrogen peroxide. The oxygen-rich peroxide destroys hydrocarbons present in the soil (O’Brien et al., 2017). Treatment process might have to be repeated until all the hydrocarbon constituents reach acceptable concentration. Chemical oxidants irreversibly convert petroleum hydrocarbons into CO_2 and H_2O depending upon the contact time with contaminants. There are different kinds of chemical oxidants in use, however, choice of chemical oxidants depends upon the understanding of the hydrogeological condition of the targeted area. Commonly used chemical oxidants are Fenton's reagent, hydrogen peroxide, permanganate of sodium and potassium, and ozone (Bajagain et al., 2020). The effectiveness of chemical oxidation can be enhanced when used in conjunction with ultraviolet light (Shiying et al. 2003). The success of chemical oxidation technology depends on prior information about the site (soil permeability, texture of soil, soil reactivity), choice of appropriate chemical oxidant, and solubility characteristics of solvents (Hakeem et al., 2016). The future effect of the process in the environment remains a threat as the continuous application might increase the lifespan of the chemical in the environment. Typical chemicals such as chlorine dioxide have been applied for treatment of petroleum hydrocarbon, but do not hydrolyse in water (Apul et al., 2016). Though the oxidant is known to impact negative on the environment, however the time frame of pollution is not investigated.

2.4.2. Solidification and stabilization

This technique combines physical and chemical process for soil remediation. Contaminants are immobilized in-situ or ex-situ by introducing chemical agents to convert mobile pollutants into strongly adsorbed form. This technology does not remove contaminants from the soil; it only prevents them from migrating. It is widely used for metallic, radioactive or highly toxic contaminants. The solidifying process encapsulates the contaminant in a solid form (Tajudin et al., 2016). Various materials can be used, including carbonates (lime), phosphates (e.g. bone flour, ammonium phosphate, apatite and hydroxyapatite), alkaline agents (e.g. Ash flywheels and calcium hydroxide), clay and minerals containing iron (e.g. bauxite, goethite, silica gel, vermiculite and zeolites) and organic matter (e.g. chitosan, starch xanthate, peat, manure, activated charcoal and bio coal) (Liu et al., 2018 ; Xu et al., 2019). Others are cement, asphalt, grey steering wheel and thermoplastics. The resulting solidified block is waterproof and prevents the migration of contaminants. Over time the solid matrix can undergo weathering, so monitoring is needed (Liu et al., 2018; U.S. Environmental Protection Agency, 2006). The stabilization process immobilizes the contaminant but does not solidify the soil. In this process the chemical agents added to the soil induce physicochemical reactions with contaminants, forming precipitated, complex or absorbing them, reducing their mobility. Stabilization of 80 g of refinery oil waste was achieved by Karamalidis & Voudrias (2007) leachability of a typical PAHs such as benzo[*a*]anthracene reduced by 84 %. Increasing the mass of cement content in the stabilizer, resulted to destabilization of the oil waste leading to leaching. Though, long chain alkanes leached more than alkanes in the range of n-C_{10} to n-C_{27}. A limitation to these techniques is that, any immobilization of organic contaminants will therefore depend on physical entrapment in the matrix porosity, and sorption, such that non-polar (insoluble) compounds are more likely to be retained by the solid, whereas polar (soluble) compounds will remain leachable.

2.5. Physical processes

Physical processes refer to the immobilization or withdrawal of contaminants from the soil or sediment by some physical means. The main technologies used include electrokinetic process and soil washing as discussed below.

2.5.1. Electro-kinetic remediation

Electro-kinetic remediation is typically an in-situ process Where in an electric field is applied to contaminated soil by passing a direct current or constant voltage through anodes and cathodes inserted in the soil (Zou et al., 2016). Contaminants migrate to the electrodes by electro-osmosis, electro-migration, and electrophoresis. For organic pollutants in soils, migration depends on the zeta potential (potential between the shearing surface and the bulk fluids) (Moghadam et al., 2016). The more negative zeta potential of the soil surface increases the flow of contaminants to the cathode. EKR experiments were undertaken on a gasoil contaminated soil (20,000 ppm). Graphite carbon electrodes were used to provide an electrical direct current. Results showed that increasing the dose of rhamnolipid, the efficiency of gasoil removal increased up to 86.7 % from 4 kg from the soil after 15 days (Gonzini et al., 2010). This method solely depends on the cation exchange capacity of the media. The process would be ineffective when the analyte of interest has low ion concentration compared to the non-target ions.

2.5.2. Soil-washing

Soil washing is an ex-situ technology that uses aqueous solutions to separate organic, inorganic, and radioactive contaminants from excavated soil (Yeung, 2010). The excavated soil is mixed with the solution that will make the extraction and is then agitated. After washing, the clean soil can be deposited at the place of origin and the extraction solution can be treated. This technique can also be performed in situ (soil flushing), in which case the injection of the washing solution can be achieved through wells. The solubilizing of contaminants in the extractive solution occurs (Xu, 2019). This must be collected after the contaminated zone, and the surface treatment of this solution should be carried out (Morillo & Villaverde, 2017). If the contaminated zone has already reached the groundwater, in-situ washing can leach the contaminants to the saturated area, and groundwater treatment should be carried out. The technology has been applied successfully to remediate soils contaminated by petroleum hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pentachlorophenol, pesticides, heavy metals, creosotes, and radioactive wastes in lab scale (Yeung, 2010). At commercial throughput washing of contaminated soils have a throughput of an average of 150 tonnes per hour (Pear & wood, 1994; Pear et al., 2006). However, disadvantages of the technology include: (1) ineffective for soils containing 30 %-50 % of silt, clay, or organic matter as contaminants tend to adsorb onto these materials.

2.6. Thermal remediation technologies

Thermal remediation of soil typically applies heat for removal of pollutants from soils and can be categorised into pyrolysis and non-pyrolysis process. Technologies applied during thermal remediation, of soil are incinerator, thermal desorption, smouldering and vitrification some of these technologies cannot be classified as a pyrolytic process, because partial all complete combustion takes place during heating process.

2.6.1. Thermal desorption

Thermal desorption refers to the volatilization of pollutants from soil without any structural changes occurring due to pyrolysis (Wang et al., 2021). There are three major processes for thermal desorption (1) Direct –fired-heat is applied directly to the surface of contaminated matrix. (2) Indirect Fired -a direct fired rotatory dryer heats an air stream which is in contact with the contaminated matrix. (3) Indirect heated- an external fired rotatory dryer volatilises the water and organics from the contaminated matrix into an inert carrier gas stream (Wang et al., 2021). Thermal desorption removes organic contaminants from soil, sludge or sediment by heating them in a machine called a thermal desorber to evaporate the contaminants. Evaporation changes the contaminants into vapours (gases) and separates them from the solid material. Many organic contaminants can be removed by thermal desorption. These include volatile organic compounds (VOCs) or semi-volatile organic compounds (SVOCs) such as hydrocarbons, polychlorinated biphenyls (PCBs). VOCs such as solvents and gasoline evaporates easily when heated whilst SVOCs require higher temperatures to evaporate and include diesel fuel, creosote (a wood preservative), coal tar, and several pesticides (Zhao et al., 2019). Ex situ thermal desorption involves excavating soil or other contaminated materials for treatment in a thermal desorber (Zhao et al., 2019). The desorber may be assembled at the site for onsite treatment may be loaded into trucks and transported to an offsite thermal desorption facility. To prepare the soil for treatment, large rocks or debris first must be removed or crushed. The smaller particle size allows heat to more easily and evenly separate contaminants from the solid materials. If the material is very wet, the water removed may require treatment using other methods (Claire, 2006). Low-temperature thermal desorption is used typically to heat the solid materials to 100-350 °C to treat VOCs. If SVOCs are present, then higher-temperature thermal desorption is used to heat the soil to 350-650 °C (Yi et al., 2016) which will result in some pyrolysis occurring . Gas collection equipment captures the contaminated vapours. Vapours often require further treatment, such as removing dust particles. The remaining organic vapours are usually destroyed using a thermal oxidizer, which heats the vapours to temperature high enough to convert them to carbon dioxide and water. At some site with high concentration of organic vapour, the vapours may be cooled and condensed to a liquid. The liquid chemicals may be recycled for reuse or treated by incineration. If the concentrations of contaminants are low enough, and dust is not a problem, the vapours may be released without treatment to the atmosphere. Many organic contaminants can be removed by thermal desorption. These include volatile organic compounds or semi-volatile organic compounds SVOCs. VOC such as solvents and gasoline evaporates easily when heated. SVOCs require higher temperatures to evaporate and include diesel fuel, creosote (a wood preservative), coal tar, and several pesticides (Ali et al., 2013; Khan et al., 2004).A typical portable thermal desorption unit can be seen in Figure 2.1.

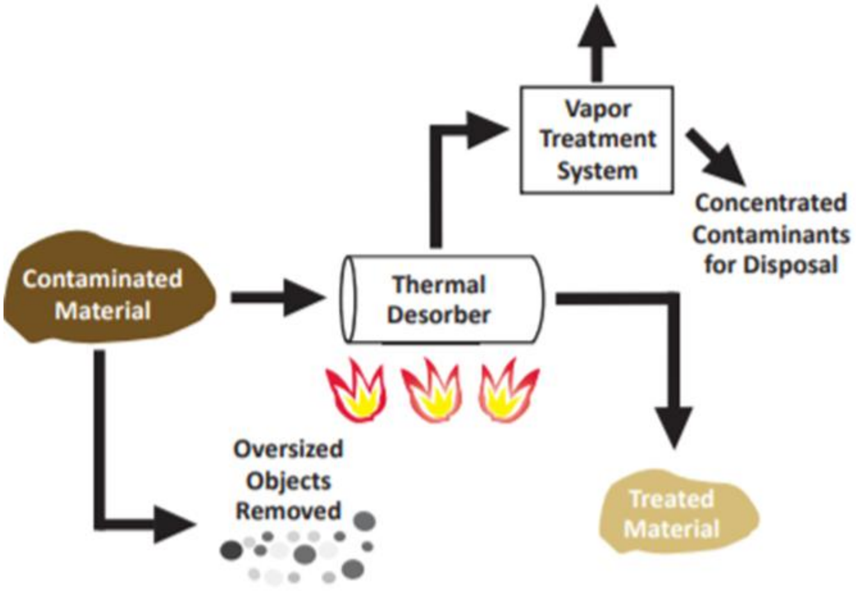


Figure 2.1. Diagram showing indirect (heat from electrical source) thermal desorption process Diagram adapted from: https://www.xdd-llc.com/thermal-desorption

After volatilization, contaminants in the gas phase are removed by a gas treatment system such as granular-activated carbon. Thermal desorption disposal of oily drilling cuttings was tested using a of 250 L/h thermal desorber (Zhang & Yao, 2019). The test was done at different temperatures (300–550 °C) and residence times of 7 min and 12 min respectively, after the optimum time, total petroleum hydrocarbon reduced to 0.3 % by weight (Zhang & Yao, 2019). Low-temperature thermal desorption treatment (LTTD) of soil contaminated by 0.51 % w/w petroleum hydrocarbon was carried out by (Yi et al., 2016) .The LTTD consisted of heating the soil to 200 °C for 15 min using heated air generated from a regenerative thermal oxidizer. Residual petroleum hydrocarbon was reduced to 0.003 % w/w.

Lab scale treatment of PAHs contaminated soil was done using an indirect thermal desorber at temperatures at temperature above 300 °C, removal efficiencies were over 99.9 % for all PAHs except for light polyaromatic hydrocarbons, such as naphthalene and fluorene (99.8 %) and acenaphthene (99.0 %) (Renoldi et al., 2003). Lab scale treatment of Different soil textures, artificially contaminated with diesel was studied by (Tatàno et al., 2013) at various desorption process conditions (heating temperature in the range of 300–390 ºC, and reactor retention time in the range of 40–120 min showed an optimum removal of 99 %, though soil texture had an influence during the remediation process. This finding was collaborated in the work of (Falciglia et al., 2011), where it took an excess of 80 ºC is sufficient to remedy diesel polluted clay soils compared to other soil texture.

Thermal desorption was used in decontaminating a coking plant with major contaminants of naphthalene, acids and organic compounds spanning land area of over 2500 sqm in the Chesterfield, Derbyshire UK. Heated air at temperatures of between 450-650 ºC is distributed through a system over the contaminated area of over a period of 5 and 14 days leading to reduction of over 70 % soil petroleum hydrocarbons.

Bykova et al (2021) in their studies revealed that soil contaminated with petroleum hydrocarbons up to levels of 2000–5000 mg/kg was subjected to thermal desorption. The treatment temperature from 25 to 250 ºC reduces the concentrations to an acceptable value. However, at heating temperature of 250 ºC , 50 % of the soil humus was destroyed.

While the goal of incineration is to oxidize contaminants in the soil, the goal of thermal desorption is to volatilize the contaminants from the soil while retaining the structure of the compound. Thermal desorption in practice often includes not only desorption, but also ancillary oxidation and/or pyrolysis, it is likely that impacts on soil properties vary spatially and from project to project, particularly for in situ applications.

2.7. Pyrolysis

Thermal decomposition and bond breakage of organic materials at high temperatures (500-1,000 °C) in an inert environment is called pyrolysis. It can be limited by various factors, such as temperature and heating rate.

2.7.1. Types of pyrolysis

Types of pyrolysis According to the parameters of the process and products, different types of pyrolysis can be distinguished. Based on the criteria (reaction temperature, heating rate, residence time), pyrolysis is classified, leading to the formation of different yield products.

2.7.2. Slow pyrolysis

Slow pyrolysis occurs at temperatures exceeding 400 °C and long residence time. With the heating rate of 1 to 5 °C/min (Desisto et al., 2010).Under these conditions the gaseous phase of the products will be high because of the complete secondary reactions. The final char yields are decreased by increasing the process temperature from 400 °C to 700 °C. The liquid products reach a maximum value at around 550 °C and decrease at the temperature of 700 °C (Desisto et al., 2010). The decrease in char yield at higher temperatures is related to the increase of volatiles from tar and is subjected to the secondary reactions, which means less production of liquid and more gas (Czernik & Bridgwater, 2004). The volatile organic fractions present in vapour phase continue to react with each other to yield char and some liquid fractions (Bridgwater et al., 1999). The quality of bio-oil produce in this process is very low. Longer residence time initiates further cracking to reduce the yield of bio-oil. It was discovered that pyrolysis of oily sludge leads to an increase in oil yield at increased temperature to an optimum temperature of 525 °C, and at a further heating above 525 °C sees a decrease due to secondary composition (Shen & Zhang, 2003). Similarly, complete hydrocarbon removal during pyrolysis of oil sludge was reported by (Anthony & Wang, 2006) to occur at 500 °C. Though, lower temperature of 450 °C was reported by (Liu et al., 2009) for removal of 80 % of total organic carbon in petroleum oil sludge. Pyrolysis reactions dominated in the temperature range of 400−500 °C during remediation of oil contaminated soil. Oil content in treated soil is less that 0.1 %w/w after treatment for 3 hr (Vidonish et al., 2018). According to the authors, complete removal of TPH was observed at temperature below 500 °C. The end product is always char, liquid, and gases depending on procedural conditions (Fonts et al., 2012; Zhang et al., 2005). Residual oil weight of 0.29 -0.6 %w/w. was observed in the samples with high clay content after pyrolysis for 30 min at 400 °C. Initial and final oil weight was determined using for n –hexane (Kang et al., 2020). According to Bulmau et al. (2014) To decontaminate PAH polluted soil, three different temperatures at 350 °C, 500 °C and 650 °C investigated at treatment time of 60 min, 90 % PAHs was removed from soil at 650 ºC. The process suffers from low heat transfer values with longer retention time leading to higher input of energy (Demirbaş, 2005; Tippayawong et al., 2008).

2.7.3. Fast pyrolysis

Fast pyrolysis of soil involves the rapid heating either in a fluidized bed, rotating cone and abrasive pyrolysis (Desisto et al., 2010). This type of pyrolysis occurs at temperatures between 600 – 1000 °C, with the heating rate of about 100-300 °C/sec and a very short time of residence (1-5 seconds) to reduce the formation of intermediate products and increase the yield of tar. This process has been used by Li et al (2018) for remediation of petroleum contaminated soil. The authors reported that with a nitrogen flow of 0.8 L/min, 10 g of the contaminated soil was heated between 250-600 °C. About 69.6 % of petroleum hydrocarbon was removed after 30 min of treatment time.

2.7.4. Flash pyrolysis

Flash pyrolysis is an irreversible process in which biomass is heated rapidly in an anoxic environment at temperature 800-1000 °C with rapid heating rate greater than 1000 ºC/sec, the resident time is shorter than that of fast pyrolysis. The feedstock is injected into the already heated fuidized bed, where fluidizing gas sweeps volatile component out of the reaction zone (Li, 2013). The process is characterized by poor thermal stability resulting in the production of 40-75 % weight liquid oil and less of non-condensable gases of initial feedstock oils with quite high viscosity and residues (Ore & Adebiyi, 2021).

Table 2.1. Pyrolysis types and operating condition

Operating parameters	Slow Pyrolysis	Fast pyrolysis	Flash pyrolysis
Pyrolysis temperature (ºC)	300-700	600-1000	800-1000
Heating Rate (ºC/Sec)	0.1-1	10-200	>1000
Particle size (mm)	5-50	<1	<0.2
Solid residence time (Sec)	300-550	0.5-10	<0.5
Reactor type	Fixed bed	Rotating cone	Fluidized bed

2.8. Fixed bed reactor for slow pyrolysis

Various types of reactors have been used including fixed bed, moving bed, rotary kiln, conical spouted bed and fluidized bed. Rotary kiln: A rotary kiln is a refractory-lined, revolving cylinder that operates as a heating chamber. Fluidised Bed Furnace:

Circulating fluidised beds make use of high-velocity air to circulate and suspend waste particles in a heating loop and operates at temperatures of 430 °C.

In fixed bed pyrolysis, a fixed bed pyrolysis is used. The feed material in the reactor is fixed and heated at high temperatures. As the feed is fixed in the reaction bed (reactor), it is called fixed bed pyrolysis. In this process, the feed material is fed into the reactor, and heat is applied externally. Usually, nitrogen is used as inert gas for making inert conditions and for helping the gaseous mixture to dispose of the reactor. The losses in fixed bed pyrolysis are relatively less than fluidized bed pyrolysis. A typical process showing pyrolysis process of hydrocarbon using a fixed bed reactor in an horizontal furnace is shown in Figure 2.2.

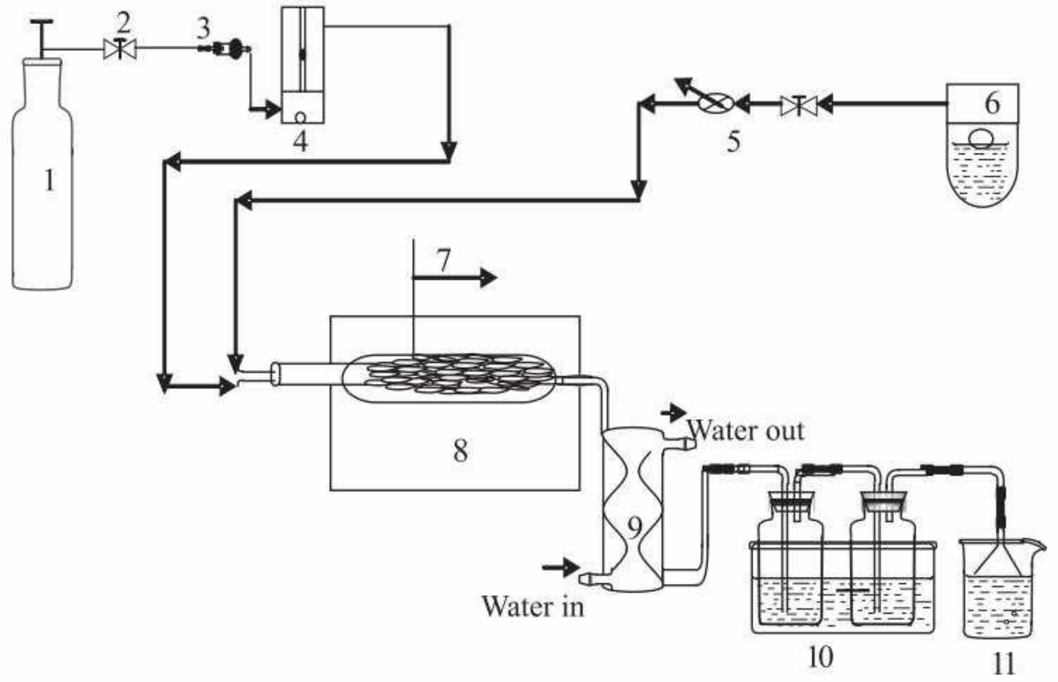


Figure 2.2. Schematic representation of laboratory-scale pyrolysis in an horizontal tube furnace using a fixed bed reactor

(adapted from Liu et al., 2009)

2.9. Lab-scale treatment of contaminated soils

In the study by Tang et al (2019), experiments were carried out at a temperature of 450 to 600 °C, at a constant residence time of 50 min. About 20 g of sludge was treated during the process of each experiment. Nitrogen was used as carrier gas at 100 mL/min. Pyrolysis of oil sludge was carried out in a fixed bed reactor at 450, 500, 550 and 600 °C, at a constant residence time of 50 min. About 20 g of sludge was treated during the process of each experiment. Nitrogen was used as carrier gas at 100 mL/min. Oil removal increased with temperature; at 600 °C, over 15 % char was formed.

Temperature is the determining factor of pyrolysis, one of the alternative technologies for oil sludge treatment. The effects of final operating temperature ranging from 350 to 550 ºC on pyrolysis products of oil sludge were studied in an externally-heating fixed bed reactor. The reactor added 150 g of the oil sludge into the furnace and allowed it to stand for 1 h with 100 mL/min sweeping rate of N_2. With an increase in temperature, the mass fraction of solid residues, liquids, and gases in the final product is 67–56 %. During the process, and the optimum temperature for oil sludge pyrolysis is 550 ºC. Heavy oil content decreases from 31.19 to 10.80 %w/w representing 65 % oil reduction (Liu et al., 2008).

Removal of total petroleum hydrocarbon of about 1.6-1.9 %w/w from soil was studied (Vidonish et al., 2018). Soil pyrolysis was conducted in a 0.5 L fixed-bed reactor heated at 420 °C in a split-tube furnace for 3 h. Nitrogen flowed through the reactor at 1 L/min. Pyrolysis reactions dominate in the 400−500 °C range releasing hydrogen and more hydrocarbons (methane, higher alkanes, and olefins) and leading to the formation of a residual carbonaceous material (char) that coats the soil particles. The process is complete at temperatures below 500 °C and effectively reduces the TPH content of contaminated soils to levels well below the regulatory requirements. According to the authors, temperatures above 500 °C led to the destruction of carbonated and significantly influenced soil pH. The pyrolysis chars and liquids were collected and weighed separately. It was found that the oil content of pyrolytic carbon was less than 0.3 %, indicating that it was basically out of the category of hazardous waste. The pyrolysis char, which has not been subjected to secondary treatment, is not suitable for applying activated carbon, but its physical properties can be utilized as an adsorbent (Tang., 2019).

2.10. Large scale pyrolysis treatment of contaminated soil

Excavated soils in 50 m^3 batches were heated at temperatures between 450-650 ºC, leading to over 70 % hydrocarbon removal (Claire, 2006). Pilot scale treatment of soil contaminated with crude oil was conducted by Song et al (2019) soil using a continuous rotatory kiln. After process time of 30 minutes at 470 ºC, initial soil total petroleum hydrocarbon reduced from 5 % w/w to 0.003 % w/w which is below contamination level. Similarly, pilot tests was conducted to treat heavily contaminated crude oil soil by Kang et al (2020). The contamination level of 5.21 %w/w was reduced to 0.28 and 0.03 %w/w after 30 and 60 min of pyrolytic treatment at 400 °C.

Fixed-bed reactors are simple, flexible, and easy to scale up. It can be concluded that the fixed bed can cope only with a limited gas flow and will gradually expand if more gas is sent through it. Fixed bed reactor technology is simple, reliable, and proven effective for fuels with biomass feed particles of uniform size. The major drawback to fixed bed pyrolysis is its batch nature; however, multiple reactors in parallel are required for larger plants, which render it noneconomic, making rotatory kiln and fluidized bed system advantageous. However, these types of reactors are mainly used for research and small-scale heat and power applications. Fixed bed reactors are used in laboratories when developing a new process.

2.11. Application by-products from soil thermal remediation

Pyrolysis by-products such char have drawn tremendous interest due to their potential to enhance soil fertility, sequester CO_2, and manage organic waste. Microscopy and elemental analysis suggest that pyrolysis leads to the formation of carbonaceous material (char) that coats the surface of soil particles. It is believed that aside char formation, some coke is formed from other fractions of oil and asphaltene. Recalcitrant heavy crude oil, as a result of pyrolysis, partially converts into char, which can further improve s soil fertility (Vidonish et al., 2016a, 2016b). Pyrolysis has the potential to fill an important niche in the remediation of weathered hydrocarbons, while restoring soil fertility and enhancing revegetation. This carbonaceous solid waste is renewable energy source and therefore the potential of converting this into useful energy such as liquid fuel should be seriously considered. The pyrolysis oil is of moderate heating value, is easily transported, can be burnt directly in the thermal power plant. The application of any reactor depends on the design and some variables such as heating temperature, resident time, vapour product and pressure. The pros and cons of these reactors are listed below.

Table 2.2. Advantages and disadvantages of different types of reactors

(Zaman et al., 2017)

Reactor	Advantages	Pyrolysis type	Disadvantages
Fixed bed	Simplicity in Reliable design results in Biomass size independent	Slow pyrolysis	High carbon conservation Long solid residence time Low ash carry over Difficult to remove char
Bubbling fluidized bed	Simple design Easy operational procedures	Fast pyrolysis	Good temperature control Suitable for large-scale application Small particle sizes are needed
Circulating fluidized bed	Well-understood technology Better Thermal control Larger particle sizes can be processed	Fast/Flash pyrolysis	Large-scale production difficult Complex hydrodynamics Char is too finer

2.12. Microwave heating

2.12.1. Scope

Microwave (MW) heating occurs in a dielectric material due to the polarization of water molecules and other microwave absorbers with electromagnetic radiation. The range of frequencies is between 300 MHz and 300 GHz wavelength (λ) is: 1cm to 1 m). At this frequency interval, microwave energy can only be transferred by a vacuum medium, waveguide (Metaxas & Meredith, 1983). The corresponding wavelength and frequency of each radiation format are shown in the electromagnetic spectrum (Figure 2.3).

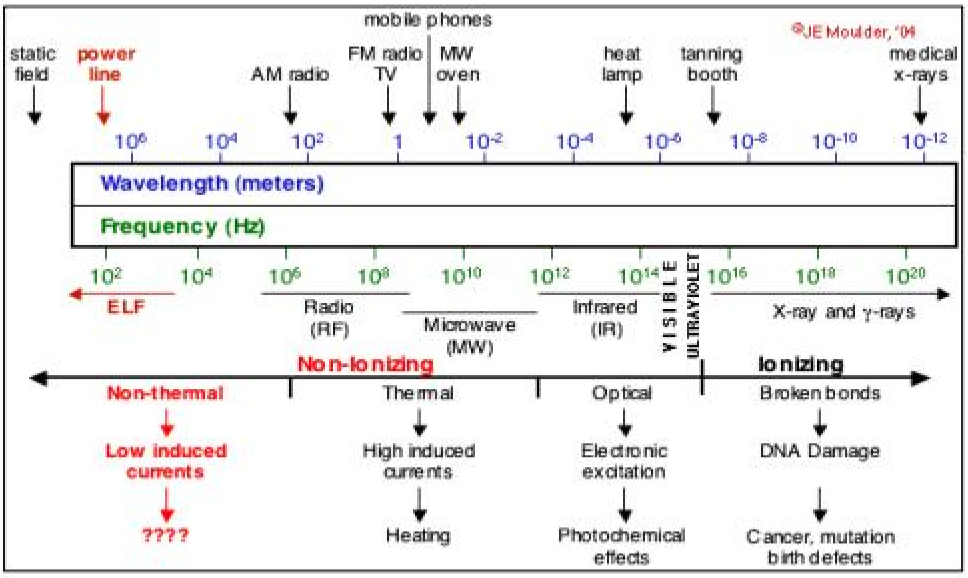


Figure 2.3. Electromagnetic spectrum

(Source:http://faculty.virginia.edu/consciousness/new_page_5.htm)

Microwave energy penetrates materials giving rise to a volumetrically distributed heat source due to molecular friction caused by dipole rotation of a polar solvent. The dipolar rotation occurs during microwave heating due to a change in polarity of electromagnetic fields inside the cavity over time (Figure 2.4).

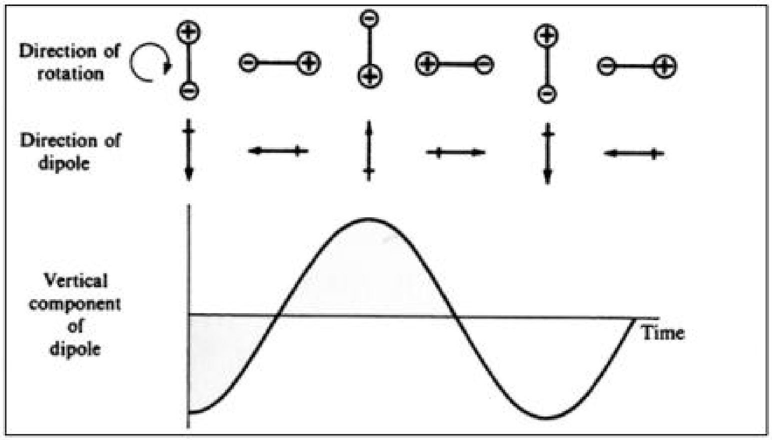


Figure 2.4. Variation of microwave propagation in time

Source ;(Pitchai, 2011)

Microwave heating is usually applied at the most popular of the frequencies allowed for industrial, scientific and medical (ISM) applications, namely 915 (896 in the UK) and 2.45 GHz. How microwaves will heat a material depends on its shape, size, dielectric constant, and the nature of the microwave equipment used. In the microwave S-band range (2450 MHz), the dominant mechanism for dielectric heating is dipolar loss, also known as the re-orientation loss mechanism. When a material containing permanent dipoles is subject to a varying electromagnetic field, the dipoles cannot follow the rapid reversals in the field. As a result of this phase lag, power is dissipated in the materials (Bradshaw et al., 1998).

2.12.2. Theory and fundamentals of microwave heating

Radiation implies transportation of energy by the force fields of electromagnetic waves, with the ability to radiate through a perfect vacuum and do not need any medium to transfer energy from one object to another. All electromagnetic waves have two components, 1) Electric field (E) and 2) Magnetic field (B). As a charge (electric or magnetic) in a medium changes its position in space, the corresponding field also produces space changes. These changes in electric and magnetic fields create an oscillatory wave, known as electromagnetic waves. The waves are characterized by factors such as velocity, electric field strength, and frequency.

Two primary characteristics of any periodic wave phenomenon are the wavelength and the frequency. The relationship between these two properties for electromagnetic waves can be represented as:

$$C=f\lambda \qquad [2.1]$$

Where C is the speed of light in the medium (m/s), f is the frequency of the wave (Hz), andλ is the wavelength (m).Maxwell (1873) discovered that electromagnetic waves are made of electric and magnetic field components 90° aligned to one another (Achard, 2005).

2.12.3. Penetration depth

The amount of power dissipated in a sample, and temperature distribution within the sample is affected by the ability of microwaves to penetrate the material. This phenomenon is the penetration depth and is defined as the distance from the surface of the material at which the incident microwave power reduces to 1/e (37%) of its value at the surface. It follows then that the absorbed power at the penetration depth is approximately 63%. Penetration depth (D_P) is affected by the dielectric properties of the treated material. Equation 2.2 showing the relationship between penetration depth and dielectric properties.

The penetration depth is estimated as:

$$D_p = \frac{\lambda \sqrt{\varepsilon'}}{\varepsilon''} \qquad [2.2]$$

Where $\lambda$is defined as the free space wavelength with value of 0.122m at 2.45GHz, ε' is the dielectric constant and ε'' is dielectric loss factor. Empirically, microwave soil penetration is dependent on soil properties such as water, oil and organic matter content. However, in this work the dielectric properties of the soil are used as an estimate.

When treating materials with a high loss factor (ε''), penetration depth is lower, and vice versa. For high loss materials where the penetration depth is small, there is non-uniformity in the heating and temperature distribution in the workload, especially workloads with appreciable depth. For example, during microwave drying of a workload with high water content (highly absorptive of microwaves), the bulk of the power will be dissipated in the water phase near the surface of the material. Nonetheless, the penetration depth improves over treatment time as water evaporates.

2.12.4. Microwave heating mechanisms

Microwave heating is often known as dielectric heating refers to heating by the electric field (E-field) component of the high-frequency electromagnetic radiation, owing to the presence of electric dipoles in polar molecules. The electric field component of microwaves is responsible for dielectric heating. Microwaves are electromagnetic waves that consist of two perpendicular components, namely electric and magnetic fields, as shown in Figure. 2.6. The electric field component of microwave interacts with materials such as (1) microwave-transparent material where microwaves pass through without any losses (2) conductor like metals where the microwaves cannot penetrate and are reflected and (3) absorber such as oils and waters where the material can absorb the microwaves (Figure 2.5). Microwave dielectrics are known as a material that absorbs microwave irradiation. Thus microwave heating is called dielectric heating.

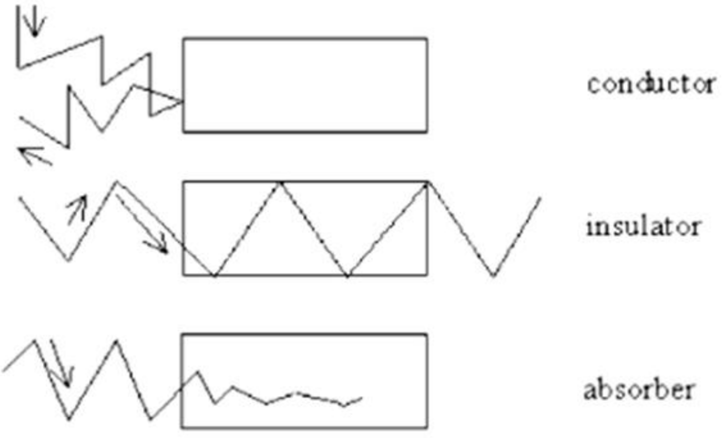


Figure 2.5. Interaction of microwave energy with different materials

Source; (Jones et al, 2002)

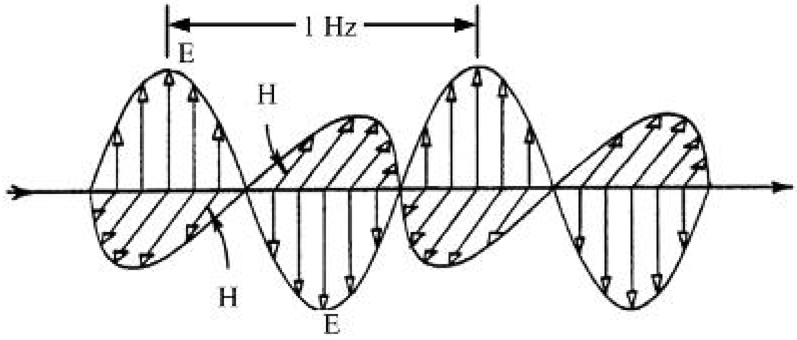


Figure 2.6. Electric (E) and magnetic field component of microwave

(Pitchai, 2011)

2.12.5. Polarization mechanism

In the polarization mechanism a dipole is sensitive to external electric fields and will attempt to align itself with the field by rotation. Under a high-frequency electric field, the dipoles do not have sufficient time to respond to the oscillating field; due to this phase lag, they collide when they attempt to follow the field. Uncompensated charges produce an electric dipole moment, and the sum of those dipoles over a unit volume is the polarization. The dipolar polarization mechanism is the primary principle of microwave dielectric heating that involves heating electrically insulating materials by dielectric loss. Materials that are amenable to microwave heating are polarizable and have dipoles that reorient rapidly in response to changing electric field strength. However, if these materials possess low thermal conductivity and dielectric loss increases dramatically, the temperature increases in "hot spots," with the possibility of thermal runaway occurring. Thus, the committee considers the conversion of microwave energy into heat, which involves interaction between microwave fields and the conductivity or dielectric properties of the material. Interactions between microwaves and materials can be represented by three processes: space charges due to electronic conduction, ionic polarization associated with far-infrared vibrations, and rotation of electric dipoles (Newnham et al., 1991).

2.12.6. Ionic conduction mechanism

In the conduction mechanism, mobile charge carriers such as electrons and ions create an electric current due to their movement through the material under the influence of the microwave E-field. The induced currents will cause heating in the sample due to electrical resistance caused by the collisions of charged species with neighbouring molecules or atoms. The electric field applies a force on charged particles, due to which the charged particles start to migrate or rotate. Due to the movement of charged particles, further polarization of polar particles takes place. The concerted forces applied by the electric and magnetic components of microwaves rapidly change in direction (2.4×10^9 per second). This causing warming because the gathering of liquid or a semi-solid cannot respond instantaneously to the field's changing direction, which creates friction that manifests itself as heat. In insulators, electrons do not flow freely, but electronic reorientation or distortions of induced or permanent dipoles can give rise to heating.

2.12.7. Dielectric properties

Dielectric properties play a critical role in deciding the interaction between the electric field and microwave absorbing materials (Buffler, 1993). The relative complex permittivity consists of two parts, real and imaginary, which are dielectric constant and dielectric loss factor, respectively.

The relative complex permittivity is given by $\varepsilon^* = \varepsilon' - j\varepsilon''$ [2.3]

The dielectric constant describes the material's ability to store electric energy (for vacuum = 1), while the loss factor indicates the material's ability to dissipate electric energy into heat. In microwave heating, the dielectric loss factor is considered the primary factor in determining a material's ability to dissipate electric energy into heat. Typically, the dielectric constant in biological materials is constant with minimal variation in temperature and frequency variation. In low-loss materials, the value of the dielectric loss factor is considered minimal, low-loss materials has the ability to absorb more energy but less ability to dissipate as heat (Metaxas and Meredith, 1983). In contrast, lossy materials dissipate any absorbed electric energy into heat energy more rapidly than low-loss materials. Dielectric materials are characterized by a quantity known as the dielectric loss tangent (tan δ) (low loss material - ≤ 0.005; medium loss material - 0.005 to 0.01 (Geyer &Baker-Jarvis, 2002). This is connoted by the ratio of dielectric loss factor to that of dielectric constant.

$$\text{Tan } \delta = \frac{\varepsilon''}{\varepsilon'} \quad [2.4]$$

Biological materials do not interact with the magnetic field component of electromagnetic waves. Magnetic materials such as ferrite, often used in susceptors and browning dishes, interact with the magnetic field, resulting in substantial heating (Buffler, 1993). Conversion of the electric component of microwaves into power dissipation in a lossy material (Goldblith & Wang, 1967) can be calculated by

$$P_d = 2\pi f \varepsilon'' \varepsilon_0 |E|^2 \qquad [2.5]$$

Where P_d is the conversion of power per unit volume (W/m^3), f is the frequency (GHz), $\boldsymbol{\varepsilon}''$ is the relative dielectric loss factor, ε_0 is the permittivity of free space (8.854×10-12 F/m), and E is the electric field strength (V/m). In theory, electric conduction and various polarization mechanisms (including dipole, electronic, atomic, and MaxwellWagner) contribute to the dielectric loss factor (Metaxas & Meredith, 1983; Kuang & Nelson, 1998).

2.13. Microwave heating systems

The transfer of energy occurs due to interaction between the molecules and atoms using the microwave. The whole process of drying is carried out in a microwave chamber connected to an electricity source. The carrier gas is inert and is also used to create an oxygen-free chamber. Among its advantages include effectiveness in heat transfer, ability to control the heating process effectively, and ability to guide against the formation of undesirable by-products. The typical microwave processing system consists of several interconnected components: (1) an energy source, usually a constant frequency microwave oscillator or a magnetron (2) transmission lines, usually waveguide (3) the applicator, and (4) the process material. An efficient processing system is designed for maximum power transfer between the microwave oscillator and the material-loaded applicator. Description of the process is well explained in the experimental section in Chapter 3.

2.13.1. Magnetron and how it works

The heart of a microwave generating system is the magnetron. It converts electrical energy to microwave radiation. To do this, a low-voltage alternating current and high-voltage direct current are used. A transformer changes the incoming voltage to the required levels and a capacitor, in combination with a diode, filters out the high voltage and converts it to direct current. Inside the magnetron, electrons are emitted from a central terminal called a cathode. A positively charged anode surrounding the cathode attracts the electrons. Instead of traveling in a straight line, permanent magnets force the electrons to take a circular path. As they pass by resonating cavities, they generate a continuous pulsating magnetic field, or electromagnetic radiation. Electrical energy, in the form of low-voltage alternating current and high-voltage direct current, is transformed and converted into direct current. A magnetron uses this direct current and generates microwaves with a frequency of 2450 megacyles per second or 2.45 GHz (gigahertz). The microwaves are directed by an antenna at the top of the magnetron into a waveguide.

2.13.2. Waveguide

Waveguide is part of the microwave setup that transmit electromagnetic wave from the magnetron to the cavity. They are typically hollow conducting pipes with either a rectangular or circular cross-section. Joints are tightly bolted and gasketed as with pipes intended to hold the water pressure. The waveguide conveys high-frequency signals with negligible loss. The propagation of waves through a waveguide is determined from solutions of the wave equations defining the signal. In a waveguide, the electric and magnetic fields are confined the space, with in the guides. Thus, no power is lost through radiation and even the dielectric loss is negligible since the guides are normally air-filled. However, there is some power loss as heat in the walls of the guide, but the loss is very small.

It is possible to propagate several modes of EM waves within a rectangular waveguide. Each transfers electric mode (TE). And transfers magnetic mode (TM) wave in a waveguide can have different field configurations. Each field configuration is called a mode. These modes correspond to solutions of Maxwell's Equations for a particular waveguide. In TEM both electric and magnetic fields are purely transverse to the direction of propagation and consequence have no 'z' directed E & H components. In TE waves, only the E -field is purely transverse to propagation, and the magnetic field is not purely transverse. In TM wave, only the H- field is purely transverse to propagation, and the Electric field is not purely transverse. Hybrid modes have both electric and magnetic field components in the direction of propagation (Asmussen et al., 1987).

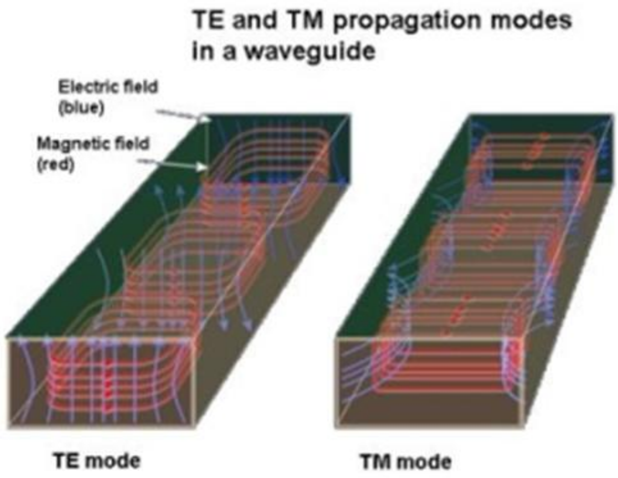


Figure 2.7. Propagation of microwaves in waveguides at TE and TM modes

Source: https://www.testandmeasurementtips.com/basics-waveguides microwavesovens/

During heating and material processing applications, resonant applicators, such as single-mode and multi-mode applicators and non-resonant waveguides, are most popular. Resonant cavities are commonly used because of their high field strengths. The type of applicator used in a microwave processing system depends on the application and type of material to be processed. Single-mode, multi-mode, and variable frequency multi-mode processing systems are commercially available and used for different microwave processing applications. Single-mode applicators are being used in specific applications such as joining ceramics and laboratory-scale study of microwave/materials interactions. Asmussen et al. (1987) presented a detailed description of single-mode or controlled multimode microwave cavity applicators for precision materials processing. Multimode cavities can be used for processing large-sized objects and are suitable for batch operations, and therefore most industrial microwave processing systems employ multimode cavity (Srinath et al., 2012).

2.13.3. Single and multimode cavities

A single-mode cavity, as its name implies, can sustain only one mode defined within the frequency range of the magnetron. The most common mode used for a cylindrical cavity is the TM_{010}, which has a uniform electric field along its cylindrical axis. A plunger is used to tune the system so that optimum power is coupled to the load. Mode TE_{10l} is the most commonly used in a rectangular waveguide. Subscript l refers to the number of half-sinusoidal variations of the field along the principal coordinate axis. The use of single-mode cavities makes it easy for materials to give workers in either the E-field or H-field maximum to find the best sintering performance. In the operation of single-mode cavities, the cavity must always stay tuned with properly matched impedance with the source. Single-mode cavities work by generating a definable Waveform (Barham et al., 2019). Compared with multimode cavities, single-mode cavities provide the advantage that E-field and H-field maxima locations can be separated. This is useful for materials with low dielectric loss. Compared to multimode applicators, single-mode applicators have higher energy efficiency and well-defined fields that can match the reactor vessel geometry and position. Generally, single-mode cavities are designed to accept one reaction vessel at a time (Kappe, 2004). Among the advantage of single-mode cavities is their high sensitivity.

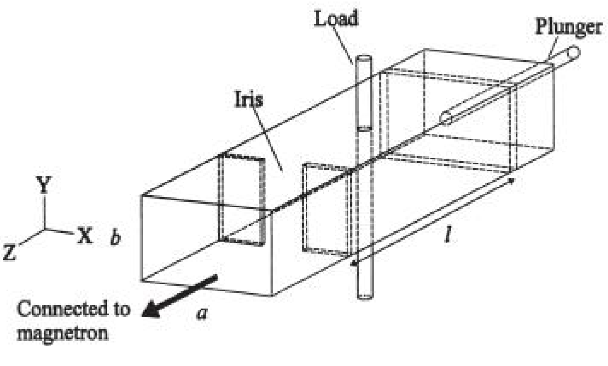


Figure 2.8. A TE$_{10l}$ single-mode cavity (Chan and Reader, 2000)

2.13.4. Multimode applicators

Multimode applicators are often used for processing bulk materials or arrays of a discrete material whose overall dimensions are too large (more significant than the wavelength of the operating frequency) to permit consideration for use in a single-mode oven. Multi-mode cavities work by accepting the broad range of MW frequencies emitted by the magnetron at various orientations (modes) and allowing them to distribute randomly within the cavity. In their most straightforward configuration, these applicators take the form of a metal box that is excited (driven) at a frequency well above its fundamental cut off frequency. Typical example of a multimode cavity is the home microwave oven. Most industrial microwave systems are simply a scaled-up version of the domestic microwave oven; however, besides being larger and more powerful than its domestic counterparts, industrial microwave systems have open ends to allow products to move from one end to the other on a conveyor belt. When multiple modes are excited, heating non-uniformity is minimized even when the field perturbing effects of the materials being processed are present. A multimode cavity is typically rectangular in shape, with large-enough dimensions to sustain many different modes over the frequency spectrum of the magnetron. The familiar domestic microwave oven is an example of a multimode applicator.

Uniform heating is difficult to obtain in a multimode oven. This difficulty arises from the unpredictable way in which the parameters were affecting uniformity change with time. As a result, several techniques, in addition to the excitation of multiple standing-wave modes, are used to promote uniform heating. They include metallic mode stirrers to ensure that all the possible modes are excited, surface scanning to direct the energy at regions of interest, product motion, and, in some cases, hybrid heating using conventional heating to replace surface losses.

However, the use of multimode is at the expense of increased circuit losses (applicator and other coupling structure and transmission-line losses) and often results in the oscillator not being adjusted to maximum power transfer. In addition, the multimode applicator is an electrically open-loop processing system, i.e., it is variable power, on-off processing system. Multimode cavities can be used to process large-sized objects and are suitable for batch operations and therefore, most industrial microwave processing systems employ multimode cavity (Srinath et al., 2012).

2.14. Leakage suppression

Suppression of microwave leakage from microwave oven doors and product openings is required for personnel safety and to reduce electromagnetic interference. Although these are two very different issues, they must be dealt with simultaneously by one choke or suppression runnel design. The current safety standard for microwave ovens is an emission specification that limits emissions at a distance of 5 cm from the surface of an oven to a maximum of 5 mW/cm^2.

2.15. Case studies on the application of microwave in soil remediation

Microwave irradiation performance can be limited by factors such as, microwave power, microwave duration, surfactant, pH, salt and some properties of the sludge (Fortuny et al., 2007). Compared to other techniques that involve heating, microwave irradiation can rapidly raise the energy of molecules within the medium resulting in higher reaction rates within a very short period of time, which make the method a high energy-efficient (Li et al., 2009).

Microwave pyrolysis has been shown to be a high-performance technique for the remediation of crude oil polluted matrices (Falciglia et al., 2014; Falciglia et al., 2016). It has been applied on a laboratory scale to decontaminate soil containing polychlorobiphenyls (Gomes et al., 2013).

A study performed by Chien (2012) successfully showed the feasibility of microwave energy for in-site remediation of petroleum contaminated soil in an oil-refinery in Taiwan. A 4-metere antenna in length was used to radiate microwave energy with power of 2 kWfor 3.5 hours and the removal efficiency was reported to be 75-99 % depending on the distance and the depth away from the microwave antenna. Energy consumption during microwave pyrolysis can be minimized by adding strong microwave absorbers (Men´endez et al., 2002).

Yuan et al. (2006) investigated the microwave remediation of the soil contaminated with hexachlorobenzene (HCB) using powdered MnO_2 as a microwave absorber. Their results revealed that a complete removal of HCB was obtained with 10 min microwave treatment by the addition of 10 %w/w powdered MnO_2 and about 30 %w/w H_2SO_4 (50%). Different additives such as carbon fibre has influence absorption of microwave by matrix such as soil.

Robinson et al (2008) worked on remediation of high-grade and low-grade oil sand; oil removal was in the range of 18-53 %. In low-grade oil sand with abundant clay, oil removal reached 53 % with an energy input of 0.8 kJ/g.

Li et al (Li et al., 2009) achieved 99 % crude oil removal at optimum condition by seeding the contaminated soil matrix with 0.02 g of carbon fiber as microwave absorber carbon-rich additives, resulting in an energy input of 6.72 kJ/g (assuming 70 % of the microwave incident power 800 watts is absorbed for 4 minutes).

Koh et al (2015) applied microwave technique for desorption of oil from soil. It is found that about 15 minutes is sufficient treatment time to satisfy the clean-up level, and the cleaning costs would be US$ 15.59/ton.

Different researchers were able to recover up to C_{16} hydrocarbons from oil-contaminated drill cuttings using a microwave heating system (Robinson et al., 2009; Pereira et al., 2011). Drill cuttings contaminated with kerosene-range hydrocarbons were successfully treated to less than 1 % w/w in a continuous ex-situ microwave system operated at 150 kg/hr (Buttress et al., 2016), and a similar system was also used to demonstrate the principle for remediating soils but organic removal was limited to 60 % (Buttress et al., 2016).

Falciglia et al (2016) Simulated MW remediation treatment for removal PAH from contaminated soil was efficient. Thus, the removal range was about 70–100 % and most efficient approximately within 10 min treatment at 1000 W-MW. At 10 min treatment time using 440 W only about 20–40 % removal was obtained, but increased to about 90 % after 60 min irradiation.

Apul et al (2016) used carbon nanoparticles to enhance treatment of hydrocarbon polluted soil compared to macroscale carbon additives. According to the authors, after a period of 60 seconds TPH concentrations reduced from 11 000 to between 2000 and 6000 mg TPH kg^{-1} soil within one minute using carbon nanomaterial additives and a 2.45 GHz, 1000 W conventional microwave oven.

Sivagami et al. (2019) reported that for an increase in magnitude of MW power from 300 to 600 W, TPH removal (%) was enhanced by approximately 50 %. TPH removals (%) were approximately 41 %, 88 %, and 91 % at MW powers of 300, 450, and 600 W.

Cho et al. (2020) investigated the removal of TPH from soils using 2.45 GHz microwave generator. The removal efficiency of the coarse soil reached 91.1 % at 15 min, whereas that of fine soil was low. A total of 30 min had passed, and a removal efficiency of 71.2 % was found for the fine soil. Residual TPH concentration was decreased when irradiation time was increased with a removal rate dependent on soil temperature variation. The surface functional groups of the contaminated soil were influenced by microwave irradiation, and changes in the hydrocarbon fraction affected contaminant removal. The results indicate that the activation energy was correlated with the influence of particle size.

Several attempts have been made on the application of a continuous process treatment of microwave treatment of drill cuttings (Pereiraet al., 2011) and soils (Buttress et al., 2016). However, it still essential to understand how some process parameters will affect batch process oil removal from different soil types. Result from the findings will enhance the economics and efficiency of continuous process treatment.

2.16. Oil removal mechanisms from soils during microwave heating

During microwave heating process, water phase is heated selectively by microwaves and converted to steam, which acts as an in-situ mass transfer media that strips or desorbs the hydrocarbons from the oil matrix.

Microwaves do not heat the oil directly as the oil is essentially transparent at microwave frequencies. However, absorbed water molecules within the soil's pores are kinetically activated, gaining energy the same as that of latent heat of vaporization of water. An increase in the internal energy of water molecules entrains oil molecules on the surface of the soil. However, bounded water molecules enhance the entrainment of high boiling point hydrocarbons (Robinson, 2014).

The removal rate is highly dependent on sweep gas flowrate, the surface area available, vapour pressure, external pressure, and temperature. The low vapour pressure of the oil phase (predominantly alkanes as shown in the previous works (Shang et al., 2005)), even at higher temperatures, and the limited available surface area for evaporation are likely to limit mass transfer and the rate of oil removal significantly. This makes the rate and extent of removal achievable through this mechanism negligible compared to both other mechanisms.

Microwaves were used to generate steam from wet soil, with the steam forming a medium to desorb or entrain the organic contaminants. The water trapped within the pores absorbs the microwave energy and converts to steam, which then entrains the contaminant oil as it passes from the pores into the bulk gas Steam penetrates the soil layer and form a mixture with the oil in it. As mentioned earlier, the boiling point of the hydrocarbons drops and flows along with steam. The feasibility of the steam stripping mechanism has been examined by different researchers (Buttress et al., 2016; Ogunniran et al., 2017) and has proved its potential for the removal of oil from contaminated soil and drill cuttings. The process has been reported to be energy economical. According to (Lord, 1998), bulk soil temperature during steam stripping of oil-contaminated soil averaged at a temperature of 100 °C. Achieving this temperature level of soil makes steam stripping a feasible technique for oil removal. Robinson et al. (2008) compared the efficiency of steam and nitrogen in streaming hydrocarbons from contaminated drill cuttings; a favourable efficiency difference of approximately 40 % regarding steam stripping was achieved. However, the application of both gases gave an outstanding efficiency in the sequestration of oil content. The authors, however, had a dilemma between steam distillation and stripping as the occurring mechanism. One of the challenges of the steam stripping mechanism, known as channelling, can affect the efficiency of the process. It occurs when water molecules restrict the movement of hydrocarbons into the gas phase within the bulk of the sample Wilkins et al., (1995). Yoon et al. (2002) corroborated Wilkins et al. (1995) by showing that hydrocarbon mass transfer can become diffusion rate-limited, even at high gas velocities. This work will investigate the extent to which steam stripping mechanism remove oil from different Nigerian soil types.

2.17. How soil texture affects microwave heating

The characteristics of soil influence contaminant–soil interaction and removal efficiency during the decontamination processes. The soil texture and consequently the specific surface area influence the interaction of the compounds with the soil and the availability and the remediation of hydrocarbon pollutants (Huang et al., 2011). Soil surface area increases with decreasing particles; this significantly influences contaminant soil interaction during microwave heating process. Changes in soil texture affect microwave energy penetration, electric field strength, and the soil sample's permittivity (Falciglia & Vagliasindi 2015). Falciglia et al. (2017a) showed significant differences in the magnitude of dielectric properties for different soil types (at the same frequency and volumetric moisture content) with a most marked difference for ε' values that is the main responsible parameter in the MW soil penetration process. Falciglia et al. (2017b) reveal the importance of determining soil compositional texture before treatment. This provides information on the amount of microwave energy to be imputed. It also aids in the design of a microwave cavity that will enhance penetration of the electric field. Dielectric constant and loss factor for dry soils shows slight variation. Different models are used for their prediction. Wang and Schmugge's models reveal an insignificant effect of bulk density on dielectric parameters. The model postulated by Hallikainen et al. (1985) uses bulk density and conductance (ρ) of soils, which can be used in estimating ε'

$$\varepsilon' = (1+0.44\rho b)^2 \qquad [2.6]$$

An increase in soil organic matter content reduces both the specific surface area and bulk density regarding soil composition. Bound water (moisture content) of soil is a function of soil texture and particle size. Hence, soil moisture is also affected, and there would be reduced microwave energy absorbed.

The comparison of calculated costs with those of other remediation technologies for hydrocarbon contaminated soils showed that the obtained short remediation times and energy costs make microwave heating a deliverable alternative to conventional thermal desorption or physical-chemical technique. Less energy costs and relatively short residence time, make MW remediation attractive as compared to conventional pyrolysis method (Table 2.3). Various authors have reported energy involve in soil treatment with different technologies and can be seen in (Figure 2.3).

Table 2.3. Overview of cost implication for different treatment technologies

Classification	Technology	Duration	Cost (USD)	References
Biological	Phytoremediation	months/years	25-100 per ton	(Gerhardt et al., 2017)
	Biostimulation	months/years (45 months)	100-300 per m^3	(Koshlaf and Ball , 2017) (Zhang et al., 2019)
Chemical	Solidification and Stabilization	8-32 months	36.6 per m3	(Kujlu et al., 2020)
	Chemical oxidation	Hours to days	6670-76920	(Li et., 2014; Bajagain et al., 2020; Chen et al., 2016)
Physical	Electrokinetics	14-15days	25-100 per m^3	(Korolev et al., 2008; Pazos et al., 2012; ERSG, 1997).
Thermal	Incineration	Seconds to hours	150-2900 per ton	(Vidonish, Zygourakis, Masiello, Sabadell, et al., 2016)(Anthony & Wang, 2006)
	Ex situ Thermal desorption	Minutes to hours	223 to 560 to per ton 330 54.12/ton	(Faisal et al., 2004; US-EPA, 2004 ; Falciglia & Vagliasindi, 2014;) Lee (1999)
	microwave heating	Minutes to hours	33–245 per ton 15.59 per ton	(Falciglia & Vagliasindi, 2014) Lee (1999)

In conclusion, microwave interacts differently with soil depending on the properties of the soil such as texture, moisture content. Previous work done in the application of the technology for treatment of typical Nigeria soil (Ogunkayode, 2016). However, it is important to see how different soil types will response to microwave. There has been different suggestion of the mechanism for oil removal from materials by different researchers (Shang et al 2005, Robinson et al 2008, Robinson et al 2009, Pereira 2011) namely physical entrainment, direct vaporisation, steam distillation, and steam stripping. There is no clear line of distinction in the application of the mechanism for hydrocarbon sequestration from soil. Knowledge of the exact mechanism for oil removal will enhance scaling up the microwave pyrolysis process upon variation of process parameters. This forms the basis of this research in examining the contribution of steam stripping oil removal mechanism of oil from soils. Overall results from soil treatment from microwave technology will be compared to the convention process.

CHAPTER THREE. Experimental Methods and Analytical Techniques

3.1. Scope

This chapter provides a detailed description where appropriate of the methods used throughout this research work; typically in the characterization of a sample before and/or after treatment.

In order to meet the research aim, a field investigation was conducted to ascertain different crude oil contaminated sites. Soil samples for this study were collected in from different locations in Delta State Nigeria. Clay and sand soils were collected is within latitude: 5^{0}24′54.765″N longitude: 6^{0}11′54.021″E. A pipeline conveying crude oil is located 120 m away from the collecting point and 500 m from a road. West of the area are occupied by some indigenes of the community (Figure 3.1). Loamy B soil was collected from the second location latitude 5^{0}28.98″N and longitude 6^{0}08.37″E. Loamy A soils collected from the third location latitude 5^{0}32.29″N and longitude 6^{0}53.68″E. The samples were collected at 10 cm depth from each site using hand-held auger, after then, the samples were mixed together. The collected samples were stored in fabric bags prior before transporting to the UK. Upon arrival they were stored in the freezer at 4°C.

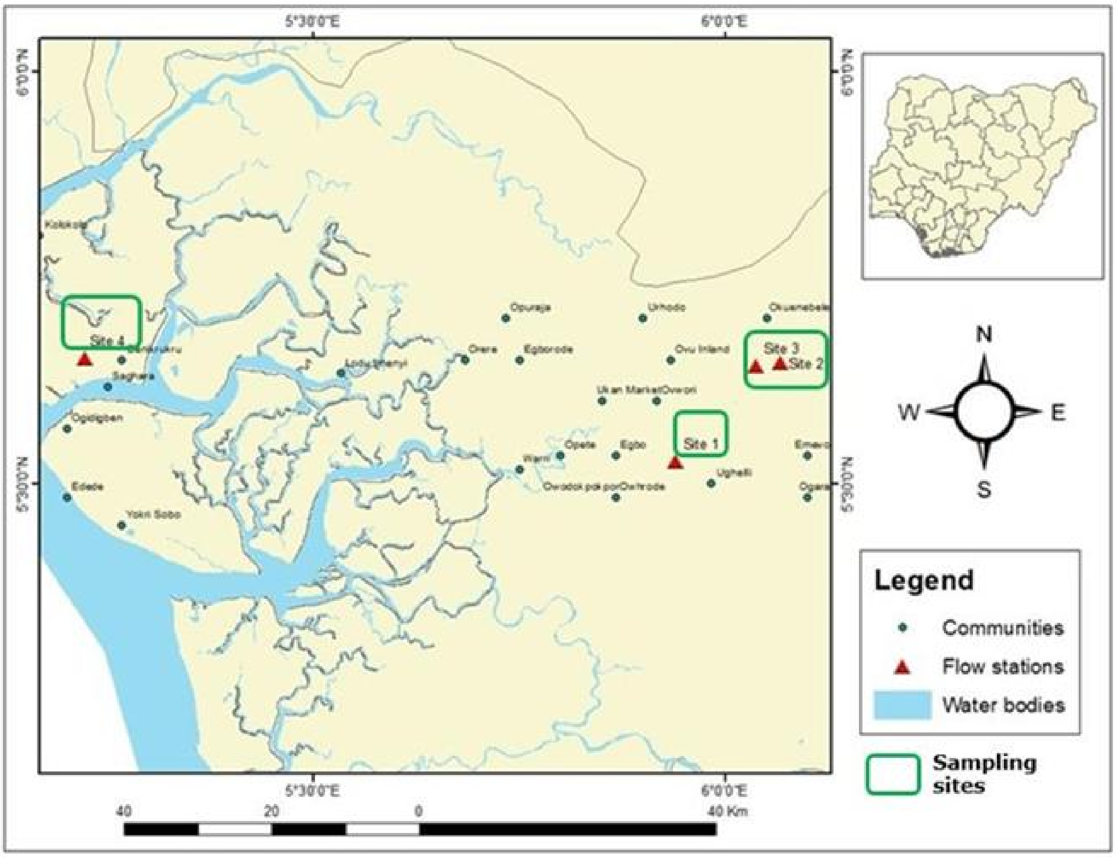


Figure 3.1. Map showing the sample collection points

The following methods are covered.

1. Soil liquid content and compositional analysis:

i. Water content determination

Soil water is important as it indicate available water required in soil for microwave processing.

ii. Oil content determination

This is a common leaching method applied during solid-liquid extraction. It is a standard method of quantifying oil content in contaminated soil.

iii. GC-MS characterization of extract

Identification of specific hydrocarbons in oil can be achieve using GC-MS. Ranges of aliphatic and aromatics group are qualitatively determined and comparatively used to connote the extent of soil treatment.

iv. Total organic carbon

v. Gas analysis

Composition and concentration of flue gases from pyrolysis reaction are determined analytically by gas chromatography. It is important to improve safety, efficiency and to monitor the process and emissions.

2. Soil particle analysis

i. Sieving

Sieving is important as it is a means of assessing particle size distribution of a given soil sample. This information is used for soil classification and to predict its behaviour.

ii. X-ray diffraction (XRD)

This technique gives detailed information about the mineral composition of soil particles. The minerals content to influence dielectric response of soils, hence, microwave absorption.

iii. Density and porosity measurement

These two parameters are indicators of available water capacity of soil. Pore space also facilitates the movement of oil contaminant in soil.

iv. Brunauer–Emmett–Teller (BET)

Soil surface area and pores are determined using BET. This test is used as a basis of comparison with (iii), furthermore, BET analysis reveals the microspores and macrospores present in each soil type. As a basis of comparison, this test

3. Dielectric response of soils to microwaves

The dielectric properties of soil are fundamental guide prior to microwave soil heating. This technique, gives the behaviour and response of soil particles when heated in a microwave cavity.

3.2. Soil sampling for extraction

Cone and quartering technique for was used to effectively quantify oil content in soils. The technique involves sampling and arranging the sample into a pile, after which the pile is flattening and subsequently divided into different quarters. The first and third quarter in a clockwise direction are combined (quarters in opposite direction). Likewise, the second and third quarter. Further coning and quartering were done to get 24 representative samples was collected for soxhlet extraction.

3.3. Soil liquid content and composition analysis

3.3.1. Oil content measurement

Soxhlet extraction is a very useful tool for preparative purposes in which the analyte is concentrated from the matrix as a whole or separated from particular interfering substances. The sample is placed in a thimble-holder and, during operation is gradually filled with condensed fresh solvent from a distillation flask. When the liquid reaches an overflow level, a siphon aspirates the whole contents of the thimble-holder and unloads it back into the distillation flask, carrying the extracted analytes in the bulk liquid. This operation is repeated until complete extraction is achieved. Soxhlet equipment consists of a thimble (sample holder), distillation flask, the extractor body, condenser, and heating mantle (Figure 3.1).

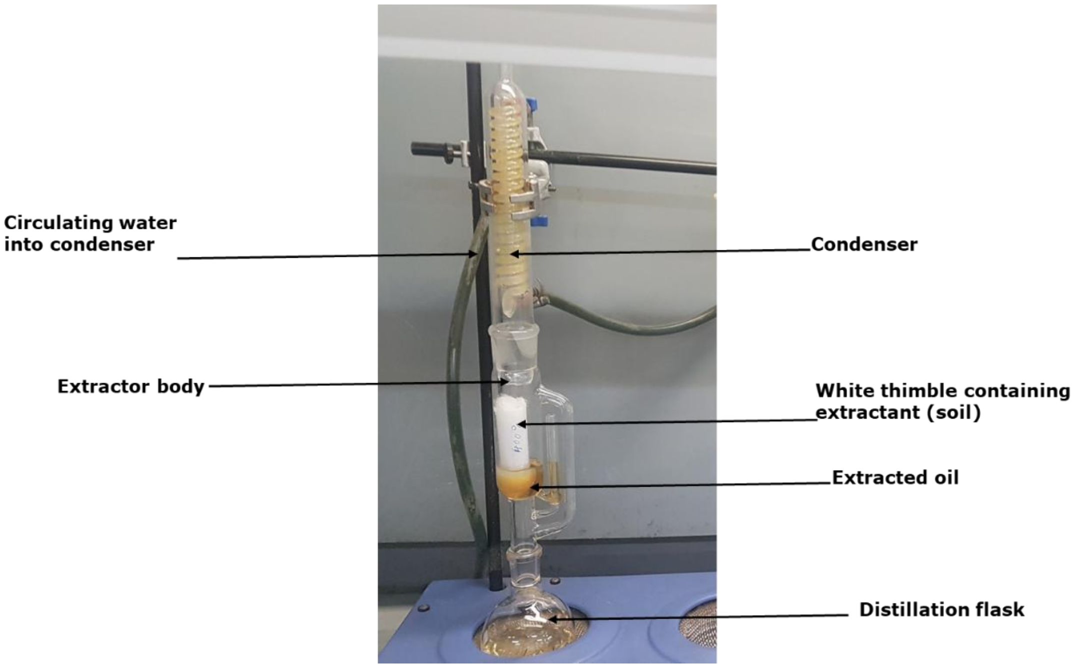


Figure 3.1. Soxhlet extraction setup

A known weight of crude oil polluted soil was loaded into a thimble and transferred to the main chamber of the soxhlet extractor. A mixture of dichloromethane (CH_2Cl_2) and methanol (CH_3OH) (93:7 % v/v) of total volume 250 ml is placed in a 500 ml distillation flask. The mixture in the distillation flask was heated continuously for 24 hours. After the extraction, the oil-solvent mixture was concentrated by removing dichloromethane. This was carried out by heating the mixture to 40 ^{0}C in a water bath under low vacuum. The concentrate was transferred to 10 ml vials, which were then allowed to evaporate in air at room temperature for 24 hours. The mass of oil extracted was estimated by taking the difference between the mass of the vial when empty and with oil after 24 hours of drying in air. The oil content can be calculated from equation 3.1;

$$A_o=\frac{M_o}{M_s}\times 100 \qquad [3.1]$$

Where A_0 is the calculated weight fraction of oil (%), $M_0$is the mass of oil extracted and M_s is the sample mass. The accuracy of this method was determined to be ±0.5 %w/w.

3.3.2. Water content measurement

The Dean and Stark (ASTM D-95-ISO 373) method was used, comprising a vertical cylindrical piece of glass, often with a volumetric graduation on its full length and a precision tap on the bottom very much like a burette as shown in Figure 3.2. The top of the cylinder is a fit with the bottom of the reflux condenser. Protruding from the top the cylinder has a sidearm sloping toward the reaction flask. At the end, the sidearm makes a sharp turn so that the sidearm's end is vertical. This end connects with the reactor. During the reaction in, vapours containing the reaction solvent and the component to be removed travel out of the reaction flask up into the condenser, and then drip into the distilling trap. Here, immiscible liquids separate into layers. When the top (less dense) layer reaches the level of the sidearm it can flow back to the reactor, whilst the bottom layer remains in the trap. The trap is at full capacity when the lower level reaches the level of the side-arm--beyond this point, the lower layer would start to flow back into the reactor as well. Therefore, it is important to syphon or drain the lower layer from the Dean-Stark apparatus as much as needed. The water contents of the soil samples were measured according to ASTM D-95 by the Dean-Stark method, where 30 g of soil was used with 100 ml of toluene heated under reflux to distil and separate the water.

The water content of the sample can be estimated as follows;

$$A_w=\frac{M_w}{M_s}\times100 \qquad [3.2]$$

Since the density of water is 1 g/cm_3, if the volume of water collected was x cm^3, then the mass of water will be x g.

Where Aw is the percentage water content, Mw is the mass of water collected and Ms is the sample mass. The accuracy of the method in measuring the water content of drill cuttings was determined to be ±0.2 %w/w.

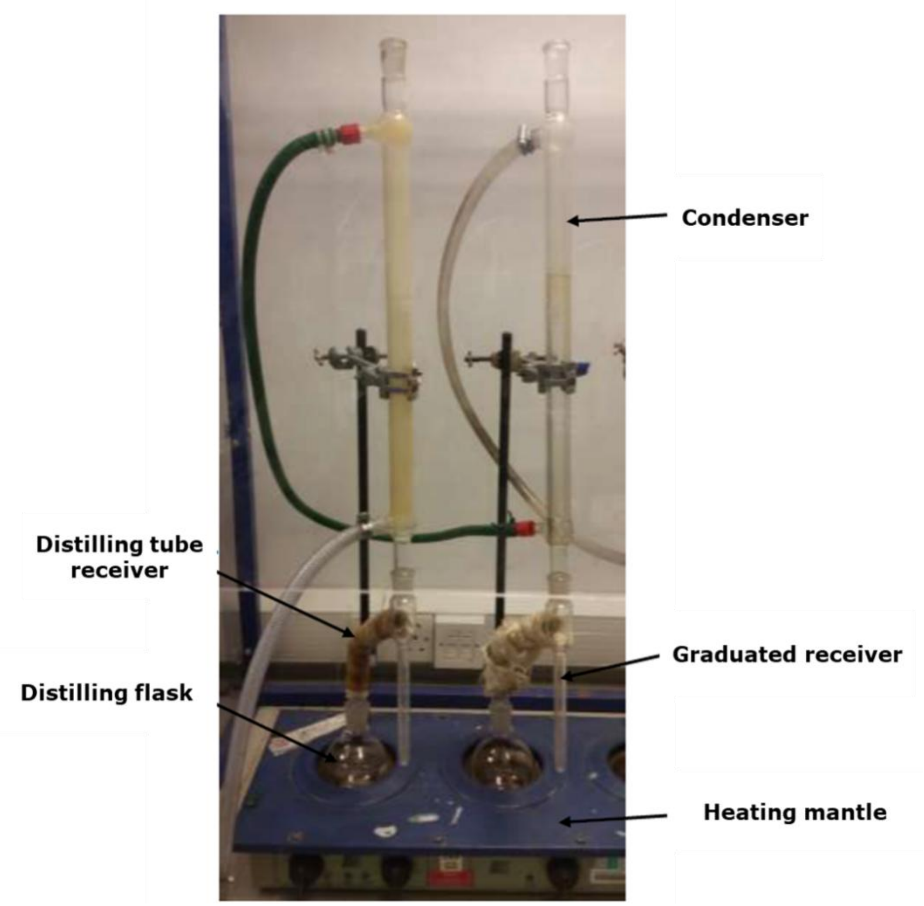


Figure 3.2. Dean stark set-up

3.3.3 Gas. Chromatography (GC): theory and techniques

The gas chromatography instrument comprises an injection port, a regulated carrier gas cylinder, a column (inert solid support) enclosed in a thermostatic regulated oven, a sample detector and a recorder as shown in Figures 3.3a and Figure 3.3b. The separation of components by GC is accomplished by a sequence of partitions between a mobile gas phase and a stationary liquid phase held in a column after the gas mixture is injected as a narrow band. The detector then monitors the composition of the gas stream as it emerges from the column carrying separated components, and the resulting signals provide the input for data acquisition (Bartle & Myers, 2002). The carrier gases such as helium, nitrogen and argon have been used to analyse the mobile gaseous phase. The volatile samples injected must be thermally stable at operating temperatures from ambient to over 400 °C, to suit the elution process (Bartle & Myers, 2002). Gas chromatographic separation is often carried out in columns that are manufactured using non-absorbent and chemically inert materials. The column can either be packed or capillary. Packed columns are usually made of glass and stainless steel. It is simpler to operate, less costly and often offers satisfactory performance. While capillary columns are made from quartz or fused silica. This type of column is very expensive, mostly give superior resolution and therefore becoming more widely used for complex mixtures (Rahman et al., 2015).

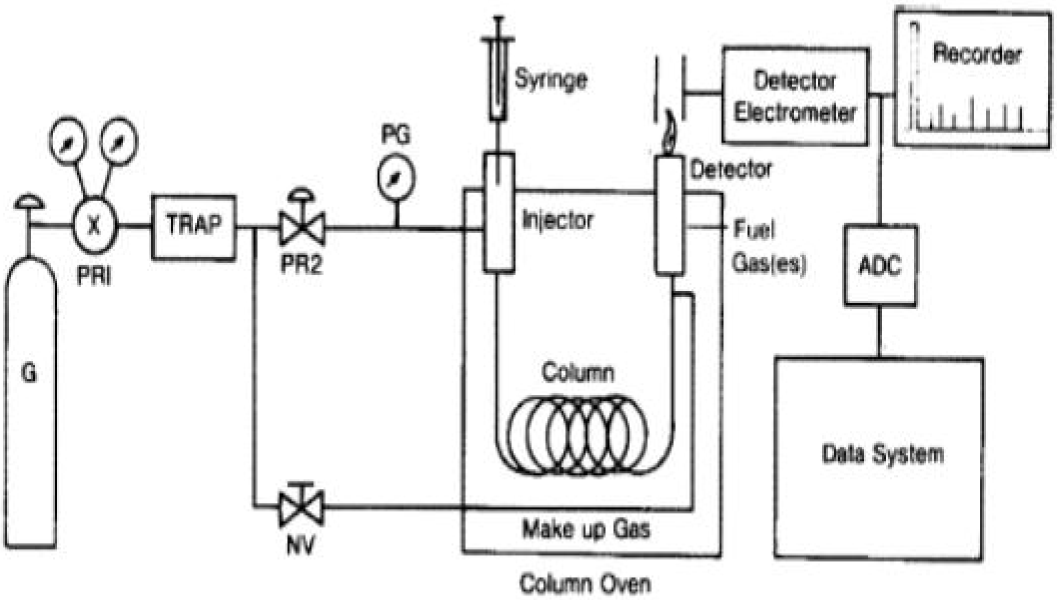


Figure 3.3a. Gas chromatography instrumentation

(Bartle & Myers, 2002)

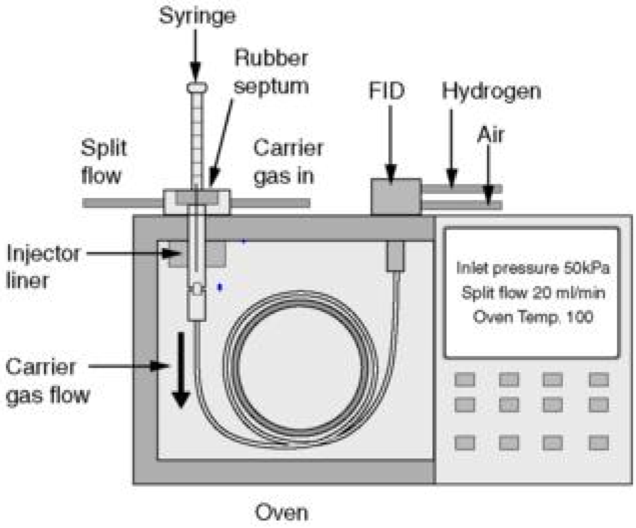


Figure 3.3b. Gas chromatography oven/controller

The process of separation and analysis start when the component of the gas mixture injected in the GC system is heated and vaporised within the sample injection unit. The heated gases together with the mobile phase (carrier gas) are then transported sequentially through the column, where it is separated into the various components. The rate of progression of each component within the column varies based on their polarity, boiling points, concentration, and thermal stability. This characteristic ensures that different chemical species elute at different retention times (Bartle, 1993). The separated eluted compound is appropriately measured by the detector located to the column exit. The detector further converts this measurement into an electrical signal which is then transferred to a data processing unit. The data obtained enables the successful determination of the number of components in the mixture, and their relative proportions. The row of peaks drawn when the electrical signals output from the GC detector are plotted on the vertical axis and the elapsed time after sample injection is plotted on the horizontal axis is called a chromatogram (Shimadzu GC, 2022). Flame ionisation detectors (FID) and thermal conductivity detectors (TCD) are two common types of detectors employed for gas compositional analysis. FID analyses the hydrocarbon gases ($C_1 – C_{5+}$)

The Perkin Elmer Clarus 580 GC system used for determination of the gaseous product composition. Before this analysis, hydrocarbon standard gas ($C_1 – C_5$).These standards were stored in gas cylinders and were drawn using a 100 µl glass gas syringe (with a needle attached) through a diaphragm. The gases were then injected into the analyser through a diaphragm in the injection line.

Gases generated from the experiments were collected in a 1 litre gas bag and immediately analysed on the gas chromatograph (GC) fitted with FID and TCD detectors operating at 200 °C. The hydrocarbon gases were analysed by injecting 100 µl of gas samples (split ratio 10:1) onto the FID at 250 °C with separation performed on an alumina plot fused silica 30 m x 0.32 mm x 10 µm column, with helium as the carrier gas. The oven temperature was programmed from 60 °C (13 min hold) to 180 °C (10 min hold) at 10 °C min^{-1}. Individual hydrocarbon gas yields were identified and quantified using C_1-C_5 gases (injected separately) as an external gas standard. Separation was performed on a Haysep N6 packed column using Argon as the carrier gas. The gas yields were also identified and quantified in relation to gases individual standards (injected separately) as a mixture of external gas standards. In each experiment, one litre of pyrolysis gas was collected for analysis.

3.3.4. Oil composition

A combination of gas chromatography (GC) and mass spectrometry (MS), is well-established to analyse complex organic and biochemical mixtures (Skoog et al., 2007). Gas chromatography separates different compounds in the sample into pulses of pure chemicals based on their volatility by flowing an inert gas (mobile phase), which carries the sample, through a stationary phase fixed in the column spectra of compounds are collected as they exit a chromatographic column by the mass spectrometer. A mass spectrometer is an analytical instrument that generates a beam of gas ions from inorganic or organic compounds. It sorts the resulting mixture of ions according to their mass-to-charge (m/z) ratios (Skoog et al., 2007), using electrical or magnetic fields as seen in Figure 3.4. It provides qualitative and quantitative output signals (peaks) from the mass-to-charge ratio and the intensity (abundance) of each detected ionic specie (Boyd et al., 2011).

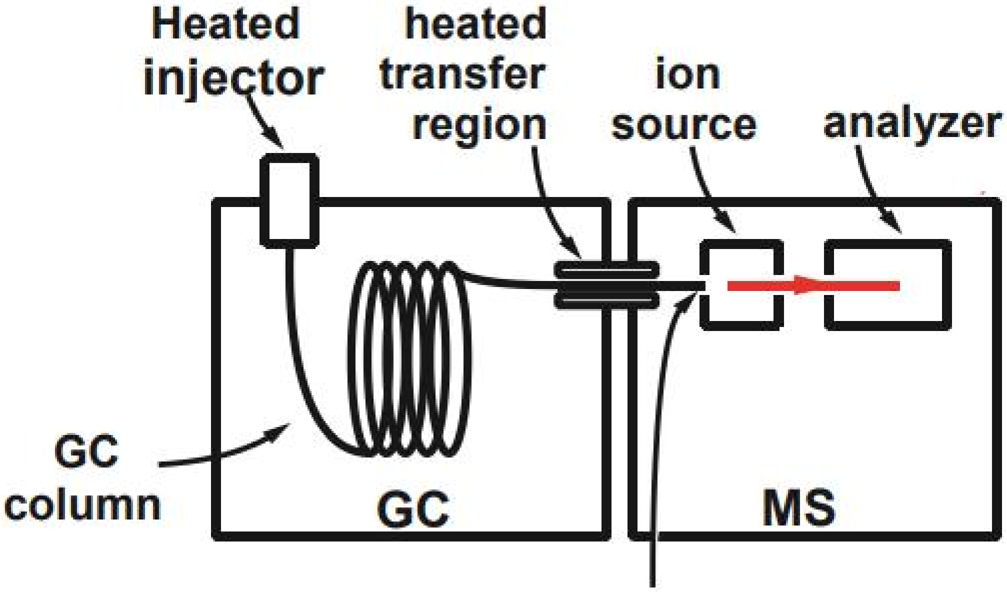


Figure 3.4. Schematic diagram of a mass spectrometry

Source: De Hoffmann & Stroobant, (2007).

Oil samples were weighed into a sample tube and diluted with dichloromethane. GC-MS in full scan mode (m/z 40-450) was performed on the samples with a Varian CP-3800 gas chromatograph, interfaced to a Varian 1200 mass spectrometer (EI mode, 70 eV). Separation was made using a ZB-1701 fused silica capillary column (60 m x 0.25 mm i.d., 0.25 mm thickness), with helium as the carrier gas, and an oven programme of 50°C (hold for 2 min) to 300°C (hold for 33 min) at 5°C/min.

Samples are introduced into the GC using a heated injector. Components are separated on a column, according to a combination of molecular mass and polarity, and sequentially enter the MS source via a heated transfer region. The analytical data consists of total ion chromatograms (TIC) and the mass spectra of the separated components.

3.3.5. Total organic carbon measurement

In elemental analysers, samples are combusted in a furnace at 1000 ^oC (Analytical Method Committee, 2006). The products: carbon is converted to carbon dioxide; hydrogen to water; nitrogen to oxides of nitrogen and sulphur to sulphur dioxide. If other elements such as chlorine are present, they will also be converted to combustion products, such as hydrogen chloride. A variety of absorbents are used to remove these additional. Combustion products as well as some of the principal elements, sulphur for example, if no determination of these additional elements is required. The combustion products are swept out of the combustion chamber by inert carrier gas such as helium and passed over heated (about 600 ^oC). Quartz oxidation column made of chromium oxide, tungsten trioxide removes any oxygen not consumed in the initial combustion and converts any nitrogen oxides to nitrogen gas (Analytical method committee, 2006). The gases are then passed through the absorbent traps in order to leave only carbon dioxide, water, nitrogen, and sulphur dioxide. An approximate soil mass of 75-80 mg was weighed into the sample holder (standard foil), and then transferred to the furnace heated for an average of 5 min as described above. Carbon, hydrogen and nitrogen content of the crude oil-contaminated soils was determined using Leco 628 CHNS elemental analyser. The soils were treated with 1 M HCl to measure the % w/w of carbonates present, and the carbon measured after that is defined as soil total organic carbon (TOC).Percentage TOC is calculated as;

$$\% \text{ TOC}=\frac{I_{toc}}{F_{toc}} \times 100 \qquad [3.3]$$

Where I_{toc} is the TOC content in the char, F_{toc} is the TOC in the untreated soil.

3.3.5. Column chromatography

The principle behind this technique is separation of mixtures based on their interaction with the stationary phase (adsorbent). The adsorbent is usually a mixture of silica and alumina in the ration of 3:2 as the stationary phase) is made into a slurry with a suitable liquid and placed in a cylindrical tube that is plugged at the bottom with a piece of glass wool or porous disc. The mixture to be separated is dissolved in a suitable solvent and introduced at the top of the column, and can pass through the column as shown in Figure 3.5. Intermolecular forces, which vary in strength according to their type, make organic molecules to bind to the stationary phase. The stronger the intermolecular force, the stronger the binding to the stationary phase, therefore the longer the compound takes to go through the column. As the mixture moves down through the column, the components are adsorbed at different regions depending on their ability for adsorption. The component with greater adsorption power will be adsorbed at the top and the other will be adsorbed at the bottom. The weakly adsorbed component will be eluted more rapidly than the other. The different fractions are collected separately (Bissada et al., 2016). Evaporation of the solvents from the different fractions provides samples for analysis.

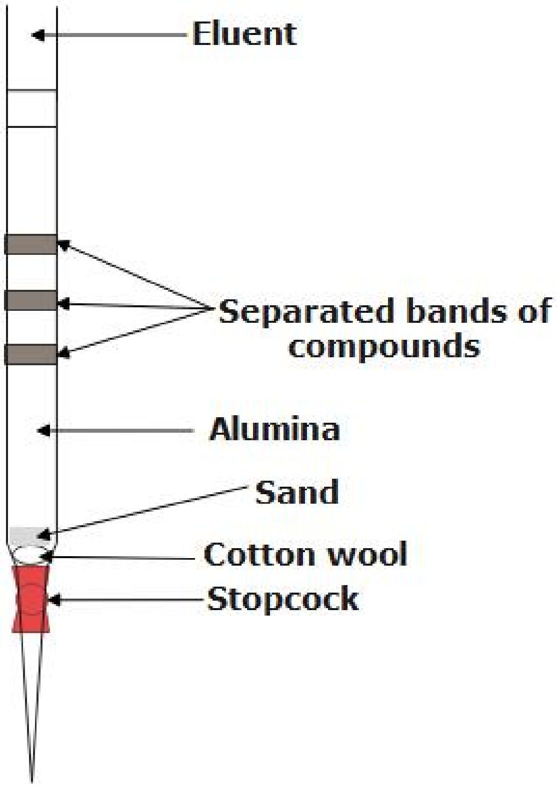


Figure 3.5. Column chromatography setup

The set-up is shown in Figure 3.5. The column, cotton wool, and other glassware are washed with dichloromethane and rinsed appropriately with the required solvent before the separation process. The column is loaded with alumina/silica (2:3) as the stationary phase, with 40 to 50 mg of the oil sample. Thereafter is flushed with n-hexane and the sample is added to the top of the wet column. Separation of the aliphatic hydrocarbons is attained by elution with 30 ml n-hexane whilst the aromatic hydrocarbon is obtained by elution with a mixture of 30 ml DCM and n-hexane (40:60). The polar species obtained by elution with 1:4 volume mixture of 30 ml DCM and methanol and the product yields. Quantitative yields of the product are done using gas chromatography coupled with mass spectrometry. Typical example can be seen in Figure 3.4.

3.4. X-ray diffraction

The mineral composition of the soil samples in this work were identified using X-ray powder diffraction analysis. This technique works on the basis of X-ray diffraction according to the space between atoms in a crystal lattice. There are several atoms in a crystal lattice, each having unique and random orientations. X-rays of known incident angle (θ) is scanned on a sample, and the angle of X-ray diffraction (Figure 3.6) from the sample is recorded. The angle of diffraction is unique to the atomic spacing in a crystal lattice, which means that each mineral can then be identified (Harris & Willie, 2008). A Bruker D8 Advance X-ray Diffractometer instrument has been used, consisting of an X-ray tube that produces monochromatic waves and can be rotated to produce incidents rays at 0-90 degrees. Soil samples are prepared by drying and sieving down to <212 μm. An electronic detector is located opposite the sample in the instrument, which detects diffracted X-rays from the sample. Diffraction only occurs when the wavelength of the incident X-rays is of the same magnitude as the distance between the atomic planes (Harris & Willie, 2008). Bragg's law gives the wavelength in equation 3.8;

$$n\lambda=2d \sin\theta \qquad [3.8]$$

By varying the angle of incident of X-rays, the d spacing in each mineral in the sample can be determined. The unique characteristic of each mineral in a sample is shown by plotting the angular positions (2θ) and the intensity of the resultant diffraction peak.

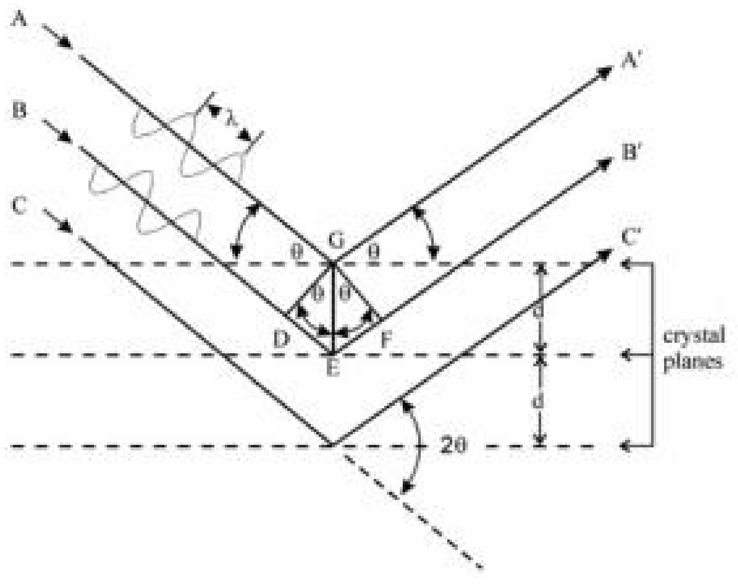


Figure 3.6. Schematic representation of XRD by regular spaced planes of atoms in crystals

Theta (ɵ) is the angle that the beam makes with the atomic planes: 2ɵ is the angle that the diffracted beam deviates from the primary beam; d is the distance between equivalent atom planes in the crystal (d-spacing): and λ is the wavelength of the radiation.

3.5. Soil analysis

3.5.1. Particle size

The samples were prepared for analysis by removing the oil (soxhlet extraction – section 3.11) and water (Dean and Stark – section 3.2.2) and drying in an oven at 105 ºC for 24 hours. A known weight of dried soils was transferred to various sieves. Clean sieves are assemble in descending order of sieve size 0.038, 0.09, 0.1, 0.125, 0.212, 0.25, 0.355, and 3 mm, 50 g of sample was loaded at a time into the top sieve size. The pan is placed below the smallest sieve size, and the soil sample is transferred into the top sieve and placed the cap over it. The stack sieves are placed in the mechanical shaker and shaken for 10 minutes. The stack is removed from the shaker and carefully weighs each sieve's weight with its retained soil. In addition, remember to weigh and record the weight of the bottom pan with its retained fine soil. The mass of soil retained on each sieve is calculated by subtracting the weight of the empty sieve from the sum of the mass of the sieve and retained soil.

$$\text{Quantity passing} = \text{Total mass} - \text{mass retained} \qquad [3.9]$$

$$\%\ \text{retained} = \frac{\text{mass retained}}{\text{total mass}} \times 100 \qquad [3.10]$$

This cycle was repeated between 5-10 times for each 50g of sample loaded in the top sieve, and continued until the entire sample was sieved.

3.5.2. Skeletal density

The instrument used to measure the skeletal density using Accupyc 1330 Gas Pycnometer (Micrometrics). Helium is used as the purge gas in the analysis. 5g of dry soil samples are filled to approximately ¾ of a 10ml sample chamber in the instrument. The instrument uses the ideal gas law, gas displacement techniques, and the difference between the gas pressure in the sample chamber and a reference chamber to calculate the actual volume of the sample. The skeletal density is then calculated from the ratio of the sample mass to the actual volume. Bulk density was determined by filling a measuring cylinder with soils to the 250 ml mark. The base of the cylinder was tapped 5 times for a uniform bulk density measurement for all samples. The bulk density was then calculated using the sample mass.

$$\text{Porosity} = 1 - \frac{\text{Soil bulk density}}{\text{Skeletal density}} \qquad [\ 3.11\ ]$$

3.5.3. Nitrogen adsorption isotherm using Brunauer–Emmett–Teller (BET) analysis

Brunauer-Emmett-Teller's (BET) theory explains the physical adsorption of gas molecules on a solid surface. It is the fundamental theory for measuring the specific surface area of materials. The theory applies to multilayer adsorption systems that use probing gases that do not chemically react with material surfaces as adsorbates to quantify specific surface areas. Nitrogen gas is the most commonly employed gaseous adsorbate used for surface probing by BET methods. For this reason, standard BET analysis is most often conducted at the boiling temperature of N_2. However further probing adsorbates are also utilized with lower frequencies, allowing surface area measurement at different temperatures and scales. These include argon, carbon dioxide, and water.

To determine textural properties of the oil-contaminated samples, N_2 sorption isotherms at -196 °C were obtained using a Micromeritics ASAP 2420 instrument. Approximately 2 g of sample was weighed into a sample tube with a filler rod. Without degassing, the sample was frozen in liquid N_2 at -196 °C for 30 mins, next the sample was evacuated manually to a vacuum setpoint of 10 µm Hg, and the isotherm started. Isotherms were acquired from 0.001 to 0.995 relative pressure (P/Po). Helium Pycnometry was used to determine the skeletal or true density of the samples, with the addition of blank N_2 isotherms on the sample tubes, warm and cold free spaces were calculated manually. The BET model was used to determine the specific surface area in the relative pressure range of 0.05-0.30, giving positive BET ‘C’ constants. Pore size distribution and volumes were also established by the Dubinin-Radushkevich model for micropores (<2 nm), BJH model (Harkins-Jura thickness curve correction) for mesopores (2-50 nm) and macropores (>50 nm, limit up to 150 nm from BJH model.

3.6. Dielectric measurements

Dielectric measurements were carried out using a cavity perturbation technique (Figure 3). The system consists of a cylindrical copper cavity connected to the network analyzer. A tube of internal diameter of 4mm containing silica fibre of 7-10 cm from the top of the tube. While in the cavity (height 55mm and width 550 mm) position and with the signal analyzer's help, the tube was calibrated within the cavity. This is achieved by moving the tube up and down, so the curve peak reaches its farthest point to the left, by observing the curve's peak displayed on the signal analyzer interface. A known weight of the sample was inserted into the tube, and a similar procedure was repeated as when the tube was empty. Low-temperature measurement was done in the cavity. In high-temperature experiments, samples are heated in a conventional electrical furnace and transferred to the cavity by the robotic arm for measurement at a frequency of 2.45 GHz. The process was repeated over a temperature range from 15 to 650 °C. Dielectric measurements were carried out using a cavity perturbation technique. The system consists of a cylindrical copper cavity connected to the network analyzer. A 4 mm internal diameter quartz tube was used to contain 0.20 - 0.23 g of the sample, which was then moved into the resonant cavity. The change in resonant frequency and quality factor upon insertion of the sample was recorded and used for calculating the dielectric constant and loss factor. For variable temperature measurements, the quartz tube was maintained in a conventional electrical furnace located above the cavity and transferred into the cavity using an automated step-motor after a pre-set temperature/time programme. All the experiments were carried out in triplicate.

3.7. Experimental rig

3.7.1. Microwave heating

Soil samples were studied in a single mode cavity with a well-defined electric field distribution. Microwaves were generated at 2.45 GHz and directed to the cavity via WR 340 waveguide and a 3-stub tuner for impedance matching to minimise reflected power. The sample comprised 20 g of contaminated soil and was contained within a quartz reactor that was located in the centre of the cavity. Nitrogen gas with a flow rate of 2 L/min was purged through the reactor to maintain an inert environment and prevent combustion of the evolved hydrocarbon vapours. Microwave experiments were carried out by placing 20 g of contaminated soil. Samples were treated at microwave powers of 1-3 kW for 5-420 s as seen Figure 3.7 and Figure 3.8. The reflected power was logged and used to calculate the absorbed energy for each test, and this used as a primary control variable rather than temperature. A condenser attached to the microwave reactor with circulating cold water was used to recover oil and water vapour from the sample during treatment.

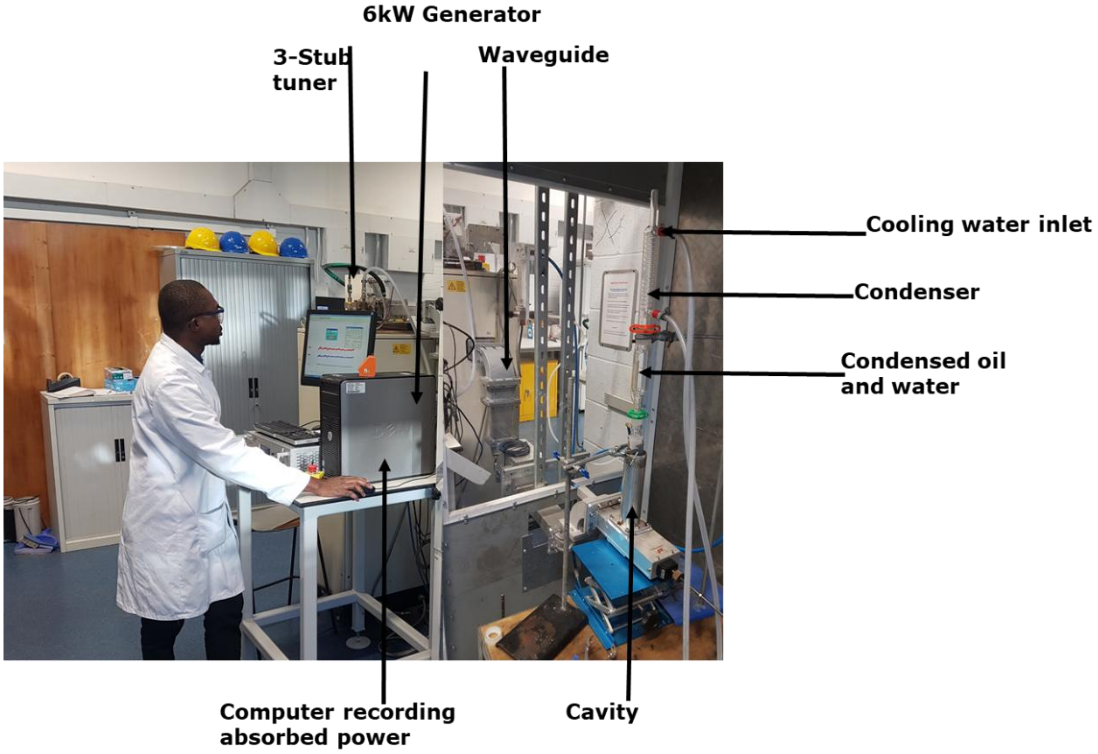


Figure 3.7. Microwave treatment set-up

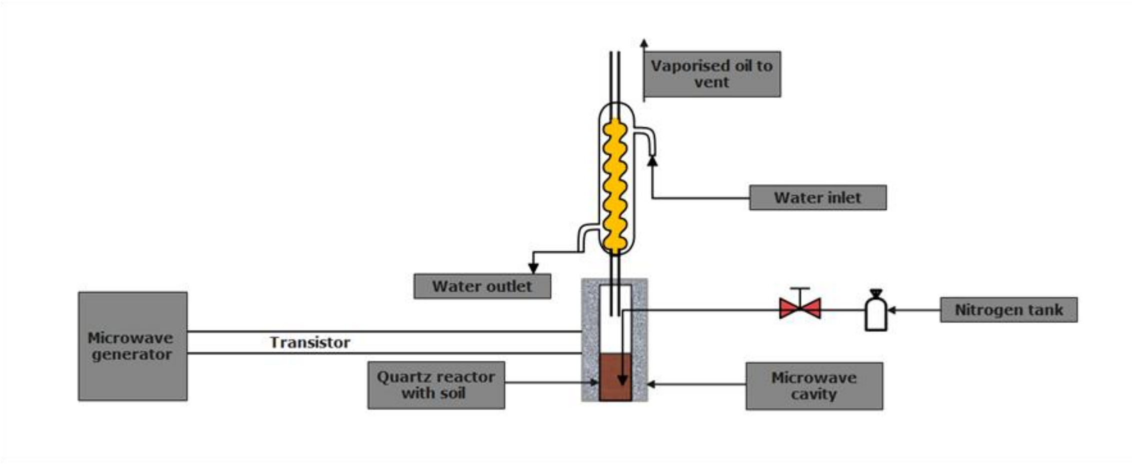


Figure 3.8. Schematic of single-mode microwave apparatus for treatment of contaminated soil

3.7.2. Conventional heating

The Gray-King retort pyrolysis is a carbonisation test that is well-established for coal (ASTM D3175; Davis & 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. The laboratory pyrolysis test 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 Gray-King test was used here 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.A 20 g of the soil, which was processed in a Gray- King retort system at temperatures from 400 - 800 ºC in accordance with ASTM D3175. The soils were kept at the final temperature for 45 minutes, and an ice bath was used to recover condensed oil.

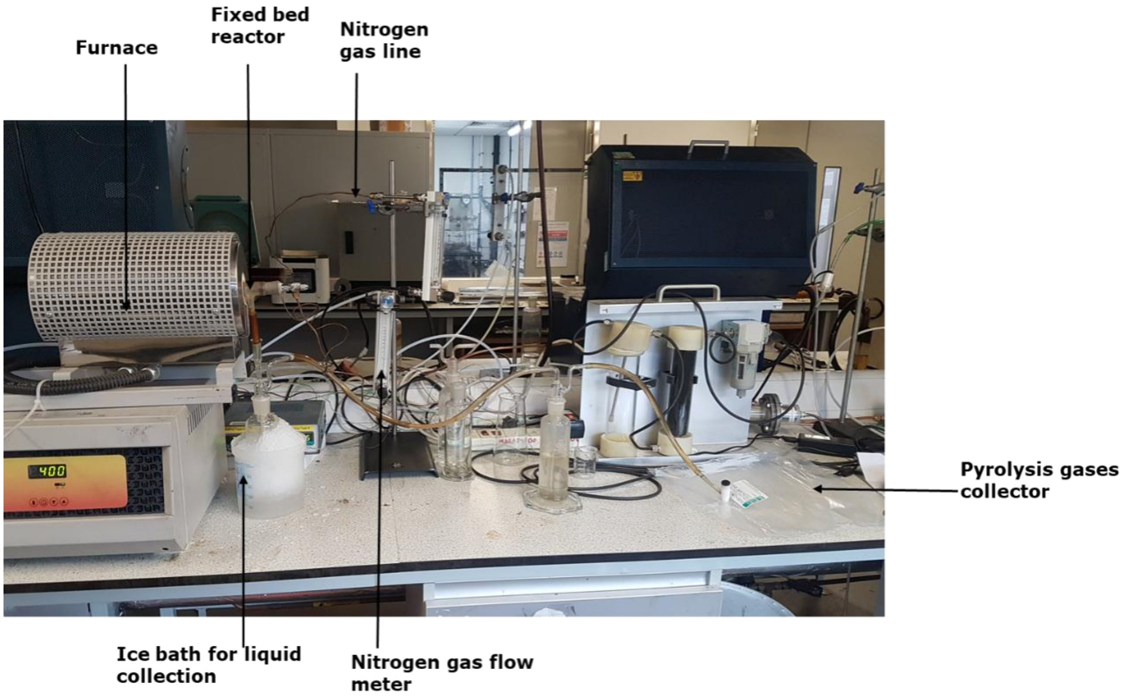


Figure 3.9. Schematic of single-mode microwave apparatus for treatment of contaminated soil

CHAPTER FOUR. Impact of Soil Properties and Microwave Power on Oil Removal from Soils

4.1. Scope

The main objectives of the work presented in this chapter are to determine the performance of a batch microwave processing system to treat oil contaminated soil to final oil content in soil that is within disposable limit. This knowledge will be used to explain the experimental observations reported in this chapter, which focuses upon identifying the key variables affecting oil removal performance during batch process treatment.

Microwaves are known to interact differently with different soil types, and soils with different physical characteristics such as water content and bulk density. Soil porosity is a significant factor influencing the water-holding capacity, and soil texture has been shown to influence the decontamination process and contaminant removal efficiency (Falciglia et al., 2016; Ngole-Jeme & Veronica, 2019). Texture also affects sample permittivity and subsequent microwave penetration, and hence the strength of the electric fields and power density within the soil matrix (Falciglia et al., 2016). Bulk densities of different soil textures in the Niger Delta of Nigeria are reported to influence their water-holding capacities (Kamalu et al., 2002), hence they would be expected to exhibit different responses to microwaves. This chapter aims to describe the different properties of soil and how it influences microwave heating. The effect of increasing microwave power on oil removal from various soils is also investigated.

4.2. Soil characterisation

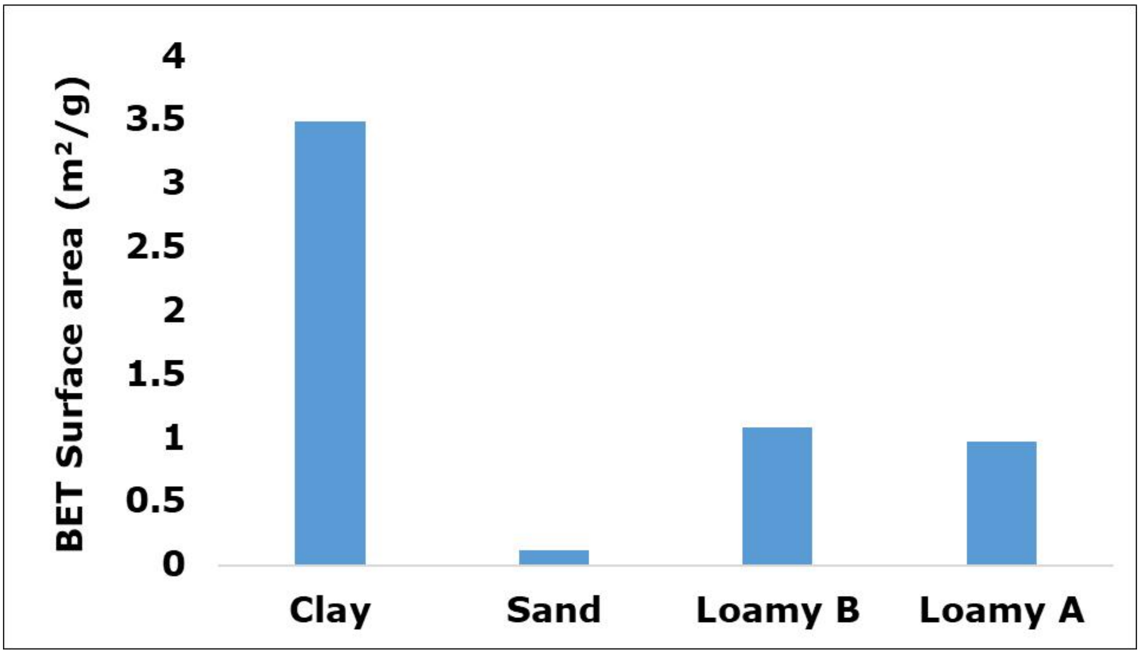


Figure 4.1. Plots of BET specific surface area for four texture based soils

Figure 4.1 shows value obtained from Brunauer Emmett Teller (BET) analysis. The properties of the solid phase largely determine the formation of the soil structure. Soils vary widely in their reactive surface because of differences in mineralogical and organic composition and in their particle-size distribution (Carter et al. 1986) and the measured surface area is largely dependent upon the amount of particle surface exposed (Mortland, 1954). Soil surface area is 0.5 m^2 /g for sand, Loamy A and B are (1 and 0.8) m^2 /g while clay soil had the highest area of 3.5 m^2 /g. They differ substantially in specific surface areas, although both loamy soils had close values. The surface properties of the soil solid phase influence the quality of the resulting soil aggregates and interaction of the solid surface with water. Other properties influencing the hydrophilicity of the soil surface and response to microwave heating can be mineralogy, as discussed below.

Results for mineral composition analysis of the contaminated soil using XRD (X-ray diffraction) can be seen in Figure 4.2. Quartz was dominant in the soil, which is hydrophobic though other agglomerates contain a blend of minerals such as kaolinite and montmorillonite bound together by clay except for sandy soil. Non-swelling clays, such as kaolinite, have only external surfaces, whereas swelling clays like montmorillonite have many internal and external surfaces. The combination of external and internal surface areas may vary simply because of the mixed layer minerals and the variations in clay mineralogy.

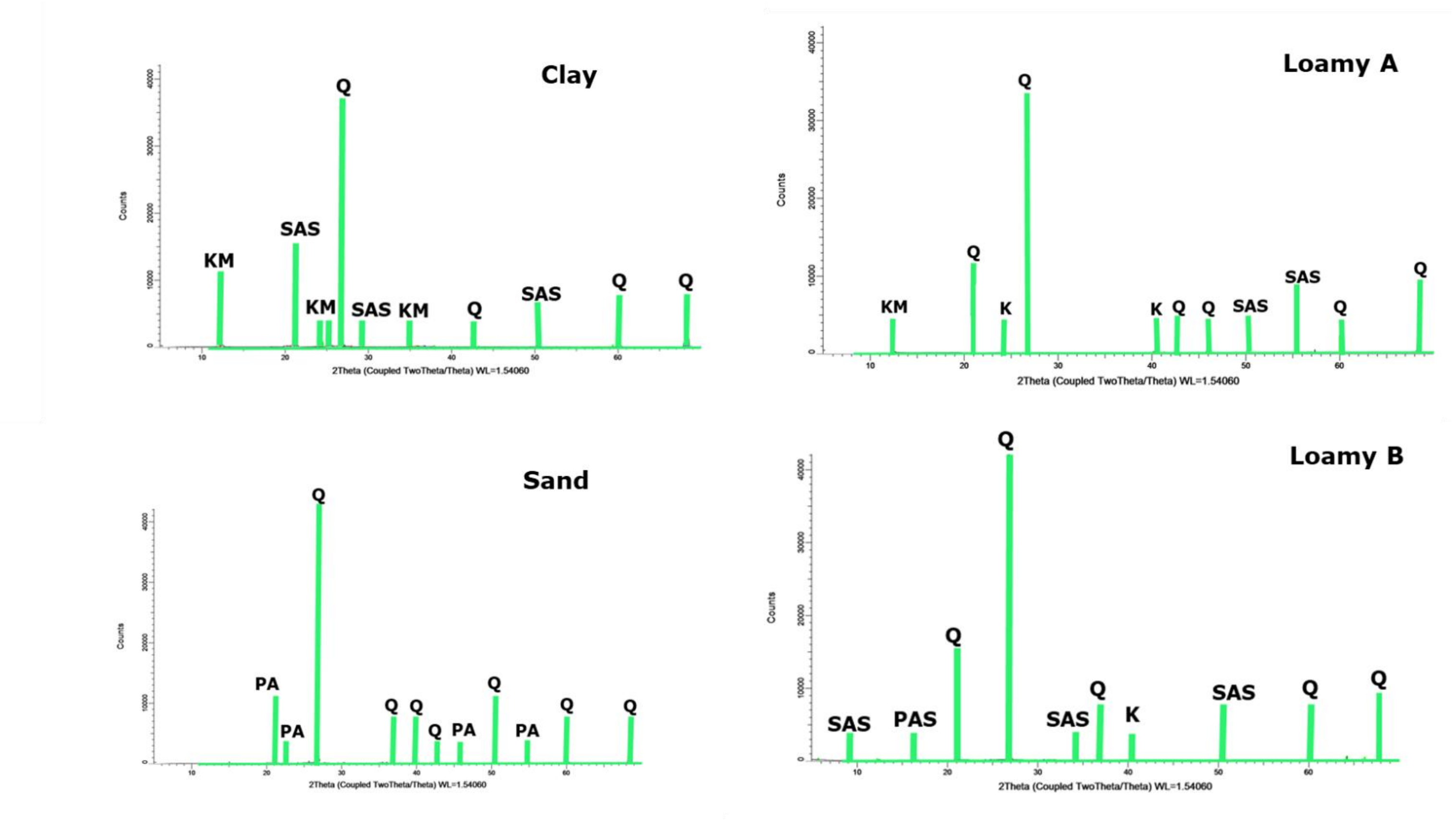


Figure 4.2. XRD showing the major mineral components of soils; KM-Kaolinite-montmorillonite, SAS-Sodium Aluminum Silicate; K-kaolinite; Q-quartz; PA-Aluminum Silicate; PAS-Potassium Aluminum Silicate

Soils with an initial oil and water content, TOC, and porosity as shown in Table 4.1 were used for these experiments.

Table 4.1. Soil and extracted oil properties

Soil type	Water content (%)	Bulk density (g/cm^3)	Skeletal density (g/cm^3)	% Porosity	Rawsoil (Untreated soil) TOC (%w/w)	Extracted oil (%w/w)	Residual C (%w/w)	C_{17}/Pr	C_{18}/Py
Loamy A	5.0	1.11	2.32	0.52	7.50±0.4	6.5±0.80	1.20	0	0
Loamy B	3.3	1.19	2.37	0.50	5.65±0.05	5.06±0.80	0.61	0.57	1.23
Sand	1.6	1.51	2.59	0.41	1.60±0.04	1.34±0.04	0.30	0.54	1.69
Clay	12.6	1.34	2.59	0.49	1.76±0.06	1.58±0.06	0.16	0.58	1.11

***Residual C= TOC after soxhlet extraction; *soil carbonate is less than 1 % of TOC**

*C_{17}/Pr: ratio of carbon-17 to pristine: C_{18}/Py: ratio of carbon-18 to phytane

Table 4.2. Particle size distribution of clay, sand and loamy soils

Particle Size (µm)	**% Volume Fraction**			
	Clay	Sand	Loamy B	Loamy A
2630	0	0.56	0.61	0.82
800-1000	1.36	8.41	6.75	8.65
300	27.82	53.32	22.61	24.82
212	17.09	23.21	34.46	33.38
106	24.09	12.94	26.10	25.25
45	14.50	1.55	6.91	6.20
20	6.56	0	0.86	0.69
<20	8.56	0	1.71	1.39

4.3. Dielectric properties of soils

Dielectric property measurements are vital to know how materials will respond to microwaves (MW). Triplicates measurement of dielectric loss factor was measured over the temperature range of 15-750 °C for various soil types, and the results are presented in Figure 4.3. Error bar shown in the graph represent standard deviation from triplicate analysis. At temperatures below 100 C, soils' dielectric loss factor is relatively high, indicating that the soils are good absorbers of microwave energy under these conditions. This is due to free moisture within the soil samples, and Table 4 1 shows the water content to be 12.2 %, 5 %, 3.3 %, and 1.6 % for clay, loamy A, loamy B and sandy soils. Between room temperature to 100 °C dielectric loss for soils ranged as 0.34-0.16 for clay soils, 0.15-0.10 for loamy A soils, 0.03-0.018 loamy B soils and 0.0063-0.004 for sand soils. The soils become much less absorbent as the free water is lost to evaporation and the remaining mineral matter and organic contaminants are relatively transparent to microwaves at 100 °C. Clay and sand soil exhibits a dielectric loss peak value of 0.35 and 0.0069 at room temperature, compared with 0.5, and 0.21 for the loamy A, loamy B soils, respectively at temperature above 600 °C, possibly due to the percentage composition of polar groups in the crude oil (Figure 4.6) (Zhang et al., 2019). At higher temperatures, the loss factor increases with increasing temperature for both soils (loamy A and loamy B), which is likely due to the decomposition of the organic contaminants. The presence of polar groups could promote loss mechanisms, making the soil more microwave absorbent at these temperatures. The loss factor for the loamy soil increased with temperature above 500 °C. The same behaviour is seen for other soils. Sandy soil has the lowest dielectric loss from room temperature to 750 °C. The rapid increase in loss factor for loamy compared to other soils could also be due to more carbonaceous material being formed due to the higher oil content. In this work, the main factors responsible for the difference in magnitude of dielectric loss factors are water (Robinson et al., 2014), polar organic compounds and carbon materials formed from oil. Clearly, the dielectric properties of the soil will continually change with time and on the extent to which the soil is treated and the contaminants decomposed or removed.

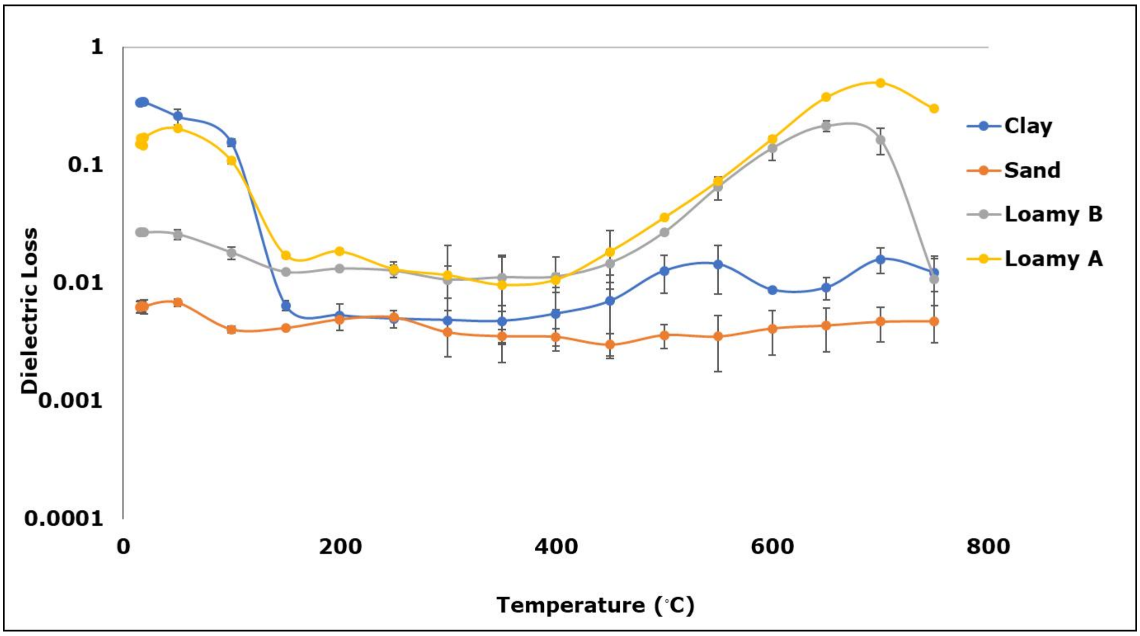


Figure 4.3. Dielectric loss for clay, loamy A, loamy B and sand soil at 2.5 GHz as a function of temperature

The dielectric constant measures the ability of soils to be polarized. As seen in Figure 4.4. Mean values from the measurement were plotted against temperature and standard deviation from triplicate measurement is used to estimate the error bar. Dielectric constant in the first 150 °C ranged as clay > loamy A > loamy B > sand, likely due to the variation in soils moisture content (Table 4.1). As the temperature increases above 450 °C a sharp increase in dielectric constant is observed for loamy soils due to the high percentage of polar groups present in the soils. This clearly shows how soil physical properties such as moisture and texture cause variation in dielectric properties. Loamy spoils with similar texture showed similar dielectric response over the range of temperature 200-750 °C. Nevertheless, the slight variation between both soils is attributed to differences in their moisture and oil content. Hence, dielectric constant can be used to predict soil response to microwave heating. The data shown in Figure 4.3 reveals that microwave heating of sandy soil may pose challenges compared to other soil types.

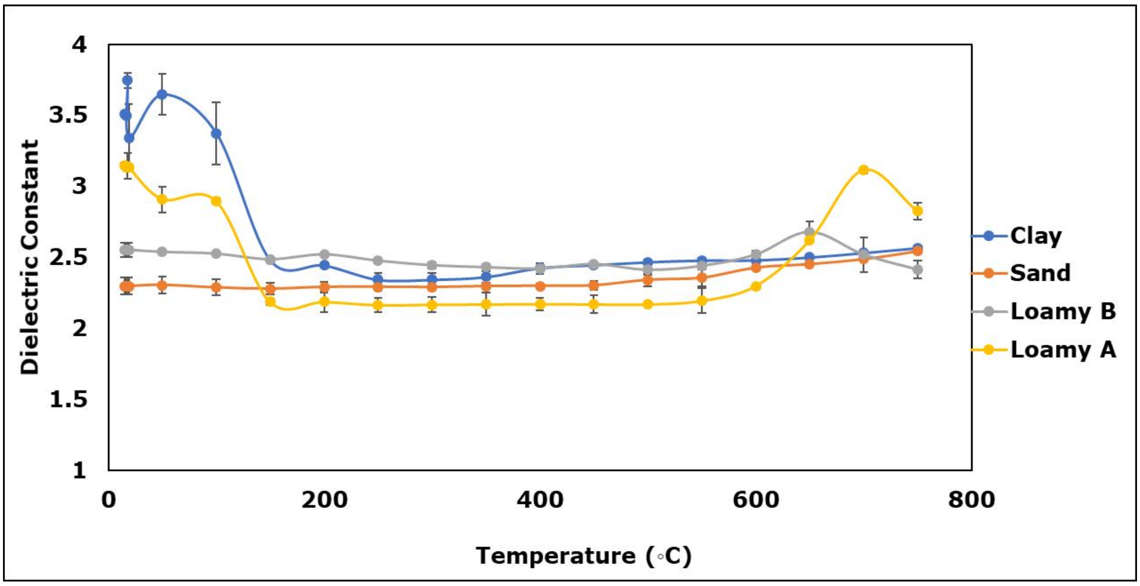


Figure 4.4. Dielectric constant of clay, loamy A, loamy B, and sand soil at 2.5 GHz as a function of temperature

The dielectric constant of soil is strongly dependent on soil moisture and soil texture, and moisture in soil significantly affects the dielectric properties of soil. Dielectric constants of solid particles, like sand, silt, and clay present in soils are essential in estimating the level to which they will absorb microwaves. Dielectric constant for clay soil has the highest value at room temperature while sand soil has the least response. At temperature greater than 600 °C loamy A and loamy B soils showed good response (Figure 4.4). The data shown in Figure 4.3 and 4.4 reveals that microwave heating of sand soil may pose challenges compared to other soil types.

4.3. Hydrocarbon composition of contaminated soils

The composition of hydrocarbons in oil extracts was compared by GC-MS, where Figure 4.5 (a and b) shows the total and single ion chromatograms (m/z 71) for extracted oil from soils. The latter highlights the linear and branched-chain alkanes present. The distribution of alkanes for the clay, loamy B, and sandy soils is very similar. The oils only differ in the intensity of the unresolved mixture arising from aromatic and polar compounds or from potential biodegradation. However, the preservation of n-alkanes across the range C_{15} -C_{35} for clay, loamy B and sand soil extract showed minimal biodegradation. The presence of n-C_{17}/Pristane and n-C_{18}/Phytane ratios gives information about the deposition environment. The ratios together with other index are used to indicate maturity of the source rock for oil generation (Peter & Moldowan, 1993). However, the ratios alone in this work (Table 4.1) is not enough to give useful information regarding level of maturity of the source rock.

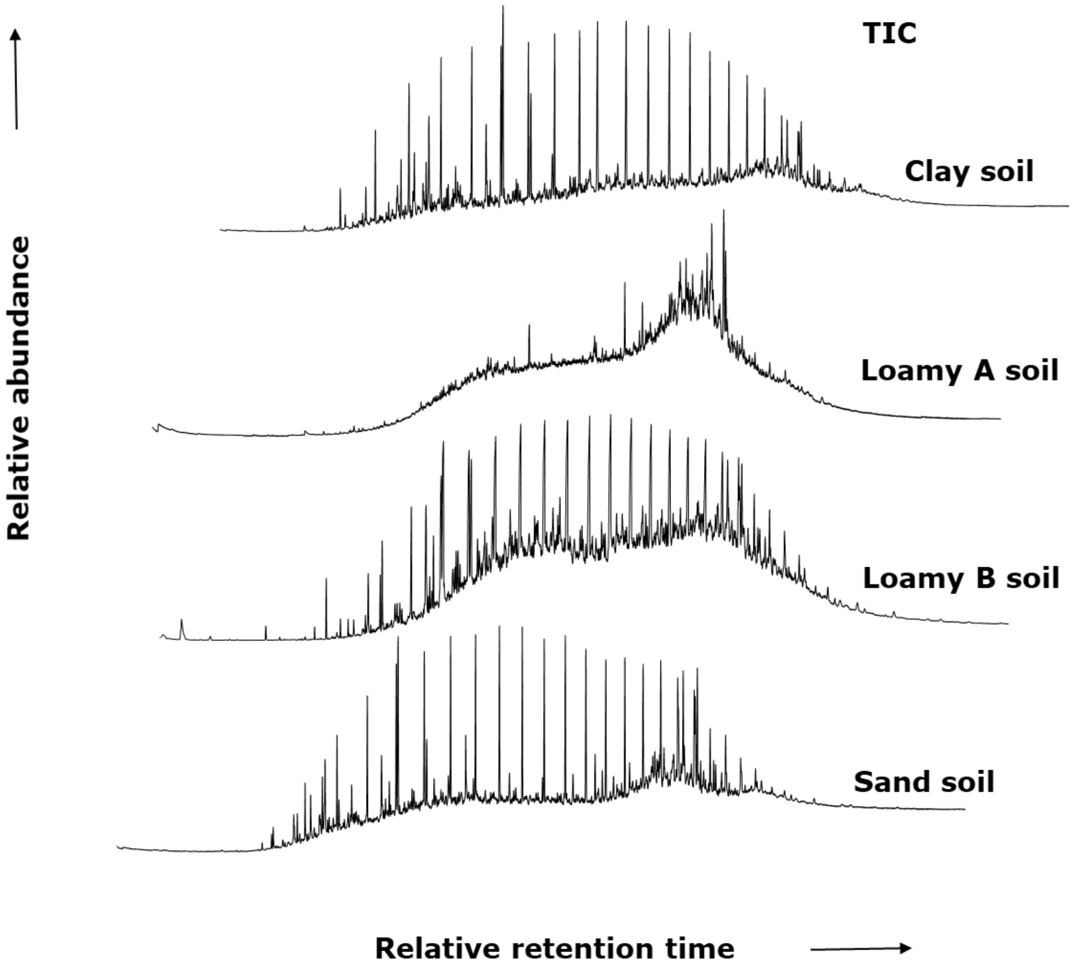


Figure 4.5a. Total ion chromatograms for oil recovered from soils through solvent extraction represent oil causing environmental pollution

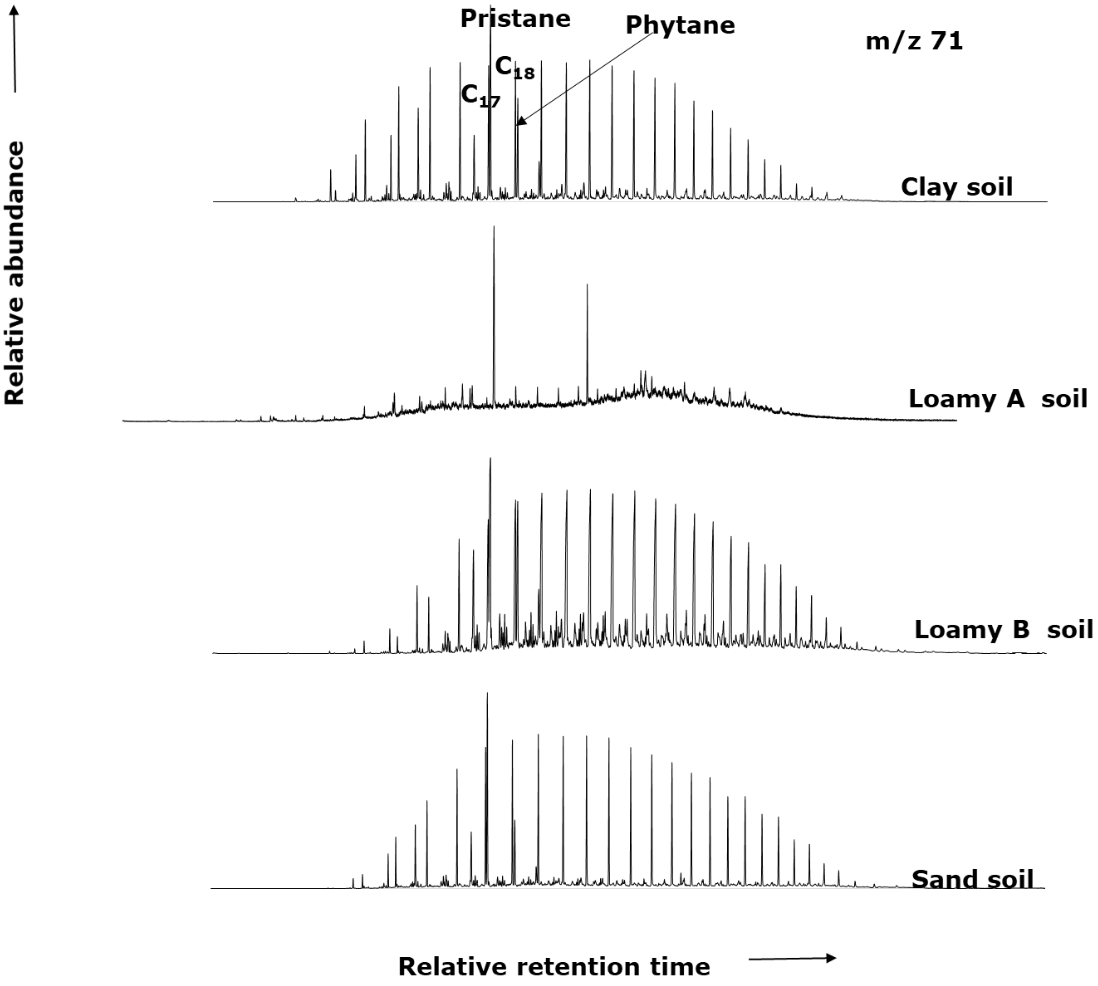


Figure 4.5b. Single ion chromatograms (m/z=71) for oil recovered from soils through solvent extraction represent oil causing environmental pollution

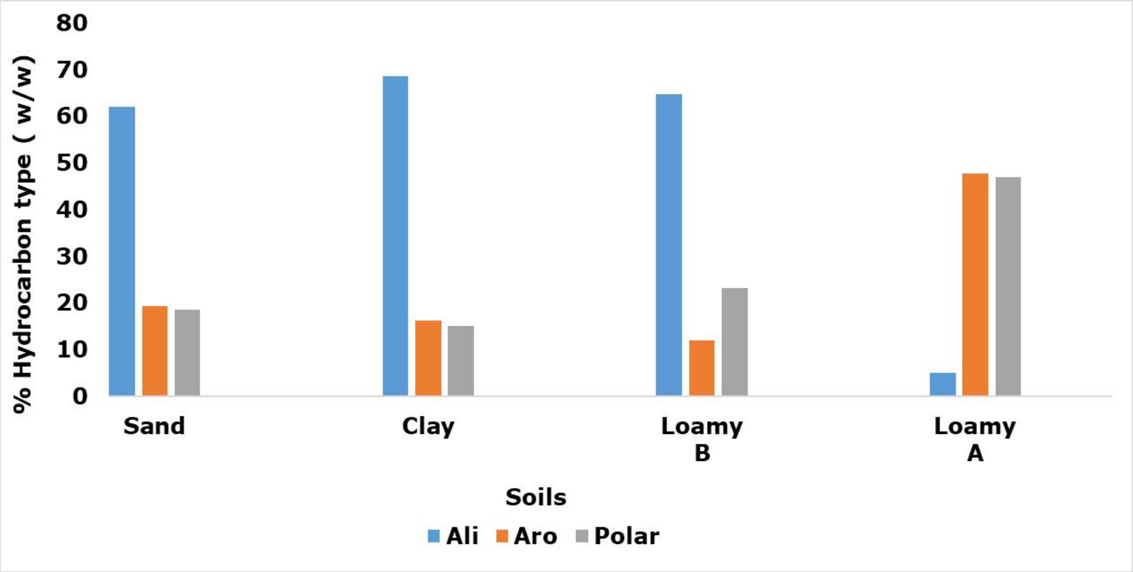


Figure 4.6. Yields of products obtained from column fractionation of crude oil extracts from soils. Ali: Aliphatic, Aro: Aromatics and Polar: Polar groups and resins

The yields obtained from the fractionation of polluting oil in soils can be seen from Figure 4.6. Loamy A soils contains less of aliphatic hydrocarbons which is may be due to degradation and loss of light ends hydrocarbons (Figure 4.4). Oil spills in soils undergo, microbial degradation therefore some of the hydrocarbon fractions are lost over time. The degradation susceptibility to microbial breakdown is as follows: linear alkanes> branched alkanes >aromatics with low molecular weight > high molecular weight polycyclic aromatic hydrocarbon (Shi et al.,2020).

4.5. Effect of microwave heating time and on oil removal from different soil types

Microwaves are known to interact differently with different soil types and soils with different physical characteristics such as water content and bulk density. Soil porosity is a significant factor influencing the water-holding capacity, and soil texture has been shown to influence the decontamination process and contaminant removal efficiency (Falciglia et al., 2016). Texture also affects sample permittivity and subsequent microwave penetration, and hence the strength of the electric fields and power density within the soil matrix (Falciglia et al., 2016). Bulk densities of different soil textures in the Niger Delta of Nigeria are reported to influence their water-holding capacities (Kamalu et al., 2002), hence they would be expected to exhibit different responses to microwaves. With constant soil sample mass (20 g), nitrogen gas flow rate (2 l/min) and cavity power (0.8, 1, 2 and 3 kW), the effect of sample irradiation time up to 420 seconds was studied. The cavity power of 6 kW was used as this allowed the maximum range of treatment times to be studied. A typical representation of the rig is explained in Chapter 3. Table 4.3shows the sample mass after microwave treatment for 0.8 kW power, for 10 experimental runs. The data shows good repeatability of the experiments. Percentage relative standard deviation (RSD) ranged from 3.92 to 7.45.

Standard deviation of triplicate is determined to examine the error in oil removal at 0.8, 1, 2 and 3 kW microwave power input.

Table 4.3. Weight losses in grams for repeat microwave experiments 0.8 kW microwave power for 120 seconds

Experiment number	**Loamy A**	**Loamy B**	**Clay**	**Sand**
1	1.43	0.55	0.48	0.29
2	1.62	0.53	0.55	0.30
3	1.75	0.57	0.51	0.33
4	1.54	0.52	0.49	0.35
5	1.48	0.58	0.50	0.29
6	1.50	0.51	0.49	0.32
7	1.66	0.55	0.52	0.30
8	1.38	0.59	0.51	0.29
9	1.56	0.50	0.52	0.31
10	1.43	0.56	0.50	0.31
Mean	1.54	0.55	0.51	0.309
Standard deviation	0.115	0.030	0.02	0.0196
% RSD	7.45	5.45	3.92	6.34

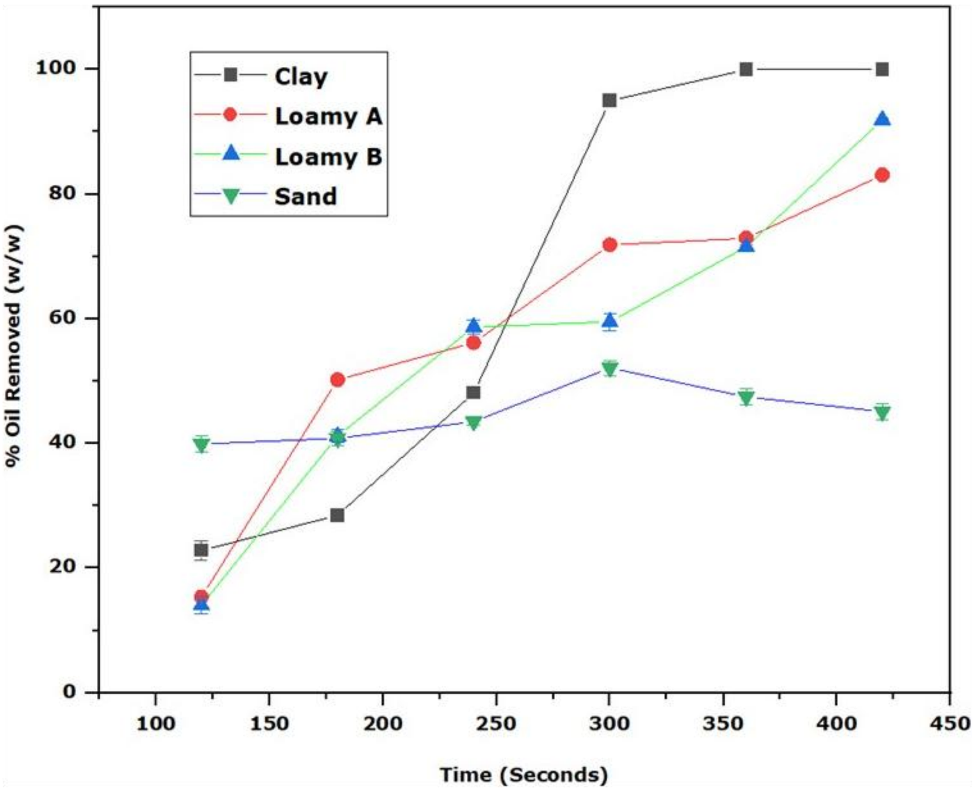


Figure 4.7. Variation of oil content vs. treatment time input for clay, loamy A, loamy B and sand soils treated using .0.8 kW for all soils

*Error bar represent standard deviation from triplicate oil extraction after MW experiment.

The percentage oil removed samples are shown in Figure 4.7 with respect to the sample treatment time. Contaminated soils were subjected to a MW power of 0.8 kW over 120 to 420 seconds. After 360 seconds, virtually all the oil was removed from the clay soil (Figure 4.7) compared to 72 % for the loamy A and loamy B soil and 48 % for the sandy soil. Further heating of the soils; loamy A and Loamy B soils for 420 seconds led to 83 and 93 % oil removal. Maximal oil removal was observed with a microwave power of 0.8 kW at 420 seconds. This suggests that increasing microwave time leads to increasing oil removal. This was not the case for the sandy soil, where little change was obtained after 200 seconds. It is apparent for sandy soil that increasing irradiation times above 360 seconds are unlikely to make significant gains in further reducing residual oil levels. This can be explained by considering the dielectric properties of the sandy soil. The ranking order achieved is entirely consistent with the dielectric properties reflecting the free moisture contents (Table 4. 1, clay > loamy A> loamy A > sand).However, oil removal from sandy soils showed good removal in the first few seconds as seen for various power input. As the moisture becomes used up as a result of fast drying rate in sand soil. Hence, depletion of moisture as microwave absorption. Other soil types hold water longer due to the capillary attraction of the tiny spaces between numerous clay particles and strongly bound water/hydroxyl groups present in clay. Some small microwaves phases present in the some samples (kaonite). Heating can lead to the formation of carbonaceous material if the oil phase starts to decompose, which enhances MW absorption and promotes more oil removal. For clay soils, inter-crystalline layers can trap water molecules that penetrate the layers. Their high porosity values with low bulk densities (Table 4.1) increase the contaminant diffusion phenomena during microwave heating. In comparison to literature Liu and Yu (2006) achieved a removal efficiency of 90 % for PCB's contamination over 15 mins. Yuan et al. (2006) achieved a removal efficiency of 94 % for 10 mins. Chien (2012) obtained 75.6 % to 98.4 % C_{10} to C_{40} organics removal in field conditions for 3.5 h of treatment water as a susceptor. Dawei et al. (2009) used carbon fiber as a susceptor to remove TPH in Soil and achieved 700°C within 4 min by adding 0.1% by wt of carbon fiber with an MW power of 800 W. Liu, and Yu (2006) achieved a removal efficiency of 90 % for PCB's contamination over 15 mins. Yuan et al. (2006) achieved a removal efficiency of 94 % over 10 mins. Similarly, most of the literature involves artificial contamination of soil under controlled conditions; hence, favourable target concentrations have been achieved within a shorter time. Li et al. (2009) achieved

99 % crude oil removal at optimum condition by seeding the contaminated soil matrix with 0.02 g of carbon fibre as microwave absorber carbon-rich additives with power for 240 seconds. Sivagami et al. (2019) reported TPH removal efficiencies (%) of 41.25, 87.77, and 91.18 at 300, 450, and 600 W after treatment time of 3600 seconds from heavy fuel oil contaminated Soil. Spent graphite was used as a microwave absorber. Cho et al (2020) worked on artificial diesel contaminated soil samples were treated at a power of 800 W for different irradiation times. The removal efficiency of the coarse soil reached 91.1 % at 15 min.MW heating could be a better choice when compared to thermal heating due to high temperatures achieved at lower operating power and the lesser time required for the remediation process. The percentage oil removal increased for soils with higher BET surface area (Figure 4.1) may be attributed to the rapid evaporation of contaminants from the soil particle surface. Clay soil had better removal at all MW power and heating time probably due to higher surface area of the soil particles. In conclusion, it can be seen from Eq. (4.1).

$P=2\pi f\varepsilon_o\varepsilon''E^2$ [4.1]

P = Power density (Kw/m^3)

F =Frequency of electromagnetic wave (Hz)

ε_o = Permittivity of free space (8.85 x 10^{-12} (F/m)

ε''= Loss factor (ability to transfer microwave energy into heat)

E (v/m) = Electric field strength with the soil which depends on the power of the microwave applied

That, in addition to the dielectric properties of the materials, the level of the microwave energy absorbed depends strongly on the electric field magnitude, which relates to the microwave power. Oil removal is strongly influenced by soil properties such as water content and also thermodynamic properties of the soils, as denser soil could permits less microwave penetration.

4.5. Effect of microwave power

Contaminated soils were further irradiated with different microwave power of 1 kW, 2 kW and 3 kW. Results are presented below.

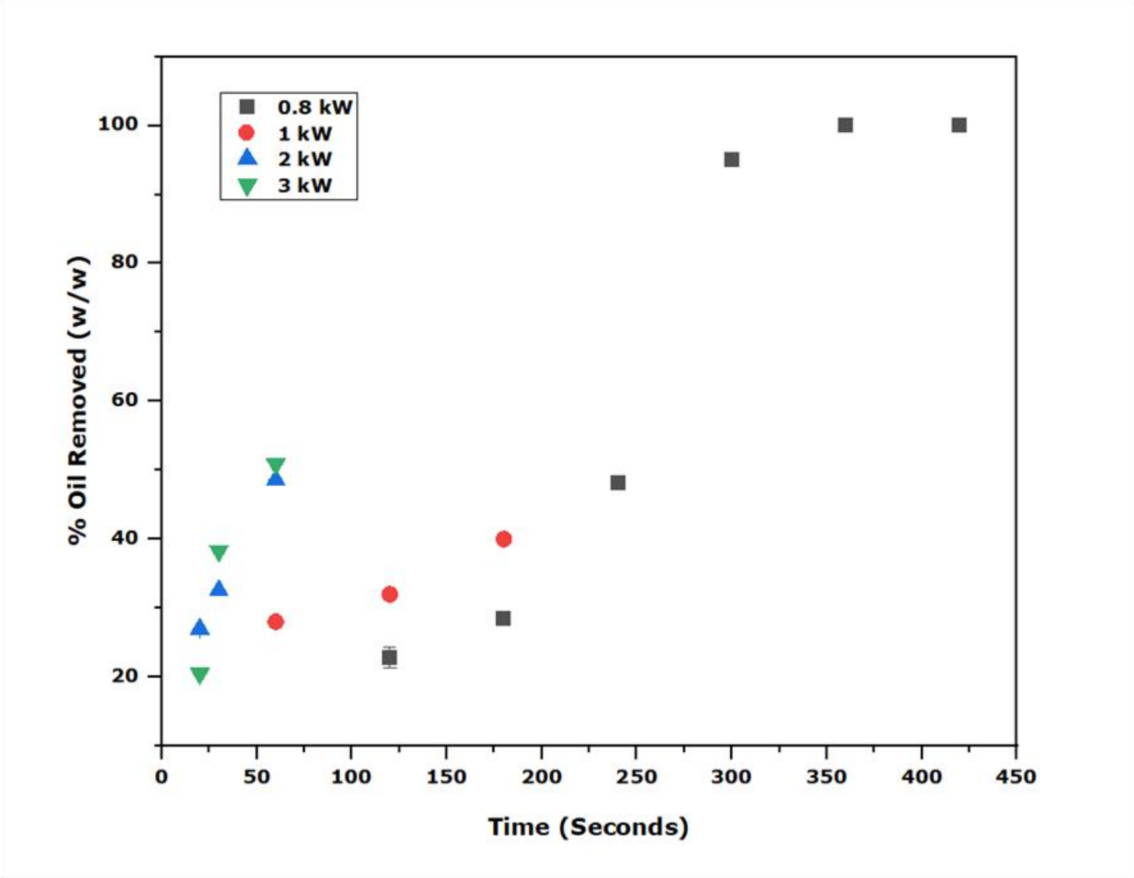


Figure 4.8. Oil removal plotted against heating times for clay soil treatment at various power input (20 g sample mass)

*Error bar represent standard deviation from triplicate oil extraction after MW experiment.

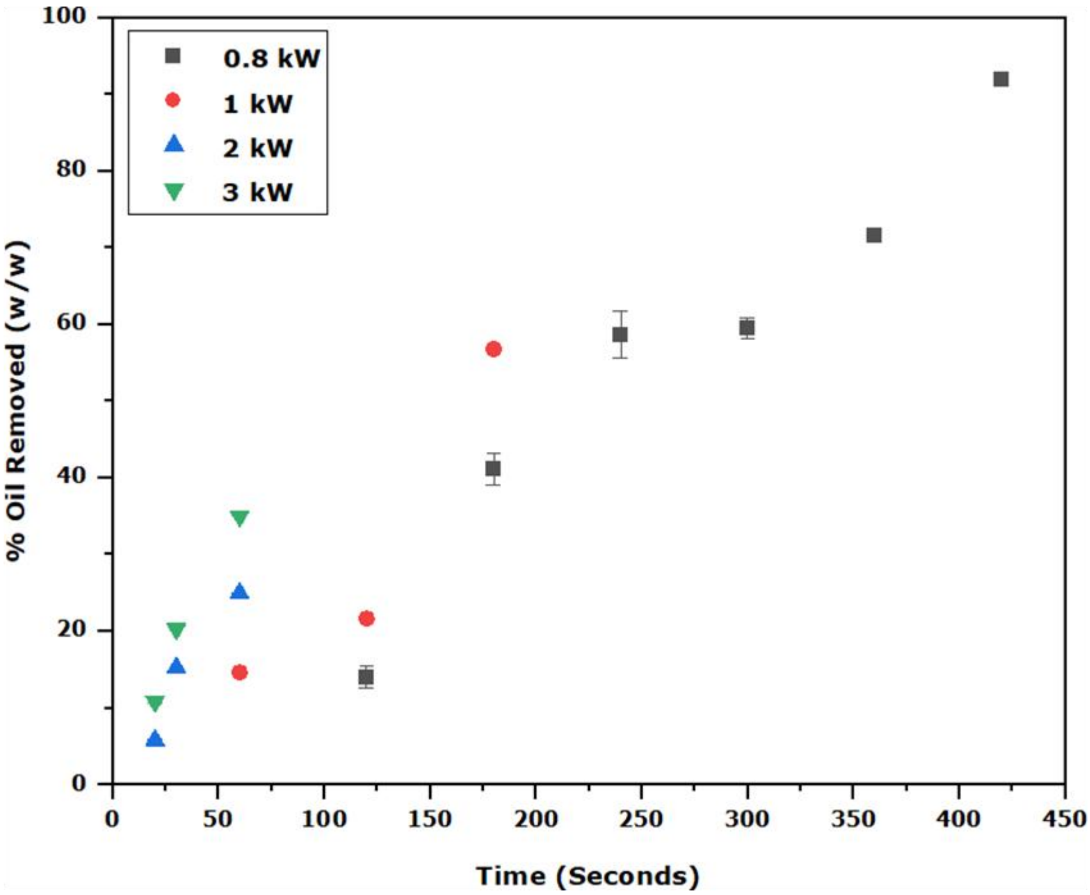


Figure 4.9. Oil removal plotted against heating times for loamy A soil treatment at various power input (20 g sample mass)

*Error bar represent standard deviation from triplicate oil extraction after MW experiment.

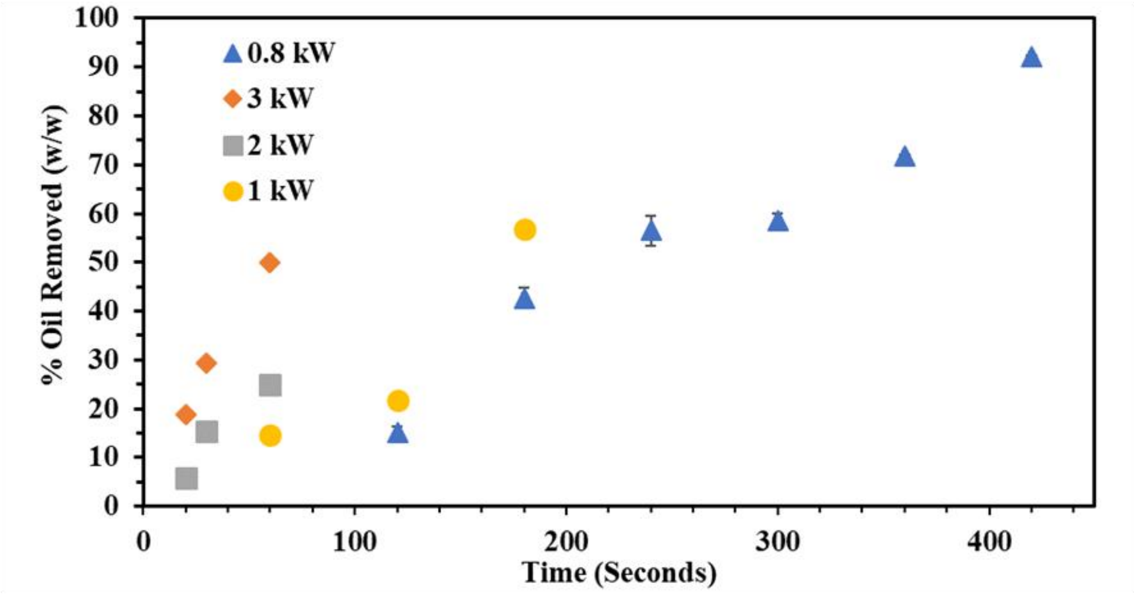


Figure 4.10. Oil removal plotted against heating times for loamy B soil treatment at various power input (20 g sample mass)

*Error bar represent standard deviation from triplicate oil extraction after MW experiment.

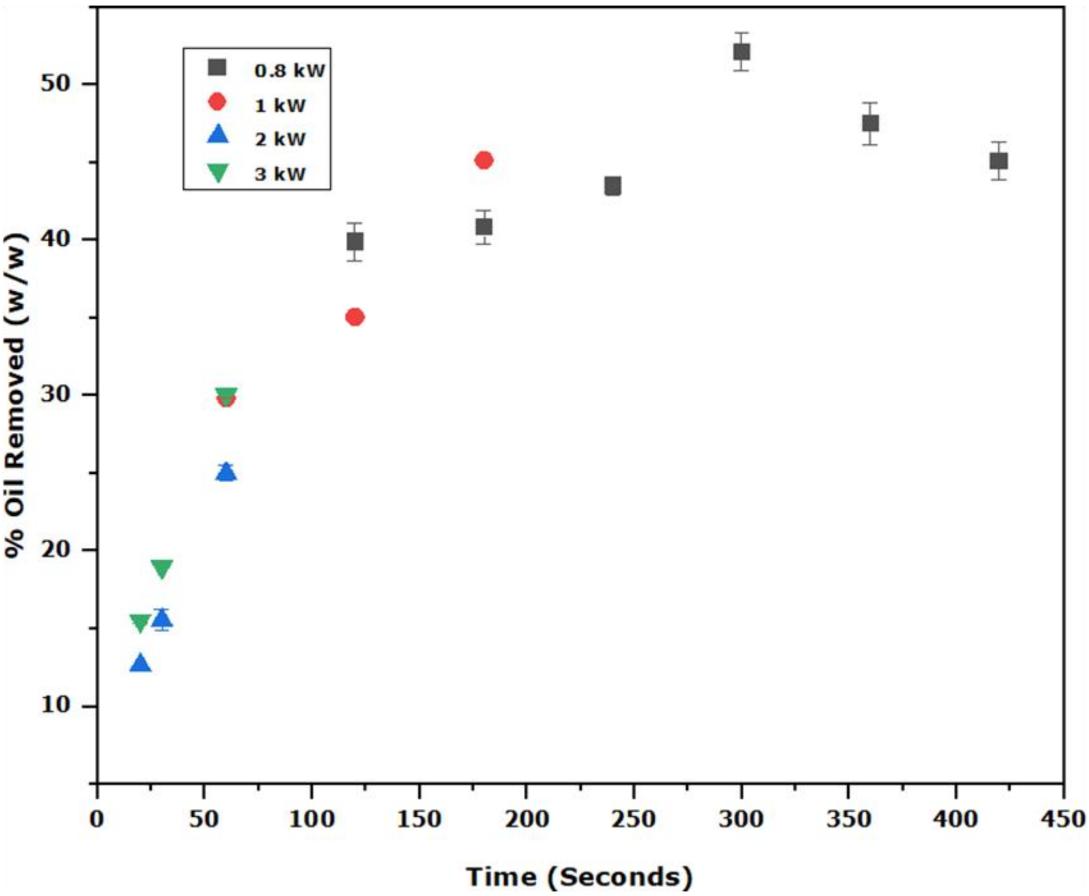


Figure 4.11. Oil removal plotted against heating times for sand soil treatment at various power input (20 g sample mass)

*Error bar represent standard deviation from triplicate oil extraction after MW experiment.

This experiment is conducted to ascertain how the variation of MW power will influence the removal of polluting oil present in the soil. The investigated power series was 0.8, 1, 2, and 3 kW, and the results are displayed in Figures 4.8-4.11. It can be seen that higher MW power led to higher remediation efficiency. It was also observed that higher power corresponds to a higher reduction of oil from soils the oil values with increasing MW power at a constant heating time of 20 seconds for power input of 2-3 kW. Oil removal ranged from 26- 28 % for clay soil (Figure 4.8), 3-5 % for loamy A soils (Figure 4.9), 6-11 % for loamy B (Figure 4.10) soils and 10 -21 %

for sand (Figure 4.11). At treatment time of 60 seconds with a power input of 1, 2, and 3 kW oil removal sand 28 %, 48 % and 50 % for clay. For loamy A 5 %, 34 % and 41 %. Loamy B 14 %, 25 % and 50 %. While for sand soil 18 %, 25 % and 41%. Oil removal increased with MW power input of 1-3 kW at a constant of treatment time of 60 seconds (Figure 4.11).

When studied at 0.8-1 kW microwave power at constant time of 120 seconds. Oil removal for clay soil is 22-38 % (Figure 4.8), loamy A soils 15-14.6 %, loamy B soils 15-22 % and sand soil 40-25 %. Heating contaminated soils at high power for a short time leads to more efficient oil removal than heating for low power at a longer time. Higher power microwave equipment will result in higher oil yields and allow much higher levels of removal than lower power systems. This finding will underpin any attempt to adopt microwave heating at a commercial scale. The percentage removal of oil in soil increased for 0.8, 1, 2 and 3 kW. These results reveal that the remediation of crude oil contaminated Soil by MW heating can be enhanced using different microwave power inputs. The maximum power used for the experiments was limited to 3 kW to prevent the risk of arcing during and formation of soot on the reactor wall. The effect of MW power plays a significant role in the remediation of contaminants from the soil. Besides the nature of the material (dielectric properties) being treated, the heat build-up within the soils depends as well as on the microwave power applied to the sample. Higher microwave powers can supply more energy to the soil, resulting in improved oil removal. Microwave power is a crucial factor because it is the sole energy source in the reaction system. The relationship between MW power and temperature is given as:

$$\frac{\Delta T}{\Delta t}=\frac{P}{\rho C_p} \qquad [4.2]$$

Where

P = Microwave power

T= Soil temperature

T= Time

C_p= Specific heat capacity

In comparison with literature Pietro et al (2013) in their work reported that an increasing operating power applied and moisture significantly influences the contaminant removal of diesel contaminant from soil. The moisture content in soil has a major effect on the final temperature reachable during MW heating. Minimal contaminant concentrations were achievable by applying powers higher than 600 W for a treatment time longer than 60 min. Treatment times shorter than 10 min resulted in a soil temperature of about 100 °C. The oil removal efficiency of 95 % was reached for the moist soils treated at 1,000 W for 60 min. Falciglia and Vagliasindi (2015) remediation of diesel polluted soils results clearly showed removal efficiency higher than 70 % are not achievable applying a minimal power of 250 W. For sandy soils, good efficiency higher than about 90 % was also reached at a power higher than 600 W for a time longer than 60 min or at power higher than 1000W for a time longer than 30 min. Sivagami et al. (2019) reported that for an increase in the magnitude of MW power from 300 to 600 W, TPH removal (%) was enhanced by approximately 50 %.

The extent of microwave distribution with the soil matrix can be measured using the penetration depth. It is defined as the distance from the surface of the material at which the incident microwave power reduces to 1/e (37%) of its value at the surface.

4.6. Penetration depth

The penetration depth is estimated as

$$D_p = \frac{\lambda\sqrt{\varepsilon'}}{\varepsilon''} \qquad [4.1]$$

Where $\lambda$is defined as the free space wavelength with value of 0.122 m at 2.45 GHz, ε' is the dielectric constant and ε'' is dielectric loss factor. Empirically, microwave soil penetration is dependent on soil properties such as water, oil and organic matter content. However, in this work the dielectric properties of the soil are used as an estimate. The penetration depth for clay, sand, loamy A and loamy B soils was estimated based on soil dielectric properties, and this data is shown in Figure 4.12. At two stages of temperature penetration was low. The first stage occurred between 20 – 100 °C for all soils due to the present of free water. The second stage occurred at temperature excess of 700 °C possibly to the presence of carbonaceous residue for the soils. Between this two stages of temperature, penetration depth is high as free water molecules evaporate with insignificant decomposition of soil organic material taking place. Soils (clay, loamy A and loamy B) with high moisture content have lowest penetration depth. The relationship between the penetration depth and temperature gives useful engineering information regarding the geometry of the reactor used during microwave treatment of soils. The quartz reactor used in this study has diameter of 0.032 m and sample bed depth of 0.05 m. This implies bed geometry parameters are less than the calculated penetration depth. Hence, penetration depths do not have any effect in the soil treatment (Figure 4.12).

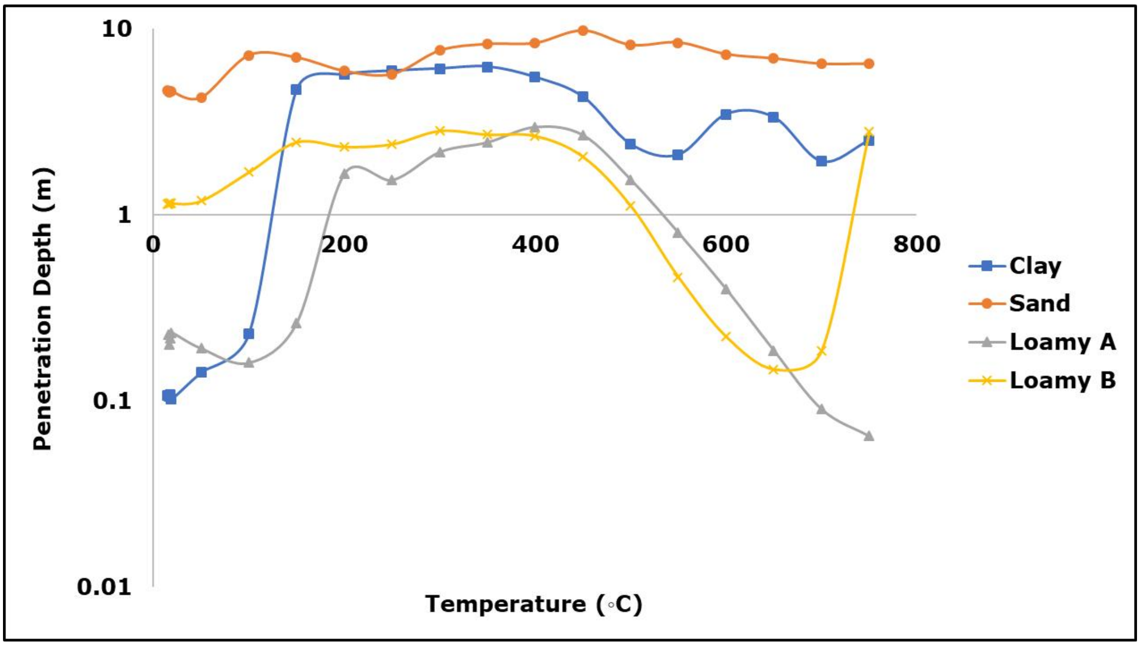


Figure 4.12. Microwave penetration depth of clay, loamy A, loamy B and sand soil

In conclusion, at higher power densities the following apply:

(1) Higher power densities equate to lower processing times and therefore heat losses to the surrounding.

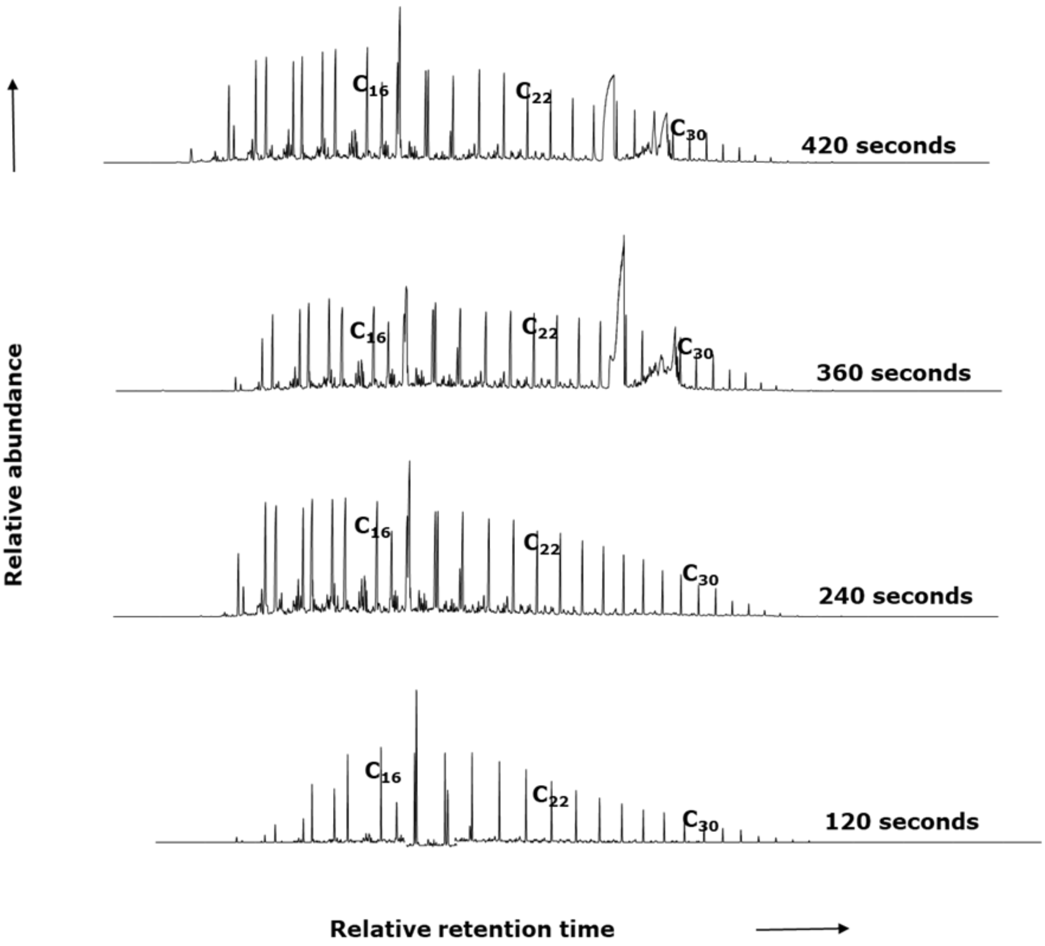
(2) At constant sample mass, when microwave power increases, the time required for oil removal decreases.

(3) The two loamy soils had similar percentage oil removal at power input studied, and different from other soils. Buttressing the fact that soil properties affects MW absorption is being influenced soil type. Hence, extent of oil removal.

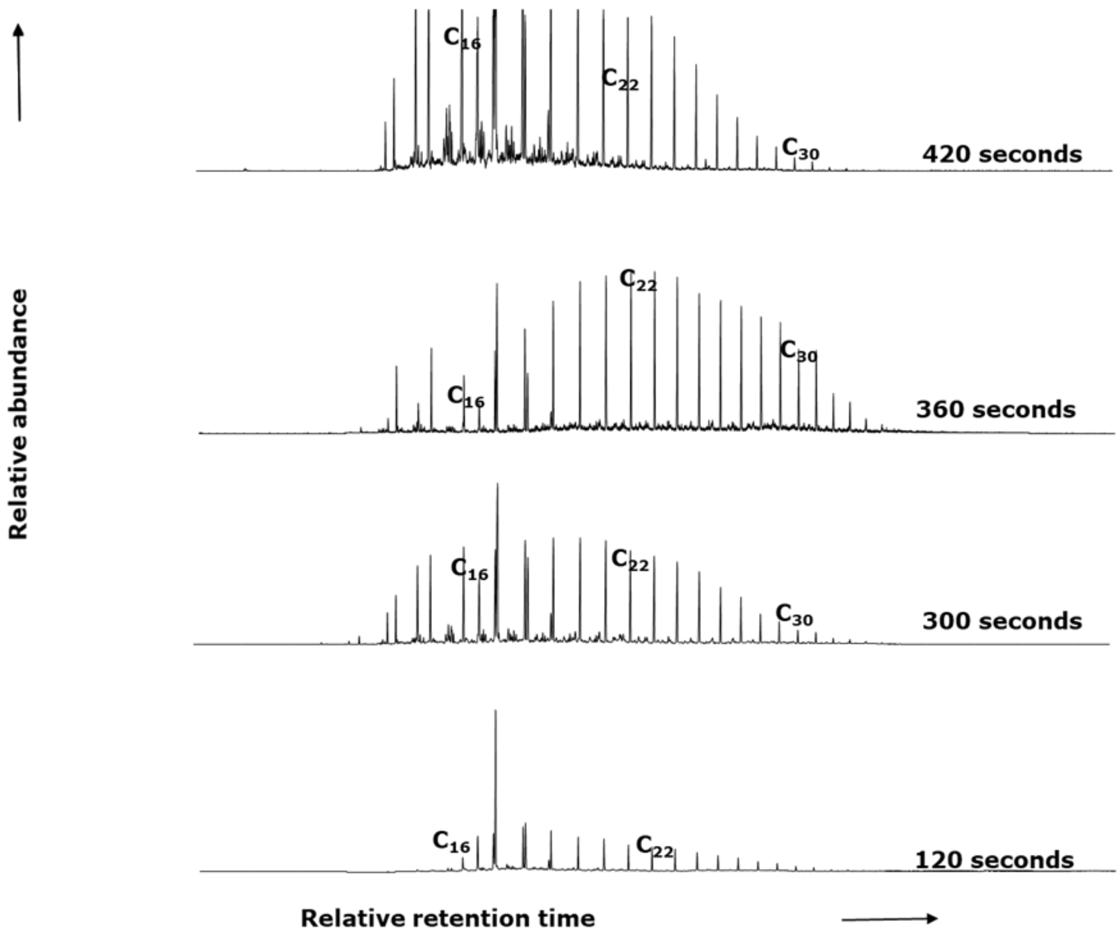
4.8. Compositions of the oils released by microwave treatment

The condensed oil from microwave heating for 420 seconds was collected to compare with the initially extracted oils. Figure 4.13 shows the TICs and m/z 71 SICs for the oils released from the three soils. The composition of the oils released by microwave treatment and the extracted oils are very similar (Figure 4.5b and

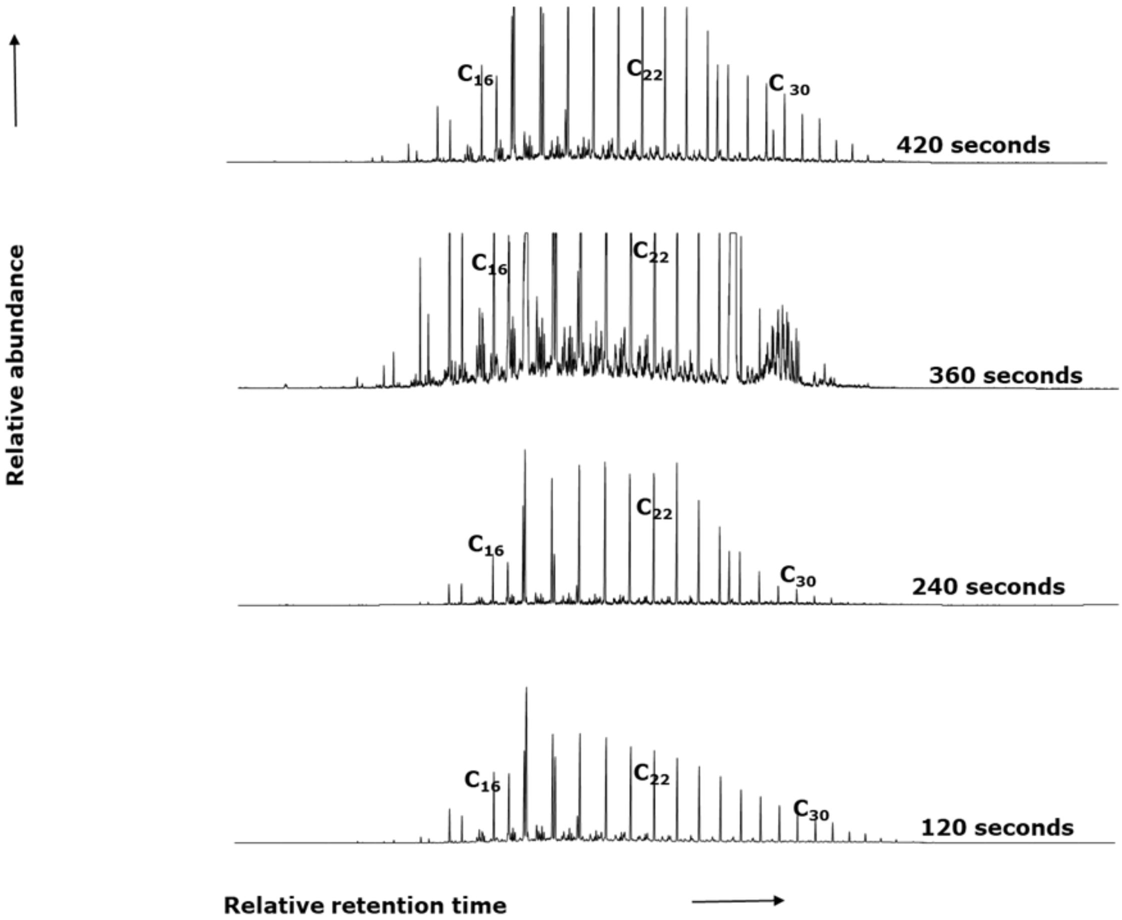
4.13). In contrast to the clay and loamy soils, the oil released from the sandy soil is lower boiling than extracted oil, reflecting the much lower yields. Since there is no formation of new carbon peaks in soil, it can be summarised that thermal desorption is the principal mechanism that occurred during the microwave heating process for all soils, and suggesting that there is no significant decomposition of the oil. In practical terms, the differences in composition between the original and recovered oils are likely to be insignificant. It also indicate that the microwave radiation has little impact on the overall oil composition, and that the predominant oil removal mechanism takes place due to thermal desorption rather than by pyrolysis. However, the distribution of alkanes in the vaporised oil was different at each treatment time with a noticeable reduction in the amount of alkanes heavier than C_{12}. This resulted, as expected, in a shift in the alkane distribution shifting to the left leading to a lighter oil mixture. This strongly suggests that there was no appreciable thermal degradation during oil release and desorption is the dominant mechanism for oil removal. The TICs of the original, product and residual oils are virtually identical. A higher concentration of lighter components is evident in the product oil from comparison of the peak values at low elution times. Similarly, the condensed oil appears to be contain a higher concentration of heavier species as evidenced by the multiple peaks at longer treatment times, which can be attributed to the inability of these components to vaporise during the microwave treatment process.


Relative abundance
C16
C22
C30
420 seconds
360 seconds
240 seconds
120 seconds
Relative retention time

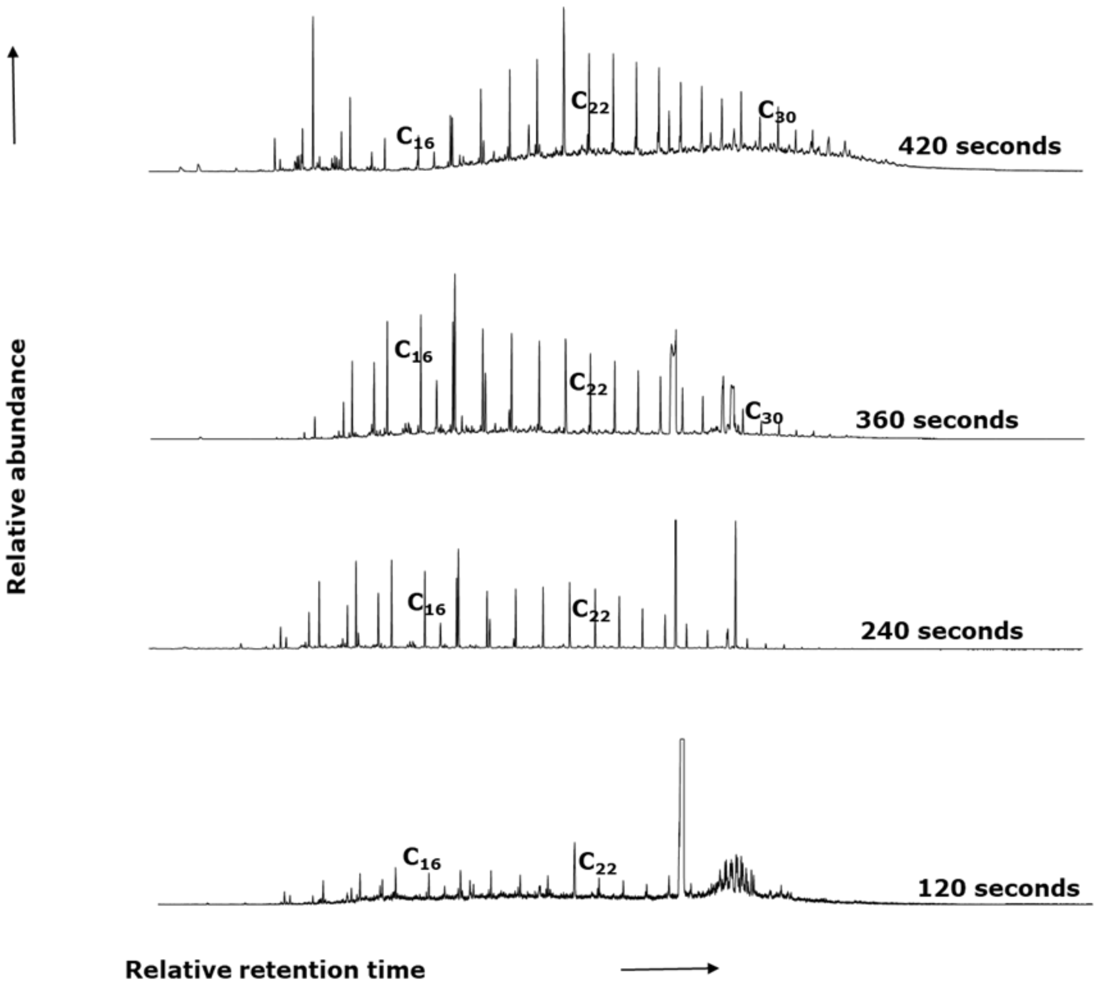
Clay


Relative abundance
C$_{16}$
C$_{22}$
C$_{30}$
420 seconds
360 seconds
300 seconds
120 seconds
Relative retention time

Sand


Relative abundance
C16
C22
C30
420 seconds
360 seconds
240 seconds
120 seconds
Relative retention time

Loamy B



Loamy A

Figure 4.13. Oil composition from the condenser section for soil samples treated at 0.8 kW MW power

An understanding of the relationship between the total organic carbon in the soils and the carbon contribution from polluting oil is presented below. The % TOC of the char from the microwave was used to determine the % TOC removed. Increasing treatment time enhance oil removal and organic carbon from all the soils, implying a linear relationship between the TOC and oil removal.

The carbon contribution is soil is from organic matter and the polluting oil. Increasing treatment time led to increases in oil and organic carbon removal for all the soils, but the extent of removal was greatest for the clay soil and lowest for the sandy soil. After 360 seconds for 0.8 kW, 94 % TOC (Figure 4.14) was removed from the clay soil compared to 49 % and 68 %, 49 %, respectively, for the loamy A and loamy B soils, 47 % for the sandy soil. Microwave heating of the loamy A and B soils for 420 seconds led to 60 % oil and 85 % TOC removal. This was not the case for the sandy soil, where little change was obtained after 200 seconds. Similar effect is observed at 1 kW (Figure 4.15), 2 kW (Figure 4.16) and 3 kW (Figure 4.17). TOC for all treated soils is less than the untreated soils. The reduction in the TOC value of the treated soil confirms the removal of adsorbed hydrocarbons. It was also evident from the literature that increasing the power density led to reduction of TOC rate (Robinson et al., 2009). Higher power heating for a shorter time was preferred for TPH contaminated soil. Similar conditions were reported by Robinson et al. (2014).

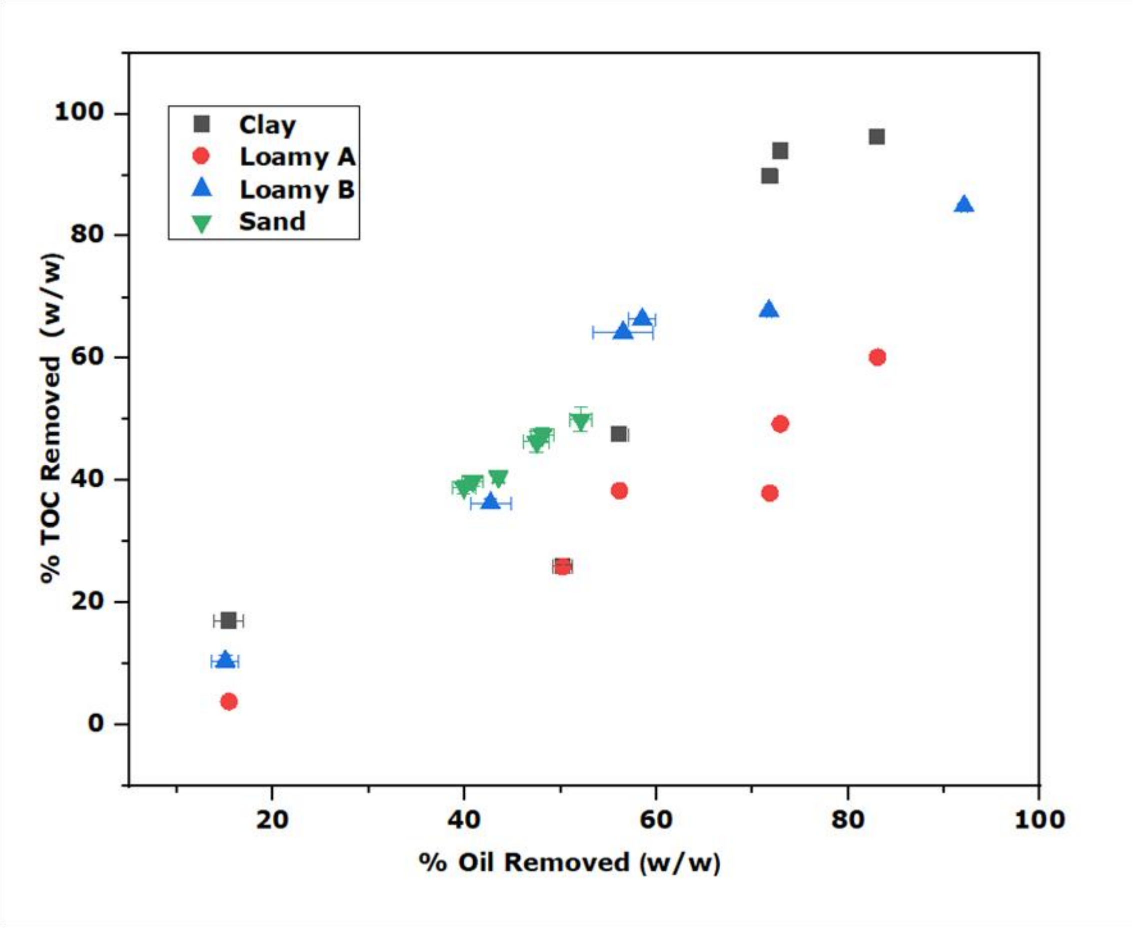


Figure 4.14. Percentage TOC versus oil removed after microwave heating at 120-420 seconds for 0.8 kW microwave power

*Error bar represent standard deviation from triplicate TOC and oil extraction after MW experiment.

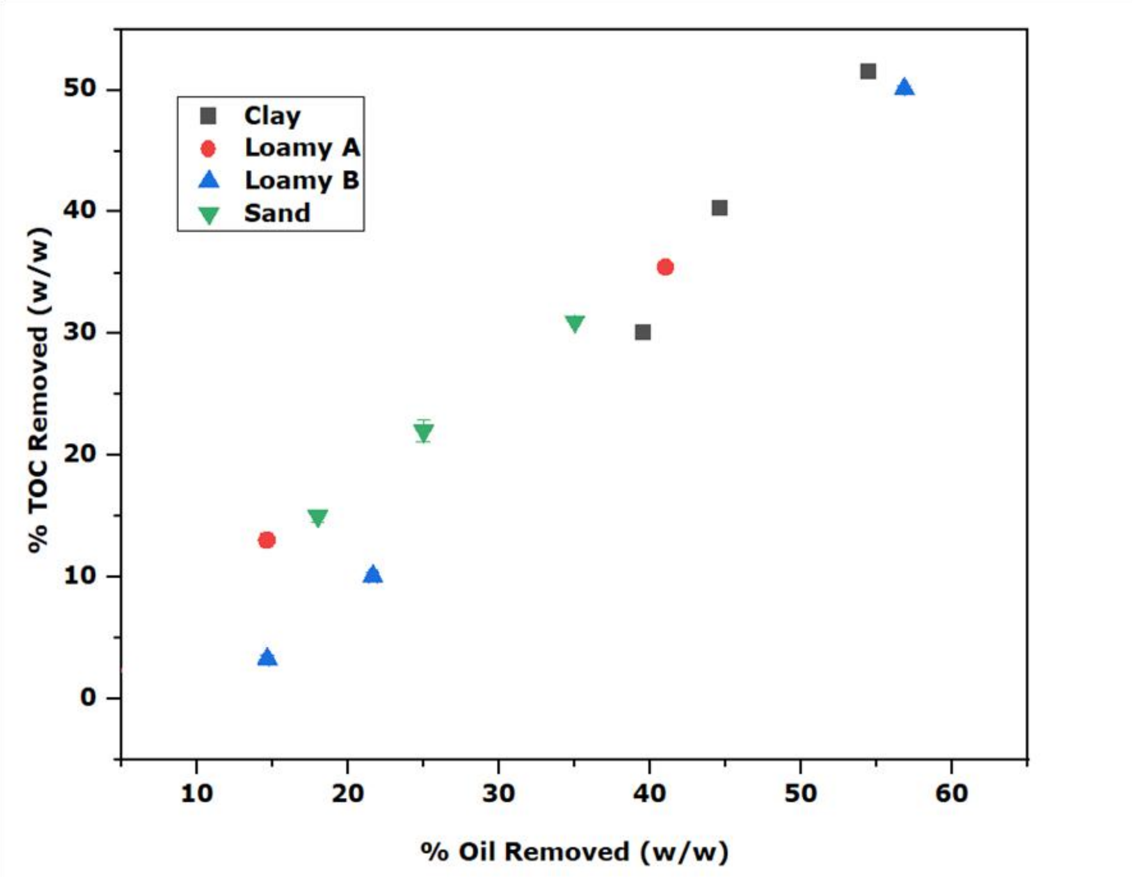


Figure 4.15. Percentage TOC versus oil removed after microwave heating at 60-180 seconds for 1 kW MW

*Error bar represent standard deviation from triplicate TOC and oil extraction after MW experiment.

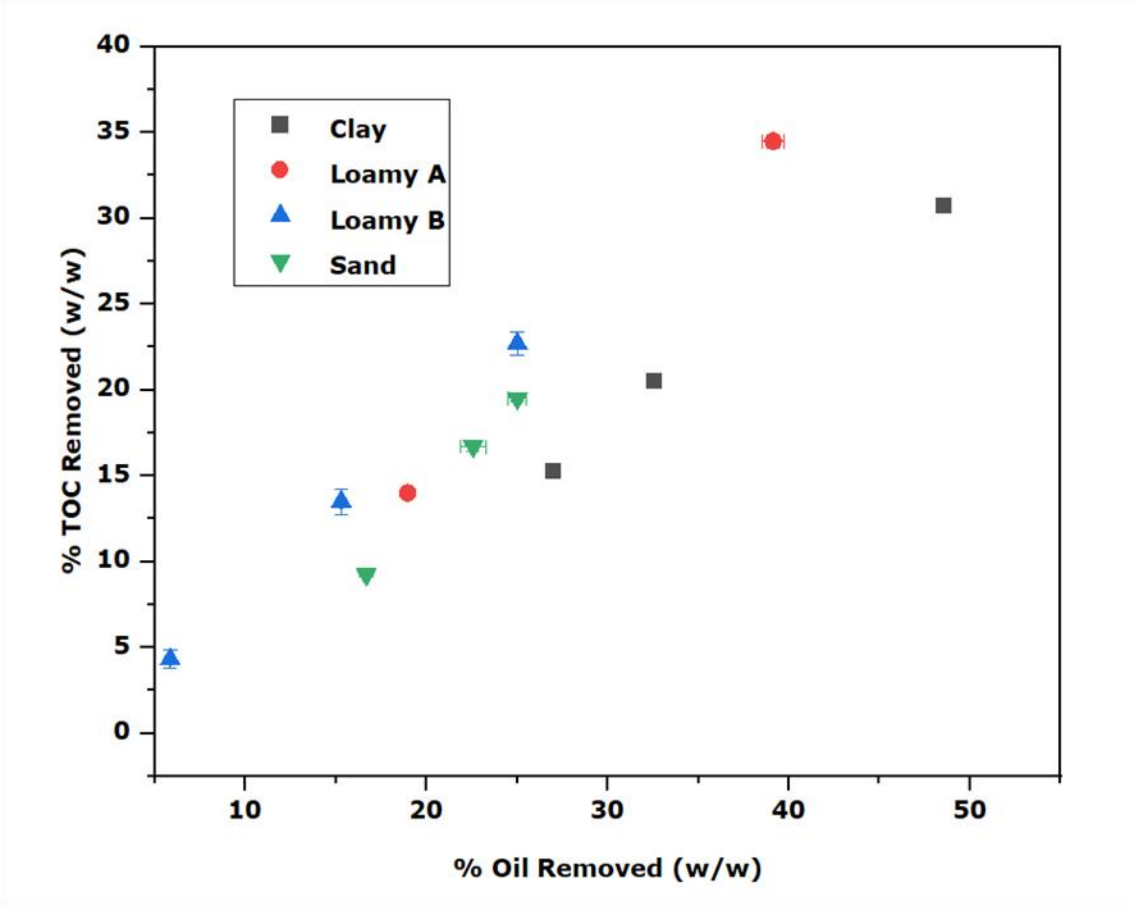


Figure 4.16. Percentage TOC versus oil removed after microwave heating at 20-60 seconds for 2 kW MW

*Error bar represent standard deviation from triplicate TOC and oil extraction after MW experiment.

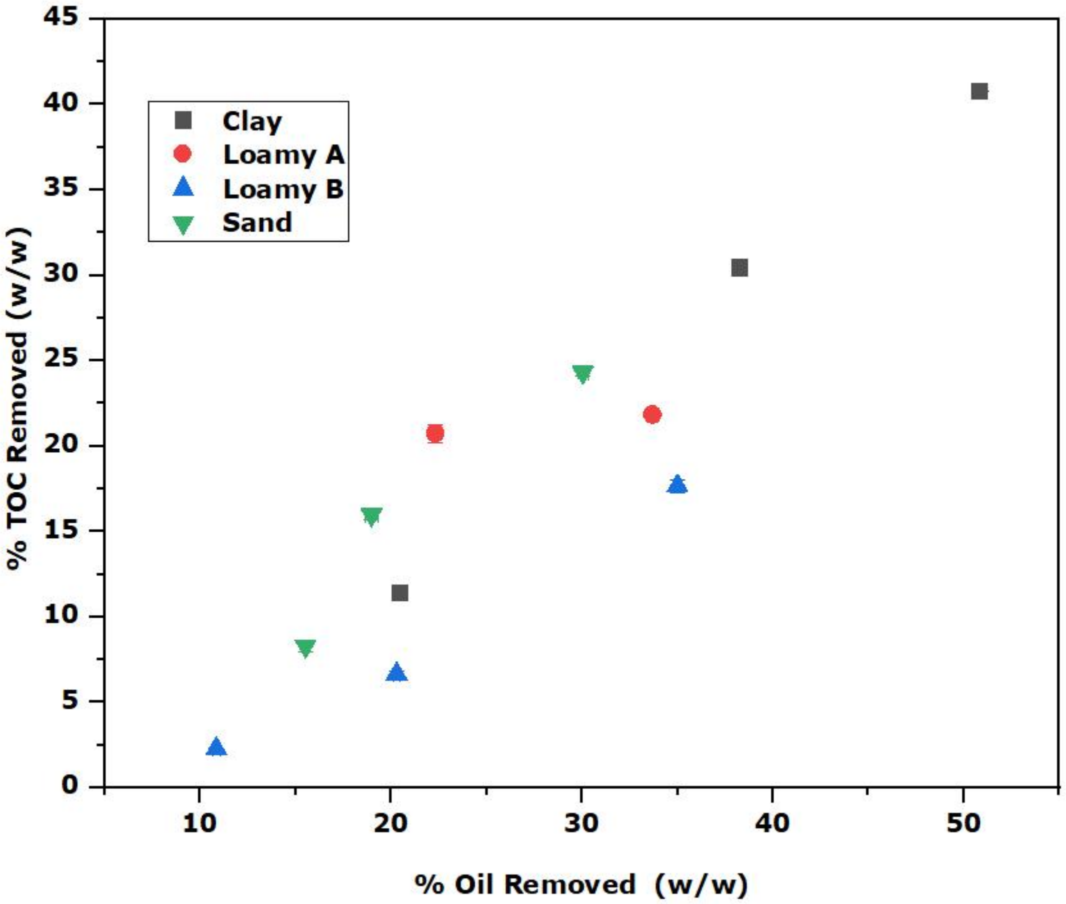


Figure 4.17. Percentage TOC versus oil removed after microwave heating at 20-60 seconds for 3 kW microwave power

*Error bar represent standard deviation from triplicate TOC and oil extraction after MW experiment.

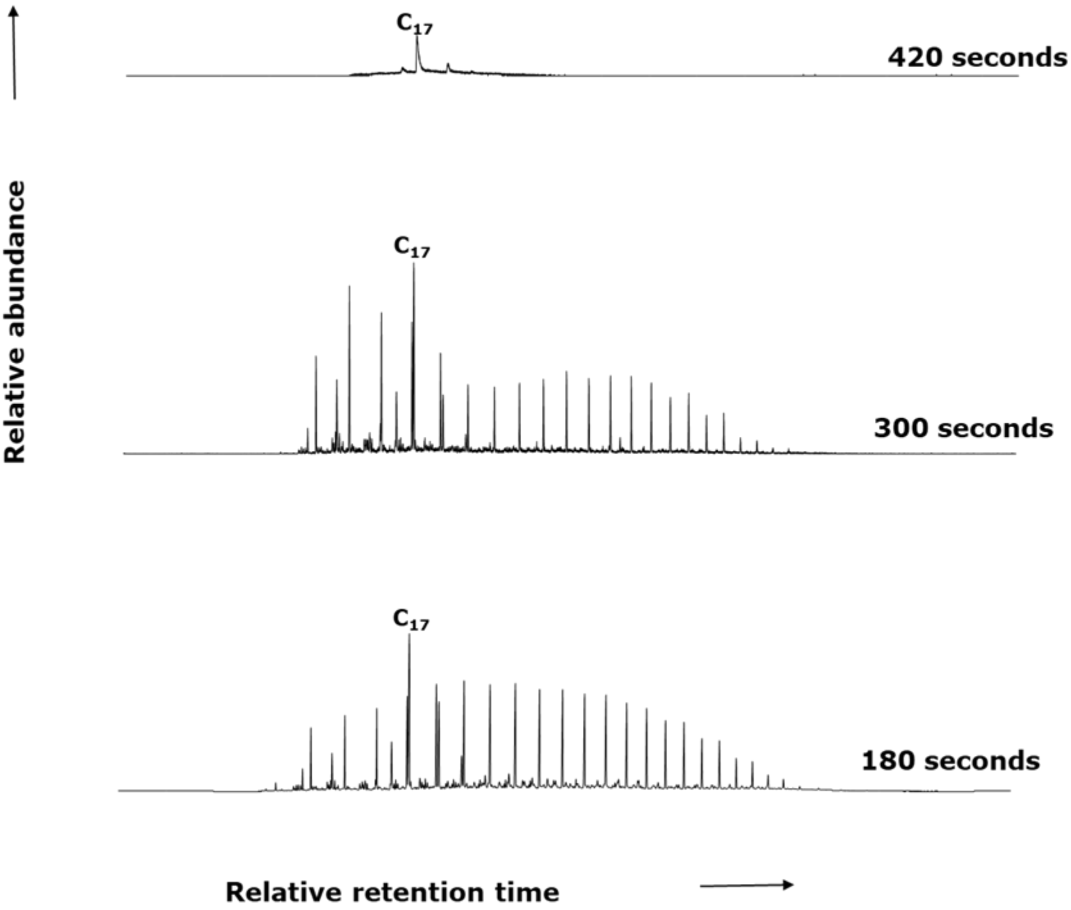
Table 4.6. Residual carbon and oil in the soil after microwave heating

Time	**Residual carbon (% w/w)**				**Residual oil yield (% w/w)**			
(second)	Clay	Loamy A	Sand	Loamy B	Clay	Loamy A	Sand	Loamy B
120	1.46±0.020	7.21±0.08	0.98±0.001	5.00±0.01	1.24±0.02	5.51±0.08	0.85±0.4	4.35±0.07
180	1.30±0.110	5.56±0.19	0.96±0.009	3.6±0.008	1.11±0.04	3.23±0.05	0.83±0.02	2.98±0.11
240	0.92±0.010	4.62±0.71	0.95±0.010	2.02±0.003	0.84±0.02	2.85±0.07	0.77±0.02	2.09±0.16
300	0.18±0.001	4.65±0.18	0.76±0.020	1.9±0.002	0.52±0.03	1.83±0.03	0.66±0.02	2.05±0.07
360	0.11±0.005	3.81±0.06	0.86±0.020	1.82±0.001	0.002±0.001	1.76±0.06	0.69±0.01	1.44±0.01
420	0.065±0.001	2.98±0.12	0.92±0.010	0.85±0.04	<0.002	1.10±0.14	0.72±0.02	0.44±0.05

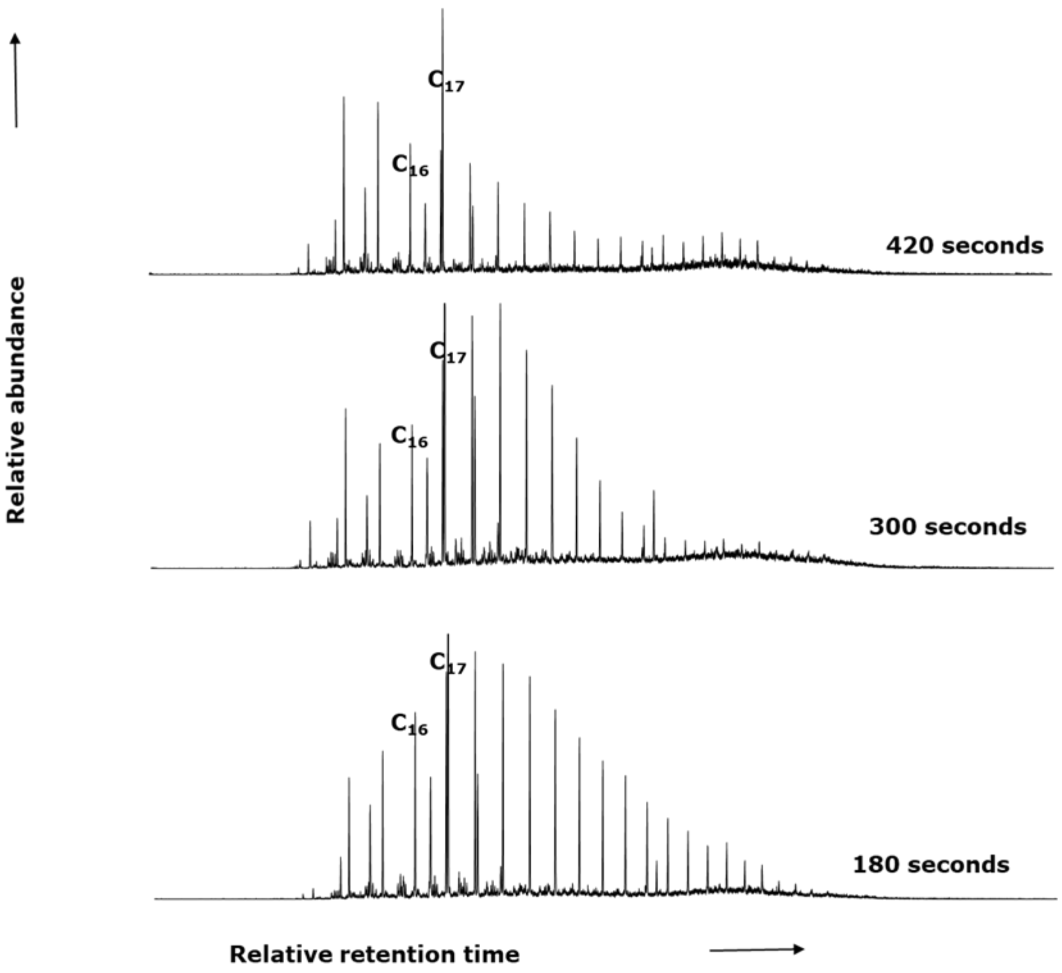
The residual oil levels obtained are shown in Table 5.6. Residual oil levels can be obtained below the 0.5 %w/w % environmental discharge limit. Increasing the cavity power results in a decrease in residual oil in soil samples, which is likely due to higher electric field strength. Hence more rapid heating of the dielectric materials within the sample prior to mass transfer of the microwave treated phase-out the sample. As seen from Table 5.6 the oil content decreased with increasing processing time for 0.8 kW MW. The oil content decreased from 1.58 w/w % to<0.002 w/w %, for clay soil, 6.50 %w/w to just over 1.1 %w/w,, for loamy A soil, 5.06 %w/w to 0.44 w /w %, for loamy B soil and 1.34 w/w % to 0.72 w/w %, for sand soils. The residual oil contents of 0.002 and 0.44 % w/w (Table 4.6) for the clay and loamy B soils and fall below the regulatory standard of petroleum hydrocarbons in Nigeria soils of 0.5 % w/w (Department of Petroleum Resources, 2002).

4.9. GCMS traces of residual oils in the soils after microwave treatment

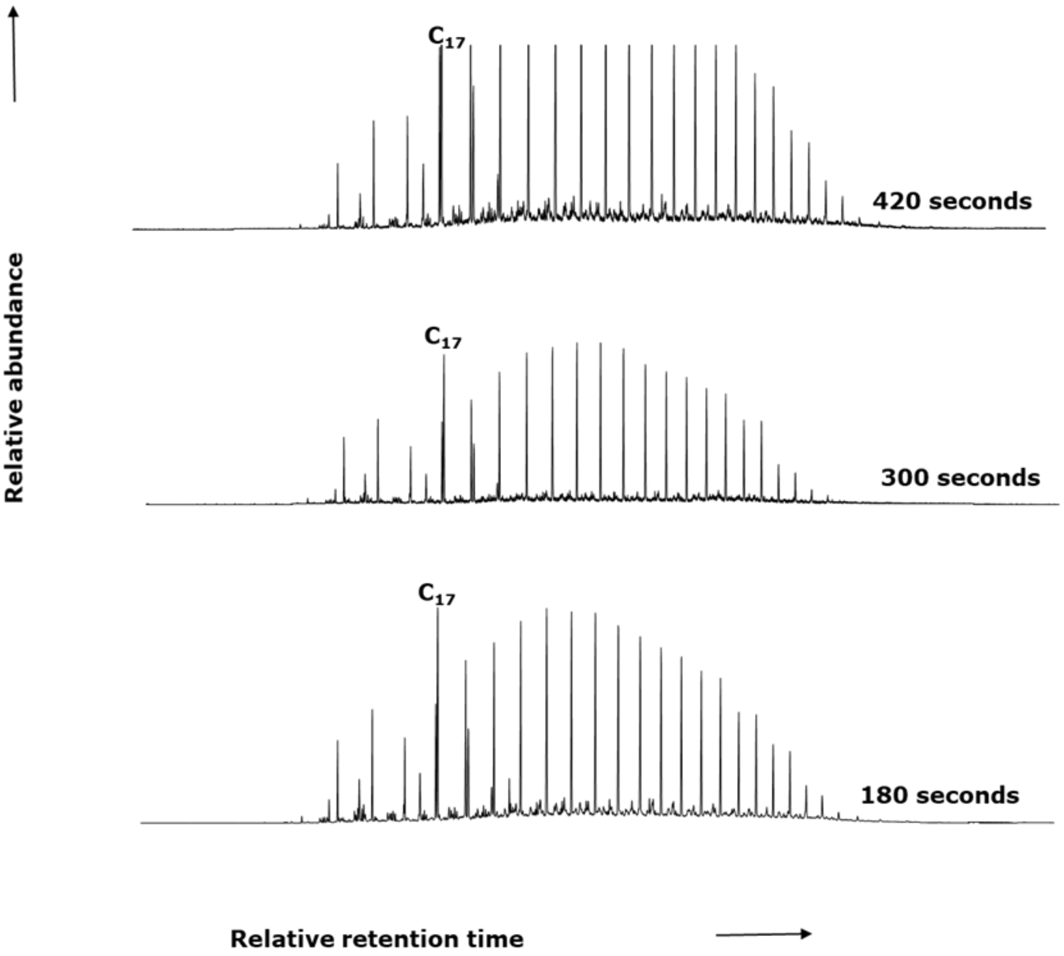
Residual soil collected after microwave treatment was extracted using the same procedure for the untreated soil. The extract was then analysed by GCMS, results are presented in (Figure 4.18).As heating time is increased; an obvious reduction in the number of peaks is can be seen in m/z 71 for clay soil. Also, reduction in the intensity of peaks for loamy A soil is observed (Figure 4.7b). Several hydrocarbon carbon peaks are lost after treatment of clay soil (Figure 4.18a). Residual oil from sand soil (Figure 4.18c) has similarities with the raw Soil (Figure 4.5a). The total ion chromatogram TIC refers to all hydrocarbons present in the oil matrix that was detected during a particular GC/MS analysis. Overall chromatogram for residual oils in soils supports the findings of severe oil lost from clay soil. More also, it presents the massive number of hydrocarbons left in sand soil.


Relative abundance
C_{17}
420 seconds
C_{17}
300 seconds
C_{17}
180 seconds
Relative retention time

Clay


Relative abundance
C_{17}
C_{16}
420 seconds
C_{17}
C_{16}
300 seconds
C_{17}
C_{16}
180 seconds
Relative retention time

Loamy A



Sand

Figure 4.17. Oil composition for residual soil after MW treatment at 0.8 kW

In conclusion, removal of crude oil from soils by microwave heating is dependent on the soil type and residence time within the microwave cavity, with complete oil removal for clay soil being achieved for the first time. The trends of the lowest extent of oil removal being obtained for sandy soil and intermediate levels for loamy soil are consistent with the microwave properties of the soil, reflecting that the clay has the highest moisture content. Although complete oil removal was not achieved for loamy A, loamy B and soils sand soils under the microwave heating investigated here. The composition of recovered oil after microwave heating remains largely unchanged, indicating that the oil is thermally desorb from the soils at optimum studied time of 420 seconds. Chapter 5 reveals that soils behave differently during microwave heating and the knowledge of their influence on remediation time and different MW power has been shown. This signifies that soil nature influences oil removal due to numerous factors one of it called penetration depth have been shown to have no effect. The mineralogy and soil moisture may greatly influences mass transfer, hence the mechanism of oil removal. Several possible mechanisms could be responsible for the oil uptake from the soils. An understanding of contribution of steam stripping mechanism and mass transfer effects are significant issues that will be addressed in the next chapter.

CHAPTER FIVE. Energy Requirement for Removal of Oil from Soil and Mechanism Study

5.1. Scope

The main objectives of the work presented in this chapter are to determine the energy required for oil removal as indication of the energy efficiency of the remediation process. Also, the extent to which steam stripping occurs during microwave remediation of crude oil contaminated soils. The knowledge of this mechanistic process of oil removal is crucial because it aids the optimisation of the microwave process and informs the selection and design of appropriate downstream processes and equipment. The work described in Chapter 4 provided an understanding of how oil is removed from different soil types during microwave treatment .The current hypothesis is to see the contribution of steam stripping mechanism in oil removal, and also how is related to the velocity of steam within the pores of the soils. This chapter investigates the energy input for oil removal from soils. The specific energy input was calculated from absorbed microwave power and the duration of each experiment as described in the equation below.

$$\mathrm{E}\left(\frac{\mathrm{kwh}}{\mathrm{t}}\right)=\frac{\text{Aborbed power }\times\text{ time}}{\text{mass of soil (g)}}\times\frac{10^{6}}{\text{tonne (t)}}\times\frac{\mathrm{kwh}}{3600\ \mathrm{kJ}} \qquad (5.1)$$

Results for oil and water removal are mean values, standard deviation represent error in oil and water measurement.

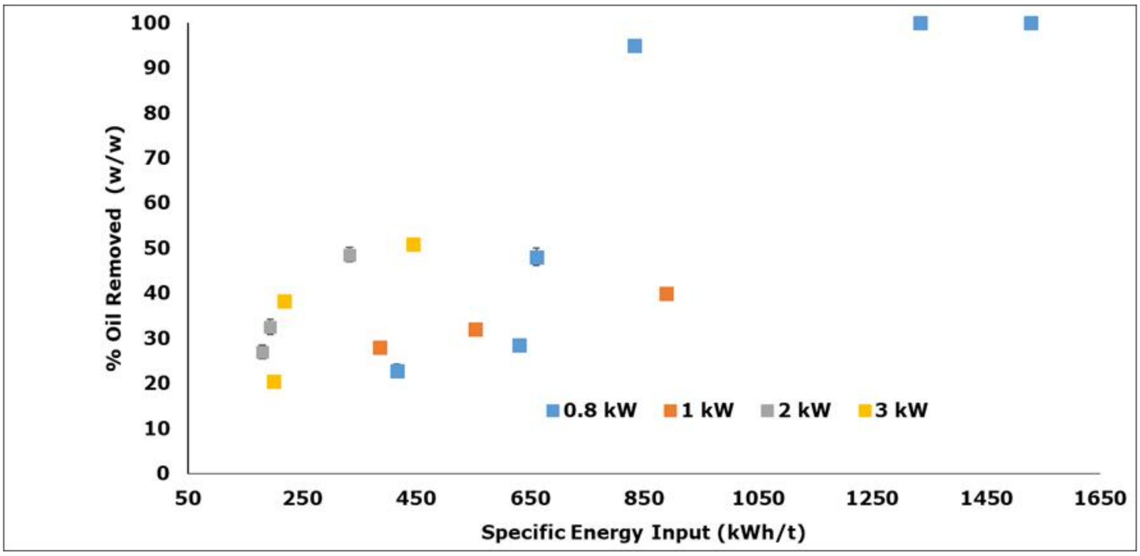


Figure 5.1. Oil removal plotted against energy input, showing that oil removal increases at high power densities and equivalent energy input for clay soil

*Error bar represent standard deviation from triplicate oil extraction after MW experiment.

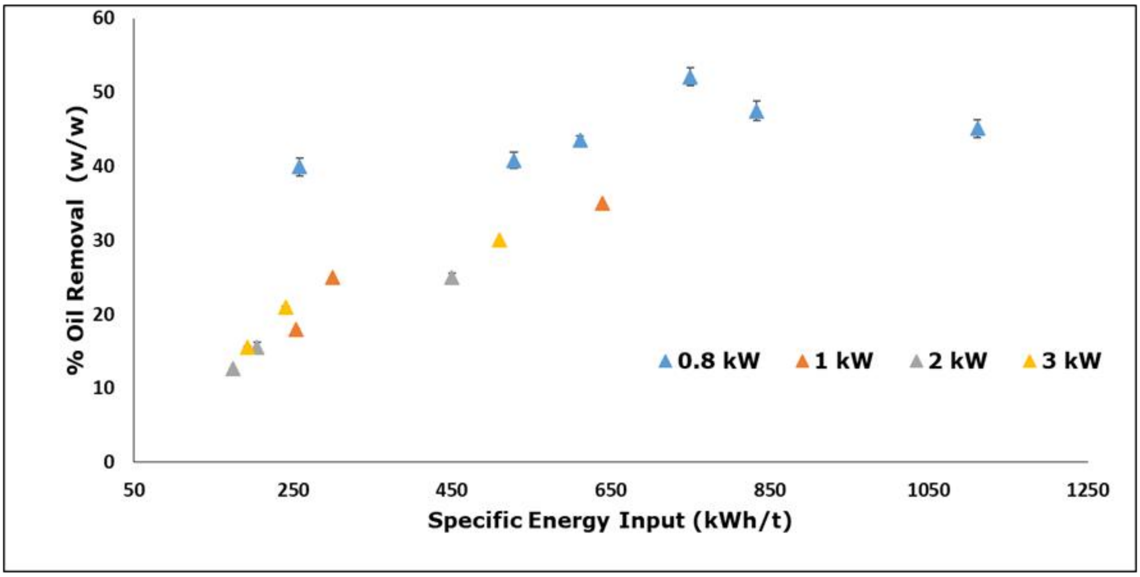


Figure 5.2. Oil removal plotted against energy input, showing that oil removal increases at high power densities and equivalent energy input for sand soil

*Error bar represent standard deviation from triplicate oil extraction after MW experiment.

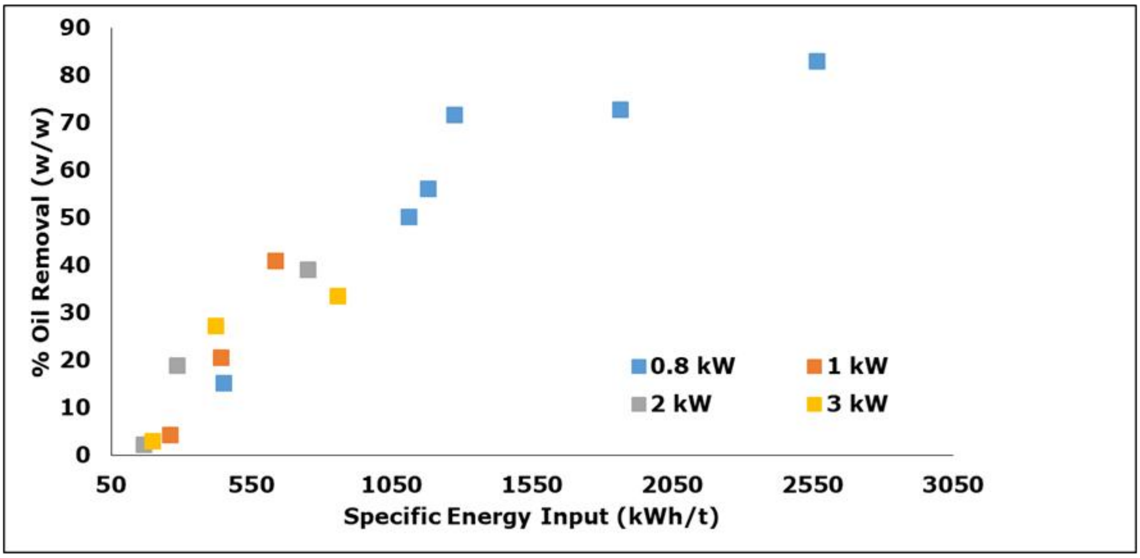


Figure 5.3. Oil removal plotted against energy input, showing that oil removal increases at high power densities and equivalent energy input for loamy A soil

*Error bar represent standard deviation from triplicate oil extraction after MW experiment.

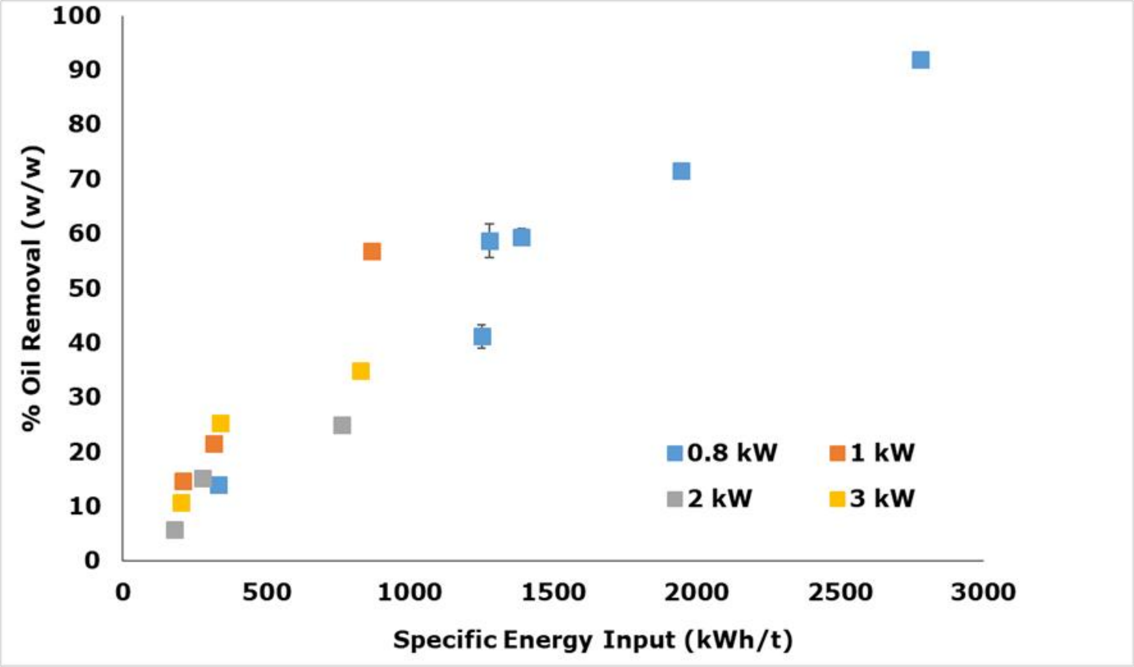


Figure 5.4: Oil removal plotted against energy input, showing that oil removal increases at high power densities and equivalent energy input for loamy B soil

*Error bar represent standard deviation from triplicate oil extraction after MW experiment.

Figure 5.1-5.4 shows that oil removal is not solely dependent on the amount of energy absorbed In all cases the amount of oil removed increases with energy input, and the maximum energy absorbed by different soils at 0.8 kW MW input are 1527 kWh/t for clay (Figure 5.1), 2565 kWh/t for loamy A (Figure 5.3), 2777 kWh/t for loamy B (Figure 5.4) and 1111 kWh/t for sand soils (Figure 5.2). It was not possible for more energy to be absorbed due to the loss of water. Energy absorbed by the soils mixture is in the range for 1 kW MW input are 386 -888 kWh/t, 258-635 kWh/t, 209-866 kWh/t and 254-639 kWh/t. With 2 kW 180-333 kWh/t, 166-750 kWh/t, 180-763 kWh/t and 175-450 kWh/t. For 3 kW MW input, 200-444 kWh/t, 196-858 kWh/t, 201-827 kWh/t and 192-590 kWh/t, for clay, loamy A, loamy B and sand soil. The corresponding oil removal is 28-40 %, 4-41 %, 14-56 % and 18-35 % for 1 kW. With

2 kW the range of oil removal is 27-49 %, 2-40 %, 6-25 % and 12-25 %. While 3 kW gave 21-51 %, 3-34 %, 10-35 % and 15-30 % for various soils. An equivalent energy input of 400 kwh/t for clay shows over 100 % increases in oil removal when heated at 3 kW input compared to 0.8 kW. From Figure shows that around twice as much oil was removed from the sample when treated at 3 kW compared with 1 kW. Other soil showed similar effect at equivalent energy input especially at power MW input greater than 0.8 kW. Higher heating rates lead to higher rates of steam generation, which improve heat transfer between the water and oil phase due to higher turbulence and better mixing (Perry & Green, 1997). This indicates that the microwave heating process is more efficient when higher powers are used at an equivalent energy input. This phenomenon has also been observed for microwave processing of oil contaminated drill cuttings (Kamalu et al., 2002; Ogunniran et al., 2017). The effect of power at a constant energy input is a key finding for this study, and has not been shown before for oil sands processing. The data imply that equivalent energy input leads to better power density and is a fundamental parameter that governs oil removal. Higher power microwave equipment will therefore result in higher oil yields as well as allowing much higher throughputs of oil removal than lower power systems at equivalent energy inputs. Although this is not the case for sand soil as increasing energy input at 0.8 kW MW higher did not result to better oil removal. However, energy input from MW power greater than 0.8 kW resulted to increasing oil removal. The energy requirements are high as heating soil samples beyond 100-120 °C were water molecules are lost requires a substantial increase in energy requirement, as lower moisture content, and consequently lower bulk dielectric properties lead to lower heating rates and greater heat loss. Influence of increased water in soil on oil removal and energy requirement are discussed below.

5.2. Effect of increased soil water content on oil removal

Water is a typical polar substance that can significantly absorb MW energy. Water in soil is essential factor, as water absorbs microwaves and helps strip pollutants from the soil through steam, which is produced as the microwaves heat it. Additionally, changes in water content will alter the conductivity and permittivity of the treated soil (Liu et al, 2008). Therefore it could be an essential factor that may influence the removal of oil from soils. This is due to the increasing dielectric properties of the soils containing water that improves the performance of the heating treatment (Acierno et al., 2003). Soil moisture plays a significant role in the absorption of microwaves and the distribution of heat (Kawala & Atamańczuk 1998). A change in moisture content alters the conductivity and the permittivity of the sample. Hence, the strength of the electric fields in the material and the power dissipated in it. The existence of moisture is conducive to the continuous absorption of microwave energy, and the evaporation of moisture will promote the removal of contaminants. Uniform distribution will assist evaporation in ensuring high removal efficiency while retaining more moisture. The moisture content in soil has a significant effect on the final temperature reachable during MW heating. Therefore, soil moisture is essential to reach high oil removal efficiency.

Diprose (2001) reported that the moisture content of a soil sample affects the final temperature. Hence, water plays a major role in the absorption of the microwaves and in the distribution of heat. When it is present, the soil temperature quickly reaches 100 °C, provided that a sufficient amount of energy is being supplied. Water is an excellent MW absorber, and its presence gives an increase of dielectric properties. Therefore, dry soil is a low energy absorbent, but its dielectric constant values allow it to reach minimal soil temperature of about 100 °C, whereas the moisture content in soil has a major effect on the further final temperature increase reachable during MW heating (Hallikainen et al. 1985; Li et al. 2009). The moisture content in material has an effect on the final temperature it attains during MW heating (Di-prose, 2001). Water has a high dielectric loss factor, so relatively small differences in moisture contents between samples will result in different temperatures (Liu et al., 2004b). In this study, contaminated soil samples with different levels of water content (clay 18 %w/w, loamy 14 %w/w and sand soil 14 %w/w) were treated by 0.8 kW microwave irradiation.

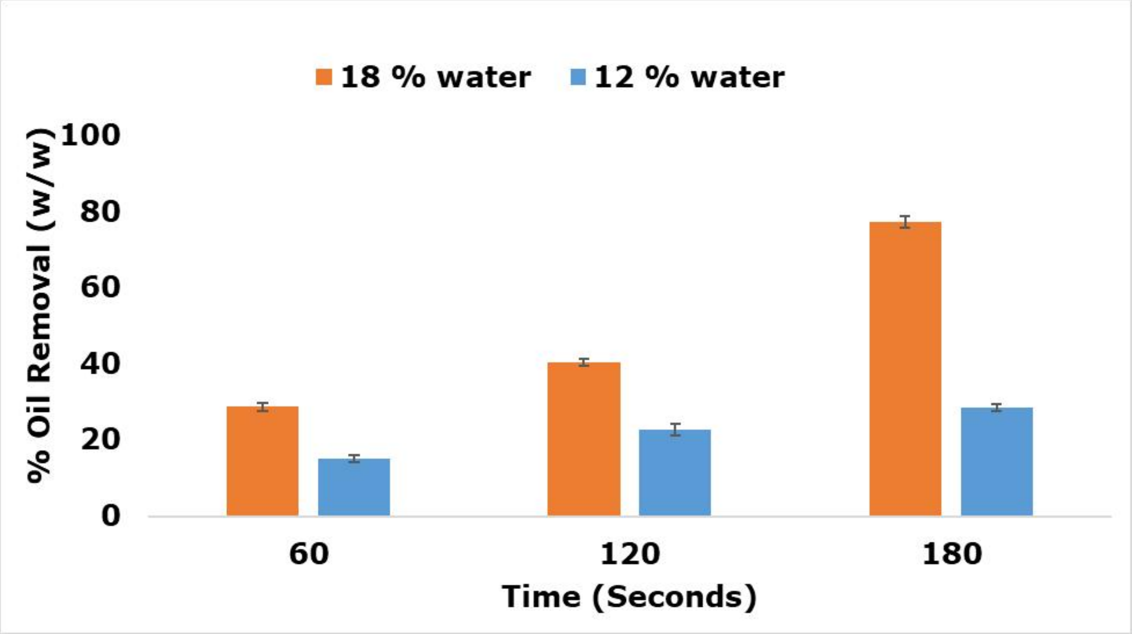


Figure 5.5. Oil removal during microwave heating at different water contents for clay soils, using 800 kW microwave

*Error bar represent standard deviation from triplicate oil extraction after MW experiment.

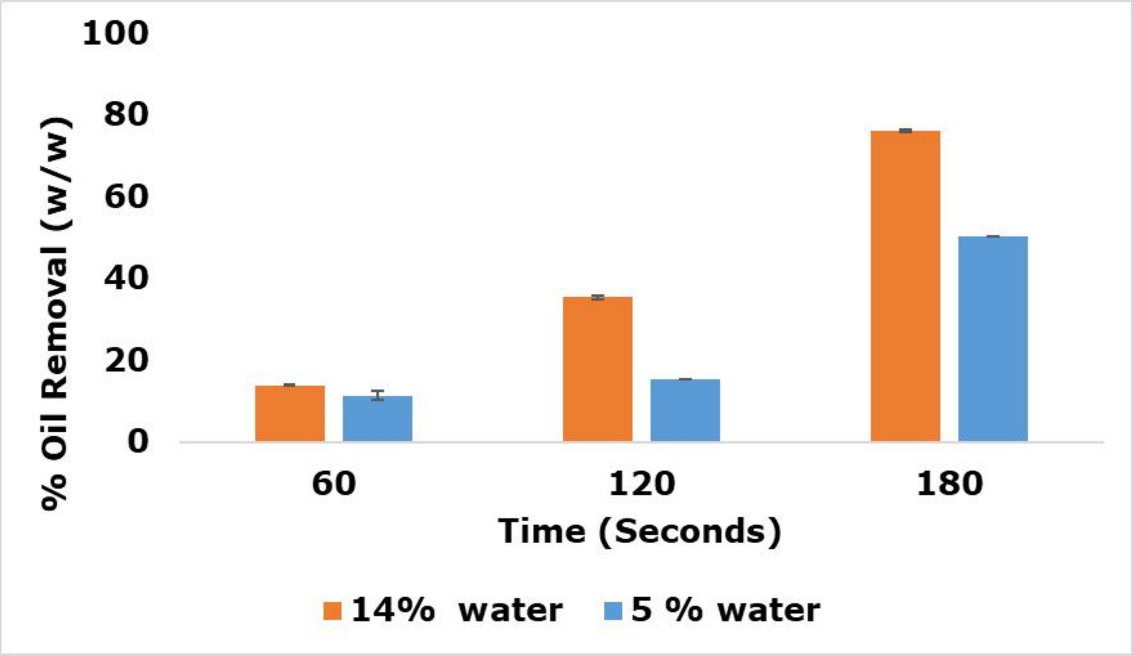


Figure 5.6. Oil removal during microwave heating at different water contents for loamy A soils, using 800 kW microwave

*Error bar represent standard deviation from triplicate oil extraction after MW experiment.

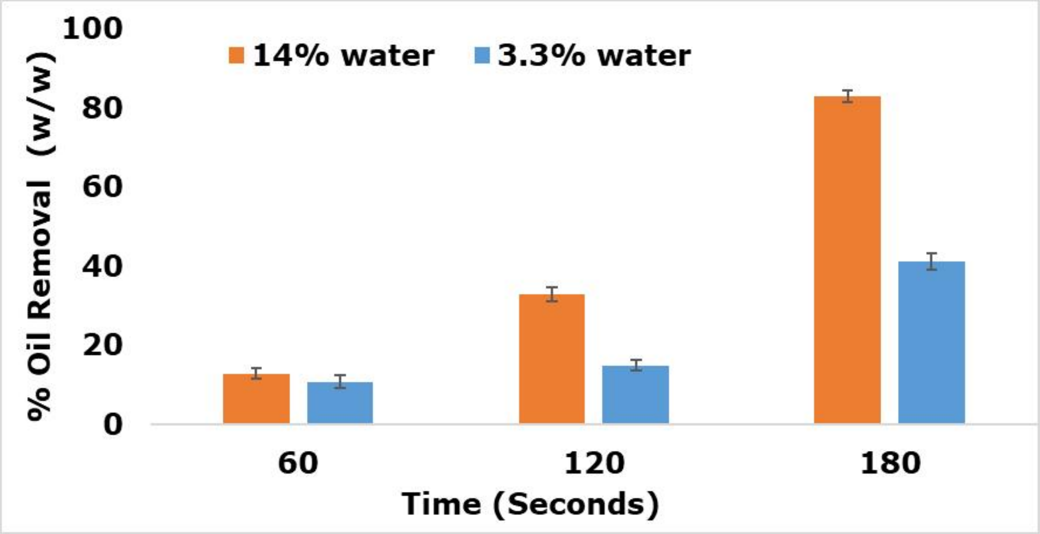


Figure 5.7. Oil removal during microwave heating at different water contents for loamy B soils, using 0.8 kW microwave

*Error bar represent standard deviation from triplicate oil extraction after MW experiment.

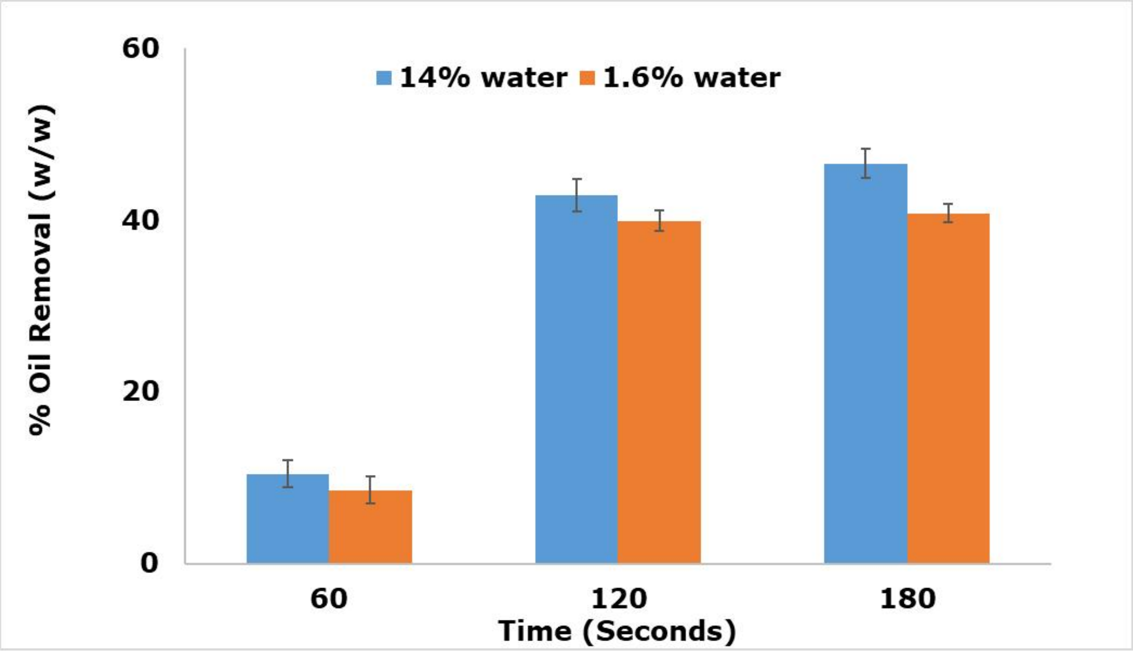


Figure 5.8. Oil removal during microwave heating at different water contents for sand soils, using 0.8 kW microwave

*Error bar represent standard deviation from triplicate oil extraction after MW experiment.

Loam A (Figure 5.6) and loamy B soils (Figure 5.7) showed similar trend. However, the marked difference observed in oil removal from various soils between the two groups of soils indicates that oil removal strictly depends also on different contaminant water adsorption processes influenced by the specific surface area, lowest for sandy soil (Figure 5.8) and highest for clayey soil (Figure 5.5). Moreover, for clayey soil, the presence of inter-crystalline layers can trap more water that penetrates the layers with high porosity values.

As seen from Figure 5.5 , the percentage water content removal increase with heating time from 18 % w/w initially present in the material, to approximately 2.7 - 7.6 % w/w after 30 seconds of drying. It followed a similar pattern to that of Figure 6.6 and 6.7 (loamy soils) , with initial water content of 14 %w/w decreasing from 7.28 % w/w to 2.1 % w/w between 0 and 30 seconds. For sand soils with an initial water content of 14 %w/w, it decreased from 6.2 % w/w to 5.18 % w/w. A change in water content of clay soil led doubled oil removal at 180 seconds of heating time. Similar behaviour is observed for loamy A and loamy B soils. Less than 5 % change in oil content is observed for sand soils. In conclusion, Adding water to soils effectively raised its ability to absorb microwave energy required to remove a good percentage of oil from soil at a shorter treatment time. This indicates that soil moisture influences a major desorption of hydrocarbons, probably due to the soil temperature increase and evaporation-contaminant stripping phenomena, which present a major influence on the more volatile contaminant fraction. The extent to which increasing soil moisture influences energy input is investigated at 0.8 kW MW power for 2 and 3 min.

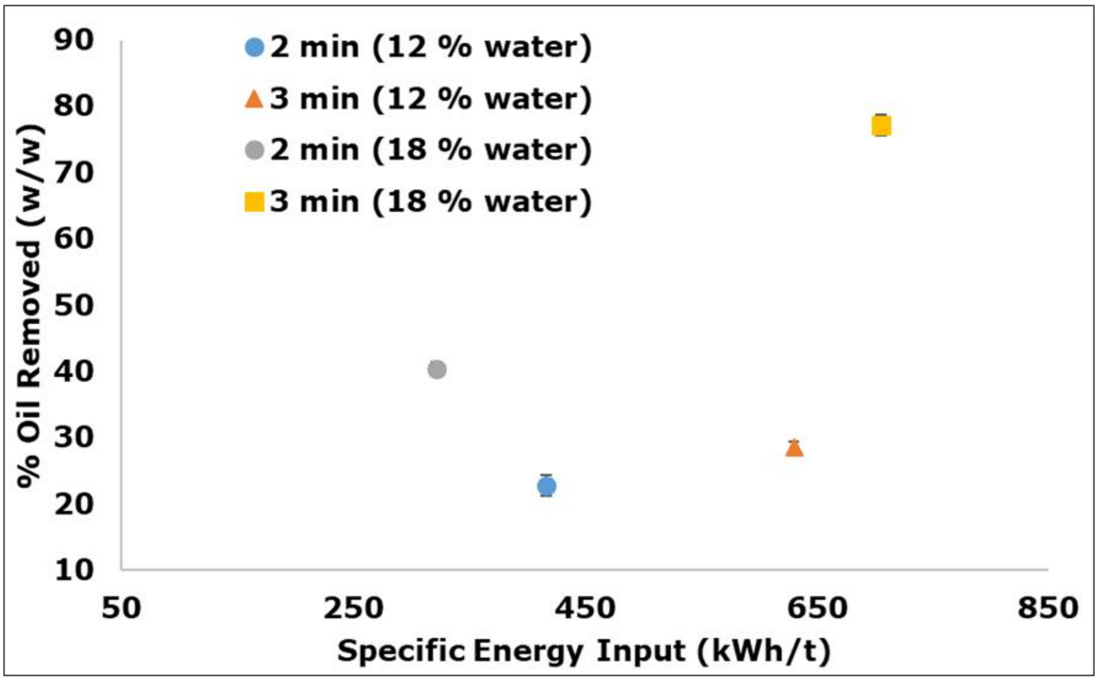


Figure 5.9. Oil removal plotted against energy input for water content of 12 and 18 %w/w for clay oil

*Error bar represent standard deviation from triplicate oil extraction after MW experiment.

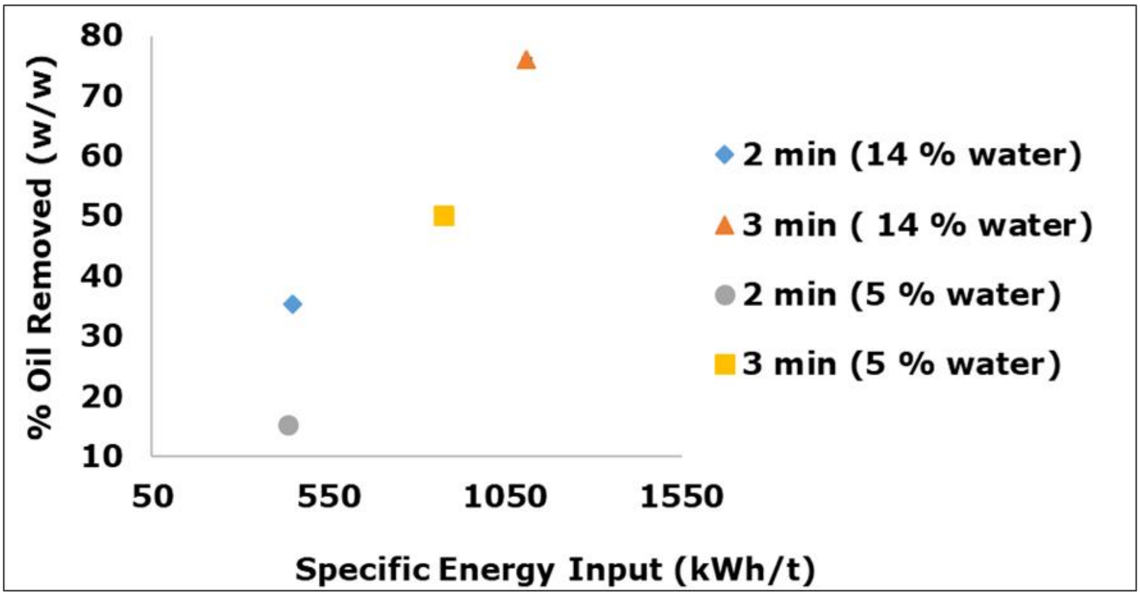


Figure 5.10. Oil removal plotted against energy input for water content of 5 and 14 % for loamy A soil

*Error bar represent standard deviation from triplicate oil extraction after MW experiment.

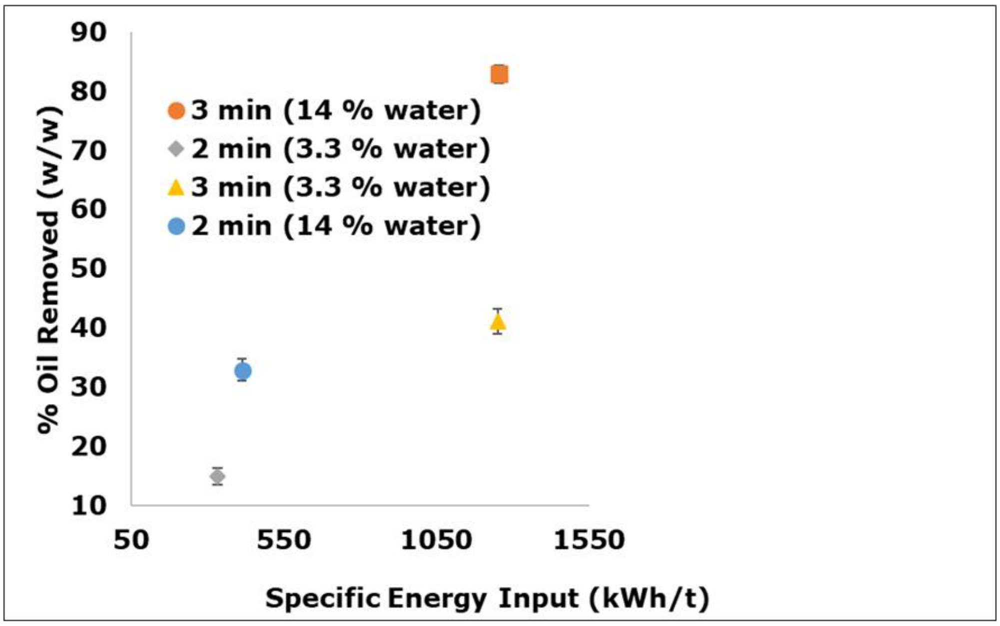


Figure 5.11. Oil removal plotted against energy input for water content of 3.3 and 14 % for loamy B soil

*Error bar represent standard deviation from triplicate oil extraction after MW experiment

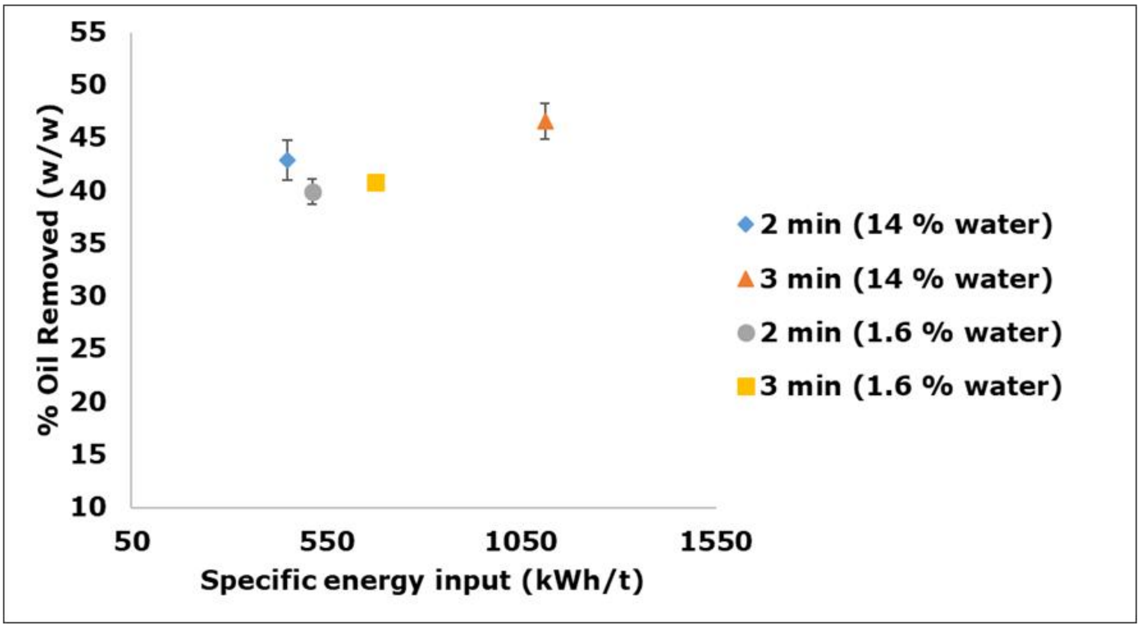


Figure 5.12. Oil removal plotted against energy input for water content of 1.6 and 14 % for sand soil

*Error bar represent standard deviation from triplicate oil extraction after MW experiment.

Calculated energy input increased for all soils at higher water content especially at 3 min of heating. For clay soils at 3min energy input increased by 11 % with 33 % change in water content (Figure 5.9). This resulted to 67 % increase in oil removal. Similar increase is observed for loamy soil A (Figure 5.10), loamy soil B (Figure 5.11) and sand soil (Figure 5.12)

5.3. Understanding oil removal mechanism and mass transfer process during microwave soil heating

The study will also establish the extent to which steam-stripping occurs during microwave remediation of crude oil contaminated solids by measuring steam velocities and mass transfer coefficients for oil removal. Different values for steam velocities will be obtained by changing the microwave power, heating time, mass and porosity of soil. Different heating time will be investigated for each variable studied, and these values used to establish the rate of water and oil removal. The residual oil and water content within the sample will be measured for each experiment. Prediction of the heat and water mass transfer is essential for equipment design, process optimization, and a contaminant's removal efficiency calculation. However, heat and mass transfer occur simultaneously within soils being irradiated by microwave energy and the two phenomena are strongly coupled processes, making the time-dependent solution of the problem highly nonlinear and difficult.

Table 5.1. Assumed parameters for estimating theoretical energy requirement for oil removal mechanism

Parameters	**values**
Specific heat capacity of materials	Oil = 2 kJ/kgK, Water = 4.2 Clay soil = [a]2.25 kJ/kgK, Sand = [b]1.61 kJ/kgK Loamy soil = [b]1.99 kJ/kgK
Latent heat of vaporisation	Oil = 800 kJ/kg Water = 2257 kJ/kg
Room temperature	20 ◦C

Diameter of reactor	32mm
Density of steam	0.59 kg/m^3
Water content	Sand= 14 ±0.35 % Loam B= 14±0.5 % Clay= 18±0.6%
Temperature of stripping of oil	^{c}20-100°C
Diffusion coefficient, D_a	3.185×10^{-10} m^2 S^{-1}
$E_{Stripping}$	Sand = 135 kWh/t Loamy = 150 kWh/t Clay = 170 kWh/t

a= Nidal & Abu-Hamdeh (2003)

b= Yadav & Saxena (1973)

c= Robinson et al. (2014)

Table 5.2. Temperature of soil component during microwave heating

Matrix	**Steam Stripping**
Water	20-100 °C
Oil	20-100 °C
Soil	20-100 °C

Source: (Arthur & Lord 1998: Di et al., 2000)

The theoretical energy required by steam tripping will give an indication of the energy efficiency of the mechanism, and a basis of comparison with the experimental result. The energy requirement for these mechanisms will be examined as:

$$E_{total}(\frac{\mathrm{kwh}}{\mathrm{tonne}}) = \mathrm{M_W C_{PW} \Delta T_W} + \mathrm{M_W L_W} + \mathrm{M_O C_{PO} \Delta T_O} + \mathrm{M_O L_O} + \mathrm{M_S C_{PS} \Delta T_S} [5.2]$$

M_w = Mass of water

M_o = Mass of oil

M_s = Mass of untreated soil

C_{pw} = Specific heat capacity of water

C_o = Specific heat capacity of oil

C_{ps} = Specific heat capacity of soil

L_w = Latent heat of vaporization of water

L_o = Latent heat of vaporization of oil

$$\mathrm{E}=\frac{\mathrm{Q_{total}}}{\mathrm{M}} \mathrm{X} \frac{10^6 \mathrm{g}}{\mathrm{tonne\ (t)}} \mathrm{X} \frac{\mathrm{kWh}}{3600\ \mathrm{kJ}} \qquad [5.3]$$

M = mass of untreated soil

As mentioned earlier preliminary analysis of soil samples have shown oil content of 5.06 %w/w and moisture content of 14 % w/w. Amount of energy required to reduce oil from 5.06 %w/w in 20 g of loamy B soil is calculated as follows.

$$\mathrm{M_o}=\frac{5.06}{100} \times 20 = 1.012\ \mathrm{g} \qquad [5.4]$$

Energy required for vaporization of oil

$$\mathrm{E_o(kJ)}=\frac{1.012}{1000} \times 2 \times 80 + \frac{1.012}{1000} \times 800 = 0.97\ \mathrm{kJ} \qquad [5.5]$$

20 g of soil contains 14 % w/w water

$$\mathrm{M_w}=\frac{14}{100} \times 20 = 2.8\mathrm{g} \qquad [5.6]$$

Energy requirement to heat 1.5 g water from 20 °C to 100 °C is given as

$$E_{water}\,(kJ) = \frac{2.8}{1000} \times 4.2 \times 80 + \frac{2.8}{1000} \times 2257 = 7.3\ kJ \qquad [5.7]$$

Energy required to heat soil from 20 °C to 100 °C

$$E_{soil}\ \frac{16.2}{1000} \times 1.99 \times 80 = 2.60\ kJ \qquad [5.8]$$

Total energy requirement = 0.97 +7.3+2.60 = 10.87 kJ

$$E_{total}\left(\frac{kwh}{t}\right) = \frac{7.3835kJ}{20g} \times \frac{10^6\ g}{tonne\ (t)} \times \frac{kWh}{3600kJ} = \frac{150.97kWh}{tonne} [5.9]$$

5.4. Investigation of oil stripping mechanisms oil

Mechanisms involved in removing oil from oil-contaminated soils using microwaves have not been studied especially in typical Nigerian soils. However, previous work by (Shang et al., 2006; Robinson, et al., 2009; Ogunniran et al., 2017) has investigated some potential mechanisms for removing oil from oil contaminated drill cuttings during microwave processing. The feasibility of the steam stripping mechanism as reported by different researchers has proved its potential for removing oil from contaminated soil. The process has been reported to be energy economical. According to (Arthur & Lord 1998) bulk soil temperature during steam stripping of oil-contaminated soil averaged at a temperature of 100 °C. Achieving this temperature level of soil makes steam stripping feasible technique for oil removal.

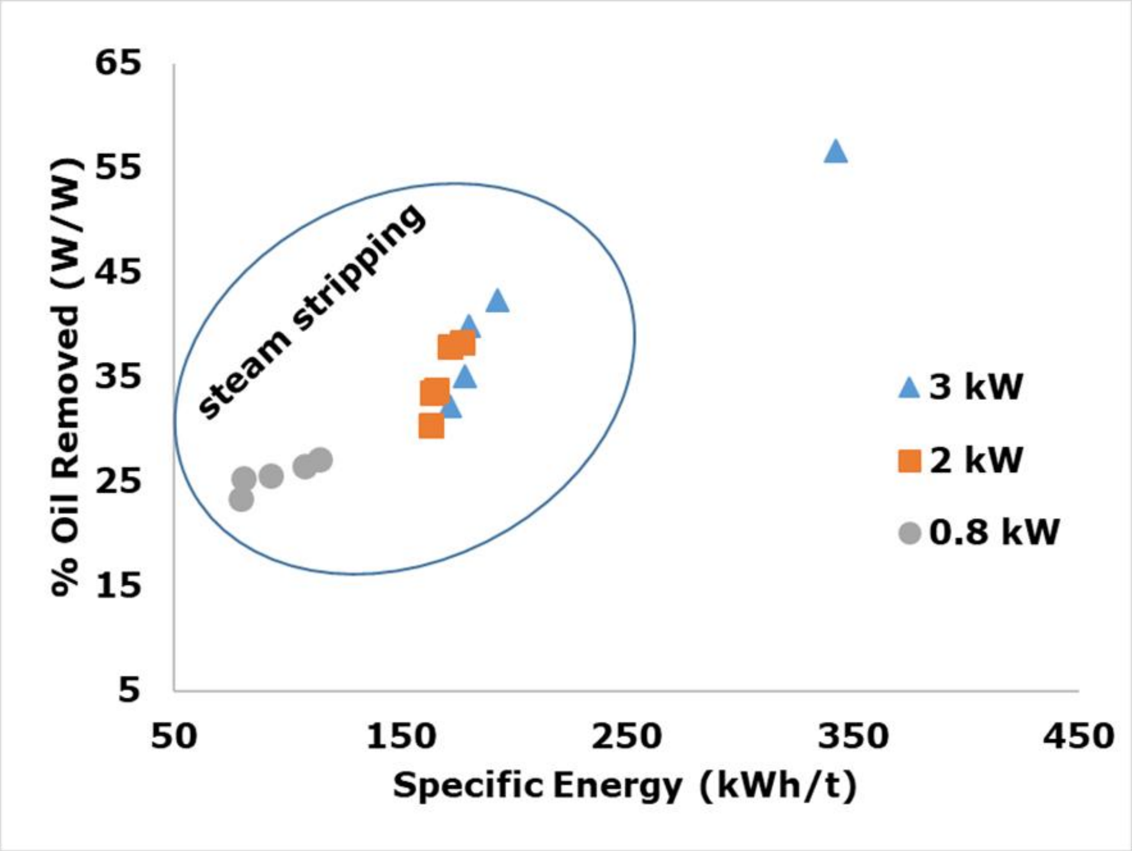


Figure 5.13. Oil removal plotted against heating times for treatment of clay soil at energy input of 50-180 kWh/t (20 g sample mass and 18 %w/w water)

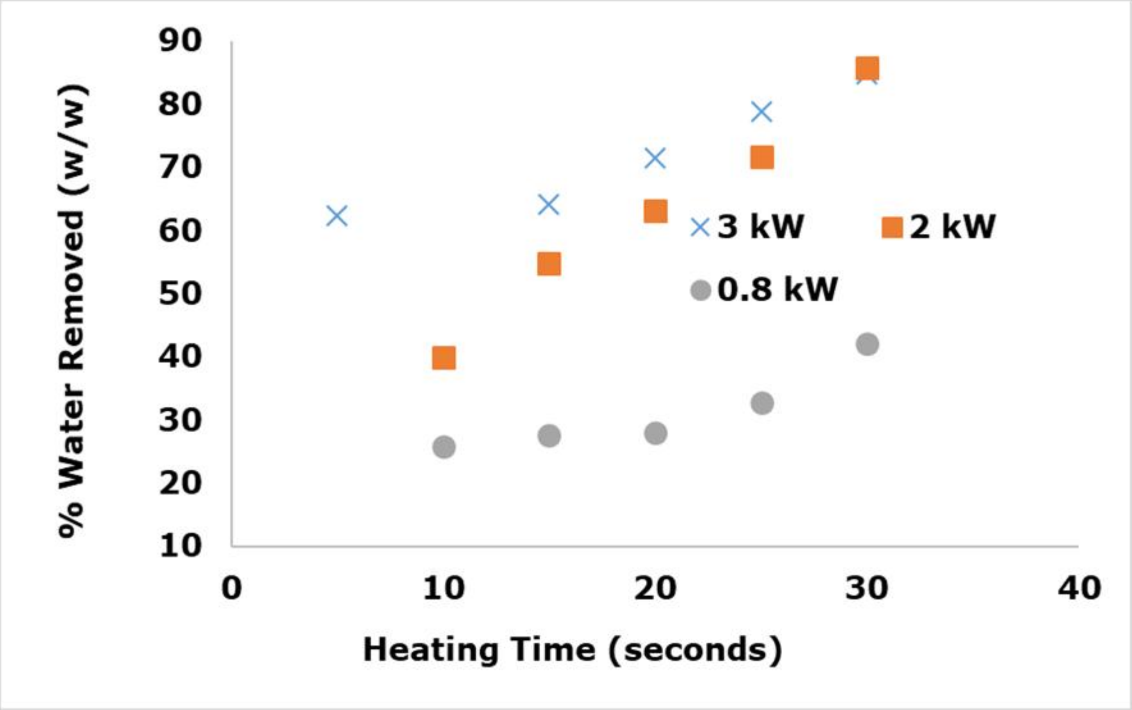


Figure 5.14. Water removal plotted against heating times during microwave treatment of clay soil

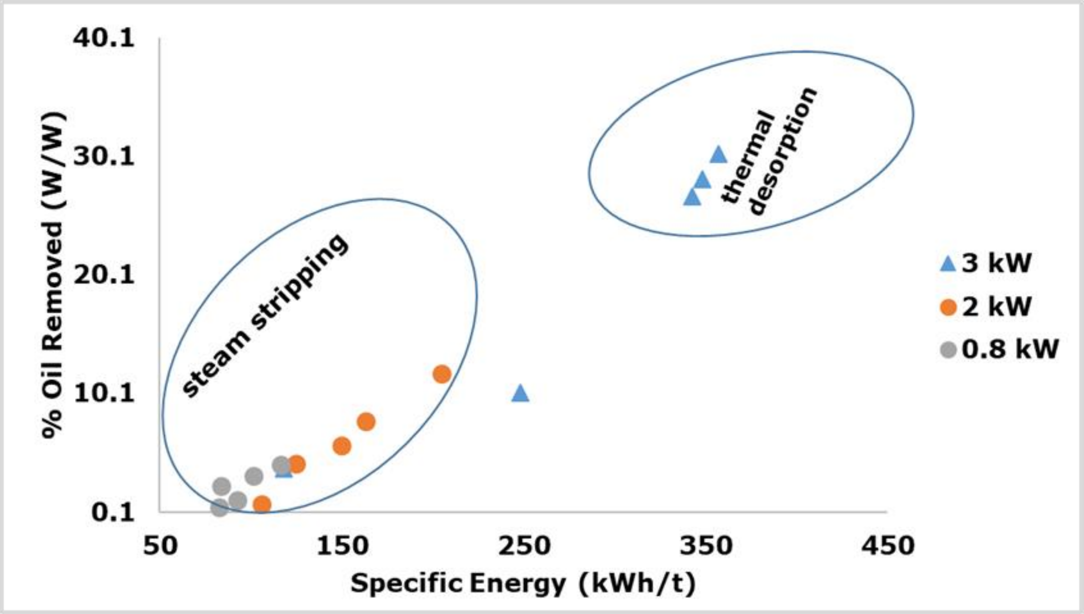


Figure 5.15. Oil removal plotted against heating times for treatment of loamy B soil at energy input of 50-180 kWh/t (20 g sample mass and 14 %w/w water)

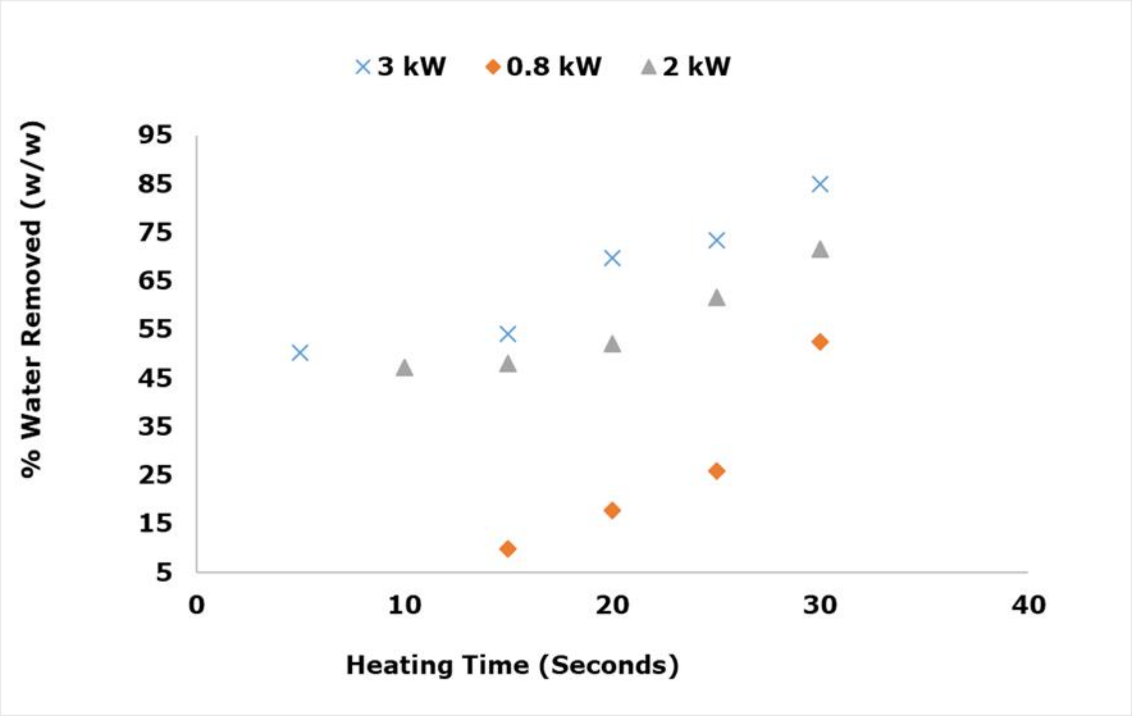


Figure 5.16. Water removal plotted against heating times during microwave treatment of loamy B soil

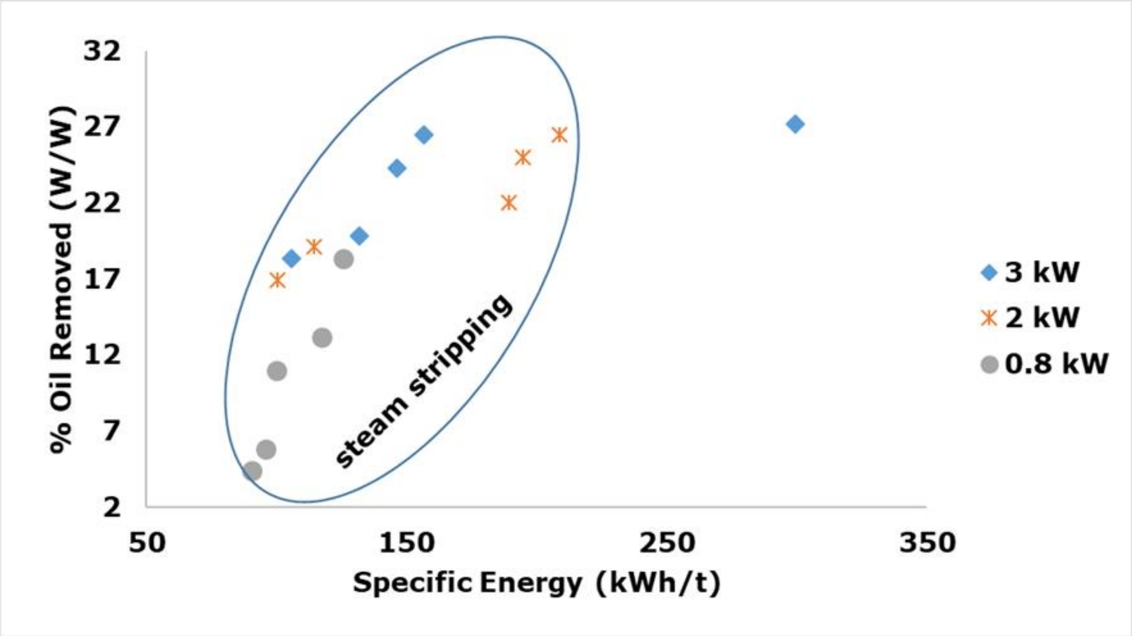


Figure 5.17. Oil removal plotted against heating times for treatment of sand soil at energy input of 50-180 kWh/t (20 g sample mass and 14 %w/w water)

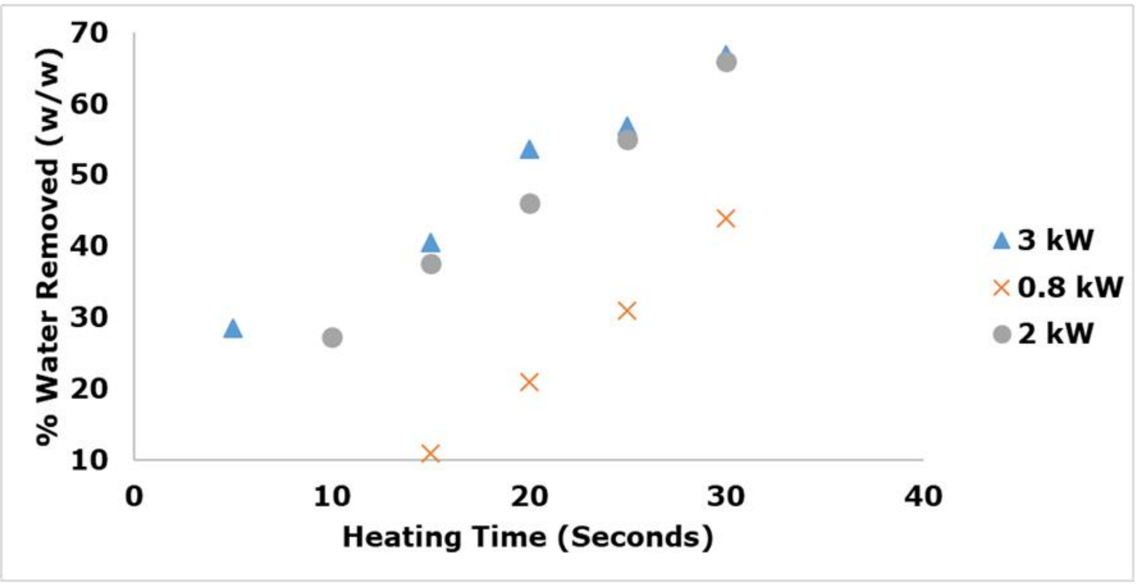


Figure 5.18. Water removal plotted against heating times during microwave treatment of sand soil

Figure 5.13 to Figure 5.18 shows corresponding energy input needed for oil and water removal by steam stripping.

5.5. Steam stripping mechanism

Power input (kW), energy input (kWh/t) and oil removal (%) are stated below for each soil. For clay soils at 3 kW energy input of 172-180 kWh/t 32-40 %. At 2 kW 30-38 % energy input of 163-177 kWh/t, for 0.8 kWh/t, 20-27 % with an energy input of 93-114 kWh/t (Figure 5.13) .Loamy B soils 3 kW energy input of 120 kWh/t 5 %. At 2 kW 3-7 % energy input of 105-163 kWh/t, for 0.8 kWh/t, 2-7 % with an energy input of 82-116 kWh/t (Figure 5.15). Sandy soils 3 kW energy input of 105-146 kWh/t 18-26 %. At 2 kW 16-20 % energy input of 100-114 kWh/t, for 0.8 kWh/t, 4-18% with an energy input of 90-125 kWh/t (Figure 5.17). Oil removal within this energy range occurred based on the fact that during steam stripping of soils, immiscible phases are created. The two immiscible phases, such as water and oil, are present together; their overall boiling point becomes less than the boiling point of the two entity that makes up the mixture (Robinson et al., 2008). The vapour pressure of immiscible liquids is function of the vapour pressures of each component; this implies that the boiling point of such a mixture is dependent on temperature and independent of the concentration of either component. The results obtained show little oil removal from loamy soils via steam stripping occurred. Similar behaviour is observed for the first 60 seconds (Figure 5.7) and 120 seconds of oil removal (Figure 4.7). Oil removal only increased for loamy soils during prolonged hearting time. Microwaves were used to generate steam from wet soil, with the steam forming a medium to desorb or entrain the organic contaminants. Oil removal from clay soil is the highest because water trapped within the pores absorbs the microwave energy and converts to steam, entraining the contaminant oil as it passes from the pores into the bulk gas steam penetrates soil layer and forms mixture with the oil in it.

Water content decreased with increasing processing time as expected. At 3 kW MW input, the water content decreased by 84 % (w/w), whereas the oil content decreased to 56.6 % (w/w) for clay soils (Figure 5.14). Loamy soils had water and oil content decreased by 85 % and 30.33 % (w/w) with oil (Figure 5.16). For sand soil water and oil content decreased by 66.9 % and 27.02 % (w/w) (Figure 5.18). The data shows a decrease in water content for samples treated at 800. 1000 and 3000 W as expected. This increase in water content with energy input suggests that the volume of water required for oil removal increases with decreasing liquid content. This is probably due to the low probability of contact between the remaining oil and water phases. As was the case with results obtained above (Figure 5.18), there is a twice decrease in water content for sand soil within the first 10- 20 seconds of processing and graduated increased slowly. The hypothesis from this occurrence is that water removal is easier in sand soil as water is present in free form and mass transfer is limited mainly by the soil bed itself.

In conclusion, this section quantifies for the first time the extent of removal through steam stripping during microwave treatment of oil contaminated soils. It then investigates how this behaviour changes for different soil samples at various treatment conditions—a hypothetical diagram presented in (Figure 5.19) explaining how oil is removed from soils micropores during microwave heating. The data presented above strongly suggests that the steam stripping mechanism is an effective process for soil oil removal.

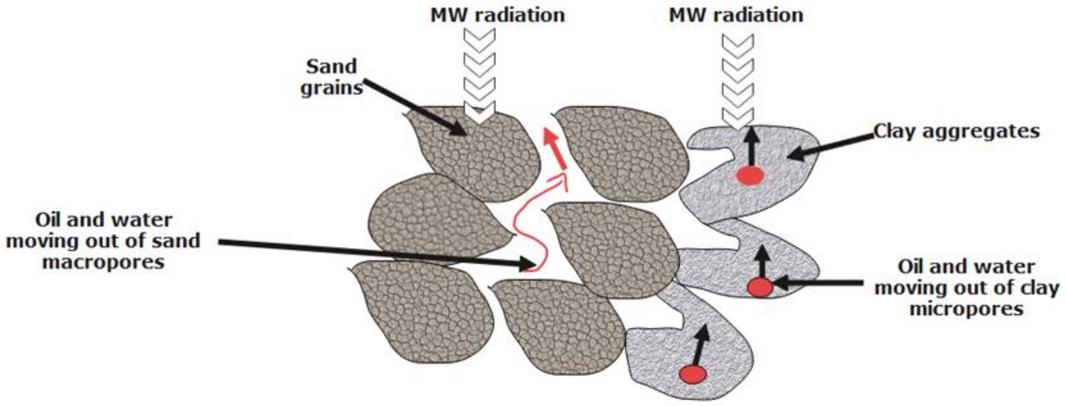


Figure 5.19. Conceptual diagram of oil and water stripping process from soils

5.6. Steam velocity: Assessment of steam stripping mechanism for oil removal from soils

The rate of water evaporation was calculated from measuring the water content of the samples before and after microwave heating. Rate of evaporation can be estimated as R (g/s)

$$R=\frac{M_1-M_2}{t} \qquad [5.10]$$

Where

M_1 is water content in untreated soil (g)

M_2 is the water content in the treated sample (g)

T is the heating time (s)

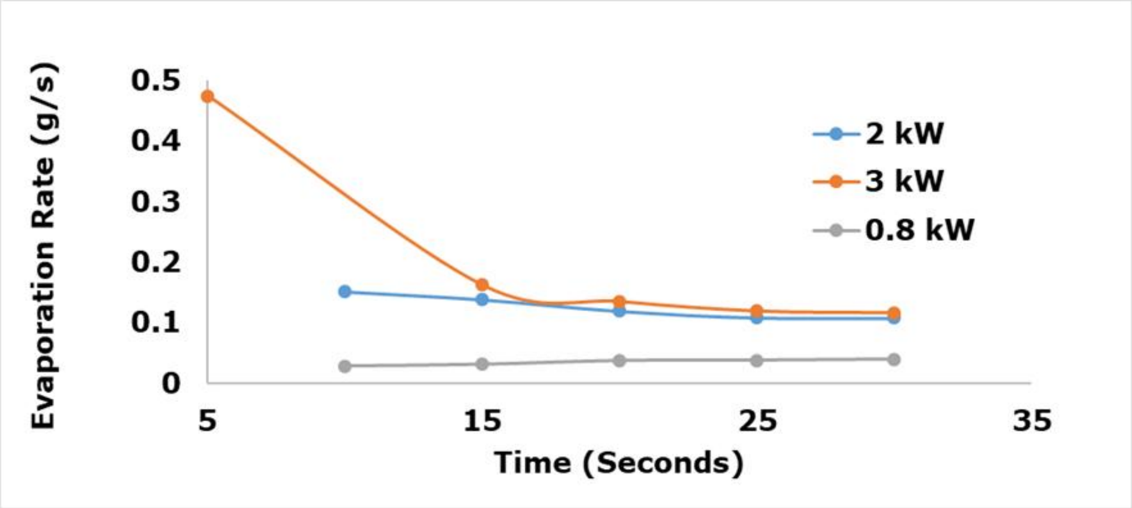


Figure 5.20. Evaporation rate of water from oil contaminated clay soil as a function of time

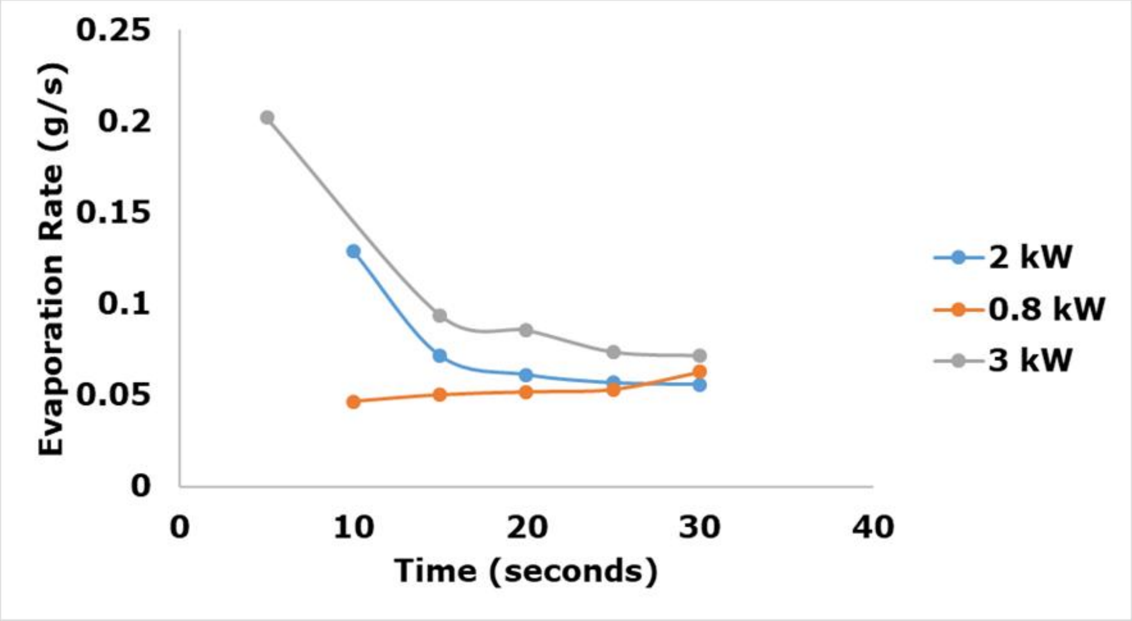


Figure 5.21. Evaporation rate of water from oil contaminated loamy B soil as a function of time

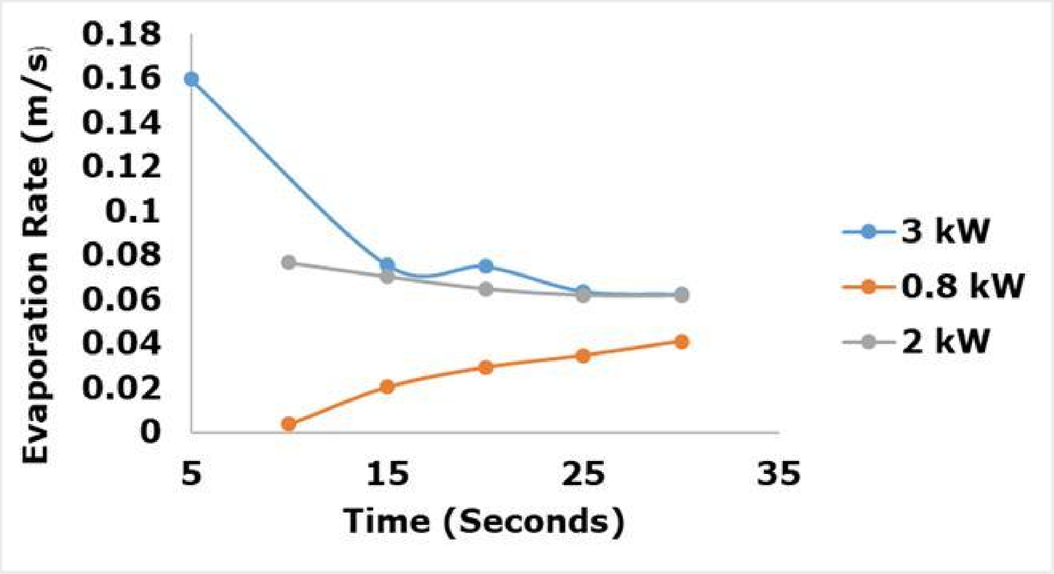


Figure 5.22. Evaporation rate of water from oil contaminated sand soil as a function of time.

Rapid rate of evaporation occurred within the first 5-10 seconds of the experiment, there after slow evaporation periods occurred. The falling rate period is characterized by low of water molecules as a result of drying. The evaporation rate differ for each soil type time and it depends on power density and heating rate. As seen in the Figures above, the rate of evaporation increased with power input for the soils. At 3 kW MW power level, initial rate is 0.45 g/s for clay soil (Figure 5.20), 0.25 g/s for loamy soil (Figure 5.21) and 0.16 g/s for sand soil (Figure 5.22). According to Constant et al (1996), faster rate of water evaporation have the tendency to partially pressurize the soil matrix hereby increasing the velocity of the steam leaving the soil pores.

5.7. Effect of microwave power and soil porosities on steam velocity

The steam velocity can be calculated as

$$u_g = \frac{Q}{A} \qquad [5.11]$$

Where

u_g = steam velocity through the pores of the material (m/s)

Q = steam volumetric flow rate (m^3/s)

A = cross sectional area of the material through which steam flows (m^2)

The steam volumetric flowrate is defined as;

$$Q = \frac{M_1 - M_2}{\rho t} \qquad [5.12]$$

ρ is the density in kgm^{-3}

t is the time taken for treatment

Microwave power and porosity of the sample have known to have effect on the velocity of steam

The relationship between microwave power and steam velocity can be express as

$$\frac{\Delta T}{\Delta t} = \frac{p_d}{Mc_p} \qquad [5.13]$$

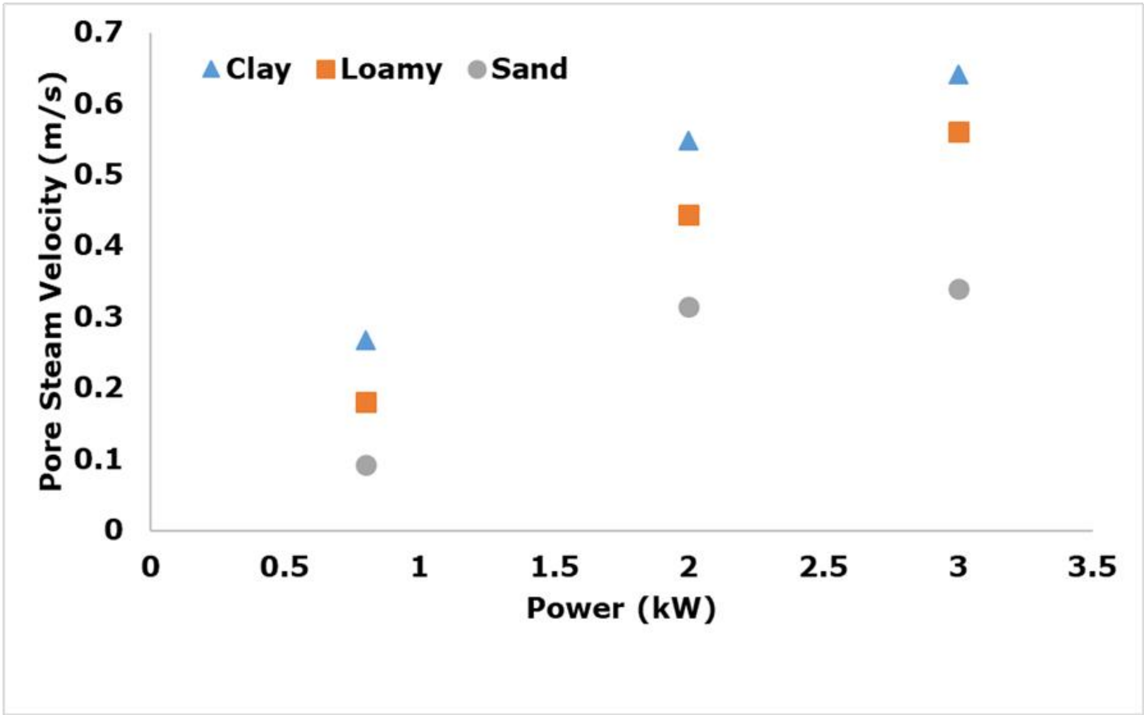


Figure 5.23. The relationship between pore steam velocity and microwave power during microwave treatment of soils at Clay 80-178 kWh/t, loamy 83-250 kWh/t, and sand 95-130 kWh/t.

Increasing Power density implies exposing soil samples to microwave energy for a longer time. This causes generation of steam at faster rate. High gas speed for uptake and movement of contaminants from soil is achieved. The effect of increasing the applied power is to increase the power density in the absorbing phases within the material, which is the water that is contained within the pore structure of soil. Microwave power is consumed in the water phase of the soil samples which heats the molecules of water and converts them to steam. At lower power densities the heating rate of water is proportionately lower, meaning that more heat is lost to the surrounding oil and soil before the water is converted to steam. The energy requirements to heat up water molecules are therefore higher at low power densities as more heat is lost to the surroundings. The size of the pores affects the interstitial steam velocity. When a material mainly consists of small pores and capillaries, the average cross-sectional area of the pores will be smaller than materials characterised by larger pores. Smaller pore cross sectional area will correspond to high steam velocity, implying reduces velocity through large pore size of a material which indicates lower steam velocity through those larger pores with greater areas. It is possible that increasing the internal pressure within the soil sample increases the driving force for steam generated especially in clay to leave, which increases the potential for high velocity steam. As shown in Figure 5.23 the volume of oil collected for clay samples with a density of 2.58 g/cm^3 was around greater at any point in time, leading to an overall improvement in oil removal. This can be attributed to the fact that greater porosity in the less dense soil sample allows for a larger number of paths to be formed within the bed, increasing the overall mass transfer. Furthermore, improved contact likelihood as a result of higher overall surface area available for contact between the steam and the oil present in the sample.

5.8. Mass transfer model

The mass transfer coefficient is linked to the velocity of the stripping medium in the generalized correlation using dimensionless groups (Ogunniran et al., 2017).

$$Sh=bRe^{C}S_{C}^{0.33} \qquad [5.14]$$

where Sh is the Sherwood number, Re is the Reynolds number, Sc is the Schmidt number, b and c are constants determined empirically. The Sherwood and Reynolds Numbers are defined as:

$$Sh=\frac{k_g d_p}{D_a} \qquad [5.15]$$

$$Re=\frac{\rho u_g d}{\mu} \qquad [5.16]$$

k_g is the gas phase mass transfer coefficient, d_p is the characteristic length (usually defined as the mean particle diameter), Da is the diffusion coefficient of the contaminant in the stripping medium, q is the density of the stripping medium, u is the velocity of the stripping medium and μ is the viscosity of the stripping medium. The mass transfer coefficient can be estimated from Fick's law (Sherwood et al., 1975):

$$J=k_g(C_i-C_b) \qquad [5.17]$$

Where J is the net molar flux of the species desorbed from the fixed bed into the gas phase, C_b is the concentration of the desorbed species in the bulk gas phase, and C_i is the concentration of the desorbed species at the interface with the stripping gas, which is related to its vapour pressure. The partial pressure at the interface is assumed to equal the vapour pressure at the stripping temperature. Partial pressure values are subsequently converted to gas phase concentration (mol/m^3) to yield k_g values (m/s) when the molar flux is known or measured. Within fixed beds it is often not possible to measure molar flux due to uncertainties in the interfacial area of the solid particles within the bed, which typically exhibit a large size distribution and poorly-defined interstitial regions. In previous studies (Wilkins et al., 1995; Yoon et al., 2002; van der Ham & Brouwers, 1998), the relationship between the mass transfer coefficient and gas velocity in fixed beds of soil has been presented in a modified equations:

$Sh_0 = bPe^c$ [5.18]

Where Sh_o is the modified Sherwood number and Pe is the Peclet number. The modified Sherwood number is defined as;

$$Sh_0 = \frac{k_g a d_p}{D_a} \quad [5.19]$$

Where a is the specific interfacial area (m^2 /m^3), and $k_g a$ is termed the overall mass transfer coefficient (s^{-1}), which is used when the interfacial area cannot be measured or estimated. Using this approach Eq. (4) can be rewritten as:

$N = k_g a V(C_i - C_b)$ [5.20]

Where N is the molar flowrate and V the bed volume.

The vapour pressure of decene at 378K (approximately bulk processing temperature) was estimated as 0.1298 atm. Concentration (kmol/m^3) as follows; At standard temperature and pressure (273K and 1atm), 1mol of gas in the material's pores occupy 22.4 dm^3. Therefore the concentration (Ci) is estimated from;

0.1298 atm

$$\frac{0.1298\text{atm}}{1\text{atm}} \times \frac{273\text{K}}{378\text{K}} \times \frac{1\text{ mol}}{22.4\text{dm}^3} = 0.0041\text{moldm}^3$$

$$N = \frac{G}{A} \qquad [5.21]$$

$$G = \frac{G_f - G_i}{t \times M_a} \qquad [5.22]$$

N= net molar flux of oil into the steam stripping medium (mol/m^2s)

k_g = gas phase mass transfer coefficient (m/s)

Gf = initial oil content (kg)

Gf = oil content after treatment (kg)

t = treatment time (s)

Ma = molar mass of oil (kg/kmol)

p_b = partial pressure of oil in the bulk gas phase (atm)

p_i = vapour pressure of oil at the interface with the stripping gas (atm) can be derived from

G is the molar flowrate, and A is the cross-sectional flow area

$$k_g = b u_g^c SC \qquad [5.23]$$

Where SC is the Schmidt number

$$S_c = \frac{\mu}{D_a \rho} \qquad [5.24]$$

Empirical mass transfer coefficient

$$J = k_g (P_i - P_b) \qquad [5.25]$$

$$D_a = \frac{3.185 \times 10^{-10} x T^{1.75}}{P_{total}} \qquad [5.26]$$

k_g = gas phase mass transfer coefficient (m/s)

d_p = characteristic length of diffusion or bulk transport, defined as the mean particle size (m)

D_a = diffusion coefficient of oil in the stripping medium (m^2/s)

ρ = density of the stripping medium (kg/m3)

u_g = steam velocity (m/s)

d = diameter of 'bulk flow' pore channel (m)

μ = viscosity of the stripping medium (kg/ms)

ε = porosity

T is the temperature of the sample in kelvin

P_{total} is the pressure of the system in bar

Gas difusivity $D(m^2S^{-1})=3.185 \times 10^{-10} \times \frac{T^{1.75}}{P_{total}}$ [5.28](Van der Ham and Brouwers, 1998)

T = temperature (kelvin 378k) at atmospheric pressure

The mass transfer rate of hydrocarbons from soils to a gas stripping medium has been investigated. The steam velocity and mass transfer coefficient data from the three soils is presented in Figure 5.24, Figure 5.25 and Figure 5.26show the effect of pore steam velocity on mass transfer coefficient. Result obtained reflects the relationship between pore steams velocities observed in this work. The gradient of the plots represents the constant c in equations 5.14. It is clear from the data that increasing steam velocity results in a higher mass transfer rate of oil from soils for clay and sand soils. The efficiency of oil removal of the system can be improved by increasing the mass transfer coefficient into the steam stripping phase. This may be achieved by increasing the power input or by improving electric field intensity within the cavity, hence higher heating rates and greater steam velocities within the samples.

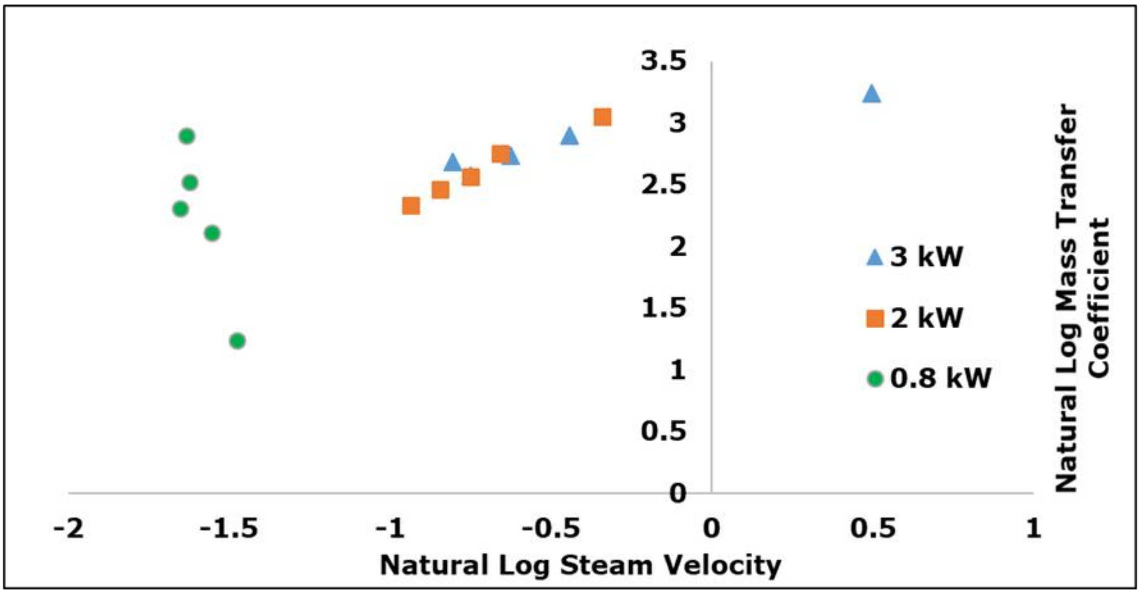


Figure 5.24. The effect of steam velocity on mass transfer coefficient during the microwave treatment of oil contaminated clay soil

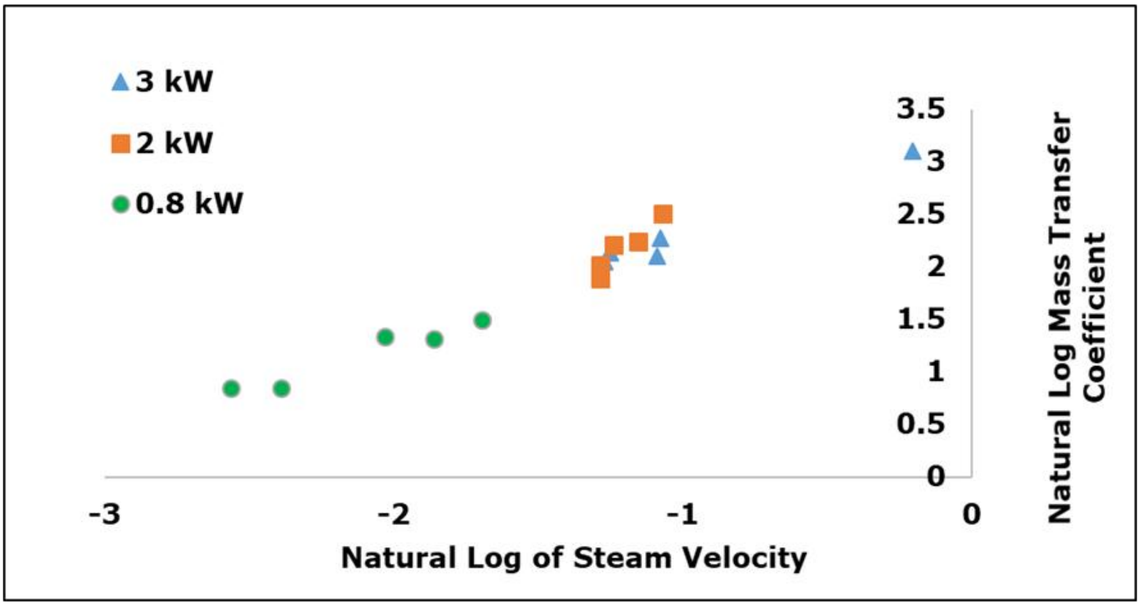


Figure 5.25: The effect of steam velocity on mass transfer coefficient during the microwave treatment of oil contaminated sand soil

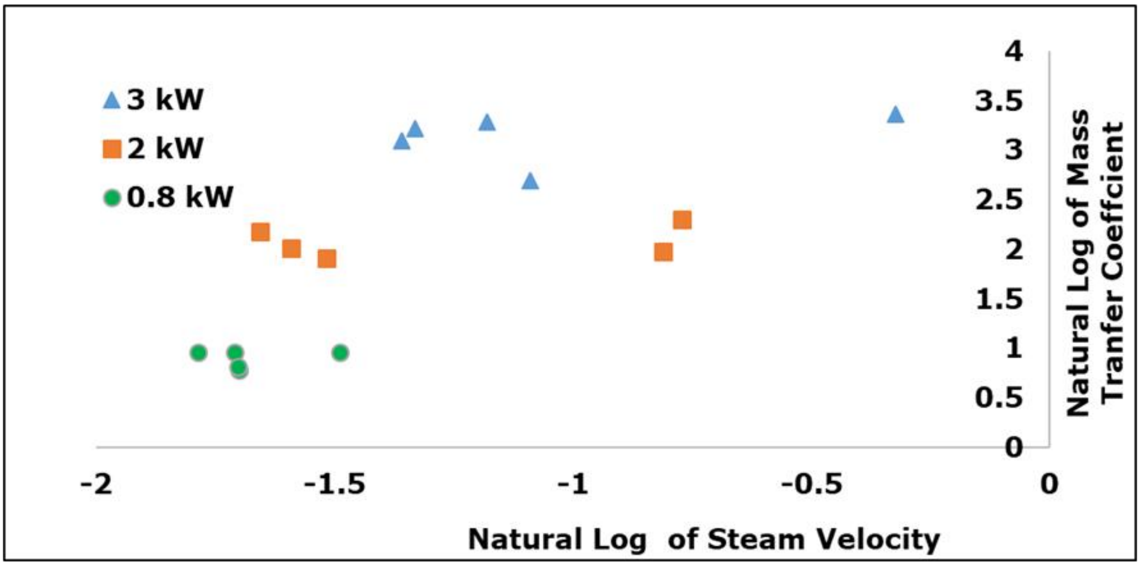


Figure 5.26. The effect of steam velocity on mass transfer coefficient during the microwave treatment of oil contaminated loamy soil

An important conclusion to note from Figure 5.24 and Figure 5.25 is the positive correlation between mass transfer coefficient and steam velocity. The mass transfer coefficient of oil into the steam stripping medium increases as the steam velocity increases. This strongly suggests that the rate of oil removal from clay and sand soil is highly dependent on the mass transfer rate of vaporised water from the material. Variables for clay and sand lie on one curve, indicating that they can be explained by steam velocity. This is important because, for the first time, it is demonstrated empirically that the rate of water removal as steam from soils (steam stripping) can be effective variable for oil removal.

Table 5.3. Steam velocity and mass transfer coefficient for clay soil at power levels of 0.8-3kW, porosity 0.49

Power (kW)	Steam generation rate (g/s)	Steam velocity (m/s)	Oil removal rate (g/s)
0.8	0.054	0.209	0.004
2	0.120	0.473	0.005
3	0.136	0.535	0.006

Table 5.4. Steam velocity and mass transfer coefficient for loamy B soil at power levels of 0.8-3 kW, porosity 0.55

Power (kW)	Steam generation rate (g/s)	Steam velocity (m/s)	Oil removal rate (g/s)
0.8	0.0531	0.182	0.001
2	0.061	0.219	0.003
3	0.086	0.307	0.012

Table 5.5. Steam velocity and mass transfer coefficient for sand soil at power levels of 0.8-3 kW. 1200 kg/me, porosity 0.41

Power (kW)	Steam generation rate (g/s)	Steam velocity (m/s)	Oil removal rate (g/s)
0.8	0.029	0.131	0.0003
2	0.065	0.290	0.003
3	0.075	0.337	0.003

The water and oil removal levels in Figure 5.5-5.8 were subsequently used to establish the rate of steam generation and rate of oil removal. Steam velocity was calculated based on the rate of steam generation (change in water content with time), bed geometry and sample porosity. For all soil steam generation rate, steam velocity and oil removal rate increased with power density Table 5.3, Table 5.4 and Table 5.5. Doubling the microwave power doubles the steam velocity for sand and clay soil, which increases the mass transfer coefficient. This may be due to the fact that higher power densities promote a higher steam velocity and subsequently increased removal efficiency of the hydrocarbon phase.

5.9. Continuous microwave processing of sand soil at 896 MHz

An attempt was for made for the first time in microwave processing of crude oil natural contaminated sand soil from Nigeria up to 1 tonne. The aim was to compare laboratory treatment and pilot-scale treatment. Crude oil contaminated sand soil was treated using an 896 MHz system located within an existing thermal desorption plant in Lowest of the UK. The industrial pilot plant was designed with a microwave power input of 80-100 kW at frequency of 896 MHz. Sandy soil with initial oil content of 1.4 %w/w (Table4.1) was loaded into a rectangular hopper. After that, the soils were discharged into a continuous rectangular conveyor belt system using a series of screw feeders. The soils were then passed at a feed rate of 700 kg/h through the microwave cavity, where it was treated, leaving the system through an outlet hopper. Nitrogen gas was used to maintain an inert system and monitor oxygen level also as a purge gas to prevent potential combustion of the oil content during microwave heating. It serves the purpose of a sweep gas to aid the removal process of possible flue gases within the applicator. Mass of soil in the microwave system's feed hopper and outlet hopper were monitored continuously and linked with the power supply. The hopper and power supply interface is to maintain equilibrium between feedstock and power level. Also, an oxygen monitoring device was linked to the power supply was only started once the oxygen content dropped below 6% v/v. The microwave cavity consisted of choke sections, which prevented microwave leakage, and the applicator region where treatment took place. The applicator was connected to a magnetron via a number of 90° bends and straight waveguide sections. The magnetron used in this case could output a maximum power of 100 kW at 896 MHz. A circulator was used to protect the magnetron and was used to absorb any reflected power that was not absorbed by the soil in the cavity. Any heated water leaving the circulator unit is cooled by an air cooled heat exchanger and recycled back in a closed loop. Arc detectors, interlocked with the power supply, were placed in the bend immediately after the applicator and just before the circulator to prevent any damage caused through arcing.

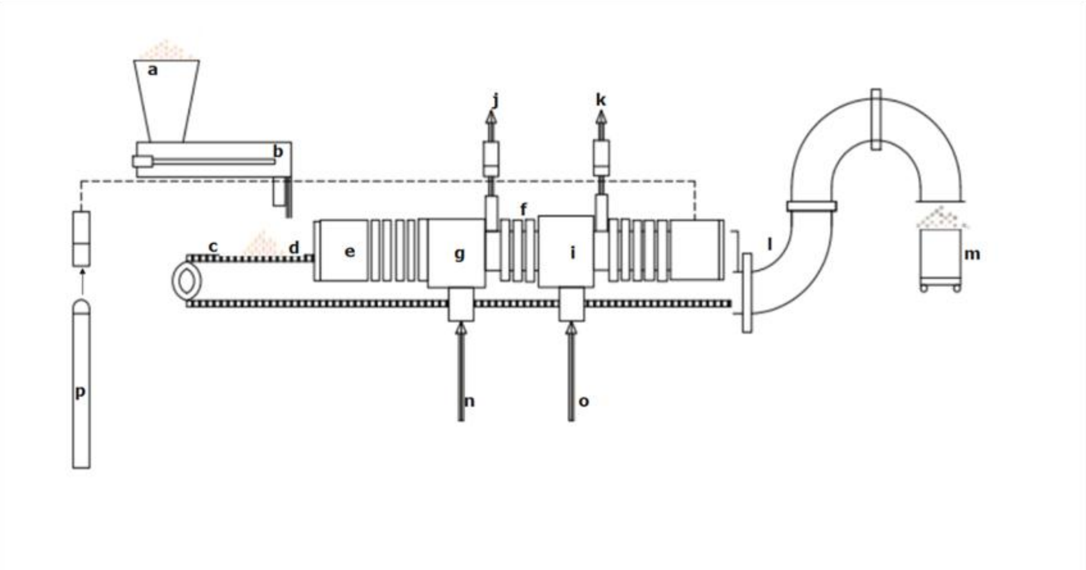


Figure 5.27. Complete diagram of pilot scale rig for the treatment of contaminated sand soil

a) hopper, b) screw feeder, c)conveyor belt, d) untreated sand soil are fed Into the microwave applicator, e) chokes used to prevent microwave leakage, f) chokes used to prevent cross-coupling, g) and i) microwave applicators where the sample is subjected to a high power density, j) and k) vapours and extracted fumes are removed to the extraction system, I) microwave treated (oil-lean) drill cuttings exit the cavity and are collected (m) at the end of the line for testing, n) and 0) microwave inlet perpendicular to belt, p) nitrogen bottle.

Steam and condensable vapours were then condensed in a heat exchanger, vapours generated within the cavity were removed at extract points. Extraction points were attached at the feed inlet between the area of discharge and the belt screw feeder, as well as at the discharge end of the cavity, where the treated soil were collected. A representative sample of the treated soil leaving the cavity was collected and stored for water and oil content testing. The result is shown below

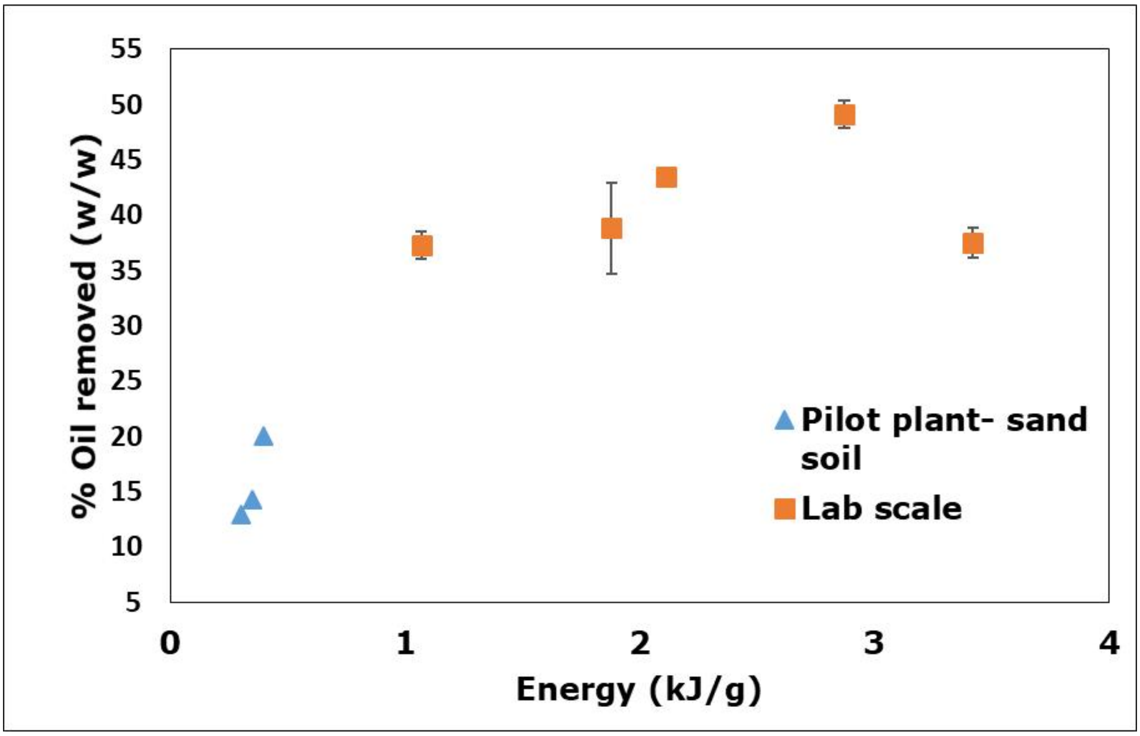


Figure 5.28. Oil removal against energy input for batch and continuous MW treatment of sand

*Error bar represent standard deviation from triplicate oil extraction after MW experiment.

An energy input of 0.3-0.4 kJ/g for continuous process treatment oil removal is in the range of 13-20%. In comparison to the batch process has energy input of 1.07 kJ/g resulted to 37.3 % oil removal. Although the batch process has about 2.5 times the energy from the continuous process (Figure 5.28).

In conclusion, this chapter has discussed that oil removal at different high microwave power can be explained by steam stripping removal mechanisms. It is known that steam velocity increases when microwave power increases, which then improves the oil mass transfer rate out of the sample. It is clear that this phenomenon is steam stripping and provides a more robust explanation of the power density and increasing soil water content effect on oil removal than has been previously suggested. The steam velocity and mass transfer coefficient data from microwave heating tests in processing different soil types were used to generate mass transfer. In conclusion it is clear, that steam velocity governs oil removal process, which in turn promotes evaporative mass transfer of the hydrocarbon phase. The importance of this process is that in with microwave heating the stripping gas is steam, which is generated in-situ from the water that is present within the solid. Steam is generated throughout the entire soil bed volume, including areas of low voidage, implying that the contact between hydrocarbon and stripping gas is more consistent throughout the bed volume and not prone to the channelling effects that occurs (Ogunniran et al., 2017). High gas velocities will occur in areas of high voidage, whereas limited gas flow will occur in areas of low voidage and thus the contact between stripping gas and hydrocarbons will be limited within these regions. Increased internal pressure, steam temperature and velocity - increasing the power density leads to pressure driven vapour flow from within the soils at higher velocity and turbulence. This can enhance both mass transfer from an entrainment point of view, as well as mass transfer from a vaporisation point of view, as better mixing can be achieved between the steam and the oil phase.

CHAPTER SIX. Comparing Conventional Pyrolysis to Microwave Heating

Pyrolytic treatment offers the potential for the rapid remediation of contaminated soils. Factors such as the pyrolysis temperature, heating rate, and residence time may affect oil removal from soil (Li et al., 2019). Therefore, these factors were examined in the treatment of oil-contained soils using a typical Gray-King fixed bed. The research objective is to illustrate the remediation degree concerning the removal of crude oil from contaminated soils at different operating temperatures and associated retention time. Repeated Gray-King pyrolysis tests for all soils was performed at 400 °C, the weight differences between the initial and final soil are listed in Table 6.1, experimental process is fully discussed in Chapter 3.

Table 6.1. Weight losses (g) for repeat pyrolysis at 400 °C

Experiment number	**Clay**	**Loamy A**	**Loamy B**	**Sand**
1	2.45	2.22	1.62	0.52
2	2.80	2.62	1.61	0.48
3	2.74	2.54	1.56	0.55
4	2.65	2.46	1.45	0.58
5	2.75	2.63	1.50	0.55
6	2.55	2.65	1.67	0.56
Mean	2.66	2.52	1.57	0.54
Standard deviation	0.13	0.16	0.08	0.035
% RSD	5.03	6.34	5.09	6.48

Footnote: Heating rate = 5 °C/min, weight of starting soil (g) = 20

The result of the influence of conventional heating on oil removal from different soil types is presented in Table 6.2.

Table 6.2. Yields of residual oil in the soil after pyrolysis

Residual oil (% w/w)				
Temperature (°C)	Clay	Loamy A	Loamy B	Sand
400	0.16	0.68	0.93	0.11
500	0.002	0.01	0.01	0.0003
600	<0.002	<0.01	<0.001	<0.0001
700	<0.002	<0.01	<0.001	<0.0001
800	<0.002	<0.01	<0.001	<0.0001

*Values are reported as mean from triplicate tests.

After pyrolytic treatment, the residual oil content was reduced to 0.16 %w/w, 0.68 % w/w, 0.93 %w/w, and 0.11 % w/w when this contaminated soil was treated at 400 °C for 45 min. Nigeria's threshold standard of 0.5 %w/w for crude oil in soil was obtained when all the soils were treated at 500 °C (Table 6.2).

Table 6.3. Percentage oil depletion after thermal heating as a function of temperature

		% Oil removed (w/w)		
Temperature (°C)	Clay	Loamy A	Loamy B	Sand
400	90.00±0.3	89.53±0.25	86.00±0.4	92.00±0.3
500	99.87±0.5	99.98±0.2	99.80±0.5	99.98±0.1
600	99.99±0.1	99.99±0.1	99.98±0.1	99.99±0.2
700	99.99±0.3	99.99±0.2	99.98±0.1	99.99±0.1

800	99.99±0.1	99.99±0.1	99.98±0.1	99.99±0.2

*Values are reported as mean from triplicate oil analysis

Table 6.3 illustrates the pyrolysis temperature influence on removal from oil-contaminated soil at different temperatures (400 ºC, 500 ºC, 600 ºC and 700 ºC) applied to the different soils. Compared with the initial oil content in the soil, the process temperature influences the concentration level of the organic pollutant from the polluted soil. When the pyrolysis temperature is 400 ºC, 90 %, 89.53 %, 86 %, and 92 % of oil is removed from clay, loamy A, loamy B, and sand soils, respectively . By increasing the pyrolysis temperature to 500 ºC, 99.9 % of oil is removed from all soils. Increasing the temperature of the process does not provide a significantly lower level of contaminants in the soil after 500 ºC (Table 6.3). Overall, the highest oil removal was observed with sand and the lowest one with clay and loamy soils. Table 3 illustrates the pyrolysis temperature influence on removal from oil-contaminated soil in case of different temperatures (400 ºC, 600 ºC, and 800 ºC) applied to the different soils. Compared with the initial oil content in the soil, the process temperature influences the concentration level of the organic pollutant from the polluted soil. When the pyrolysis temperature is 400 ºC, 90 %, 89.53 %, 86 %, and 92 % of oil is removed from clay, loamy A, loamy B, and sand soils, respectively . By increasing the pyrolysis temperature to 500 ºC, 99.9 % of oil is removed from all soils. Increasing the temperature of the process does not provide a significantly lower level of contaminants in the soil after 500 ºC (Table 6.3). These findings are similar to Kang et al. (2020) reported that 94.4 % of crude oil was removed by batch pyrolysis after 30 min of heating. Removal of total petroleum hydrocarbon of about 1.6-1.9 % weight from soil was studied (Vidonish et al., 2018). Soil pyrolysis was conducted in a 0.5 L fixed-bed reactor heated at 420 °C in a split-tube furnace for 3 hours. The residual soil TPH content in the soil is less than 0.5 % w/w. The results also demonstrated that the oil removal rates almost reached 100% at 500 °C. The residual oil from soils was calculated and is discussed below.

The TOC from recovered pyrolysis char is seen in Table 6.3, it is used for determining the percentage TOC of recovered oil and gas in Table 6.4 – Table 6.7. Values reported for char and oil are from triplicate analysis. The highest yield was used from triplet analysis was used for gas studies.

Table 6.4. Residual TOC of char (%w/w)

Temperature (°C)	**Clay**	**Loamy A**	**Loamy B**	**Sand**
400	0.28	2.85	1.35	0.30
500	0.13	2.20	0.70	0.18
600	0.10	2.20	0.60	0.17
700	0.08	2.25	0.59	0.10

*Values are reported as mean from triplicate TOC analysis

Total gas yield (ml) is calculated as:

$$GY = \frac{GC \times V}{GI} \qquad [6.1]$$

Where GY= gas yield in ml

V = volume collected in gas bag

GI = volume of gas injected into the gas chromatogram

Equations for the conversion to percentage TOC is explained in the appendix.

Table 6.5. Percentage TOC removal from the oils as a function of temperature clay

Temperature (ºC)	400	500	600	700
% TOC in gas yields	0.04	0.07	0.13	0.20
% TOC of char	15.90	4.55	5.68	3.98
% TOC of oil recovered from soil	84.04	92.70	94.09	95.47
% Total TOC	99.98	97.32	99.9	99.65

Table 6.6. Percentage TOC removal from the oils as a function of temperature Loamy A

Temperature (ºC)	400	500	600	700
% TOC in gas yields	0.013	0.14	0.18	0.20
% TOC of char	38.00	31.07	29.33	30.00
% TOC of oil recovered from soil	55.98	66.43	68.09	69.02
% Total TOC	93.99	97.64	97.6	99.22

Table 6.7. Percentage TOC removal from the oils as a function of temperature loamy B

Temperature (ºC)	400	500	600	700
% TOC in gas yields	0.016	0.043	0.043	0.11
% TOC of char	23.89	12.39	10.61	10.44
% TOC of oil recovered from soil	74.82	86.99	87.89	88.32
% Total TOC	98.73	99.42	98.543	98.87

Table 6.8. Percentage TOC removal from the oils as a function of temperature sand

Temperature (ºC)	400	500	600	700
% TOC in gas yields	0.006	0.12	0.22	0.25
% TOC of char	18.75	10.91	10.63	6.25
% TOC of oil recovered from soil	79.71	88.18	88.34	92.97
% Total TOC	98.52	98.93	99.19	99.47

The percentage TOC in char reduced with temperature (Table 6.5-6.8), the value for range as 15.90-3.98 %; loamy A soil; 38-38 %, loamy B soil; 23.89-10.44 % and sand soil; 18.75- 6.25 %. TOC content at 700 ºC is highest for loamy A soils due to the high content of the heavier end PAHs and polar compared to other soil types (Figure 4.6). Percentage reduction for all soils is greater between 400-500 ºC. The % TOC for 100 ml of pyrolysis gas collected ranged from 0.04- 0.2 % for clay (Table 6.5), 0.013-0.20 % for loamy A (Table 6.6), 0.016-0.11 % for loamy B (Table 6.7) and 0.006-0.25 % for sand (Table 6.8). The total % TOC recovered oil from the fixed bed Gray-King pyrolysis process at 45 minutes treatment time increased with an increase in the peak temperatures and remained almost constant beyond 500 °C peak temperature for all treated soils. Total percentage TOC recovered from the Gray-King pyrolysis is less than 100 %, the reason is due to number of factors which may include loss of differing amounts of lighter constituents in recovered oil. A Comparison of residue TOC in w/w% in Table 6.5, and the initial TOC from dichloromethane/method mixtures extractable soil (Table 4.2) shows that former is less in value. This buttress the previous fact that losses of some volatile component after heating occurred. The composition of the oil was analysed using GC-MS and discussed in the next section.

6.1 Composition of pyrolysis oil

Condensed oil collected after pyrolysis has been analyzed using a GC-MS and the chromatograms showing the n-alkanes are shown in Figure 6.1 (a, b, c and d).

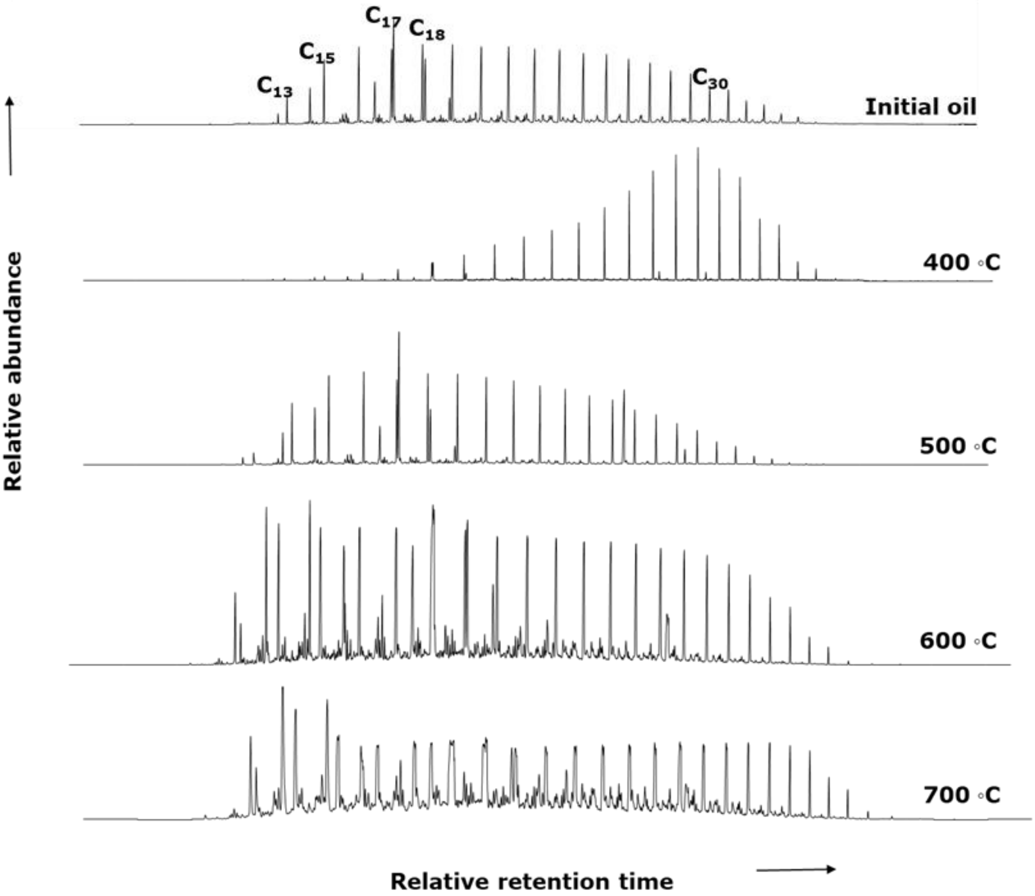


Figure 6.1 a. (Clay soil)

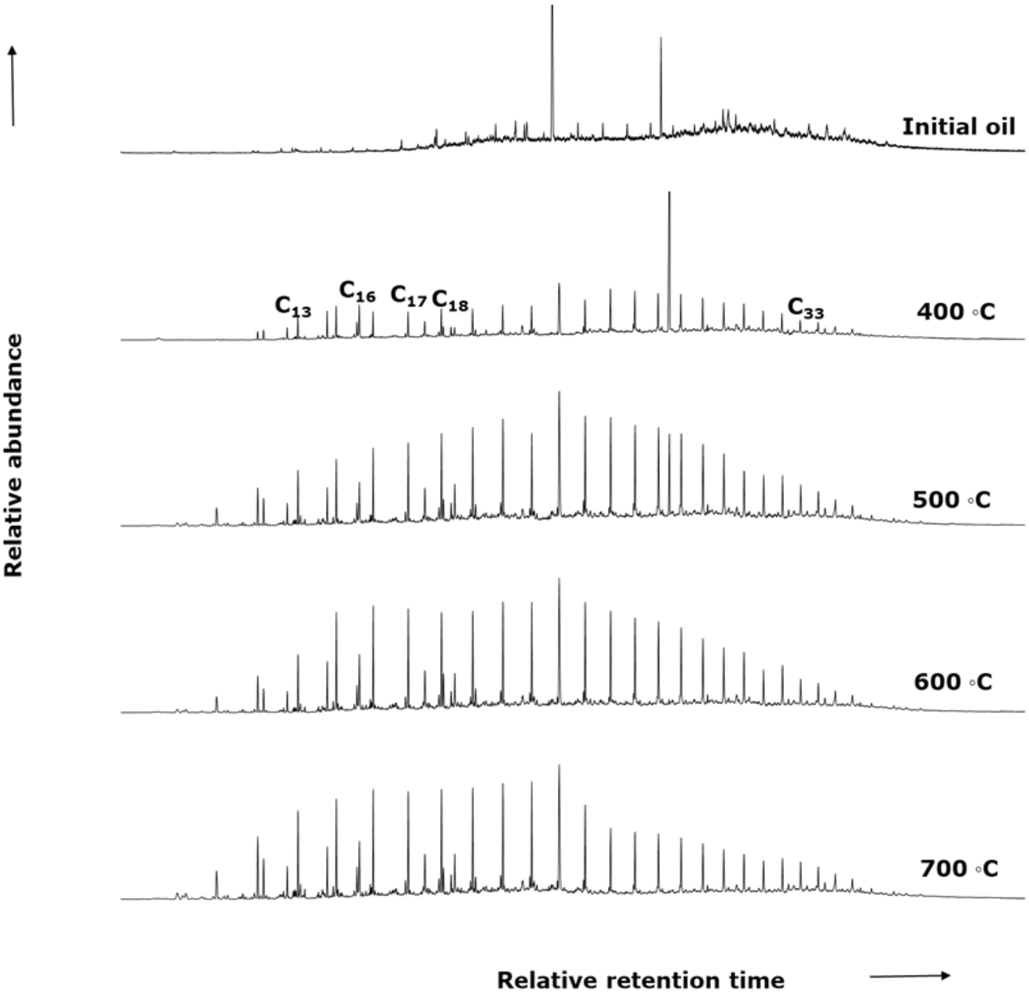


Figure 6.1 b. (Loamy A)

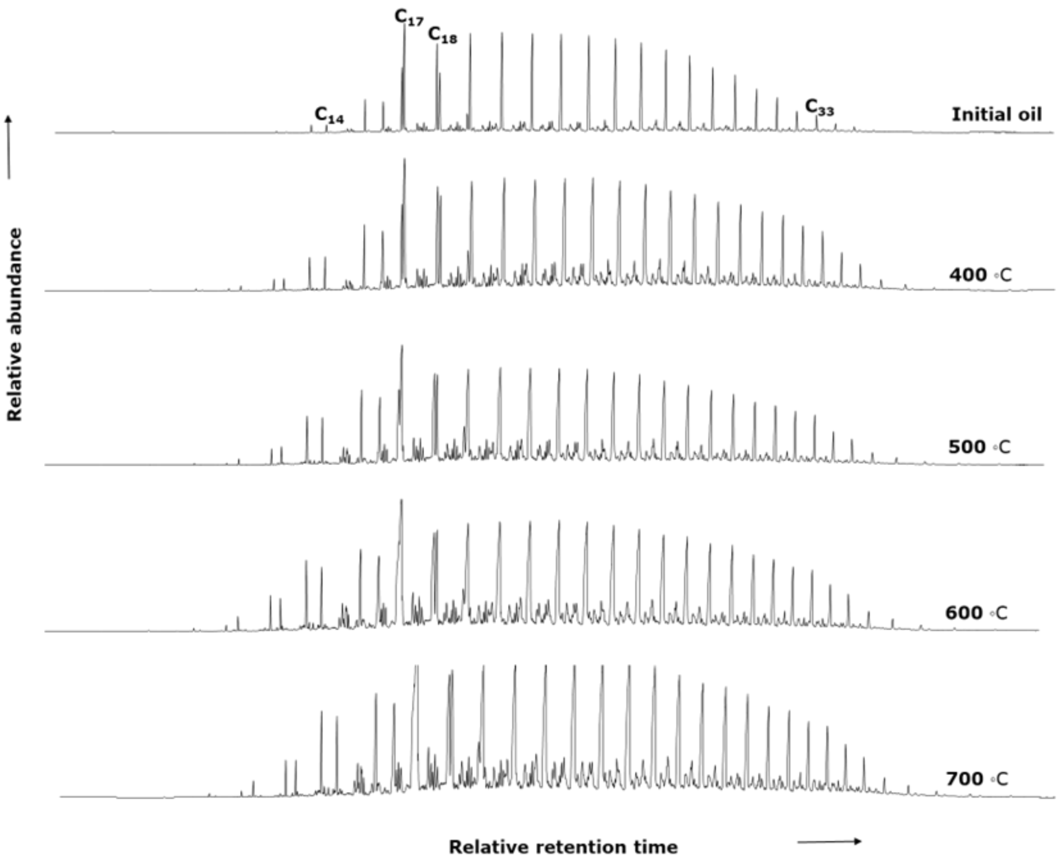


Figure 6.1c. (Loamy B)

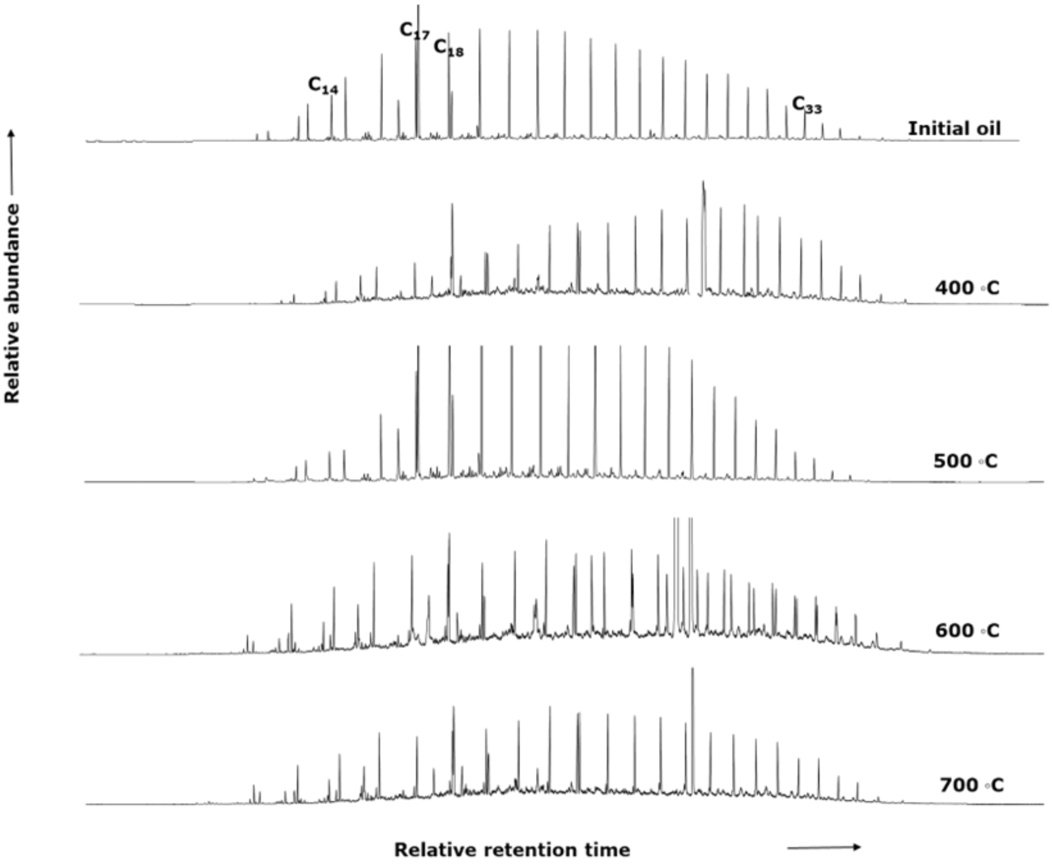


Figure 6.1 d. (Sand)

Figure 6.1. (a, b, c and d). GC-MS single ion chromatograms (m/z=71) of the oils obtained from clay, loamy A and loamy B and sand soils

The GC-MS chromatogram in Figure 6 .1 (a, b, c and d) show the temperature effects over the range 400 – 700 °C. There is a significant cracking effect as light fraction increases with temperature. Heating above 500 °C showed an abundance of lower molecular alkanes (> C_{14}) compared to the initial. This indicates that lower boiling point alkanes are generated as the temperature continues. The unresolved complex mixture (UCM) is very evident in the treatment of loamy A soil (Figure 6.1 b) as severe cracking of the UCM occurred to form lighter hydrocarbons. The increase in (> C_{33}) abundance can be due to a combination reaction involving higher and lower molecular weight hydrocarbons, especially in loamy A, loamy B, and sand soils.

Clay soils (Figure 6.1 a) behaved differently after 400 ºC, an abundance of (> C_{33}) reduces as temperature increases—combination reaction results in the formation of heavy n-alkane resulting in increased peak intensity. Analysis of the gas yields obtained from pyrolysis is used to explain this phenomenon further.

6.2. Gas yields

The GC-FID traces for pyrolysis gases are shown in Figures 6.2-6.5. Methane was the major product, and the yield increased with temperature for all soil types. The mass (µg) of hydrocarbon gases (methane and ethane) recovered at 400 ºC ranged as 15.34, 7.98 for clay (Figure 6.2), 42.52, and 17.54 for loamy A (Figure 6.3), 21.52 %, 95.43 for loamy B (Figure 6.4) and 9.4, 0 % for sand soil (Figure 6.5). Mass (µg) of typical olefin (ethene) recovered ranged as 7.98 for clay, 11.64 for loamy A, 7.18 for loamy B soil, and 0 for sand soil. The difference in percentage gas obtained for each soil shows how the oil content and other soil composition affects the type of off-gases recovered. Soils with higher oil content had greater value for recovered methane gas. Unsaturated hydrocarbon gases such as ethene, propene, butene increased for all soil type especially at high temperature, though pentene behaved differently as it reduce with increasing temperature.

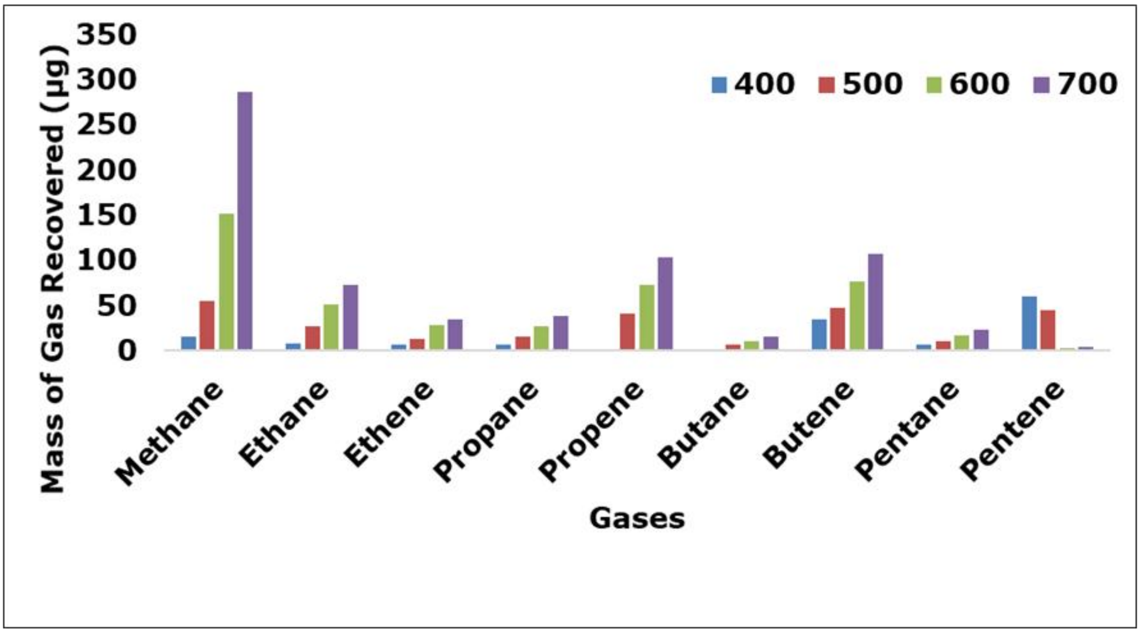


Figure 6.2. Gas composition from pyrolysis of the clay soil at various pyrolysis temperature

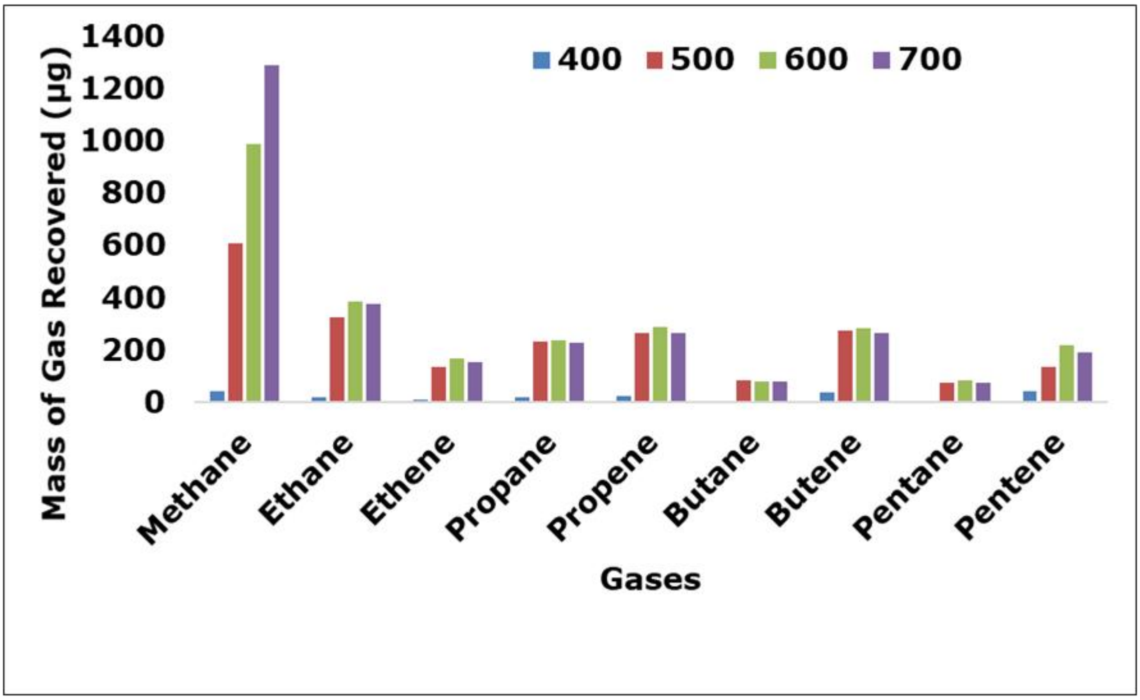


Figure 6.3. Gas composition from pyrolysis of loamy A soil at various pyrolysis temperature

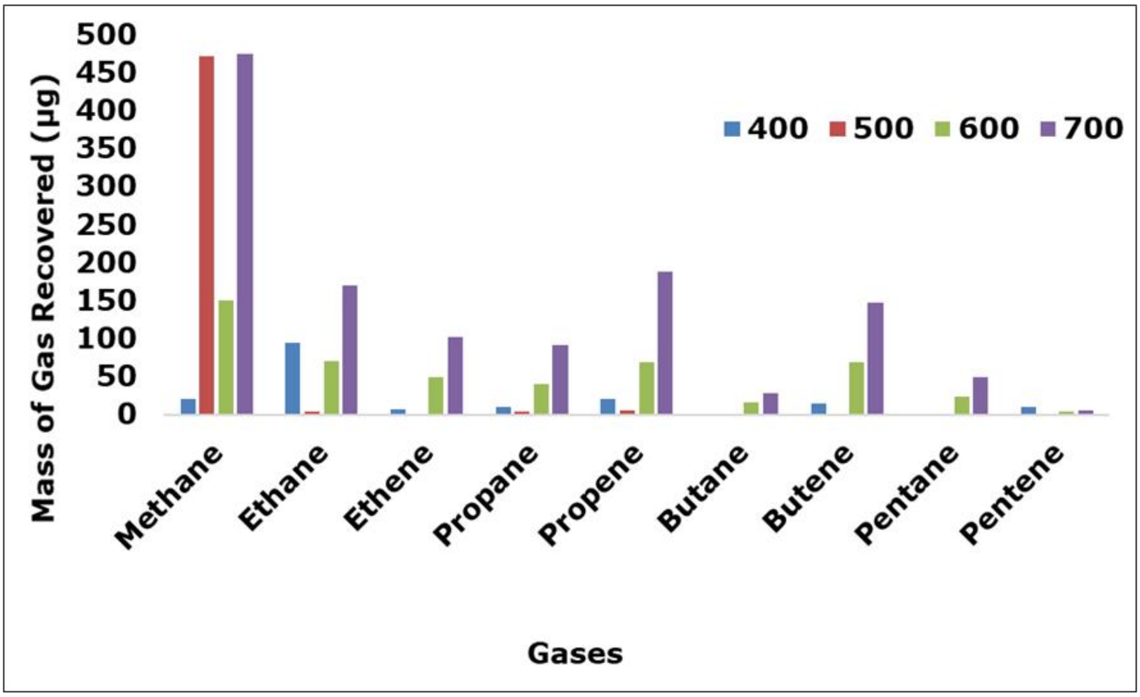


Figure 6.4. Gas composition from pyrolysis of loamy B soil at various pyrolysis temperature

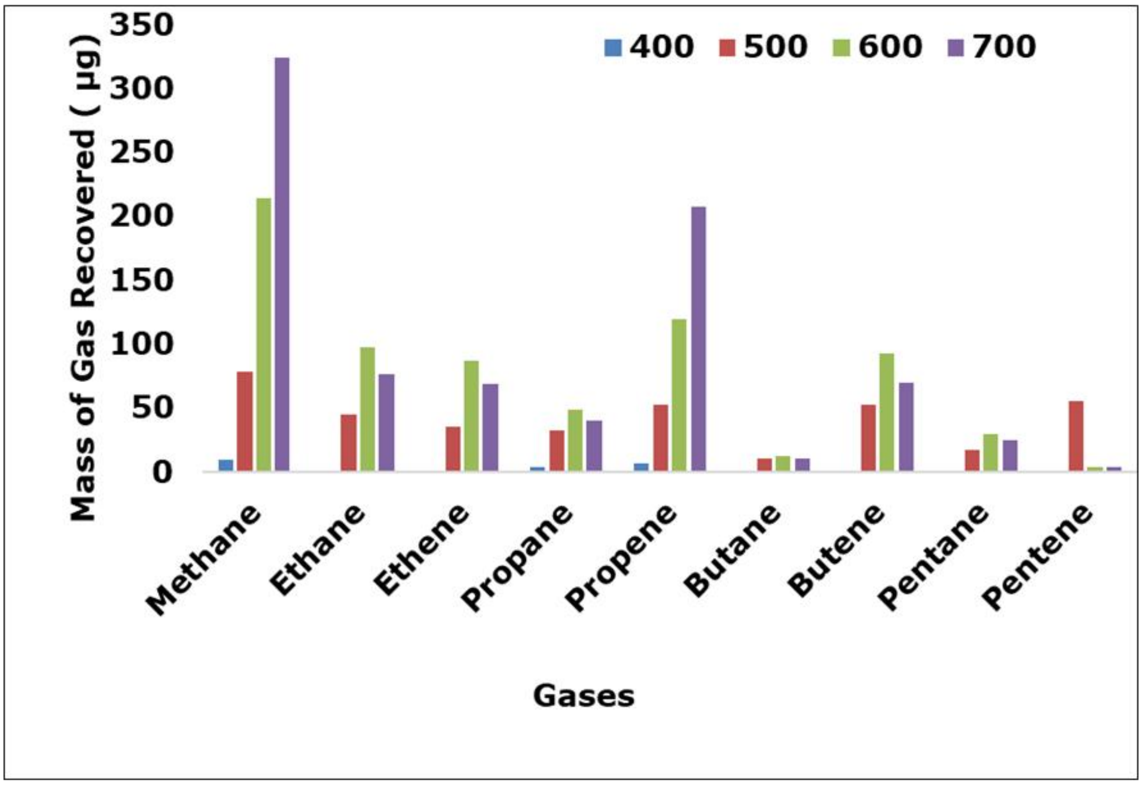


Figure 6.5. Gas composition of pyrolysis from the sand soil at different pyrolysis temperature

The increase in yield of olefins with increasing temperature shows that thermal cracking of hydrocarbons took place. It is possible that competing reactions such as thermal cracking of heavy molecular weight hydrocarbons and combination reaction between pyrolysis gases and pyrolysis oil also occurred due to the decrease in the yield of pentene. However, cracking reactions seems to be the favoured reaction. The high yield of oil (Table 6.2) in comparison to yield of gases (Figure 6.2-6.5) is in agreement with the description of a typical slow pyrolysis process. A typical conceptual secondary reaction involving pyrolysis gases and liquid hydrocarbon in oil is shown in Figure 6.6.

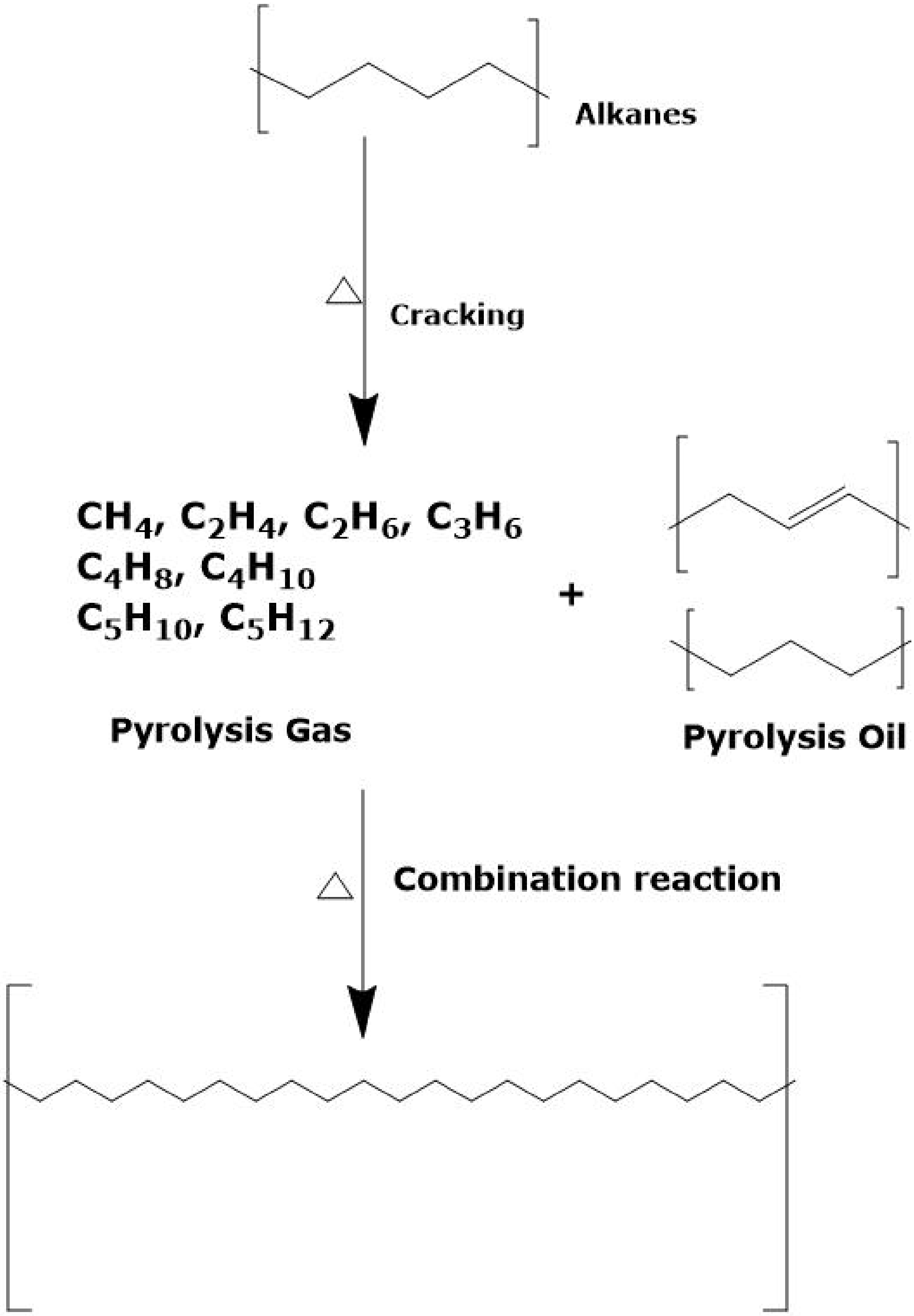


Figure 6.6. Conceptual diagram of reaction occurring during pyrolysis

Alkene/alkane doublets formed at higher temperatures is an evidence of dehydrogenation. The hydrogen and the hydrogen is used in radical reactions. Figure 6.7 shows the TIC for oil recovered at 600 ºC.

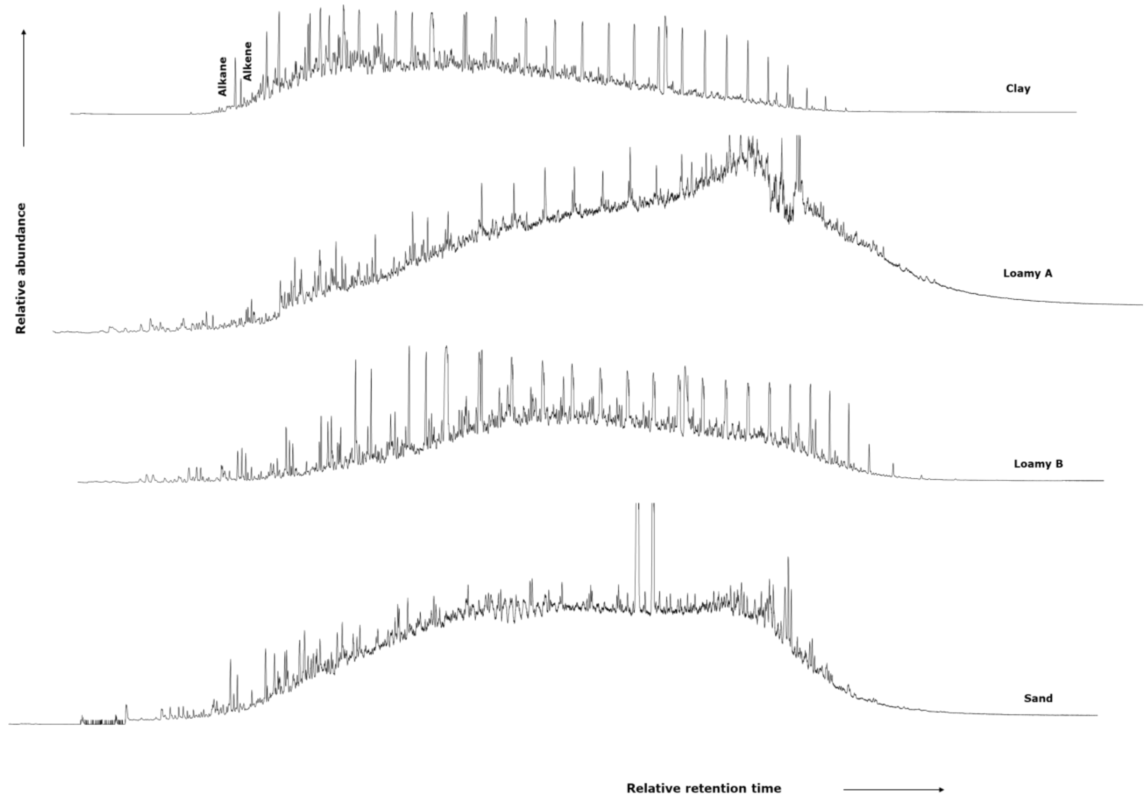


Figure 6.7. GC-MS total ion chromatograms of the pyrolysis oils obtained from clay, loamy A and loamy B and sand soils at 500 °C

It reveals the presence of unsaturated alkenes hydrocarbon in the oil and are capable of promoting other reactions mentioned in (Figure 6.7).

6.3. Comparison conventional pyrolysis with microwave heating

A few research studies have shown a relationship between conventional and microwave heating in soil oil removal. A similar mass of contaminated soil was used in the two systems. Information regarding the differences/connections between the technologies will enhance the development of soil treatment processes.

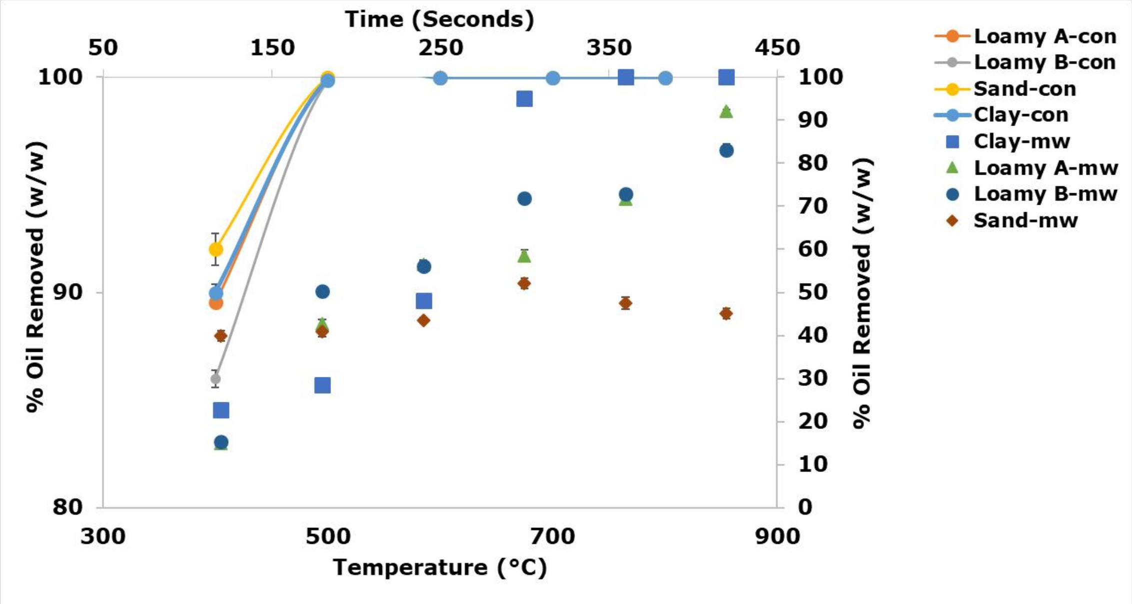


Figure 6.8. Percentage oil removal in the soil after microwave and conventional soil treatment

The oil removal pattern from soils for conventional (400 ºC after 45 minutes) and microwave system (7mins: 420 seconds) are Clay soil 90% and 99.99 %; sand 92% and 50 %, loamy; 86 % and 90 % (Figure 6.8). A higher percentage of oil removal is obtained for loamy and clay soils with microwave heating at optimum time of 420 seconds than conventional pyrolysis at 400 ºC. However, conventional pyrolysis favoured oil removal from sandy soil. It is possible that clay minerals tend to retard oil release during conventional pyrolysis due to adsorptive effects. Temperatures of 500 °C and effectively reduce the oil content of contaminated soils to levels well below the regulatory requirements.

In conclusion, pyrolysis can reliably reduce crude oil contamination of soils to levels below current regulatory requirements of 0.5 %w/w. This can effectively occur at temperatures below 500 ºC for sand and clay, while at temperatures above 500 ºC for loamy soils. Direct data comparison between conventional and microwave technology is challenging since the pyrolysis temperatures of the two systems are different, and the reactor size and configuration are also different. Nonetheless, the comparison in this work is based on heating time and oil removal process. Compared with conventional pyrolysis for loamy soils at 400 ºC, microwave techniques are 6 times faster with better removal for a typical fixed bed Gray-King furnace. The composition of recovered oil after microwave heating remains essentially unchanged, indicating thermal desorption is the primary mechanism for oil removal. The heating process did not alter the stereochemistry of hydrocarbons compared to extensive cracking occur during conventional pyrolysis using a Gray-King furnace.

CHAPTER SEVEN. General Conclusion and Future Work

Treatment of crude oil contaminated soil using microwave technology can reduce the oil content in clay soil to disposal Nigeria standard of 0.5 % w/w. Residual level in loamy soil below 1 %w/w but above disposables standard. This work has contributed to the following area in terms of microwave engineering.

1. Understanding of how soil texture affects soil removal from different soil
2. Contribution of low energy steam stripping mechanism to oil removal and mass transfer processes.
3. Comparing conventional pyrolysis to microwave heating.

7.1. Understanding of how soil texture affects oil removal from different soil

Treatment of crude oil-contaminated soils has been demonstrated using a microwave cavity. Removing the contaminant oil depends on the soil type and resident time within the microwave cavity. Soil properties such as mineral composition and, soil texture are critical factors for remediation of soils during microwave heating. Other factors such as penetration depth due to textural differences had no influence. Mineral content in soils is a contributing factor influencing oil removal from soils. The microwave heating behaviours of the medium are more dependent on the initial liquid content in the soil. Furthermore, is dependent on the soil type and residence time within the microwave cavity, with complete oil removal for clay soil being achieved for the first time. Soil dielectric properties and moisture could affect the optimal microwave power density. The amount of water in the soil is dependent on the soil type. More water in the soil enhances a better percentage of oil removal. This is evident in their different dielectric properties, of most significant to water contribution occurred from room temperature to 100 ºC. It was found that the water content of sand soil was not enough to reduce the oil content to the disposal limit.

The amount of water in the soil is dependent on the soil type. More water in the soil enhances a better percentage of oil removal. This is evident in their different dielectric properties, of most significant to water contribution occurred from room temperature to 100 ºC. It was found that the water content of sand soil was not enough to reduce the oil content to the disposal limit MW effectiveness is limited by low soil moistures as sand had soil had least water content of 1.6 %w/w, which had influence in oil removal. The following summary is made during oil removal from various soils are summarized below.

1. The amount of initial water in soils greatly affects the dielectric properties of each soil type. dielectric constant in the first 150 °C ranged as clay > loamy A > loamy B > sand.

2. Higher power densities resulted to lower processing times and therefore less heat losses to the surrounding. At corresponding treatment time, microwave power of 0.8 kW, 1 kW, 2 kW and 3 kW showed similar removal for each soil type.

3. At constant sample mass, when microwave power increases, the time required for oil removal decreases. At 420 seconds of heating, 99.9 % of oil was removed from clay soil, 85 %, and 92 % for loamy A and loamy B soils. For sandy soil, 50 % of oil is removed.

4. The two loamy soils had similar percentage oil removal at the studied power input and were different from other soils. Buttressing the fact that soil properties affect MW absorption is being influenced by soil type. Microwave power density, operating time and soil water content as mentioned above was significant in assessing changes in energy input. A change in the water content of clay soil led to double oil removal at 180 seconds of heating time. Similar behaviour is observed for loamy A and loamy B

soils. Less than 5 % change in oil content is observed for sand soils. However, energy input increased for all soils at higher water content. For clay soils at 180 seconds, energy input increased by 11 %, with 33 % change in water content. This resulted to a 67 % increase in oil removal. A similar increase is observed for Loamy soil A and sand soil. A change in initial water content led to increased energy inputs, with added benefits in oil removal. The energy requirement (50-180 kWh/t) for the steam mechanism of oil removal from soils and clay soil had the highest value as compared to other soil types. The water content in clay soil of 18 % accounts for up to 50 % oil removal. Water content of 14 % in sand and loamy B soils accounts for 7- 30 %. Water content were also shown to have a significant impact in the overall energy input requirements of the sample. This suggested the conversion of energy from microwaves to heating improved, which was expected as the bulk dielectric properties of the sample increase with increasing water content. Higher oil removal was observed at high power densities as a result of the pore steam velocity within the soils. This phenomenon is as a result of the bulk movement of steam in the material, with the oil removed by steam stripping. It was found that the steam stripping mechanism provided an explanation for greater oil removals observed at high power densities. This is particularly relevant to the industrial system because the industrial microwave treatment systems operate at high power densities.

7.2. Contribution of low energy steam stripping mechanism to oil removal and mass transfer processes

Understanding the contribution of the steam stripping mechanism and mass transfer effects are significant issues. Furthermore, the steam stripping phenomenon provides a more robust explanation of how soil water content affects oil removal. The steam velocity is directly proportional to the mass transfer process and governs oil removal from clay soil and sand soils. Overall, oil in clay soils oil was removed via a physical mass transfer process rather than pyrolysis, with the water present within the soils being sufficient to affect oil removal during the heating process. Mass transfer models were developed showing the relationship between steam velocity and mass transfer rate of oil from soils during microwave heating. It was shown that power density and porosity affect steam velocity, with high velocities observed at lower porosities and higher power densities. An opportunity was identified for developing a cost-effective microwave heating thermal desorption system, which could be retrofitted to existing platforms, providing an onsite soil treatment solution.

7.3. Continuous microwave soil treatment

Microwave processing of oil contaminated sand soil at 896 MHz was carried out for the first time and showed a significant improvement over continuous processing at 2.45 GHz and batch scale processing. Sandy soil with an oil and water content of approximately 1.4 w/w % and 3 w/w % respectively were treated continuously to oil weight of 1.1 w/w % with an energy input of 0.3-0.4 kJ/g, which was significantly lower than the > 1.07 kJ/g energy required for treatment when using a bench scale setup. The residual oil in soil after continuous and batch process was similar. This can be explained by the higher electric field strength and higher absolute power forward, which could be achieved using the continuous setup in comparison to the bench scale setup. This knowledge will be used to explain the experimental observations reported in this chapter, which focuses upon identifying the key variables affecting oil removal performance during continuous processing at pilot scale.

7.4. Comparing convention fixed bed pyrolysis to microwave heating

Pyrolysis of crude oil contaminated soil using a fixed bed takes considerably higher residence time compared to microwave heating. The mechanisms for both processes are different as pyrolysis in a fixed bed majorly involves oil cracking. In comparison to microwave heating oil removal is majorly through thermal desorption. The oil removal pattern from soils for conventional (400 ºC after 45 minutes) and microwave system (7mins: 420 seconds) are Clay soil 90 % and 99.99 %; sand 92 % and 50 %, loamy; 86% and 90%. A higher percentage of oil removal is seen for loamy and clay soils with microwave heating at an optimum time of 420 seconds than conventional pyrolysis at 400 ºC. Conventional pyrolysis favoured oil removal from sandy soil. Temperatures of 500 °C can effectively reduce the oil content of contaminated soils to levels well below the regulatory requirements. In conclusion, pyrolysis can reliably reduce crude oil contamination of soils to levels below current regulatory requirements of 0.5 % w/w. Microwave pyrolysis resulted in time and energy savings due to lower energy input required to conduct the pyrolysis process. Based on the investigation and analysis covered, the following conclusions and recommendations can be drawn and put forward. Microwave heating is basically a novel method for the in-situ processing of oil waste soils. This issue makes microwave heating a viable route for oil recovery and for recycling these wastes into useful products. The fact that oil recovered from conventional pyrolysis yielded oil from cracking could be an additional cost in terms of recycling. The use of MW heating with respect to a conventional ex situ thermal desorption treatment could significantly decrease the treatment time needed for the removal of hydrocarbon contaminants from soils. Therefore, the MW treatment could represent a suitable cost-effective alternative to the conventional thermal treatment for the remediation of hydrocarbon-polluted soil.

7.5. Future work

1. Different sample textures tend to arise from differences in sample mineralogy and initial oil and water content. The difference in texture can significantly impact oil and water removal as it affects the structure of the soil samples. Particle size is also important from a mass transfer and industrial point of view, as size could affect the mechanism of removal or directly impact the performance of a particular mechanism. Hence there is need to investigate the effect of particle size in soil treatment.

From an industrial point of view, it is essential to determine how large-scale operation varies from bench-scale operation and how the variables identified affect oil removal at larger scale processing. Results obtained at a larger scale can then be compared to bench scale experiments to validate the initial observations regarding mass transfer mechanisms of oil and water removal. This should allow data obtained at the bench scale to calibrate larger-scale processing. The robustness of larger-scale operation also needs to be determined as most experiments carried out thus far have only used short treatment periods.

An investigation to determine the extent to which both conventional pyrolysis and microwave heating can affect the quality and soil fertility will help facilitate the re-greening process of the environment.

2. Understanding the required amount of microwave absorber such as water or biochar will be necessary to obtain better oil removal from sand and loamy soil. The removal of the contaminant crude oil by microwave heating is dependent on the soil type and residence time within the microwave cavity, with complete oil removal for clay soil being achieved for the first time. The trends of the lowest extent of oil removal being obtained for sandy soil and intermediate levels for loamy soil are consistent with the microwave properties of the soil, reflecting that the clay has the

highest moisture content. Although complete oil removal was not achieved under the microwave heating investigated here, carbonaceous additives, such as biochar, will overcome this, especially for sandy soils.

3. Further investigation of the product chemistry and mechanisms produced by microwave pyrolysis will provide a definitive insight into any benefits of microwave heating compared with conventional processing techniques.

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Appendices

Appendix 1. Chromatogram for recovered oil from soils at 60 seconds treatment time

Oil recovered from soils with the percentage water content of 14 (clay), 14 (loamy A, loamy B, and sand soil) after 60 seconds with 0.8 kW MW treatment is shown below.

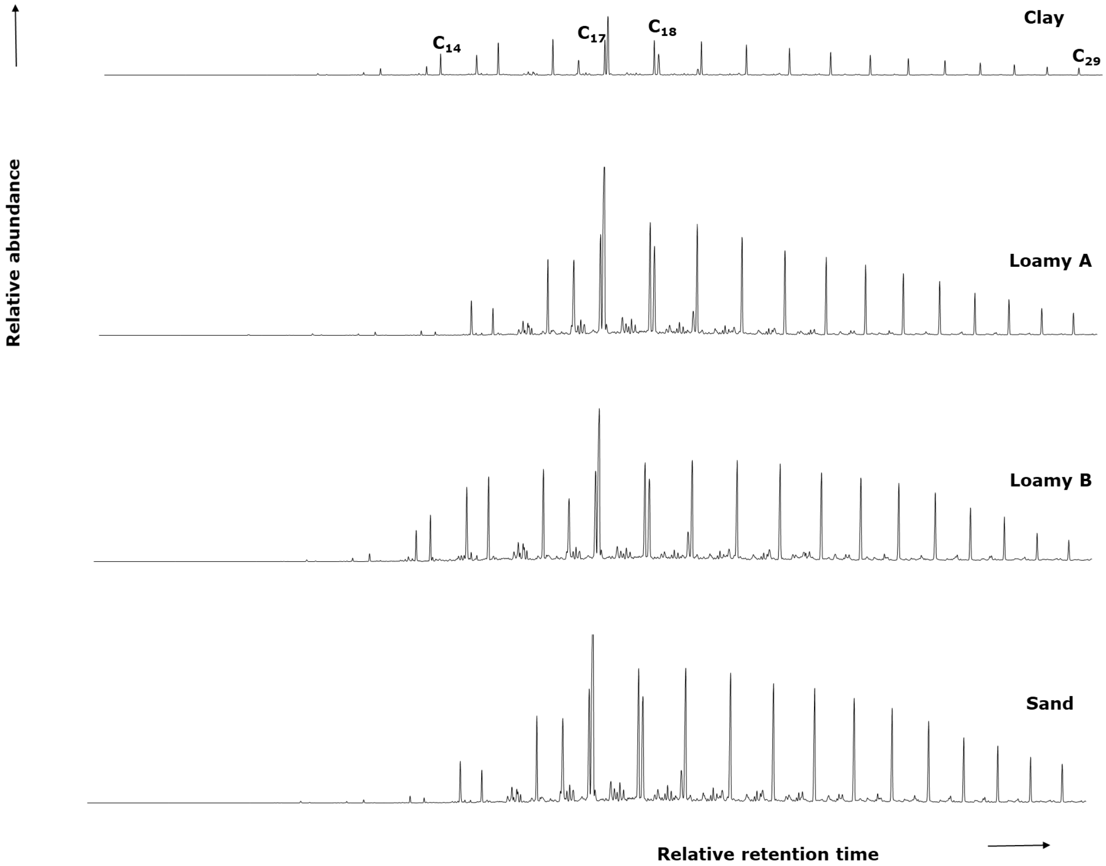

Figure 1A. GC-MS single ion chromatograms (m/z=71) of the oils obtained from clay, loamy A and loamy B and sand soils at 60 seconds treatment time

Appendix 2. Chromatogram for Recovered Oil from Soils at 120 seconds Treatment Time

Oil recovered from soils with the percentage water content of 14 (clay), 14 (loamy A, loamy B, and sand soil) after 120 seconds with 0.8 kW MW treatment is shown below.

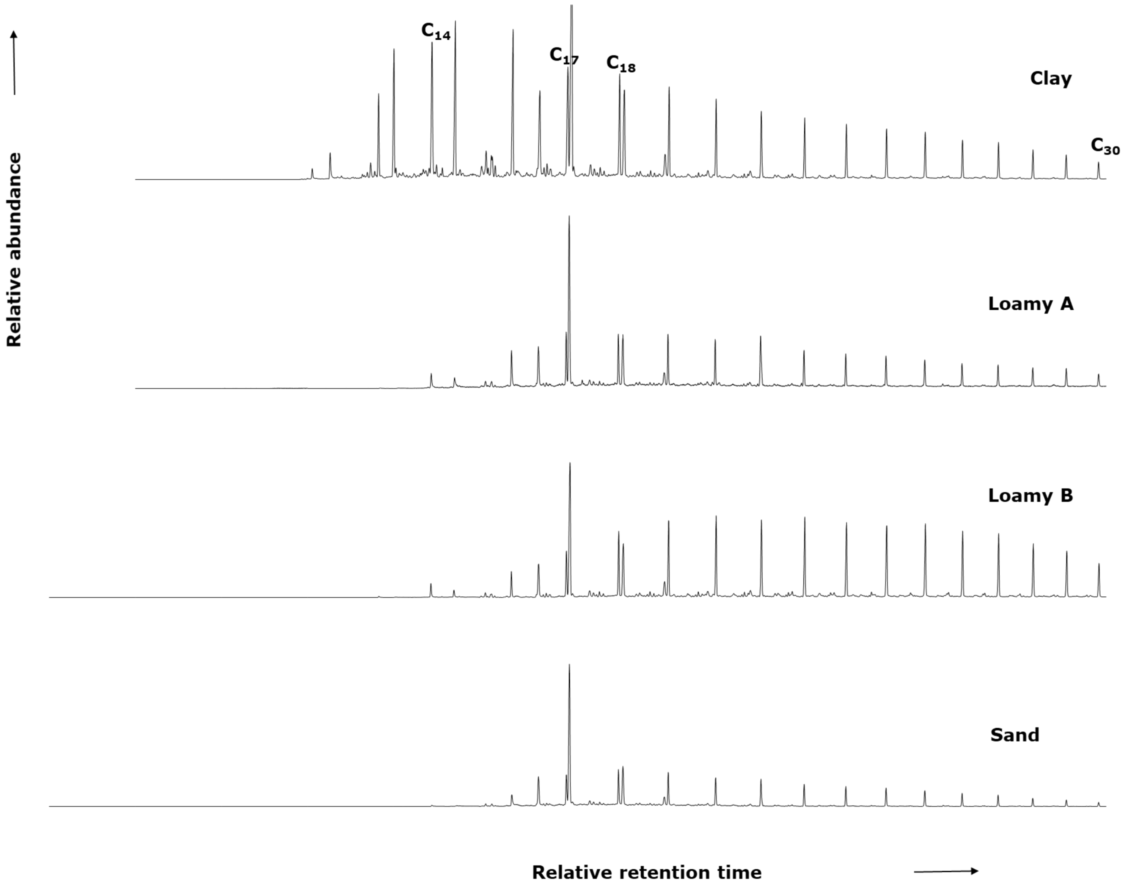

Figure 1B. GC-MS single ion chromatograms (m/z=71) of the oils obtained from clay, loamy A and loamy B and sand soils at 120 seconds treatment time

Appendix 3. Calculation of TOC in gases

TOC in gases

The TOC is gases was calculated using the following steps;

$$GY = \frac{GC \times V}{GI} \qquad [3.1A]$$

Where GY= gas yield in ml

V = volume collected in gas bag

GI = volume of gas injected into the gas chromatogram

1. The percentage of gas component using the sample and standard in 10 µl injected into the GC using;

$$\%\ \text{gas} = \frac{\text{Sample area}}{\text{Standard area}} \times \%\ \text{of}\ \%\ \text{of standard} \quad [3.2C]$$

2. The volume of gas component in 10 µl injected;

$$V_1\ (\mu l) = \frac{\%\ \text{of gas} \times \text{volume of gas injected}}{100} \quad [3.3]$$

3. The volume of gas component in 100 ml of total gas generated;

$$V_2(\text{ml}) = \frac{V_1(\mu l) \times 100\ \text{ml}}{1000 \times 0.01\ \mu l} \qquad [3.4D]$$

4. Amount in mol/dm^3 of gas generated at S.T.P;

$$N_1 = \frac{V_1(\text{ml})}{22400\text{ml}} \qquad [3.5E]$$

5. Amount of gas generated in g/dm^3

$N_2 = N_1 (\text{moldm}^{-3}) \times$ Relative molecular mass of gas [3.6F]

6. Amount of gas generated in mg/dm^3

$$N_3 = N_2\ (\text{gdm}^{-3}) \times 1000 \qquad [3.7G]$$

Appendix 4; TOC and oil weight removed by 0.8 kW microwave extraction

Clay

Time (seconds)	TOC removal (%w/w)		Mean (%w/w)	STD	Oil removal (%w/w)		Mean (%w/w)	STD
120	1.2242	1.46	0.3	0.020365	1.22	1.25	1.235	0.021213
180	1.088175	1.302849	0.457151	0.165781	1.13	1.08	1.105	0.035355
240	0.77171	0.923952	0.836048	0.011582	0.82	0.85	0.835	0.021213
300	0.15	0.179592	1.580408	0.001	0.5	0.54	0.52	0.028284
360	0.089	0.106558	1.653442	0.005	0.01	0	0.005	0.007071
420	0.054	0.064653	1.695347	0.001	0	0	0	0

Loamy A

Time (seconds)	TOC removal (%w/w)		Mean (%w/w)	STD	Oil removal (%w/w)		Mean (%w/w)	STD
120	7.1571	7.2691	7.2131	0.079196	5.56	5.45	5.505	0.077782
180	5.6958	5.4247	5.56025	0.191697	3.2	3.27	3.235	0.049497
240	5.1291	4.1157	4.6224	0.716582	2.8	2.9	2.85	0.070711
300	4.7775	4.5266	4.65205	0.177413	1.81	1.85	1.83	0.028284
360	3.85	3.76	3.805	0.06364	1.72	1.8	1.76	0.056569
420	3.0661	2.9032	2.98465	0.115188	1	1.2	1.1	0.141421

Loamy B

Time (seconds)	TOC removal (%w/w)		Mean (%w/w)	STD	Oil removal (%w/w)		Mean (%w/w)	STD
120	4.95	5.06	5.005	0.077782	4.3	4.4	4.35	0.070710678
180	3.07	3.6	3.335	0.374767	2.9	3.05	2.975	0.106066017
240	2	2.02	2.01	0.014142	2.2	1.98	2.09	0.155563492
300	1.98	1.9	1.94	0.056569	2.1	2	2.05	0.070710678
360	1.76	1.82	1.79	0.042426	1.43	1.45	1.44	0.014142136
420	0.9	0.85	0.875	0.035355	0.4	0.42	0.41	0.014142136

Sand

Time (seconds)	TOC removal (%w/w)		Mean (%w/w)	STD	Oil removal (%w/w)		Mean (%w/w)	STD
120	0.805256	0.88	5.005	0.077782	0.805256	0.88	0.842628	0.052852
180	0.793012	0.85	3.335	0.374767	0.793012	0.85	0.821506	0.040297
240	0.7571	0.78	2.01	0.014142	0.7571	0.78	0.76855	0.016193
300	0.641726	0.67	1.94	0.056569	0.641726	0.67	0.655863	0.019993
360	0.703634	0.69	1.79	0.042426	0.703634	0.69	0.696817	0.009641
420	0.73566	0.71	0.875	0.035355	0.73566	0.71	0.72283	0.018144

Appendix 5; TOC and oil weight removed by 1 kW microwave extraction

Clay

Time (seconds)	TOC removal (%w/w)		Mean (%w/w)	STD	Oil removal (%w/w)		Mean (%w/w)	STD
60	1.25	1.28	1.265	0.006159	0.93	0.98	0.955	0.035355
120	0.98	1.12	1.05	0.002843	0.85	0.9	0.875	0.035355
180	0.8825	0.8275	0.855	0.048295	0.74	0.7	0.72	0.028284

Loamy A

Time (seconds)	TOC removal (%w/w)		Mean (%w/w)	STD	Oil removal (%w/w)		Mean (%w/w)	STD
60	7.382	7.301	7.3415	0.106066	6.42	6	6.21	0.296985
120	6.543	6.5003	6.52165	0.11243	5.4	5.7	5.55	0.212132
180	4.85	4.837	4.8435	0.054659	3.75	3.92	3.835	0.120208

Loamy B

Time (seconds)	TOC removal (%w/w)		Mean (%w/w)	STD	Oil removal (%w/w)		Mean (%w/w)	STD
60	5.446	5.437	5.4415	0.314663	4.65	4.5	4.575	0.106066

120	5.087	5.083	5.085	0.310986	4.73	4.35	4.2	0.268701
180	2.815	2.809	2.812	0.162352	2.33	2.3	2.315	0.021213

Sand

Time (seconds)	TOC removal (%w/w)		Mean (%w/w)	STD	Oil removal (%w/w)		Mean (%w/w)	STD
60	1.2	0.9	1.05	0.005296	0.93	0.95	0.94	0.014142
120	0.9985	0.9736	0.98605	0.009702	0.89	0.85	0.87	0.028284
180	0.8455	0.8209	0.8332	0.043063	0.75	0.72	0.735	0.021213

Appendix 6: TOC and oil weight removed by 3 kW microwave extraction

Clay

Time (Seconds	TOC removal (%w/w)		Mean (%w/w)	STD (%w/w)	Oil removal (%w/w)		Mean (%w/w)	STD
20	0.3450	0.3397	0.34161	0.053655	1.11	1.15	1.13	0.028284
30	0.8753	0.8558	0.86956	0.1184	0.65	0.7	0.675	0.035355
60	1.0246	1.0540	1.03365	0.08349	0.58	0.53	0.555	0.035355

Loamy A

Time (seconds)	TOC removal (%w/w)		Mean (%w/w)	STD	Oil removal (%w/w)		Mean (%w/w)	STD
20	7.35	7.38	7.365	0.021213	6.34	6.25	6.295	0.06364
30	5.9633	5.9335	5.9484	0.021072	5.2	4.9	5.05	0.212132
60	5.783	5.975	5.879	0.135765	4.5	4.12	4.31	0.268701

Loamy B

Time (seconds)	TOC removal (%w/w)		Mean (%w/w)	STD	Oil removal (%w/w)		Mean (%w/w)	STD
20	5.515	5.529	5.522	0.002404	4.2	4.5	4.35	0.212132
30	5.3	5.267	5.2835	0.13999	3.68	3.9	3.79	0.155563
60	4.657	4.664	4.6605	0.366918	2.59	2.77	2.68	0.127279

Sand

Time (seconds)	TOC removal (%w/w)		Mean (%w/w)	STD	Oil removal (%w/w)		Mean (%w/w)	STD
20	1.23	1.25	1.24	0.014142	0.98	1.15	1.065	0.120208
30	1.08	0.98	1.03	0.070711	0.95	0.9	0.925	0.035355
60	0.95	0.9	0.925	0.035355	0.8	0.78	0.79	0.014142

Appendix 7; Oil weight removed by 0.8 kW microwave extraction

Clay (18 %w/w water)

Time (seconds)	Oil removal (%w/w)		Mean (%w/w)	STD
60	1.05	1.125	0.106066	1.05
120	0.88	0.94	0.084853	0.88
180	0.32	0.36	0.056569	0.32

Loamy A (14 %w/w water)

Time (seconds)	Oil removal (%w/w)		Mean (%w/w)	STD
60	6.1	6.4	6.25	0.212132
120	5.8	5.2	5.5	0.424264
180	1.4	1.7	1.55	0.212132

Loamy B (14 %w/w water)

Time (seconds)	Oil removal (%w/w)		Mean (%w/w)	STD
60	4.53	4.57	4.55	0.028284

120	3.97	4.1	4.035	0.091924
180	0.62	0.6	0.61	0.014142

Sand (14 %w/w water)

Time (seconds)	Oil removal (%w/w)		Mean (%w/w)	STD
60	1.23	1.25	1.24	0.014142
120	1.18	1.05	1.115	0.091924
180	0.88	0.84	0.86	0.028284