Remediation of Petroleum Hydrocarbon Contaminated Soils Using Microwave Processing Systems

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ABSTRACT

The rise in the world's energy demand has led to an increase in oil and gas exploitation and exploration activities. During these processes, spillages from crude oil and its refined products occur, resulting in major environmental problems such as land pollution. In Nigeria's Niger Delta, Total Petroleum Hydrocarbons (TPH) is identified as a key land contaminant from these spillages that has led to the destruction of vegetation, posing severe health risks to the local population. This research carried out a robust and systematic technology evaluation for removing TPH from the contaminated soils.

A decision matrix was developed to choose the remediation technology classification with the best potential to address this challenge. Important remediation criteria like remediation efficiency, speed, environmental impact, cost, and suitability for TPH removal were selected and assigned weights based on the peculiarity of contaminated site characteristics of the Niger Delta. Thermal methods emerged as a viable technology option with the best potential to contribute towards addressing this problem. Out of the nine thermal technologies evaluated, ex-situ microwave heating (MW) and ex-situ thermal desorption (TD) scored the highest. However, there were uncertainties about how these technologies would perform with varying soil type and composition. This could potentially impact their overall effectiveness and the technology selection decision. Therefore, investigating the viability of ex-situ microwave heating was the primary focus of this study which was also compared with ex-situ TD.

Selected heavy and light oil-contaminated solids from the United Kingdom and Nigeria's Niger Delta were collected and used. These materials were characterised for dielectric properties, moisture content, oil content, contaminant composition, and particle size distribution. The dielectric properties indicated that the dipolar and ionic/conductive loss mechanisms played a role in heat generation between

20 and <200°C (drying stage). However, ionic/conductive loss was the dominant loss mechanism between ≥450 and 700°C (char formation stage).

The soils were subjected to the microwave 'dry' heating system at various specific energies using 2.45 GHz to understand how they would interact with microwave energy. Oil removal up to 94% (at 3.8 kJ/g and 6 minutes), 37% (at 1.5 kJ/g and 3 minutes), 44% (at 4.2 kJ/g and 8 minutes), and 30% (at 4 kJ/g and 10 minutes) were achieved for filter cake, road planings, Bodo and K-Dere soils respectively. The hydrated clay layers and texture of the filter cake played a significant role in the high oil removed as temperatures >250°C were attained which enhanced oil removal via the steam stripping mechanism. To improve oil removal, contaminated materials were wetted with 5% ethylene glycol and treated (wet microwave heating system). This significantly increased oil removal in road planings to 87%. However, its effect on the other materials was insignificant.

Thermal runaway was a significant challenge that limited material processing, degraded contaminated materials, and damaged equipment during the dry and wet microwave treatments. To overcome this, the solids were treated in an inert liquid system that submerged the materials in hexane before microwave processing. For the first time, the inert liquid system addressed thermal runaway in all the materials and increased the oil removal yields of road planings, Bodo and K-Dere soils compared with the dry heating system due to the combined effect of microwave heating and the inert liquid (hexane). However, it came with a trade-off as higher specific energy inputs were required.

The overall re-evaluation of the initial technology selection decision showed that the remediation of road plainings, filter cake, Bodo and K-Dere soils were best achieved using the microwave wet heating system, microwave dry heating system, thermal desorption, and inert liquid system respectively. The inert liquid system successfully reduced the hydrocarbon contamination in Bodo and K-Dere soils to concentrations within acceptable limits set by the Environmental Guidelines and Standards for the Petroleum Industry in Nigeria (EGASPIN). While the wet microwave heating system reduced the concentrations in road planings to the set guideline, thermal desorption reduced the contamination of all the materials to acceptable limits.

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Abbreviations

AT	Autotuning
DCM	Dichloromethane
EC	Equivalent Carbon Number
EGASPIN	Environmental Guidelines and Standards for the Petroleum Industry in Nigeria
EPA	Environmental Protection Agency
FME	Federal Ministry of Environment
GC-MS	Gas Chromatography-Mass Spectrometry
ID	Internal Diameter
ISM	Industrial, Scientific and Medical
LTTD	Low-Temperature Thermal Desorption
MASE	Microwave-Assisted Solvent Extraction
MC	Moisture Content
MDH	Microwave Dry Heating
MIL	Microwave Inert Liquid heating
MTTD	Medium Temperature Thermal Desorption
MW	Microwave
MWH	Microwave Wet Heating
NAPL	Non-Aqueous Phase Liquids
OD	Outer Diameter
PAH	Polycyclic Aromatic Hydrocarbons
PFAS	Per- and Poly-Fluoroalkyl Substances
RENA	Remediation by Enhanced Natural Attenuation
RF	Radio Frequency
ST	Step Tuning
STDI	Step Tuning at Drop Intervals
SVOC	Semi-Volatile Organic Compounds
TD	Thermal Desorption
TPH	Total Petroleum Hydrocarbons
TPHCWG	Total Petroleum Hydrocarbons Criteria Working Group
VNA	Vector Network Analyser
VOC	Volatile Organic Compounds
XRD	X-Ray Diffraction

Nomenclature

A	Outer surface area of furnace, m^2
c_i	Specific heat, kJ/kg.K
D_p	Penetration depth
E	Electric field strength, V/m
E_d	Energy density, kJ/kg
ε	Permittivity
ε'	Dielectric constant
ε''	Loss factor
ε_∞	Dielectric constant at high frequency
ε_∞	Dielectric constant at zero frequency
f	Frequency, Hz
λ_o	Irradiation wavelength
K	Thermal conductivity of furnace insulation, W/m.K
L_w	Latent heat of water
ρ_b	Bulk density, g/cm^3
P	Porosity, %
Pd	Power density, W/m^3
Q	Quality factor
r	Furnace heating rate, K/s
R	Recovered oil
R_L	Radiation loss factor, kW/m^2
S_d	Skeletal density
tan δ	Loss tangent or dissipation factor
τ	Relaxation time, s
U	Heat transfer coefficient
W	Thickness of furnace insulation, m
ω	Angular velocity
$\Delta T/\Delta t$	Heating rate, °C

CHAPTER 1

1. GENERAL INTRODUCTION

Energy sources from fossil fuels like oil and gas have contributed immensely to global economies' rapid industrialisation and growth. In the last two decades, the world’s oil consumption has risen by 18 million barrels per day and is projected to reach its peak in 2030 (IEA, 2023). However, the processes associated with petroleum exploration, refining and transportation have negatively impacted the environment, posing severe risks to human health and socio-economic conditions, especially within the oil-producing communities. During upstream, midstream, and downstream processing of crude oil and its refined products, land contamination occurs from the releases of these products due to equipment failures, accidental or intentional oil spillages, leakages from pipelines and above and underground storage tanks (Falih et al., 2024; García-Rincón, 2023). This causes land pollution that results in groundwater contamination, environmental degradation, and the loss of flora and fauna.

Petroleum hydrocarbons are known to be the most widespread subsurface contaminants from the spillages of crude oil and its derivatives especially in urban and industrialised environments (García-Rincón, 2023). They consist of a large range of hydrocarbons with more widely known ones being alkanes, aromatic hydrocarbons including polycyclic aromatic hydrocarbons (PAH), and other complex substances like resins and asphaltenes and can persist in the subsurface as pollutants for decades (García-Rincón, 2023; Zhang et al., 2020). Their carcinogenic, mutagenic, and teratogenic effects make them pollutants of major concern drawing global attention (Zhang et al., 2020; You et al., 2024).

Several large sites where petroleum hydrocarbons are the key pollutants of concern have been identified globally. For example, about 2.8 million potentially contaminated sites in Europe are estimated, from which mineral oil, aromatic hydrocarbons and PAHs combined constitute more than 50% of the contaminants (EEA, 2017; EEA, 2022). From the approximately 160,000 polluted sites in Australia, petroleum hydrocarbons are identified as the key contaminants of concern (Khudur et al., 2018). On average, more than 100,000 barrels of oils containing petroleum hydrocarbons are spilt annually in the United States (Vidonish et al., 2016b). According to the United States Environmental Protection Agency (US-EPA), about 50% of the estimated 450,000 brownfield sites in the United States are impacted by petroleum, predominantly from leaking underground tanks at old gas stations (US-EPA, 2024). In Nigeria's Niger Delta, the Federal Ministry of Environment and other activist groups reported 9-13 million barrels of oil spills estimated from about 6,800-12,000 recorded oil spills (FME et al., 2006; Purefoy, 2010; Chinedu and Chukwuemeka, 2018).

Like many other developing countries, Nigeria relies heavily on petroleum as a major energy source to propel the development of its economy. Nigeria's oil prospecting began in 1908 by the Nigerian Bitumen Corporation at Araromi community of the present-day Ondo state (Onyena and Sam, 2020). In 1956, Shell British Petroleum discovered oil in commercial quantity at Oloibiri (Bayelsa state) leading to the production of about 6,000 barrels per day of oil in 1958 (Brown et al., 2017; Okotie, 2018; Onyena and Sam, 2020; Okotie et al., 2018). Oil production then rose to a maximum of 2.5 million barrels per day, placing Nigeria among the global players in the oil and gas industry with 36.97 billion barrels and 5.91 trillion standard cubic meters of proven crude oil and natural gas reserves respectively (NNPC, 2020; OPEC, 2021)[1].

Although crude oil exploration and exploitation brought about economic growth and development in infrastructure, Nigeria's environment had to pay dearly for it (Okotie et al., 2018). Presently, sites across Nigeria's Niger Delta are contaminated

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[1] NNPC is the Nigerian National Petroleum Corporation that regulates activities within Nigeria's petroleum industry. OPEC represents the Organization of the Petroleum Exporting Countries.

with petroleum hydrocarbons from over 6 decades of oil exploration which contributes the largest share of its economy (75-90% of its foreign exchange earnings). This has posed major environmental and socio-economic risks to its approximately 31 million inhabitants whose major employment includes agriculture, food production and fisheries (Sam et al., 2017). The contamination has also destroyed large areas of the region's mangroves (Lindén and Pålsson, 2013).

In 2011, an environmental assessment conducted by the United Nations Environmental Programme (UNEP) as requested by the Nigerian government revealed an urgent need for the cleaning and restoration of the bio-resource-rich Niger Delta (UNEP, 2011; Zabbey et al., 2017). In response to this report, a clean-up was launched by the Nigerian government in 2016 to implement UNEP's recommendations. This remediation exercise is estimated to take 30 years (Hegarty, 2016). Contaminated land remediation aims to sever the linkage between pollutants and receptors by addressing the source, altering the pathway, or eliminating the receptor. This is typically accomplished by removing, destroying, stabilising, or detoxifying the pollutant source, disrupting its pathway, or managing/changing the receptor's behaviour (Nathanail and Bardos, 2004; McKendry, 2019). The ultimate goal is to mitigate the adverse impact of pollutants on the environment and human health while ensuring sustainable development and returning land to beneficial use. Therefore, remediating contaminated soils has become necessary to make them fit for their intended purposes or meet legislative requirements for disposal.

Soil remediation could be done on-site (confined to the contaminated land site) or off-site (excavating and treating contaminant material away from the site). It could be ex-situ (excavating soil/extracting groundwater for treatment) or in-situ (treating without excavation leaving the soil relatively undisturbed) (Nathanail and Bardos, 2004). While on-site remediation methods for contaminated lands may be in-situ or ex-situ, all off-site techniques are ex-situ. Although a clean-up of Nigeria's Niger Delta was launched, the major challenge lies in the fact that no specific remediation approach was identified as most effective for the clean-up of these sites (Zabbey et al., 2017). This is likely because UNEP's investigation focused more on environmental impact assessment than remediation. Nevertheless, it is however clear that like in any other country, the successful clean-up of the contaminated sites across Nigeria's Niger Delta would require a mix of various remediation technology approaches based on specific site characteristics and the nature and level of contamination. Khan et al. (2004) reported that no single remediation technology is appropriate for all contaminant types and the various site-specific conditions at different polluted sites since the choice of a remediation strategy and technology is dependent on several factors like contaminant type and source, site conditions, and the potential impact of the remediation approach considered.

Presently, there exist several remediation technology approaches which can be broadly classified into biological, chemical, physicochemical, thermal technologies and civil engineering methods depending on their working principles (DEFRA, 2010; Khan et al., 2004; Lim et al., 2016; O'Brien et al., 2018). Thermal technologies have gained attention over the years due to their ability to decontaminate various types and concentrations of pollutants to a very high efficiency within a short time using heat energy. However, these technologies have some downsides especially when using the conventional heating system that remediates soils principally by conductive, and convective heat transfer mechanisms, as they can be energy intensive leading to high remediation costs and can also impact soil organic matter from the point of post-remediation usage (Vidonish et al., 2016b; O'Brien et al., 2018). Maximising the pros of thermal technologies while minimising their cons would create an effective, robust, and more environmentally friendly thermal technology remediation approach.

Microwave heating utilises dielectric heating, which involves the transfer of radiative energy. It presents a promising alternative to conventional heating methods due to its direct and instantaneous energy transfer to microwave-susceptible molecules. This approach offers the benefits of volumetric heating, ensuring that individual molecules of dielectric materials are heated when exposed to the microwave electromagnetic field, and selective heating, which targets microwave-absorbing molecules of materials like water without directly heating their surrounding environment. Volumetric heating facilitates rapid material processing, while selective heating maintains lower bulk material temperatures during processing.

In contrast to conventional heating methods, the distinctive heating process in microwaves has the potential to facilitate the removal of contaminants at temperatures below their boiling points, consume less energy (up to 20% less), significantly decrease the time required for remediation by up to three orders of magnitude, overcome limitations related to heat and mass transfer, reduce overall remediation costs, and minimise the impact on soil revegetation (Luo et al., 2019; Robinson et al., 2014; Falciglia and Vagliasindi, 2014; Falciglia et al., 2018a; Robinson et al., 2009a; Robinson et al., 2009b). Also, it can be powered by renewables to support net zero.

Microwave technology has a wide range of applications, including biomass pyrolysis, drying, food processing, catalysis and synthesis of materials, mineral processing, oil processing (including biodiesel and hydrogen production), waste valorisation and resource recovery, and environmental applications for remediating or detoxifying pollutants (Falciglia et al., 2018a; Jie et al., 2019; Slocombe and Porch, 2021; Adam et al., 2021; Robinson et al., 2022; Mao et al., 2023).

Even though there is now an increasing global awareness and focus on the need to shift from fossil fuel consumption to renewables, the impact of the decades of reliance on fossil fuels like oil is still with us. It is not expected to end anytime soon during this energy transition. Furthermore, oil demand in emerging markets and developing economies like Nigeria is predicted to grow continuously until 2050 (IEA, 2023). As a result, remediating soils contaminated with petroleum hydrocarbons has become necessary to preserve and protect human health, wildlife, and the environment. Therefore, the microwave technology solution for the remediation of petroleum hydrocarbon-contaminated solid materials like soils forms the focus of this study.

CHAPTER 2

2. LAND CONTAMINATION REMEDIATION APPROACHES

In this chapter, background information on soil materials and their different textures is provided using the texture triangle. The importance of soil properties and how they influence contaminant removal mechanisms were explained. The causes of land contamination are outlined, and the primary soil contaminant resulting from petroleum exploration activities in Nigeria's Niger Delta is identified. Additionally, existing approaches for the remediation of contaminated solid materials such as soils are reviewed to inform technology screening and selection. Some technologies with high potential for remediating the Niger Delta soils were selected for further investigation using a decision matrix.

2.1. Soil Structure

Soils are natural resources that occur on the uppermost layer of the earth's crust and consist of minerals, organic matter, water, air, and living organisms, essential for plant growth and the functioning of the ecosystem (Morgan and McBratney, 2024; Sposito, 2024). They provide a suitable footing for plants' roots thus enabling them to grow. Soils are generally classified based on their texture as they have various shapes, a distinct particle size distribution, and specific and bulk densities. They range from fine to coarse materials such as clay (≤0.002 mm), silt (>0.002 to ≤0.063 mm), and sand (>0.063 to ≤2 mm). Other larger rock fragments that can be found on soils include gravel (>2 to ≤63 mm), cobble (>63 to ≤200 mm), and boulder (>200 mm) (BS-EN-ISO-14688-1, 2018; USDA, 2017). However, the most dominant soil particles that directly affect the behaviour and texture of soils are clay, silt, and sand. The clay mineral fraction is known to exist both as discrete particles and as coatings on more coarse particles (Hallikainen et al., 1985). The soil texture triangle is a common way of classifying soils based on the fractions of their clay, silt, and sand compositions. The United States Department of Agriculture’s (USDA) texture triangle comprises twelve major texture classifications (USDA, 2017). However, it does not account for very coarse materials like gravel (Figure 2-1).

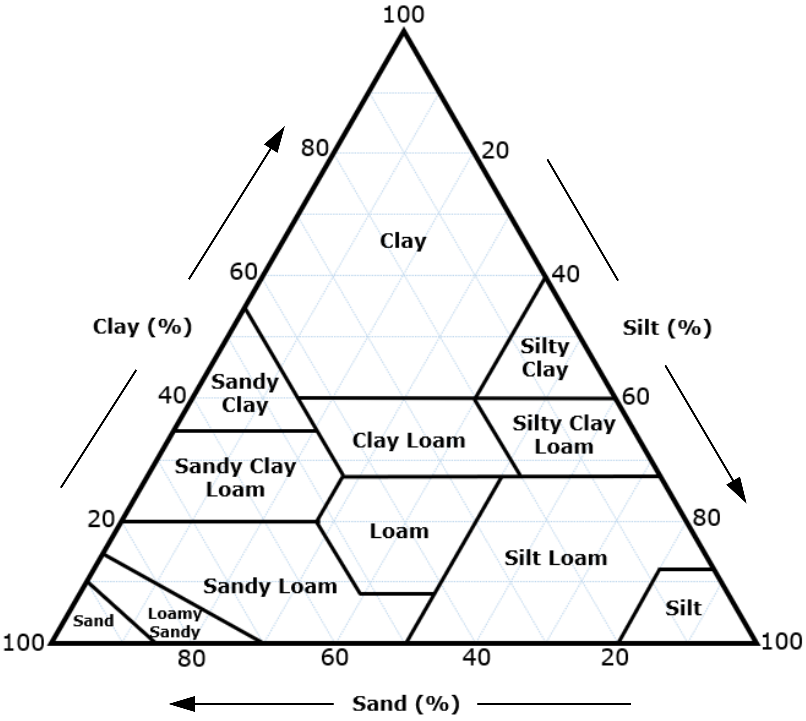


Figure 2-1: Soil classification using the texture triangle (USDA, 2017)

The soil particle or grain size increases with coarser particles i.e. clay < silt < sand. Their aggregate structures influence their ability to transport and retain water, air and nutrients (Sposito, 2024). The pore size constitutes the radii or space between soil particles. It is linked to the soil’s ability to retain air and water (i.e. porosity), and the ease with which it transports fluids (permeability). The finer the soil texture (i.e. smaller grain-sized soils) the higher its porosity, whereas the smaller the average soil pore size the smaller its permeability (Sposito, 2024). Therefore, clayey soils generally have higher water retention ability than silty and sandy ones but have lower ability for fluid transport because of their small particle and pore size.

When soil materials become polluted, the contaminant gets onto the surfaces and infiltrates into the pores of the soil grains as shown in Figure 2-2. These soil properties can be vital in understanding the infiltration of these contaminants into soil materials.

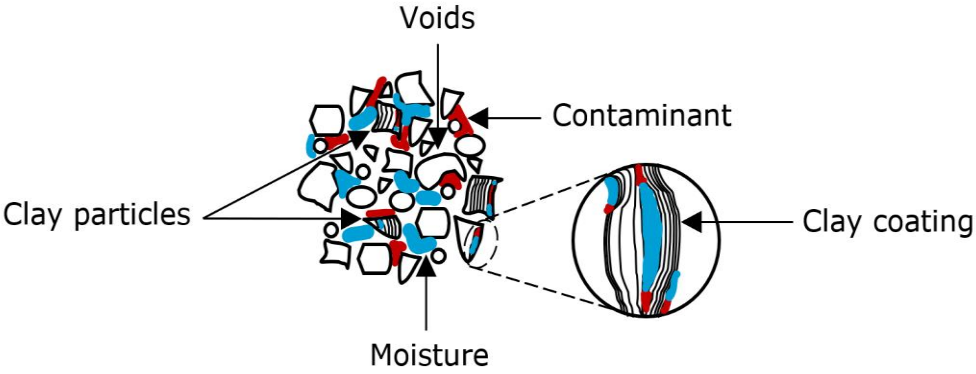


Figure 2-2: Schematic diagram of contaminated soil medium. Modified from Dobson et al. (1985)

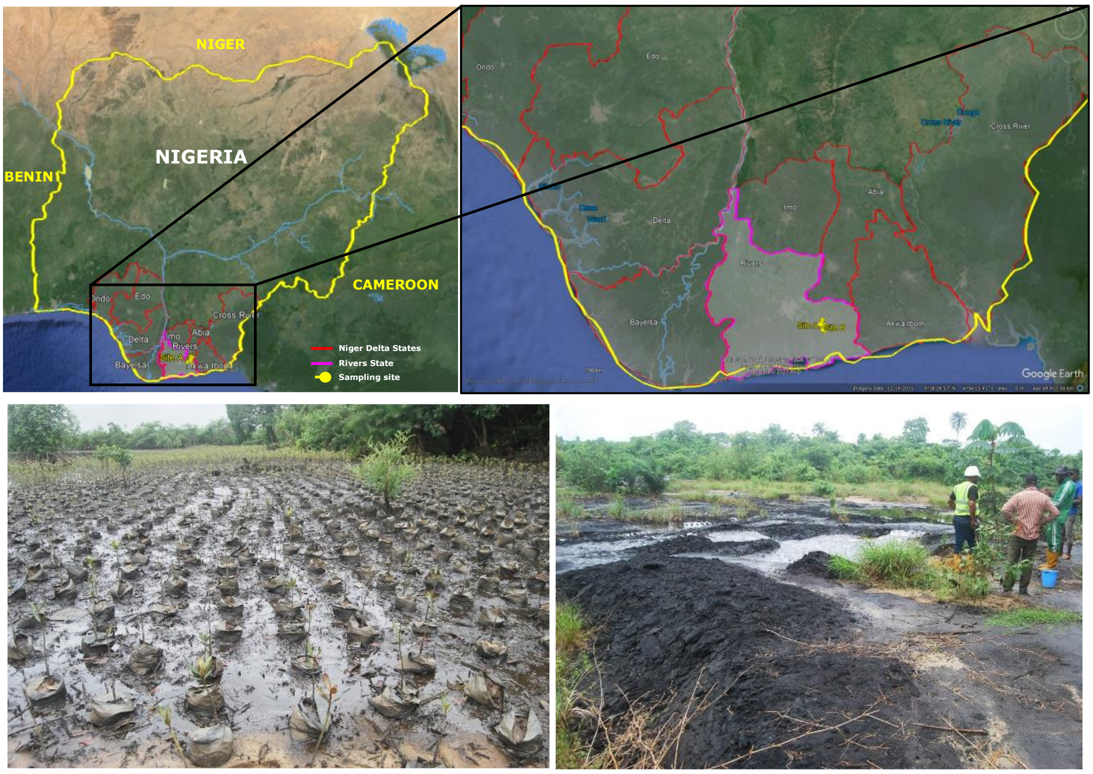
Soil and groundwater remediation technologies exploit the difference between the properties of soil and those of its contaminants to treat them (Nathanail and Bardos, 2004). As a result, soil properties are significant in selecting suitable and cost-effective soil remediation technology. For example, finer particles of contaminated soils often retain more pollutants than coarser ones. Therefore, soil washing relies on the distribution of these contaminants across various particle size ranges to separate and produce a concentrated fraction for remediation or disposal - this technique is not cost-effective when fine soil particles exceed 30-40% (Nathanail and Bardos, 2004).

Additionally, the moisture content of soils is important during microwave heating as this improves its dielectric properties (since soil moisture is a good microwave absorber) making it easier for the selective heating and conversion of water into steam to occur which acts as a mass transfer media for stripping or desorbing pollutants like hydrocarbons (Meredith, 1998; Robinson et al., 2014; Robinson et al., 2009b). Unlike sandy soil that is composed of quartz and feldspars, high moisture contents are expected in clay soils especially as they are composed of predominantly hydrophilic clay minerals like kaolinite, montmorillonite, and illite (Robinson et al., 2014; Sposito, 2024). Soil properties can influence the removal mechanism of contaminants from soils, along with factors like soil geology and the type of pollutant (or oil type in the case of petroleum hydrocarbons). For instance, because of their larger pore sizes, coarse soils like sand would enable the easy transport and removal of water in the form of steam through their pores during thermal remediation via microwave heating. When this happens, it is unlikely that the steam would facilitate the removal of a significant amount of contaminant (e.g. heavy oil) along with it. However, the fluid transport in clayey materials could be limited due to their poor permeability. Consequently, pressure build-up may be necessary for steam to escape through the soil pores, potentially resulting in significant oil removal.

2.2. Land Contamination Causes and Remediation Approaches

Land contamination is the pollution of land surfaces with hazardous materials that renders them unfit for purpose. Typical contaminants include organics (e.g. petroleum hydrocarbons, per- and poly-fluoroalkyl substances (PFAS)), heavy metals (e.g. lead, cadmium), metalloids (e.g. arsenic), and inorganics (e.g. sulphate and nitrate)(Nathanail and Bardos, 2004; US-EPA, 2023). Land pollution usually impacts the environment negatively and poses severe risks to plants and animals. Organic contaminants like petroleum hydrocarbons are derived from crude oil and its fractions. These non-polar organic compounds are relatively immiscible with water and are often present as non-aqueous phase liquids (NAPLs)(García-Rincón, 2023). They are also present as dissolved phases in groundwater and within soil. Crude oil is a complex mixture of both hydrocarbon and non-hydrocarbon compounds naturally occurring within subsurface deposits or geological formations (Chinedu and Chukwuemeka, 2018). Sophisticated processes are usually required to refine them into useful products such as gasoline, diesel, and kerosene - a process that involves the addition of additives like antioxidants, depressants, viscosity and friction modifiers, detergents, corrosion inhibitors etc. to enhance performance.

In Nigeria, oil spillages are caused by leakages from ageing, dilapidated, and abandoned facilities, poorly maintained engineering equipment, spills during transportation in pipelines and other means, bunkering and pipeline sabotage, and artisanal refining of stolen oil under poor process conditions (Lindén and Pålsson, 2013; Chinedu and Chukwuemeka, 2018). Figure 2-3 shows a typical environmental impact of land contamination within Nigeria's Niger Delta where some of the soil samples (Bodo and K-Dere soils) were collected and used for this work were obtained.



Site A: St. Patrick Waterside, Bodo

Site B: Nupene, K-Dere

Figure 2-3: Land contamination from oil exploration activities in the Niger Delta, Nigeria

Total petroleum hydrocarbons (TPH) are known to be the biggest contaminants resulting from these leakages (Table 2-1). They comprise the aliphatic (C_{10}-C_{40}) and sixteen United States Environmental Protection Agency (USEPA) priority Polycyclic Aromatic Hydrocarbons (PAH) (Okparanma et al., 2017). Several oil spill clean-up attempts were made in the Niger Delta before the clean-up launch in

2016, the largest being Remediation by Enhanced Natural Attenuation (RENA). This bioremediation approach ploughs contaminated soils to increase aeration, adds fertiliser to supplement the nutrient requirements of the hydrocarbon-utilising bacteria that break down contaminants, and then piles ploughed soils into neat windrows to further enhance the aeration (Okparanma et al., 2017; UNEP, 2011).

Table 2-1: Physicochemical properties of typical soil samples of Bodo West, Ogoniland (Chikere et al., 2019)

Parameter	Contaminated soil	Pristine soil
pH	7.8	6.5
Electrical conductivity ($\mu S/cm$)	2020	105
Total organic carbon ($\%$)	0.80	0.60
Total petroleum hydrocarbons (mg/kg)	7591	199.70
Polycyclic aromatic hydrocarbon (mg/kg)	26.12	2.76
Moisture content ($\%$)	30.00	26.00
Nitrate (mg/kg)	1.30	10.80
Phosphate (mg/kg)	1.01	11.60
Zinc ($\%$)	5.50	0.66
Potassium (mg/kg)	26.70	26.70
Lead (mg/kg)	48.70	0.09
Nickel (mg/kg)	0.07	<0.05

RENA was considered inefficient likely due to the chronic nature of contamination toxic to bacteria, the clayey nature of soil leading to a reduction in oxygen transfer, and rainfall causing leaching and running off of hydrocarbons hence contaminating other larger areas (UNEP, 2011; Lindén and Pålsson, 2013). However, it is crucial to note that each site needs to be evaluated individually to determine the most suitable remediation approaches. A one-size-fits-all approach would not be appropriate, as RENA might have been effective for some contaminated sites but not all. This underscores the need for an alternative approach. Table 2-2 outlines typical land contamination cases and some remediation attempts in Nigeria.

Table 2-2: A case study of contamination source, type, and remediation technology attempts in Nigeria (UNEP, 2011)

Source	Location	Year	Contaminant	Remediation attempts/Technology
Damage of SPDC[a] Pipeline right-of-way during the Nigerian Civil War	Ejama-Ebubu, Eleme LGA[b]	1970,1992, 2009	Crude oil (TPH[c]) Max. soil TPH: $49,800\ mg/kg$ Max. water TPH: $485,000\ \mu g/L$ The $85,000\ m^2$ contaminated area was secured with concrete blocks	A mobile Thermal Desorption Unit (TDU) was brought onsite but never used. Burnt and highly contaminated soil was excavated and deposited in two large piles ($5,000\ m^3$ each) at opposite ends of the site- this contract which seemed to be RENA[d] was later abandoned.
Spills from SPDC suspended facilities- Bomu manifold	K-Dere, Gokana LGA	1970, 1990 (twice), 2001, 2003	Crude oil spill covering $24\ 000\ m^2$ land area and up to $4-5\ m$ soil depth. Max. soil TPH: $63,600\ mg/kg$ Max. water TPH: $3,410\ \mu g/L$	Two remediation projects were said to have been carried out (remediation technique(s) used is unknown). The site is still heavily contaminated.
Oil spills from SPDC legacy site station ($area \approx 7,000\ m^2$)	Korokoro, Tai LGA	1986 (four spills), 1990	Oil spill (TPH) contamination reaching $5\ m$ soil depth. Max. soil TPH: $14,200\ mg/kg$ Max. water TPH: $769\ \mu g/L$	Superficial decontamination using RENA. Remediation was considered ineffective.
NNPC[e] refined product line spill (includes gasoline, diesel, or kerosene)	Nsisioken Agbi, Eleme LGA	2005	Contains free-phase and dissolved hydrocarbons, Benzene, and MTBE[f]. Groundwater was contaminated to a distance of at least $600\ m$. Max. soil TPH: $7,310\ mg/kg$ Max. water TPH: $86,100\ \mu g/L$	None
Fly tipping of oilfield waste containing TPH & Barium	Oken Oyaa, Eleme LGA	2010	$1,000 - 1500\ m^3$ Oil waste mixed with grey clay & rock fragments (likely drill cuttings). Max. TPH in waste: $54,300\ mg/kg$ Max. Barium in waste: $2,630\ mg/kg$	None
SPDC well-3 remediation site	Korokoro, Tai LGA	1992,1993, 2000,2003	Crude oil contamination of $12,000\ m^2$ the land area containing mobile phase hydrocarbons in monitoring wells. Max. soil TPH: $11,200\ mg/kg$	RENA was completed but was inefficient as remediation did not meet the minimum $5,000\ mg/kg$ set by EGASPIN[g].

[a] Shell Petroleum Development Company (SPDC); [b] Local Government Area (LGA), [c] Total Petroleum Hydrocarbons (TPH); [d] Remediation by Enhance Natural Attenuation (RENA); [e] Methyl tertiary butyl ether (MTBE); [f] Nigerian National Petroleum Corporation (NNPC); [g] Environmental Guidelines and Standards for the Petroleum Industry in Nigeria (EGASPIN)

2.3. Remediation Technology Evaluation and Choice of Approach

Land remediation aims to remove contaminants from soil materials to restore and make them fit for purpose or disposal. Currently, various remediation technologies for the decontamination of oil-polluted soils exist (Lim et al., 2016; DEFRA, 2010; Khan et al., 2004). Based on the uniqueness of their working principle, these technologies can broadly be classified into biological like bio-piles, RENA, and phytoremediation; chemical methods such as chemical oxidation and reduction; physicochemical methods e.g. solvent extraction/soil washing and soil vapour extraction; thermal remediation technologies such as thermal desorption and microwave heating; civil engineering methods such as excavation for disposal to landfill, and containment walls, and the integrated strategy that combines two or more technologies for site-specific remediation (O'Brien et al., 2018; Lim et al., 2016; DEFRA, 2010). Table 2-3 summarises these technology classifications.

Table 2-3: Classification of remediation technologies by process (DEFRA, 2010)

Biological (B)	Physical (P)	Chemical (C)	Thermal (T)
In situ*			
Permeable reactive barriers^{B,P,C}			Thermal treatment
Flushing^{B,P,C}			
Enhanced bioremediation		Chemical oxidation and reduction	
Phytoremediation	Electro-remediation^{P,C}		
Monitored natural attenuation	Stabilisation/Solidification^{P,C}		
Sparging^{B,P}			
Venting^{B,P}			
		Vitrification^{P,C,T}	
Ex situ**			
Biological treatment	Soil washing and separation processes^{P,C}		Thermal treatment
	Stabilisation/Solidification^{P,C}		
	Venting^{P,C}		
		Chemical oxidation and reduction	
	Vitrification^{P,C,T}		
Water and gas/vapour treatment^{B,P,C}			
Civil engineering methods e.g. excavation/abstraction, landfill, containment			

*Remediation activities taking place in the subsurface, **Remedial actions applied to excavated soil or the treatment at surface of contaminated water or gaseous emissions. ^{B,P,C} means the technology could be classified as biological (B), physical (P) or chemical (C) depending on how it is applied.

A robust remediation strategy will be needed to address NAPL, groundwater and soil. Some technologies may treat one or more of these phases at a time but usually, more than one technology is required to address all the unacceptable risks at the site. Rather than dealing with the contaminant, civil engineering methods isolate or contain them to break possible linkages to receptors. Biological methods utilise the natural metabolism process of living organisms (bacteria and fungi) to destroy or convert pollutants into less toxic forms by feeding on them (i.e. acting as proton donors) or during respiration (i.e. acting as proton acceptors) (Golder, 2018). While physical methods such as soil washing separate contaminated media from uncontaminated materials using the differences in one or more physicochemical properties, chemical methods employ chemical reagents to transform, concentrate or destroy contaminants. On the other hand, thermal approaches apply heat to destroy or increase the contaminant phase's vapour pressure to promote vaporisation and separate contaminants from soils.

A more comprehensive comparative evaluation of these remediation technologies based on their efficiency, cost, remediation speed, suitability for application on various soil types, contaminant types and concentration is outlined by Khan et al. (2004), Summersgill (2006), and DEFRA (2010) is shown in Table 2-4[2], Table 2-5, and Table 2-6. In-situ or onsite biological methods (e.g. RENA and aeration/windrows) have low costs (up to 10 US$/tonne) and have less environmental impact however, they are limited to long treatment durations that could last 30 years, they are only suitable for biodegradable contaminants, low contaminant concentrations, and depend on many environmental factors. On the other hand, ex-situ biological methods like enhanced bioremediation can give a much shorter time (0.5 to 3 years) but are more expensive with average costs of

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[2] At the top section of the table, each criterion is assessed using letters from A to I. These letters are explained and/or quantified in the lower section of the table. For example, the cost and efficiency of thermal desorption are graded as C-E (10-75 US$/tonne of water treated) and A (>90%) respectively.

Table 2-4: A typical comparative evaluation of soil remediation technologies (Khan et al., 2004)

Technique	Development status	Contaminant	Soil type	Cost	Efficiency	Duration			
Soil washing	F	B-F	F-I	A-B	A	A			
Soil vapour extraction	F	A-B	F-I	C	A	B-C			
Landfarming	F	B-C	A-I	C-D	B	B-C			
Soil flushing	F	A-F	F-I	C-F	B-C	A-B			
Solidification/stabilization	F	C, E-F	A-I	A-B	A	B			
Thermal desorption	F	A-F, except C	A-I	C-E	A	A-B			
Biopiles	F	A-D	C-I	E-F	A-B	A-B			
Bioventing	F	B-D	D-I	C-E	A	A-B			
Phytoremediation	P	A-F	Independent	D-E	C-D	D-E			
Bioslurry system	F	A-D	D-I	A-C	A	A			
Encapsulation	F	C-F	A-I	B-D	B	B-C			
Aeration	F	A-B, D	C-I	E	B	C-D			
Contaminant		Soil type		Cost		Efficiency		Duration	Rank
Type	Rank	Type	Rank	Range, US$/t of water treated	Rank	Range	Rank	Range	Rank
VOCs	A	Fine clay	A	>150	A	>90%	A	1-6 months	A
SVOCs	B	Medium clay	B	75-150	B	75-90%	B	6-12 months	B
Medium to heavy hydrocarbons	C	Silt clay	C	50-75	C	50-75%	C	1-2 years	C
Insecticides	D	Clay loam	D	25-50	D	<50%	D	2-5 years	D
Inorganic	E	Silt loam	E	10-25	E			>5 years	E
Heavy metals	F	Silt	F	<10	F				
		Sandy clay	G						
		Sandy loam	H						
		Sand	I						

F, full scale; technology used in real site remediation; **P**, pilot scale; studies conducted in the field or laboratory to fine-tune the design of the technology.

Table 2-5: Average cost of remediation technologies in Europe (Summersgill, 2006)

Technique	Ranked by cost (Euro/cubic metre)		
	Minimum	Maximum	Average
Off-site incineration	148	2850	885
In-situ vitrification	518	814	666
On-site thermal treatment	26	935	238
Off-site landfilling	10	979	231
Off-site thermal treatment	15	600	229
Off-site soil washing	30	608	226
Ex-situ vitrification	44	380	220
In-situ steam injection	50	300	175
Off-site biological treatment	20	665	167
On-site biopiling	10	570	142
On-site Immobilization	15	400	139
In-situ Immobilization	25	270	128
In-situ Electro reclamation	44	207	126
On-site Phytoremediation	22	222	122
On-site bioslurry reactor	89	222	122
On-site soil washing	15	456	116
Off-site immobilization (sqm)	50	270	112
Encapsulation	30	178	104
In-situ bioslurping	20	162	92
In-situ air sparging	11	360	91
On-site biological treatment	11	222	76
In-situ bioremediation	15	200	73
Pump and treat	10	228	71
Chemical oxidation	30	126	68
On-site land farming	15	114	62
Reactive walls	40	70	55
In-situ soil venting	10	152	54
Containment walls	40	60	50
Hydrogeological containment	22	80	49
Dual vapour extraction (DVE)	20	70	45
Confinement	20	40	34
Free product recovery	10	70	30
On-site windows	7	44	26
In-situ natural attenuation	15	25	20

Table 2-6: Typical timescale for in-situ remediation processes (DEFRA, 2010)

Technique	Remediation timescale (year)
Chemical oxidation and reduction	<1
Electro-remediation	1-3
Enhanced bioremediation	0.5-3
Flushing	1-3
Thermal treatment	<1
Monitored natural attenuation	1-30, highly dependent on specific contaminant and remediation design
Permeable reactive barriers	>10
Phytoremediation	>10
Sparging	0.5-3
Stabilization/solidification	<1
Venting	1-3
Vitrification	<1

up to 167 €/m^3 for offsite biological treatment (Lim et al., 2016; DEFRA, 2010; Khan et al., 2004). Chemical methods (e.g. chemical oxidation) have high efficiencies, can have less than a year remediation timescale in addition to low operational costs, but require high soil permeability, are pH dependent, and can destroy soil microorganisms (Lim et al., 2016; Fox, 1996; DEFRA, 2010). Their average overall costs can be up to 68 €/m^3 (Summersgill, 2006). Physicochemical technologies such as soil washing using liquids (usually water or other solvents) combined with mechanical processes are fast and easier to implement with high efficiency (>90%), however, they consume a lot of solvents some of which are not environmentally friendly and would require treatment for wash water after use leading to high cost of remediation up to an average of 226 €/m^3 and 116 €/m^3 for offsite and onsite treatments respectively (Khan et al., 2004; Lim et al., 2016; Summersgill, 2006).

Thermal technologies (especially ex-situ) like thermal desorption have very high efficiency, reliability, and speed (< 1 year or a matter of minutes and hours when using microwave heating), and can treat large volumes of soil and a wide range of contaminants; however, they require more infrastructure leading to higher remediation costs (Lim et al., 2016; O'Brien et al., 2018). Additionally, they are generally considered limited by material handling problems and increased energy costs when clay-rich soils are involved and when treating soils with high moisture content respectively (Nathanail and Bardos, 2004). Even though conventional heating systems like thermal desorption can be energy intensive leading to high remediation costs of up to 238 €/m^3 (or more for incineration), microwave heating technology can reduce this energy consumption to about one-fifth and also reduce process equipment footprint due to its advantage of selective and volumetric heating (Robinson et al., 2014; Summersgill, 2006). It can also overcome the limitations of remediating clay-rich soil materials and soils with high moisture content. This is because microwave irradiation is known to leverage the inherent soil moisture as the microwave-absorbing phase that supports mass transfer and contaminant removal during microwave heating (Lim et al., 2016; Robinson et al., 2008; Ogunniran et al., 2017; Buttress et al., 2016). Furthermore, Robinson et al. (2014) showed that while the presence of hydrated clay minerals in soils makes them undesirable for conventional thermal processing, they are amenable to microwave heating.

For the same technology, the ex-situ remediation approach when compared with their in-situ approach may (but not always) incur additional costs and environmental impacts from its extra processing steps like excavation and transportation of the contaminated soils for treatment. While the data reported by these authors have allowed for the comparison of various remediation technologies, it must be noted that these are based on typical undertaken remediation projects and are meant to be used for initial screening purposes. This is because every remediation project is unique, and the actual costs, timescales and effectiveness/efficiency might vary depending on site-specific characteristics. Nevertheless, these data were sufficient for this work's technology evaluation and screening purpose. Therefore, a remediation technology decision matrix based on important criteria selected in line with the Niger Delta’s specific contaminated site characteristic was carried out employing the data and information reported by the authors (Summersgill, 2006; Lim et al., 2016; Khan et al., 2004; DEFRA, 2010; Robinson et al., 2014; O'Brien et al., 2018; Fox, 1996). Weights were allocated to each criterion based on their relative importance to the overall remediation goal and site characteristics. The site characteristics include the high total petroleum hydrocarbon concentrations of up to 63,600 mg/kg, and soil contamination depth of up to 5 meters (see Table 2-2). The result of this decision matrix is presented in Table 2-7.

Table 2-7: Remediation technology classification decision matrix

Decision Model Criterion	Remediation technology options										
	Weight (%)	Biological methods		Chemical methods		Physico-chemical		Thermal methods		Civil eng. methods	
		Rating	Score	Rating	Score	Rating	Score	Rating	Score	Rating	Score
Efficiency/effectiveness	17	3	0.50	3	0.50	4	0.67	5	0.83	3	0.50
Low remediation cost	10	5	0.50	3	0.30	4	0.40	2	0.20	5	0.50
Low environmental impact	17	5	0.83	2	0.33	3	0.50	2	0.33	3	0.50
Applicability for various soil types	10	4	0.40	5	0.50	3	0.30	5	0.50	3	0.30
Safety considerations	10	4	0.40	3	0.30	3	0.30	2	0.20	4	0.40
Suitability for high contaminant concentrations	13	1	0.13	4	0.53	4	0.53	5	0.67	2	0.27
Speed of remediation	10	1	0.10	2	0.20	3	0.30	5	0.50	4	0.40
Suitability for VOCs/SVOCs removal	13	4	0.53	5	0.67	4	0.53	4	0.53	3	0.40
Total score	100		3.40		3.33		3.53		3.77		3.27
Rank		3		4		2		1		5	
Recommendation		No		No		May be		Yes		No	

Rating: 1 - Poor, 2 - Fair, 3 - Good, 4 - Very good, 5 – Excellent.

$\text{Total score} = \sum_{i=1}^{n} \text{Rating}_i * \%\text{Weight}_i$

The scoring system is derived from both quantitative and qualitative assessments of the remediation technology comparison reported in literature Summersgill (2006); Lim et al. (2016); Robinson et al. (2014); Khan et al. (2004); DEFRA (2010); Fox (1996); O'Brien et al. (2018).

Thermal methods emerged as a viable technology with the best potential to address Nigeria’s Niger Delta hydrocarbon pollution problem. It scored 3.77 ahead of physicochemical methods (3.53) and biological methods (3.40). Thermal methods are therefore selected as the focus of this research for their suitability and effectiveness for removing high concentrations of volatile and semi-volatile organic compounds (VOCs/SVOCs) like total petroleum hydrocarbons from a wide range of soil types over a short time. Since physicochemical methods also have good prospects (the second viable option), integrating soil washing with thermal treatment would be investigated and compared with the thermal method. A typical soil-washing remediation process is shown in Figure 2-4.

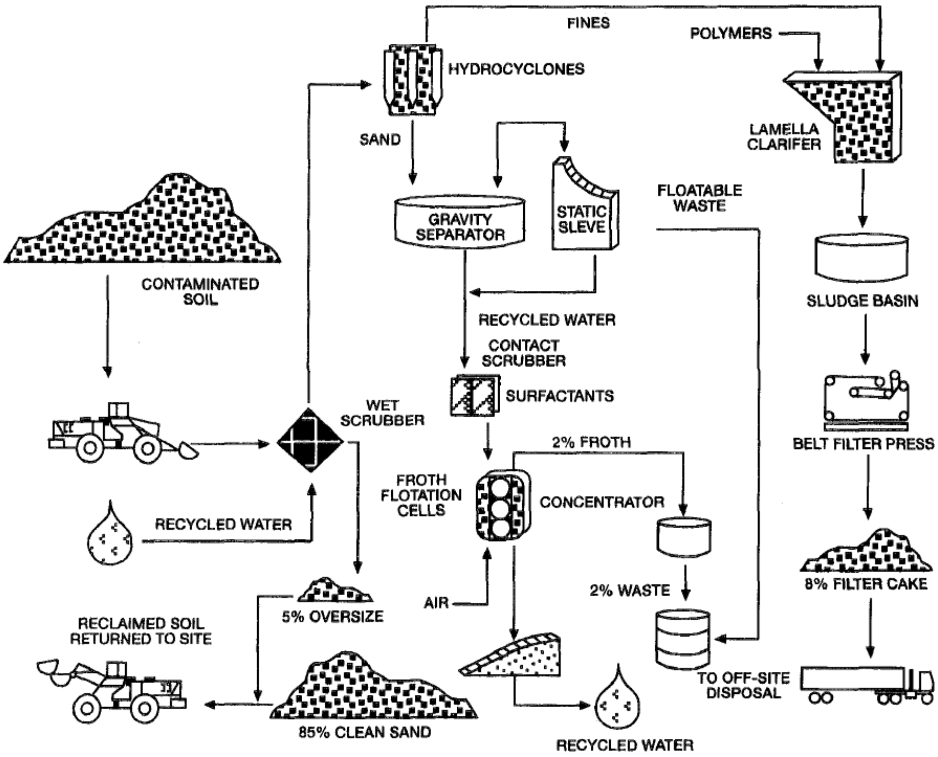


Figure 2-4: Soil washing remediation process (Fox, 1996)

Soil washing is considered a waste minimisation approach for excavated soils (Nathanail and Bardos, 2004). This means that it can be used to reduce the amount of contaminated soil that needs to be treated, and the larger fractions can be reused at the site. Filter cakes are common waste products from the soil washing remediation process. They are challenging to treat and are often taken offsite for disposal as hazardous wastes. The waste comprises a concentrated slurry of soil fines with many contaminants. Therefore, a method that can clean this material at waste processing centres would complement existing technologies. Valuable products could be recovered from filter cake including further mass reduction of this waste. This waste material that comprises a high concentration of petroleum hydrocarbons is one of the contaminated materials used in this work to establish experimental methods as discussed later in Chapter 4.

2.4. State-of-the-Art Technology Comparison for Thermal Remediation Methods

The heating principle in thermal methods can either be by conventional heating (i.e. conduction, convection, or radiation) or by electrical volumetric heating. Incineration, thermal desorption (TD), smouldering, vitrification, and pyrolysis use the former whereas, conduction (resistance) and induction, ohmic, radio frequency (RF), and microwave (MW) heating are governed by the latter. Table 2-8 compares the key thermal technology approaches that are considered for the decontamination of oil-polluted soils.

Although thermal technologies offer advantages over non-thermal methods, there are concerns about their impact on soils at high temperatures (>300°C) and long heating times. O'Brien et al. (2018) reported a rapid deterioration in soil organic matter, an increase in soil pH, collapse of soil mineralogy, and particle size distribution when heated at >450°C for 30 min, causing diminished plant and microbial biomass production. Additionally, Zhao et al. (2019) reported that high-temperature thermal desorption will destroy soil structure, volatilise and pyrolyse soil organic matter and the carbonate in soil minerals. The authors recommended improving oil removal efficiency at a low heating temperature. This was overcome using low temperatures (≤300°C) as demonstrated by Falciglia et al. (2011) who studied the thermal desorption of diesel-polluted soils and successfully removed

Table 2-8: Comparison of thermal technologies for remediating contaminated soils

Remediation Technology	Removal mechanism	Treatment location	Technology maturity	Cost of remediation	Safety consideration	Environmental considerations	Efficiency (%)	Merits	Limitations	Reference
Incineration	Destroys contaminants by oxidation. Temp.: 600-1,600°C	Usually ex-situ as in-situ (on-land burning) is difficult, costly, and unpredictable.	Full commercial scale	$150-2,900/metric tonne	Risks from handling hazardous by-products and high temperatures.	Produces hazardous by-products (bottom ash) and air pollutants. Requires re-moisturizing soils after treatment to control dust.	Up to 100	Directly destroys organic contaminants. Capable of treating large volumes and a wide range of contaminants.	Requires excessive energy for adequate heat transfer from the outer to the core of the soil layer. Unsuitable for high soil moisture.	(Ding et al., 2019; Lim et al., 2016; Vidonish et al., 2016b)
Thermal desorption (TD)	Desorption of contaminant. Often accompanied by pyrolysis and oxidation. Temp.: 100-550°C	In-situ Ex-situ	Full commercial scale Full commercial scale	$46-99/metric tonne $70-460/metric tonne	Improper handling and treatment of off-gas could cause serious secondary pollution.	Emits little or no contamination into the atmosphere.	98-100	Able to recover and recycle contaminants, less expensive than incineration.	Only separates volatile/semi-volatile hydrocarbons from contaminant matrix but does not destroy.	(Ding et al., 2019; Lim et al., 2016; Vidonish et al., 2016b; Zhao et al., 2019)
Pyrolysis	Contaminant pyrolysis, desorption, and char formation. Temp.: 400-1,200°C (<500°C for hydrocarbons)	Ex-situ	Lab scale only	$300/tonne	Volatile products could be reused.	Carbon content from produced char in soil could facilitate re-greening efforts.	>99	Effectively treats heavy-weight hydrocarbons at lower temperatures with less impact on soil properties due to char formation.	Requires anoxic conditions.	(Vidonish et al., 2016b; Ding et al., 2019)

Radio frequency heating (RF) Frequency used: 45 Hz to 10 GHz	Desorption from a decrease in the viscosity of contaminants. Temp.: 150->300°C	In-situ	Full commercial scale	\$320/m^3	Radio frequency heating amplifiers are touchy and unreliable.	Requires treatment of concentrated extracted gas stream.	90-99	Dielectric heating is independent of subsurface thermal conductivity or permeability.	Not suitable for soils with high moisture, non-volatile organics, and other inorganic contaminants.	(Ding et al., 2019; Vidonish et al., 2016b; Riser-Roberts, 1998; Noyes, 1994)
Microwave heating (MW) Frequency used: 0.3 to 300 GHz	Desorption from decreased viscosity of contaminants, Temp.: 150-800°C	In-situ and Ex-situ	Lab and pilot scale	\$34-250/tonne (energy cost)	Care is needed to prevent thermal runaway and arcing. Leakages could be kept below the required levels.	Environmentally friendly due to no products of combustion, energy saving.	75-99	Rapid, selective, volumetric heating, compactness of equipment, easy start-up and shutdown.	The challenge of working effectively at full scale as its increased frequency reduces radiation range.	(Ding et al., 2019; Lim et al., 2016; Vidonish et al., 2016b)
Vitrification	Entrapment of contaminant in molten glass, desorption, pyrolysis, oxidation. Usually aims to break pollutant-receptor linkage. Temp.: 1,600-2,000°C	In-situ Ex-situ	Full commercial scale Full commercial scale	\$300-450/tonne \$250-2,200/tonne	Risks associated with complex operations and extremely high temperatures.	Emission control and design requirements are not fully defined for large site applications. Causes a reduction of soil volumes by 20 to 40% requiring backfill.	99.9	Treats a full range of hydrocarbons, simultaneous treatment of organic and inorganic contaminants.	Complexity of operation, is energy-intensive and slow due to the required time for vitrified material cooling. Do not treat materials with organic content >5% and metal content >16%.	(Ding et al., 2019; Vidonish et al., 2016b; Riser-Roberts, 1998; Calabrese and Kostecki, 2019; Reid and Clark, 2001)

>90% diesel in 18 minutes from sandy and silty soils at 175°C, and from clayey soil at 250°C. Additionally, Luo et al. (2019) removed 98% of Total Petroleum Hydrocarbons from petroleum-impacted soil using microwave heating at 250°C for 20 minutes. Reusing the soil for vegetation growth showed an 80% germination rate thus confirming the maintenance of good soil fertility and quality. Microwave irradiation could preserve soil quality more than conventional heating as microwaves selectively heat the water phase within soils while the latter heats soils directly by conduction.

Much research has been done on the remediation of contaminated soils using thermal technologies (Table 2-8). However, there is little or no consensus on which technologies work best. A major reason for this is that technologies are typically studied individually, with little in the way of a robust comparison with others. Often, different technologies are assessed with varying soil types, with inherent differences in the nature and level of contamination, water content, mineral matter, and humic substances. There is therefore a need for a systematic technology evaluation which this research aims to achieve. Using the comparison in Table 2-8, a decision matrix was developed which informed the choice of potential thermal technology approach for the remediation of Niger Delta soils (Table 2-9).

From the technology screening in Table 2-9, the three top technologies are ex-situ microwave heating (3.46), ex-situ thermal desorption (3.21), and in-situ thermal desorption (3.14). Although ex-situ microwave heating had the best remediation potential ahead of ex-situ thermal desorption with 0.25, there exist uncertainties on how they would perform with variations in soil types and composition like moisture content and particle size. Also, thermal desorption is a more mature soil remediation technology already developed for full-scale commercial application (Figure 2-5).

Table 2-9: Decision matrix for the choice of thermal remediation technology

Criterion	Thermal remediation technology options																		
		Ex-situ Incineration		In-situ TD		Ex-situ TD		Ex-situ Pyrolysis		In-situ RF		In-situ MW		Ex-situ MW		In-situ Vitrification		Ex-situ Vitrification	
	Weight (%)	Rating	Score	Rating	Score	Rating	Score	Rating	Score	Rating	Score	Rating	Score	Rating	Score	Rating	Score	Rating	Score
Efficiency/Effectiveness	18	5	0.89	5	0.89	5	0.89	5	0.89	3	0.54	3	0.54	4	0.71	5	0.89	5	0.89
Low remediation cost	11	1	0.11	4	0.43	3	0.32	3	0.32	3	0.32	3	0.32	2	0.21	3	0.32	2	0.21
Low impact on the environment	18	2	0.36	3	0.54	2	0.36	3	0.54	4	0.71	4	0.71	3	0.54	2	0.36	2	0.36
Safety considerations	18	2	0.36	2	0.36	2	0.36	2	0.36	3	0.54	3	0.54	2	0.36	2	0.36	2	0.36
Ease of use	14	2	0.29	2	0.29	4	0.57	2	0.29	1	0.14	2	0.29	5	0.71	3	0.43	3	0.43
Speed of remediation	7	4	0.29	3	0.21	4	0.29	4	0.29	3	0.21	3	0.21	5	0.36	1	0.07	2	0.14
Suitability for application	14	4	0.57	3	0.43	3	0.43	2	0.29	2	0.29	2	0.29	4	0.57	3	0.43	3	0.43
Total score	100		2.86		3.14		3.21		2.96		2.75		2.89		3.46		2.86		2.82
Rank		6		3		2		4		9		5		1		6			8
Recommendation		No		No		May be		No		No		No		Yes		No			No

TD: Thermal desorption, MW: Microwave, RF: Radio frequency

Rating: 1 - Poor, 2 - Fair, 3 - Good, 4 - Very good, 5 – Excellent

$\text{Total score} = \sum_{i=1}^{n} \text{Rating}_i \text{ x } \%\text{Weight}_i$

The scoring system is derived from both quantitative and qualitative assessments of the thermal remediation technology comparison carried out in Table 2-9 (Ding et al., 2019; Lim et al., 2016; Vidonish et al., 2016b; Zhao et al., 2019; Riser-Roberts, 1998; Noyes, 1994; Calabrese and Kostecki, 2019; Reid and Clark, 2001)

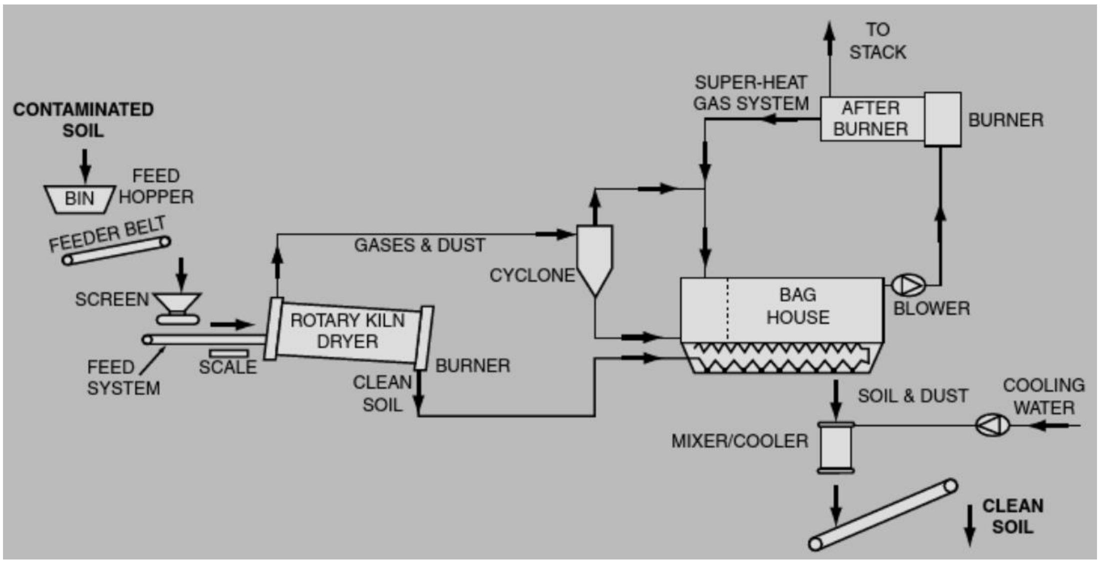


Figure 2-5: Thermal desorption unit for contaminated soil remediation (Nathanail and Bardos, 2004)

These uncertainties could affect the overall technology effectiveness and impact the decision as to which technology would work best. Therefore, while ex-situ microwave technology is the primary focus of this work, ex-situ thermal desorption will also be briefly studied to serve as a basis for comparison especially since microwave and thermal desorption differ in heating principle. Their performances will be used to re-evaluate this remediation technology decision.

CHAPTER 3

3. MICROWAVE PROCESSING SYSTEMS

In Chapter 2, it was established that microwave processing systems have the potential to effectively clean up soil contaminated with petroleum hydrocarbons. It is important to understand how this technology works to use it successfully for soil remediation. Chapter 3 discusses microwave processing systems and their heating mechanisms. It also explores the dielectric properties of materials that affect how they interact with microwaves. The chapter includes a thorough review of how microwave heating is currently used for soil remediation. It also highlights the challenges in scaling up this technology for commercial use and the opportunities for improving microwave heating, from which the research's aim and objectives were drawn.

3.1. Background

Microwaves are high-frequency electromagnetic waves with frequencies from 0.3 to 300 GHz in the electromagnetic spectrum (Lopez-Avila, 2000). Like other electro-heat (electrothermal) technologies, they utilise specific frequencies within the spectrum for various applications as shown in Figure 3-1 (Meredith, 1998; Metaxas, 1991).

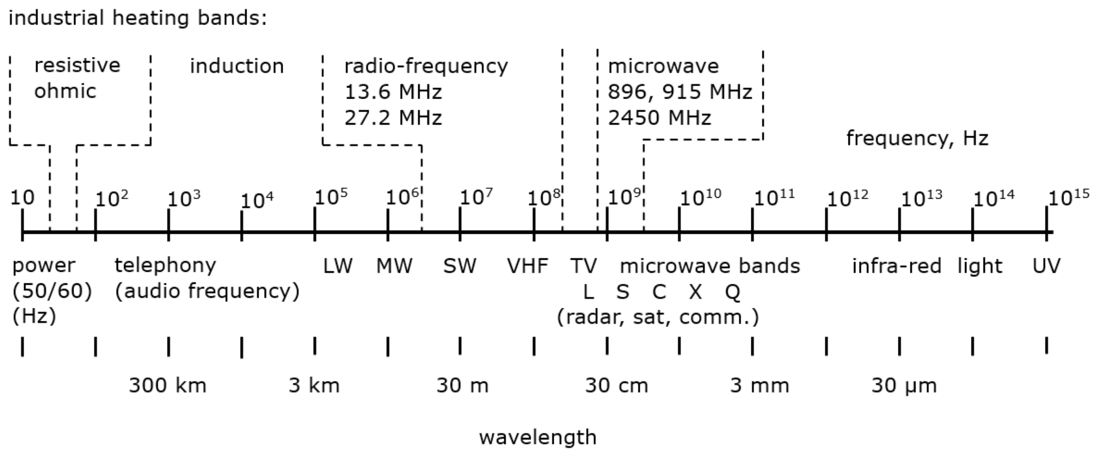


Figure 3-1: The electromagnetic spectrum showing various volumetric heating techniques (Meredith, 1998)

They are widely known for their application in cooking food items. Also, they have been used to process materials, synthesise organic compounds, remediate contaminated soils and for drying because of their rapid heat transfer, volumetric and selective heating, compactness of equipment, environmental friendliness, easy start-up and shut-down etc. (Metaxas, 1991; Lopez-Avila, 2000; Buttress et al., 2016). Among the twelve internationally reserved frequency bands for Industrial, Scientific and Medical (ISM) applications chosen to prevent interference with telecommunication services, the two commonly used frequencies for microwave heating are 896 MHz (915 ± 15 MHz in the USA) and 2,450 ± 50 MHz with wavelengths of 33.3 and 12.2 cm respectively (Meredith, 1998; Li and Yang, 2008; Ofcom, 2022). However, dielectric materials can be heated with microwaves at frequencies other than the allocated ISM frequencies. The 896 MHz (915 MHz in the USA) and 2,450 MHz frequencies are often the basis for equipment design as most types of equipment are purchased at these frequencies. However, for industrial processing, the 915 MHz has an advantage of better penetration depth (since penetration depth is inversely proportional to frequency), generator power and efficiency compared with the 2,450 MHz (Hui et al., 2008).

Interaction of materials with electromagnetic fields is classified as either transparent, opaque, absorber or mixed absorbers (Robinson et al., 2008; Gude et al., 2013; Li and Yang, 2008; Mishra and Sharma, 2016).

1) Transparent (insulators): allows little absorption of microwaves by materials with low dielectric loss e.g., fused quartz, borosilicate glasses, ceramics, and Teflon.
2) Opaque (conductors): reflects microwaves without allowing penetration into the materials, such as bulk metals and alloys e.g., copper.
3) Absorbers (dielectric materials): absorb microwave radiation based on their electric field strength such as aqueous solutions and polar solvents like water and ethylene glycol.

4) Mixed absorbers: usually advanced/composite materials with a combination of phases containing at least one good absorber phase and another insulator phase(s) e.g. wet soils, ceramic matrix composites and polymer matrix composites. They absorb microwaves via localised energy conversion.

Understanding these interactions informs material selection in microwave system design. For example, insulators are good supports and holders, conductors are used as walls and waveguides in cavities, and absorbers are good microwave susceptors. Unlike conventional heating, microwave heating delivers energy directly to absorbing bodies by molecular interactions with an electromagnetic field thus achieving heating instantaneously (Robinson et al., 2008; Zhang et al., 2018). This causes the heating of individual material elements rather than the entire matrix, thus reducing heating times to <1% compared with that required in conventional thermal processing (Meredith, 1998). Figure 3-2 compares the heat transfer in microwave heating with those in conventional heating systems.

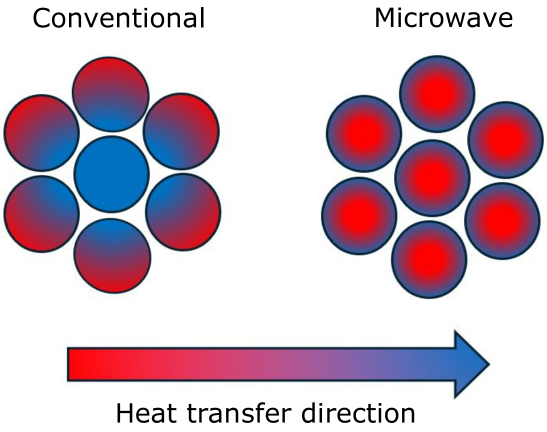


Figure 3-2: Microwave versus conventional heating systems

3.2. Microwave Heating Equipment: Generators, Applicators and Waveguides

Apart from the control and automation components, microwave processing systems are characterised by three major elements that enable them to function. They consist of a microwave generator, a waveguide, and an applicator (Metaxas, 1991; Meredith, 1998). Microwave heating systems are expected to meet some essential requirements like the high conversion efficiency of power input to usable output, operate within the prescribed frequency band, low capital and running costs, simplicity to operate and maintain, robustness for industrial operation, and comprehensive and accurate documentation to allow for easy installation, service and operation (Meredith, 1998).

3.2.1. Microwave generators

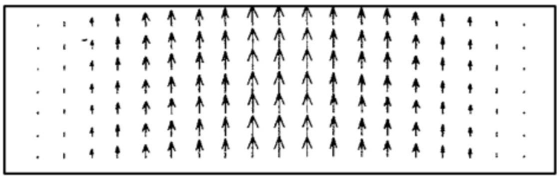
Generators are the power source of the heating systems and are used for generating microwaves at the required frequencies. For industrial applications, microwave heating systems often require powers beyond 10 kW and into the range of 100 kW and 1 MW to operate (Meredith, 1998; IMS, 2024). The common power tube generators include magnetrons, klystrons, and solid-state generators. Solid-state generators are transistor-based amplifiers that increase power in steps (Adam, 2017). They have very high costs and low output power as a result, they are not commonly used for heating applications (Adam, 2017; Meredith, 1998). Klystrons on the other hand use resonant cavities and electron bunching to amplify microwave signals. They generate adequate power however, they are more widely used in radar, communication, television, and scientific research. Their advantages of spectrum purity, tunability over a wide frequency band, and freedom from distortion of modulated signals are however not relevant for industrial heating purposes (Meredith, 1998).

Magnetrons on the other hand are considered overwhelmingly advantageous compared with solid-state generators and klystrons as they satisfy the essential requirements for microwave heating systems outlined in Section 3.2 (Meredith, 1998). They are high vacuum electronic valves that accelerate electrons in a circular path within a magnetron thus generating microwave power from a high-voltage direct current (DC) power source. High-efficiency magnetrons operating at 2,450 MHz and 600 – 1,500 W power output range are mass-produced at low costs constituting the most used microwave generators found in domestic microwaves. The transfer of power in magnetrons is extraordinarily efficient and higher-power magnetrons at 900 MHz and 2,450 MHz have typical efficiencies of >88% and >70% respectively (Meredith, 1998).

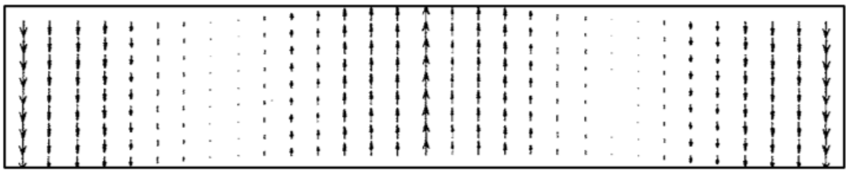
3.2.2. Waveguides

Waveguides are suitable for transmitting microwave power from the generator to the load or heating material. They are rectangular or circular-shaped hollow metal pipes usually made from aluminium to reduce weight. The most used waveguides are rectangular, and they support two types of propagation modes for electric and magnetic fields. These propagation modes include the transverse electric mode (either $TE_{m,n}$ or $H_{m,n}$ modes) in which the electric field in the direction of propagation is zero, and the transverse magnetic mode (either $TM_{m,n}$ or $E_{m,n}$ modes) where the magnetic field in the direction of the propagation is zero. Where m and n are the mode numbers that show the number of half cycles along the coordinate directions normal to the propagation direction (Adam, 2017).

The rectangular waveguide is designed to support a TE_{10} mode which is the least order mode for rectangular waveguides (Meredith, 1998; Metaxas and Meredith, 1983). The electric field patterns for a TE_{10} mode in a rectangular waveguide are presented in Figure 3-3.



E-field: transverse section across waveguide



E-field: longitudinal view along the axis of propagation

Figure 3-3: The electric field pattern in a TE_{10} mode rectangular waveguide (Meredith, 1998)

The electric field is maximum at the centre of the rectangular waveguide, as depicted in the transverse section. Some standard waveguides that can be used at around the 915 and 2,450 MHz industrial frequencies are presented in Table 3-1.

Table 3-1: Selected standard waveguides within the industrial microwave frequencies of 915 and 2,450 MHz (Metaxas and Meredith, 1983)

Frequency range (GHz)	Internal dimensions		Official designations		
	inches	mm (approx.)	IEC	RCSC	EIA
0.64 – 0.96	11.5 x 5.75	292.0 x 146.0	-	WG3	WR1150
0.75 – 1.12	9.75 x 4.875	248.0 x 124.0	-	WG4	WR975
1.7 – 2.6	4.3 x 2.15	109.0 x 55.0	R22	WG8	WR430
2.2 – 3.3	3.4 x 1.7	86.0 x 43.0	R26	WG9A	WR340

EIA: The Electronic Industries Alliance; RCSC: The Radio Components Standardisation Committee; IEC: International Electrochemical Commission

When choosing a suitable waveguide, the microwave power transmitted via the waveguide is an important criterion. Higher powers at certain frequencies would require larger waveguides to prevent arcing. Additionally, the waveguide dimensions should be chosen to ensure that the frequency is bigger than the cut-off frequency (minimum value)(Adam, 2017).

3.2.3. Microwave applicators

Applicators are where the microwaves meet and subject the heated materials (workloads) to intense microwave fields. They are designed in various types and sizes tailored for processing solids, liquids, gases, and plasmas. The major classes of applicators include travelling waves, near-field, and resonant applicators (or cavities). The travelling wave applicators are waveguides that are connected to a microwave generator on one side and a terminating load on the other side (Adam, 2017). Part of the power fed by the generator is absorbed by the workload whereas the remaining is absorbed by the terminating load (also known as dummy loads). Near-field applicators have a small distance between the workload and the applicator compared to the wavelength and can be open-ended waveguides, antennas, or slotted feed waveguides. The most popularly used applicators within microwave systems are the resonant applicators which comprise single-mode and multimode applicators (Nayik et al., 2023).

Domestic microwave ovens are an example of multimode applicators, and they are designed to support the TE_{mn} and TM_{mn} modes simultaneously. They are the most commonly used form of microwave heating applicator and can process a wide range of bulk materials with different sizes and properties and whose general proportion is greater than the working frequency’s wavelength for processing in single-mode cavities (Meredith, 1998; Nayik et al., 2023). The major challenge with multimode cavities is the difficulty in achieving uniform heating due to the non-uniform distribution of field strength, as a result, would require the employment of other techniques such as using metallic mode stirrers to overcome this (Nayik et al., 2023).

The single-mode cavity allows only one mode of propagation thus microwave energy is distributed efficiently within a predetermined space of a particular volume. They have numerous advantages such as a well-defined field, capable of achieving high fields, function in a standing or travelling wave mode, fields that can be tailored to match the product geometry, can heat both high and low-loss materials, highly efficient process and support a continuous product flow (Nayik et al., 2023). However, their small size design limits the size of the heated material to below half the arriving microwave energy wavelength. The simplest and widely used single-mode cavity functions at the TM_{010} mode.

3.3. Microwave Heating Mechanisms

The dissipation of electromagnetic energy into heat when dielectric materials interact with microwaves is complex. However, it could be explained by various loss mechanisms caused by microwave components' electric and magnetic fields. Understanding this behaviour would largely depend on the nature of the processed material - whether it is classified as transparent, opaque, absorber (dielectric material) or mixed absorber. When dielectric materials are exposed to electromagnetic waves, they heat via various loss mechanisms like the dipolar, electronic, atomic, interfacial, and conductive (ionic) loss mechanisms (Figure 3-4.

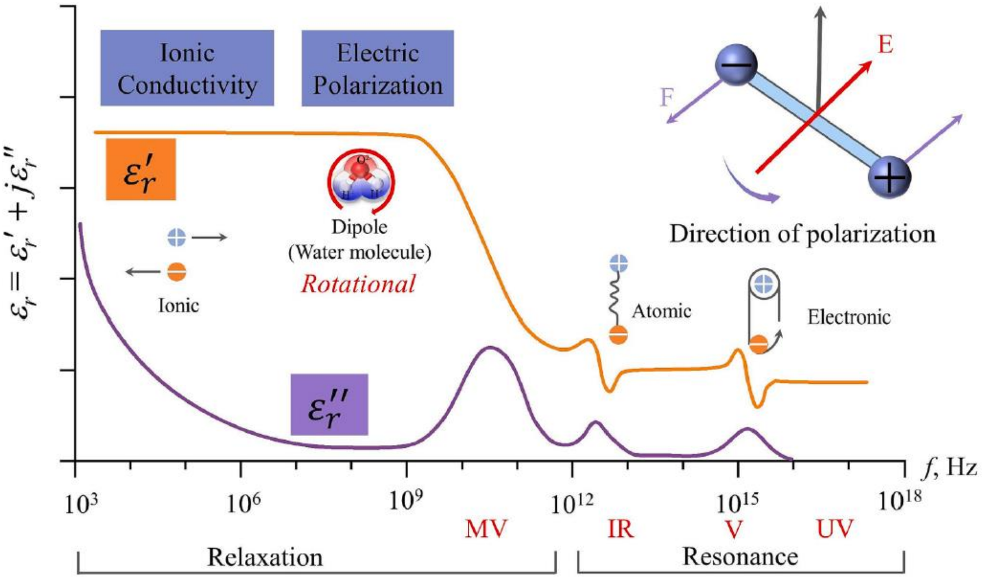


Figure 3-4: Common polarisation loss mechanisms (Fan et al., 2024)

However, the effect of electronic and atomic polarisation (also known as distortion polarisation) is only in the infrared and visible parts of the electromagnetic spectrum and plays no part in high-frequency heating i.e. radio frequency and microwave heating systems (Metaxas and Meredith, 1983; Qin et al., 2022). As a result, they don’t constitute the mechanisms of interest within the industrial high-frequency heating band, particularly the microwave heating frequency range (0.3 – 300 GHz). Within this range, the most common heating mechanisms for non-metals like liquids and heterogenous moist materials (e.g. soils) are dipolar polarisation, ionic or conductive loss (that includes both ion and electron charge carriers), and interfacial polarisation which is the combination of both mechanisms (Curtis et al., 1995; Mishra and Sharma, 2016; Sun et al., 2016). The loss factor is frequency dependent and for a given frequency one or two loss mechanisms would dominate over the others (Metaxas and Meredith, 1983).

Ionic conductivity is effective in dielectric materials like aqueous solutions whose molecules are charged when irradiated with an electric field. The charged ions travel back and forth oscillating through the dielectric material creating an electric current which causes the material to heat due to electrical resistance as the charged species collide with neighbouring atoms and molecules (Sun et al., 2016). The movement and collisions of these charged species generate heat due to ionic conductivity. The dipolar loss mechanism often dominates in dipolar liquids which contain dipole moments (e.g. water and alcohols like ethylene glycol). Upon exposure to an alternating electromagnetic field, the dipole moments become polarised as they try to align themselves with the applied field by rotation. The oscillating field causes the constant reorientation of the dipoles as they continuously try to realign themselves with the electric field. At a high-frequency electric field, these dipoles phase lag due to their inability to respond to the oscillating field in time thus colliding with each other and resulting in friction and heat dissipation (Sun et al., 2016; Gude et al., 2013).

Interfacial polarisation occurs from the accumulation of charges at the interface between a conductive and a lossless phase. When subjected to an external electric field, electrons within the conductive phase can induce polarisation within the lossless phase. If the electrons in the conductive phase become too free or mobile to generate any meaningful loss within the microwave region, heating would majorly occur within the lossless phase. Examples of this loss mechanism can be seen during the microwave irradiation of a conducting material scattered in a non-conducting medium e.g. in the dispersion of metal oxide in polar solvents, and in aqueous electrolyte solutions (Anwar et al., 2011; Gude et al., 2013; Sun et al., 2016).

The contribution of ionic (conductive) loss is known to increase at lower frequencies (Adam, 2017; Hallikainen et al., 1985). This is because, at lower frequencies, the movement of ionic constituents like salts results in the flow of conductive currents within the dielectric material leading to the transfer of energy from the microwave field to the material by the ionic/conductive loss mechanism. At high microwave frequencies, the dipolar loss mechanism is dominant (Metaxas, 1991).

For moist materials that also contain ionic salts, the ionic conductivity would have a stronger effect than dipolar polarisation in terms of their heat production capacity (Anwar et al., 2011). This is because aqueous solutions have increased dielectric loss compared with distilled water or salt alone. For example, at 25°C and 2.45 GHz, the loss factor of distilled water is 13, whereas it is 20 and 54 for 0.1 and 0.5 molal aqueous NaCl solutions respectively (Meredith, 1998). While the dipolar rotation is limited to molecules that can rapidly reorient themselves making it less efficient for heat generation, ions are highly mobile, and their mobility could increase with temperature. Furthermore, their translational motion through an aqueous solution allows for an efficient energy transfer. The higher the ion concentration, the stronger the ionic conduction and heat generation during microwave irradiation. This makes their effect more dominant when compared with the dipolar loss mechanism.

Hallikainen et al. (1985) and Dobson et al. (1985) studied the dielectric properties of soil materials with different textures from 1.4 - 18 GHz and 0 – 50% moisture content. At low frequencies ≤5 GHz, the authors attributed the high ε” to the dominant effect of ionic conductivity from the presence of liquids of salts (mainly calcium) within the soils whose concentration increased with clay content thus resulting in the highest loss factors in clay soils when compared with other soil textures. Curtis et al. (1995) showed that, ionic conductivity in soils results when the soil’s salts are dissolved in their inherent water content and travel through the soil pore spaces when subjected to an external electric field. The author confirmed ionic conductivity as the dominant loss mechanism in moist heterogeneous materials at low frequencies. However, it should be noted that apart from the contribution of aqueous solutions, the presence of high conductivity absorbing materials like carbon-rich or decomposition by-products e.g. char or graphene could also promote the conductive loss mechanisms when present in a dielectric material (Qin et al., 2022). In soils containing petroleum hydrocarbons, these highly absorbing carbonaceous materials are formed from the decomposition of the organic contaminants at high temperatures ≥500°C (Robinson et al., 2014; Robinson et al., 2009b; Robinson et al., 2012)

3.4. Dielectric Properties and Factors Influencing Them

3.4.1. Dielectric properties of materials

Dielectric properties of materials are important in understanding how they would interact with an electromagnetic field during microwave heating. Dielectric materials have an organised arrangement of charge carriers which could be displaced or polarised when exposed to an electric field. This exposure causes the positive and negative charges to move in opposite directions to compensate for the charges from the electric field (Fan et al., 2024). When an electric field is applied to a dielectric material, some energy is stored due to charge polarisation while some is dissipated into heat (Adam, 2017). The stored and dissipated energies can be expressed as a complex quantity known as the dielectric permittivity, ε, as shown in Equation 3-1 (Meredith, 1998).

$$\varepsilon = \varepsilon' - j\varepsilon'' \qquad 3\text{-}1$$

The real part of the complex permittivity, ε', is the dielectric constant which represents the stored energy, whereas the imaginary part also known as the dielectric loss factor, ε'', represents the power dissipated into heat. The loss tangent or the dissipation factor, tan δ, indicates the efficiency of a material to convert the absorbed energy into heat energy, and is the ratio of the loss factor (ε'') to the dielectric constant (ε') as shown in Equation 3-2.

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} \qquad 3\text{-}2$$

ε′, ε″, and tan δ are important parameters for characterising the dielectric properties of a material. For a specific volume of material, the power absorbed per unit volume (power density) depends on its dielectric properties as shown in Equation 3-3 (Meredith, 1998).

$$Pd = 2\pi f \varepsilon_o \varepsilon'' /E/^2 \qquad 3\text{-}3$$

Where: Pd, is the power density of the heated space (W/m^3); f, is the frequency of an electromagnetic wave (Hz); ε_o, is the permittivity of free space (8.85×10^{-12} F/m); ε'', is the dielectric loss factor of a certain phase; and E , is the electric field strength within the volume of the material (V/m). Equation 3-3 implies that, during microwave heating, the power absorbed by a material is directly proportional to its dielectric loss factor and the square of its electric field strength. Where other parameters are constant, it is also proportional to frequency.

However, it is important to note that the internal electric field (*E)* within the material is always smaller than the applied electric field as a result of depolarisation effects that occur when an electric field crosses a boundary between regions of different permittivity (Morgan et al., 2013). This effect is stronger in materials with higher dielectric constants (Steiner et al., 2020). This is why the loss tangent is sometimes a more appropriate way to compare the microwave susceptibility of various dielectric materials. Although the dielectric constant ε′ is excluded from Equation 3-3 since it does not directly contribute to the conversion of microwave power into heat, it however does affect the distribution of the electric field intensity within and around the dielectric material (Nelson, 1999; Adam, 2017). Higher dielectric constants would have a greater reduction in the wavelength of the electric field inside the material resulting in lower electric field intensity inside the material and higher outside its boundaries. This phenomenon is known as depolarisation.

When a wave propagates into a dielectric material, its amplitude diminishes because of the absorption of power as heat. Additionally, its field intensity and associated power density fall exponentially with distance from the surface of the dielectric material unless the waves in the material are reflected. The rate of decay of the dissipated power is a function of the dielectric constant and the loss factor (Meredith, 1998). The propagation of an electric field (*E*) through a dielectric material is shown in Figure 3-5.

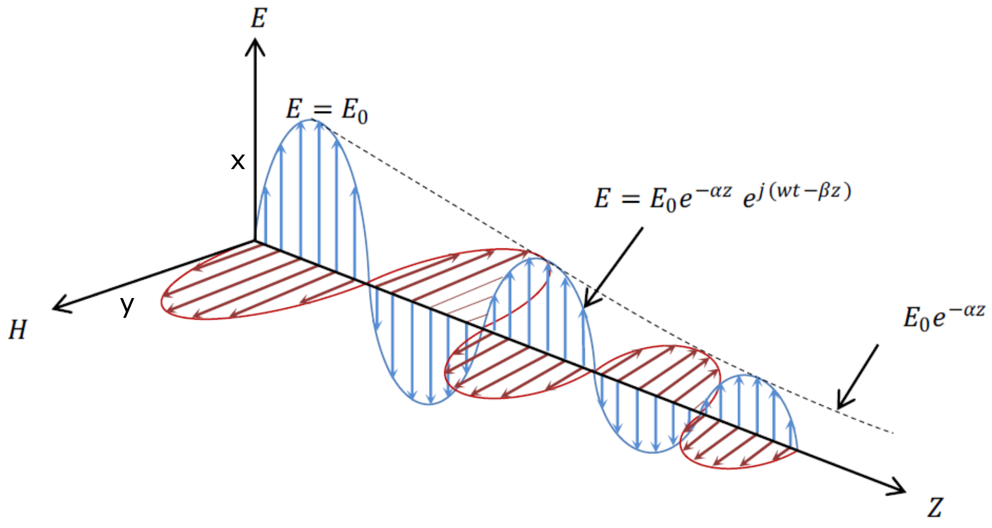


Figure 3-5: Propagation of an electromagnetic field in a dielectric medium (Metaxas and Meredith, 1983; Adam, 2017)

Where E_o is the incident electric field, whereas α (attenuation factor) and β (phase factor) are functions of the dielectric constant and loss factor (Metaxas and Meredith, 1983). The penetration depth (D_p) is another important parameter during the interaction of a dielectric material with electromagnetic energy as it indicates the immediate heat distribution within the material. It is the distance from the surface of a material at which the power drops to 1/e (i.e. ~0.368) from its surface value (Meredith, 1998). For a low-loss dielectric material, i.e. with $\varepsilon''/\varepsilon' \ll 1$, it can be represented mathematically as shown in Equations 3-4.

$$D_p = \frac{\lambda_o}{2\pi} \frac{\sqrt{\varepsilon'}}{\varepsilon''} \tag{3-4}$$

Where λ_o is the irradiation wavelength, ε' and ε'' are the dielectric constant and loss factor respectively. At distances beyond D_p, heating could still occur as around 37% of the power is dissipated into the material (Adam, 2017; Meredith, 1998). Larger wavelengths (or lower frequencies) increase penetration depths (Metaxas and Meredith, 1983). At frequencies close to the microwave heating range, penetration depths are correspondingly smaller (in centimetres and are often the size of the heated load) when compared with those at frequencies below 100 MHz (in meters). For example, at room temperature and 2.45 GHz, the penetration depth of water is 1.3 cm (Adam, 2017). For very wet materials, the size of the material is many times larger than D_p and microwave heating could result in unacceptable non-uniformities in the temperature distribution (Metaxas and Meredith, 1983).

3.4.2. Factors influencing dielectric properties

Dielectric properties are essential for estimating power density and the associated electric field strength (Meredith, 1998). They are influenced by the material's moisture content (for wet materials like soils), physical state (solid or liquid), temperature, density, composition, and frequency (Nelson and Trabelsi, 2012; Meredith, 1998). Some key factors are discussed.

3.4.2.1. Moisture content

Naturally, soils contain moisture which forms an integral part of design consideration for microwave heating systems, especially for application in soil remediation, as microwave processing of soils involves the removal of moisture in the process. Water existing in the liquid state is very polar and can readily absorb microwave energy and convert it into heat (Metaxas and Meredith, 1983). When mixed with other materials like soil it is called absorbed water. Significant differences exist between the dielectric properties of free and bound water - the two principal states that absorbed water exist within a water-containing material like soil. Free water is found within the capillaries and cavities of soils while bound water is chemically combined with other molecules or physically adsorbed to surfaces of dry materials e.g. kaolin clay ($2SiO_2 \cdot Al_2O_3 \cdot 2H_2O$) (Metaxas and Meredith, 1988). Much higher dielectric losses are associated with the free water of soils when compared with the molecules of 'bound' water that are less rotationally free as shown in Figure 3-6 (Metaxas and Meredith, 1983).

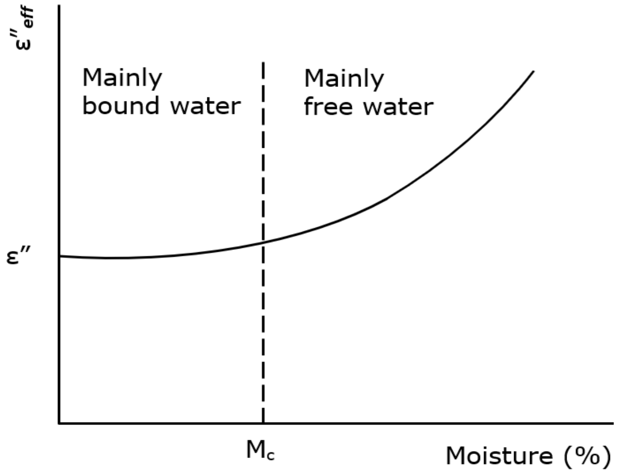


Figure 3-6: Relationship between the effective loss factor (ε''_{eff}) and moisture content for wet solids. M_c is the critical moisture content of the solid (Metaxas and Meredith, 1983)

From Table 3-2 which shows the dielectric properties of different materials, the dielectric loss factors for dry and wet (14% water content) loamy soils at 2.45 GHz are reported as 0.004 and 2.5, respectively (Meredith, 1998). This demonstrates the significant influence of water content on dielectric properties because the moisture content of 14% increased the loss factor by more than three orders of magnitude. Therefore, moist soils are expected to maintain high dielectric properties during processing until their moisture contents are completely evaporated at high temperatures ≥100°C and before any decomposition by-products such as carbonaceous materials are formed.

Table 3-2: Dielectric properties of selected solvents and different soil materials at 20 – 25°C and 2.45 GHz

Material	Moisture (%)	Density (g.cm^{-3})	ε'	ε''	tan δ ($\varepsilon''/\varepsilon'$)	Reference
Distilled water	-	1.00	77	13	0.17	(Meredith, 1998; Elmatic-Ltd, 2024)
Ethylene glycol	-	1.10	12	12	1.0	
Sandy soil	0	-	2.55	0.007	0.003	
	17	-	17	0.3	0.018	
Loamy soil	0	-	2.44	0.004	0.002	
	14	-	20	2.5	0.130	
Sandy loam	20	2.66	10.91	1.69	0.155	(Hallikainen et al., 1985)
Loam	20	2.70	10.53	1.67	0.158	
Silt loam	20	2.66	8.88	1.71	0.193	
Silty clay	20	2.56	7.40	1.85	0.249	
Sand	20	1.51	14.3	2.95	0.206	(Palta et al., 2022)
Loam	20	1.48	13.7	3.2	0.234	
Clay	20	1.35	13.2	3.4	0.258	
Drill cuttings*	6-12	1.43-2.00	4.8-6.7	1.0-1.8	0.21-0.27	(Robinson et al., 2010b)

*Results from a wide range of drill cuttings studied

Comparing distilled water with ice, at 2.45 GHz, the dielectric constant/loss factors of ice water and snow are 3.2/0.003 (at -12°C) and 1.2/<0.001 (at -20°C) respectively, which are much lower than those of distilled water 77/13 at 25°C (Meredith, 1998). This is because the water molecules in ice and snow are restricted in mobility due to their crystalline structure as a result, they are less polarised under an alternating electric field thus their low dielectric properties.

3.4.2.2. Frequency

Microwave frequencies for industrial applications are carefully selected to avoid interference with other frequency bands such as those used in telecommunication, defence and maritime applications (Metaxas and Meredith, 1983). The variation of dielectric properties (i.e. ε' and ε") of most materials with frequency is significant except for materials that are microwave transparent or lossless (Nelson and Trabelsi, 2012). This frequency dependence of dielectric properties is contributed by the loss mechanism (polarisation effects) involved during microwave heating (Nelson and Trabelsi, 2012; Adam, 2017). The permittivity of polar materials like water can be expressed mathematically using the Debye equation (Equation 3-5),

$$\varepsilon = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + j\omega\tau} \qquad 3\text{-}2$$

Where $\omega = 2\pi f$ represents the angular velocity, ε_∞ and ε_s are the dielectric constant at very high frequency and zero frequency (i.e. d.c. or static value) respectively. The relaxation time τ (in seconds) represents the time required for the dipoles to revert to a random orientation upon removing the applied electric field. Separating Equation 3-5 into real (ε') and imaginary (ε'') parts give the dielectric constant and loss factor in Equations 3-6 and 3-7.

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (\omega\tau)^2} \qquad 3\text{-}3$$

$$\varepsilon" = \frac{(\varepsilon_s - \varepsilon_\infty)\omega\tau}{1 + (\omega\tau)^2} \qquad 3\text{-}4$$

Graphically, the Debye equation is shown in Figure 3-7.

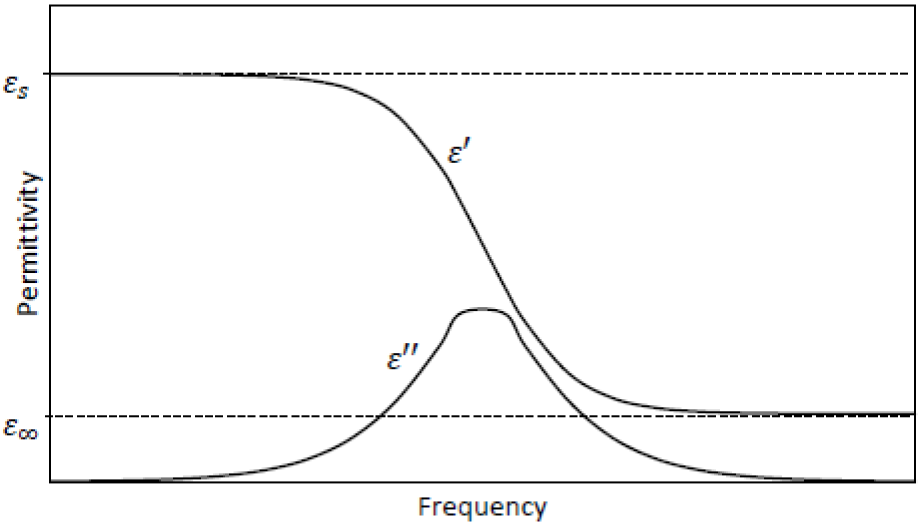


Figure 3-7: The dielectric permittivity of a materials that follows the Debye's equation (Adam, 2017; Metaxas and Meredith, 1983)

At very low frequencies, the dielectric constant has a constant high value of ε_s whereas, at very high frequencies, it has a constant low value of ε_∞ as a result of the inability of the molecules to rotate significantly before the electric field is reversed (Adam, 2017). On the other hand, the dielectric losses are zero at very low and very high frequencies. However, at intermediate frequencies, it has a peak loss value at its relaxation frequency, $\omega = 1/\tau$. Unlike dielectric materials that exhibit the dipolar loss mechanism, the frequency dependence of heterogeneous dielectric materials is complex especially when more than a single loss mechanism is exhibited e.g. the dipolar and conductive losses. In such a case, the conductive loss mechanism is dominant at lower frequencies and the dipolar loss mechanism is dominant at higher frequencies as shown in Figure 3-8 (see Section 3.3 for detailed discussion).

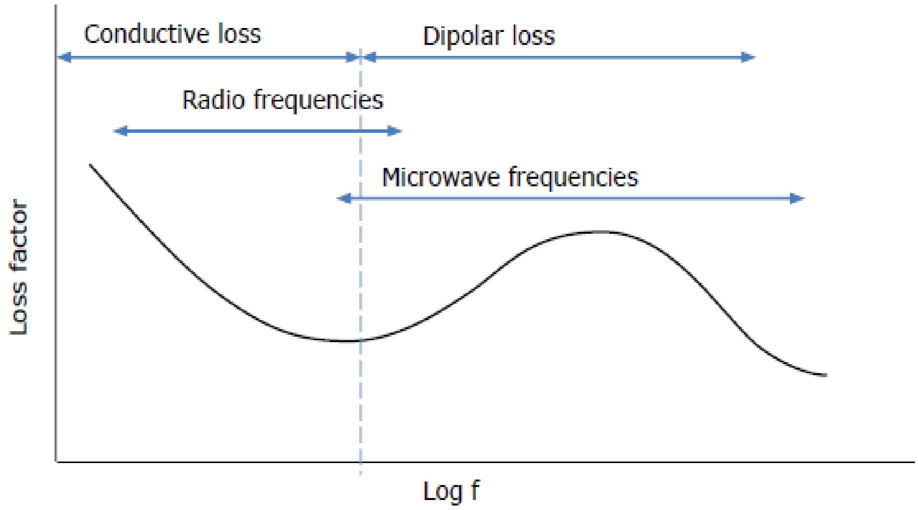


Figure 3-8: Typical loss factor of a heterogenous dielectric material exhibiting dipolar and conductivity losses (Metaxas and Meredith, 1983; Adam, 2017)

3.4.2.3. Temperature

When dielectric materials are irradiated with microwaves, heat is generated in the process. This results in changes in the temperature of the materials and can also influence their dielectric properties. Considering the graphical illustration of Debye’s equation for polar materials shown in Figure 3-9, when the temperature is increased, a decrease in the relaxation time occurs, resulting in a shift in the loss factor peak to higher frequencies.

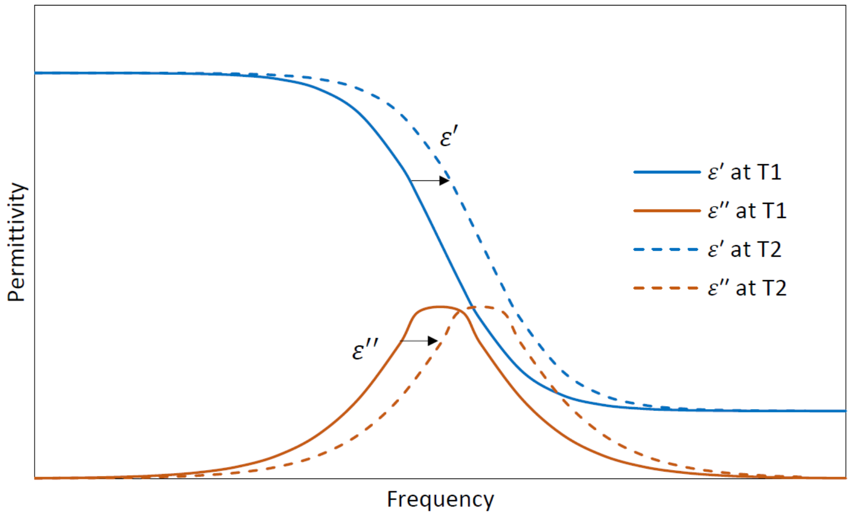


Figure 3-9: Permittivity at two different temperatures, T_1 and T_2, where $T_2 > T_1$. Adopted from Adam (2017)

Beyond the region of dispersion, the dielectric constant tends to increase with temperature increment and a reduction in the relaxation time (i.e. increase in relaxation frequency), however, the loss factor may increase or decrease depending on whether the operating frequency is more or less than the relaxation frequency (Nelson and Trabelsi, 2012; Vijay et al., 2015). If the operating frequency is below the relaxation frequency, then an increase in temperature will decrease the loss factor. However, if the operating frequency is above the relaxation frequency then an increase in temperature would increase the loss factor (Adam, 2017). In the case of pure water (a polar material that exhibits a polarisation loss), its relaxation frequency is ~20 GHz at 25˚C, therefore, at an operating frequency of 2.45 GHz, its loss factor would decrease with increasing temperature (Vijay et al., 2015; Adam, 2017). For example, Vijay et al. (2015) reported that increasing the temperature of water from 30˚C to 60˚C shifted the relaxation frequency from ~20 GHz to 38 GHz as shown in Figure 3-10.

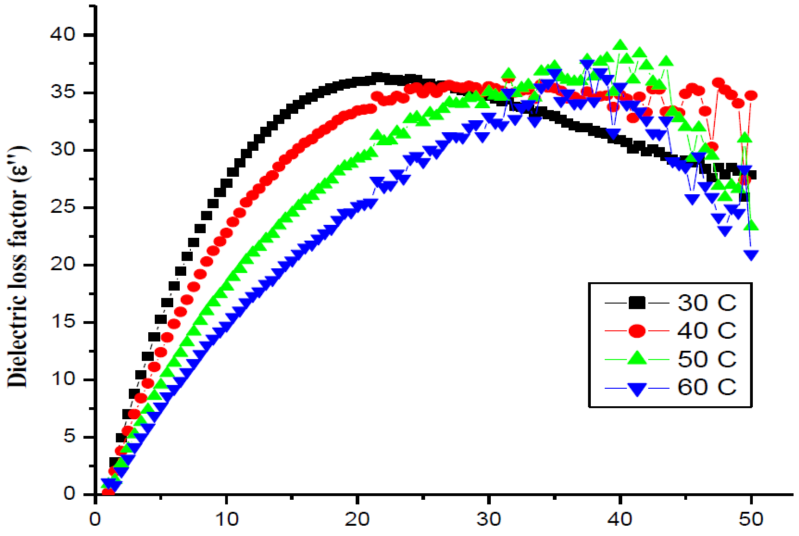


Figure 3-10: Frequency dependence of the dielectric loss factor of water between 30°C and 60°C (Vijay et al., 2015)

However, other mechanisms may dominate the dielectric relaxation effects in complex dielectric materials like food and soils (Nelson and Trabelsi, 2012). For example, Palta et al. (2022) found that the dielectric constant (ε′) and loss factor (ε″) of loamy soil (20% moisture content) behaved differently at 5 to 75°C. At frequencies between 0.2 GHz and 14 GHz, an increase in temperature resulted in a decrease in ε′ however, ε″ was found to increase due to the contribution of the bound water and thermal agitations to the dielectric losses. Robinson et al. (2014) studied the dielectric behaviour of oil sands (4.3% moisture) between 20 and 700°C at 2.45 GHz and observed a significant non-linear variation in their loss factors. The authors observed a similar behaviour as Palta et al. (2022) at temperatures <75°C. The ε′ decreased from around 2.6 to 2.2 while the ε″ increased from around 0.25 to 0.3. The ε″ later dropped to <0.03 between 100°C and 550°C when water was evaporated and then increased sharply beyond 550°C due to the formation of strong microwave-absorbing carbonaceous deposits from the decomposition of the hydrocarbon phase of the soils. This indicates that high temperatures can lead to changes in the soil’s composition - in this case, the decomposition of hydrocarbons and the formation of good dielectric materials that lead to high dielectric properties.

3.4.2.4. Density

The packing density of solid dielectric materials like soil is an important parameter contributing to their overall dielectric properties. This is because higher permittivity in solids is obtained at a higher packing density (Adam, 2017). At a higher packing density, the pore spaces and air fractions of soils become smaller. Since air has a smaller permittivity when compared with solid materials like soils, the overall permittivity of the mixture increases.

The packing density of soils would vary with texture i.e. from sand, loam/silt, clay, and other larger materials like rocks. Palta et al. (2022) showed that at any given moisture content (between 10-25%), the bulk densities of sandy soil > loamy soil > clayey soil. Additionally, the bulk densities decrease with increasing moisture content. Robinson et al. (2010b) found that at higher bulk densities of drill cuttings containing 10% moisture, fewer air voids exist compared with lower densities hence more drill cuttings are contained within the same volume resulting in higher dielectric constant and loss factors of the material. A robust design of a microwave processing system for the decontamination of hydrocarbon-polluted soils would consider the bulk densities of the feed material to ensure good dielectric constant and loss factors that would enhance microwave heating.

To conclude, it is well known that for a given temperature and frequency, soil materials with a dielectric loss factor >0.1 will readily absorb microwave energy and those with a dielectric loss factor <0.005 are considered microwave transparent (Robinson et al., 2009b; Meredith, 1998; Buttress et al., 2016). However, it must be noted that some materials with loss factors below 0.1 could still absorb microwave energy and be readily heated at high electric field intensities when high microwave power levels are used (see Equation 3-3). Zhang et al. (2018) and Adam et al. (2021) found that heavy oils with dielectric loss factors 0.015 and 0.004 are challenging to heat at room temperature and between 900 MHz to 3.0 GHz, however, their loss factors increased with increasing temperatures up to 300°C due to a reduction in their viscosity which makes them more microwave susceptible.

3.5. Contaminant Removal Mechanism Using Microwave Heating

It is widely recognised that hydrocarbon contaminant molecules in soils are relatively transparent to microwaves at room temperature (Robinson et al., 2008; Lim et al., 2016; Ogunniran et al., 2017; Robinson et al., 2012). However, when heated, the water phase or other microwave-susceptible components mixed with the soil absorb and convert the energy to heat. This heat is then transferred to the contaminant phase, promoting their removal. Rather than the direct absorption of microwaves by the contaminant, hydrocarbon removal would therefore depend on the physical properties of the hydrocarbon phase, their distribution within the soil material and the mass transfer characteristics of the soil (Buttress et al., 2016).

Various mechanisms for hydrocarbon removal during microwave soil processing are reported in the literature, including physical entrainment, steam stripping, steam distillation (or co-distillation), and thermal desorption (Robinson et al., 2012; Ogunniran et al., 2017; Falciglia et al., 2018a; Luo et al., 2019). Although entrainment, steam stripping and steam distillation are the common mechanisms associated with microwave heating due to their selective heating ability, thermal desorption is more prominent in conventional heating systems. The latter utilises heat to directly raise the volatility of contaminants to separate them from the soil matrix either below or at their boiling points. Physical entrainment occurs when vapour velocities are high to cause excessive sweeping or (carrying along) of contaminant liquid droplets/particles. In conventional separation/distillation columns, this excessive carryover of liquid droplets to the next plate leads to flooding and reduces actual plate efficiency. However, in soil remediation, it is thought that more contaminant droplet entrainment in the high-velocity vapour would enhance soil remediation.

In literature, steam stripping and steam distillation are often used interchangeably, however, Ogunniran et al. (2017), showed that these hydrocarbon removal mechanisms are based on different physical principles. In steam distillation also known as co-distillation, steam lowers the partial pressure of the volatile components which must be immiscible with water (Towler and Sinnott, 2022). When non-aqueous phase liquids (NAPL) such as petroleum hydrocarbons are present, the combined vapour pressure of the NAPL and soil water determines the boiling temperature of the two liquids, which occurs below the boiling point of the water. This means that many contaminants can be easily removed in vapour at steam temperature even if their boiling temperatures exceed 100°C (Kozlowska et al., 2009). On the other hand, steam stripping occurs when contaminants separate from soil phases and are transferred into the vapour/steam phase. This prevents the solid soil phases from reaching equilibrium with the vapour phase, allowing for continuous vaporisation at maximum rates (UFC, 2006). The removed contaminants are then condensed along with the steam in the condensation unit. Steam stripping effectively removes organics with boiling points less than 150°C and can typically achieve 99% contaminant removal (Goldberg and Min, 2014). Overall, while steam distillation results from the boiling of hydrocarbons below their boiling points within an immiscible phase like water, steam stripping removes the hydrocarbon phase into a stripping gas media by evaporation (Ogunniran et al., 2017). Steam distillation depends on the boiling temperatures whereas steam stripping relies on steam velocities. Entrainment on the other hand is a physical process and relies on vapour velocities and not the boiling or evaporation of contaminants into gas media. In conventional heating, live steam is injected counter current into the base of the column containing the contaminated soils or is generated in-situ with the aid of a heater. However, microwave heating generates steam in-situ by selectively heating the moisture within the contaminated soil matrix.

Ogunniran et al. (2017) measured the mass transfer coefficients during the decontamination of drill cuttings and compared them with existing mass transfer correlations. They conclusively showed for the first time that steam stripping rather than steam distillation is the dominant contaminant removal mechanism during microwave heating. This was because there was a positive correlation between the velocity of steam during processing and the contaminant removal unlike in steam distillation (which is not velocity dependent and results in the concurrent removal of both water and oil by boiling) (Ogunniran et al., 2017).

Therefore, the selective heating of the inherent water phase trapped within the soil pores and capillaries can result in its conversion to high-velocity steam which drives the stripping of hydrocarbon contaminants as they pass from the soil pores into the bulk gas (Buttress et al., 2016; Ogunniran et al., 2017; Robinson et al., 2008). It is expected that high-velocity steam can easily be generated when the soil's pore sizes are smaller (e.g. in clayey soils) thus causing mass transfer limitation during the escape of the rapidly generated steam. However, for larger soil pore sizes (e.g. sandy soils) that pose no mass transfer limitation, the generated steam leaves the pore spaces freely at low velocities. When this happens and the contaminants are immiscible with water, they would likely be removed by steam distillation, especially below thermal desorption temperatures. It should however be noted that due to the heterogeneous and complex nature of contaminated soil matrices, more than a single mechanism may contribute to the overall contaminant removal.

To maintain a thermodynamic advantage during microwave heating, the water phase must be converted into steam before a significant heat transfer can take place which implies that the heating rate $\Delta T/\Delta t$ in Equation 3-8 must be as high as possible (Robinson et al., 2010b).

$$\frac{\Delta T}{\Delta t} = \frac{Pd}{\rho Cp} \quad \text{3-8}$$

Where $\Delta T/\Delta t$ is the heating rate (°C/min), Pd is the power density (W/m^3), ρ is the density of the medium (kg/m^3), and Cp is the heat capacity (kJ kg^{-1} °C^{-1}).

3.6. Microwave-Assisted Solvent Extraction (MASE) Systems

Solvents are widely known for their suitability in extraction processes. In soil remediation, they are known for their application in soil washing of excavated soils (Gautam et al., 2020). Integrating microwave heating and solvent extraction offers advantages over conventional solvent extraction for its reduced volumes of organic solvents, reduced extraction time, increased sample throughput, precise temperature control during extraction and ease of use (Lopez-Avila, 2000). Microwave-assisted solvent extraction (MASE) involves immersing contaminated soil samples into the solvent placed in an open or closed system and heating them with microwave energy (Lopez-Avila, 2000).

Saim et al. (1997) recovered 1,587 and 1,492 mg/kg of PAHs from coal-contaminated soils (particle size <2 mm) using the pressurised MASE (2 g soil, 40 mL acetone, 30% of MES-1000 microwave power at 120^{o}C for 20 min with the aid of a pressure sensory equipment) and the atmospheric MASE (2 g soil, 70 mL DCM, 99% of 300 W power for 20 min) respectively. Microwave-assisted solvent extraction systems are more commonly used in sample preparation for analysis. As a result, small quantities of soil are used. A good solvent selection process for application in microwave-assisted extraction should consider the microwave-absorbing property of the solvent, the interaction of the solvent with the soil matrix and the contaminant's solubility in the solvent (Lopez-Avila, 2000).

3.7. Applications of Microwave Heating Systems for Soil Remediation

The utilisation of microwave heating in treating contaminated solid materials is versatile. It encompasses soil preparation for environmental analysis, decontamination of sludge and toxic wastes, and soil remediation. There is growing interest in exploring the potential of microwave heating as an alternative to traditional heating methods for decontaminating soils, drill cuttings, and the recovery of valuable resources, such as in oil sand processing (Buttress et al., 2016; Mutyala et al., 2010; Ogunniran et al., 2017; Robinson et al., 2010b). This is attributed to microwaves' rapid heating, penetration, selectivity, and efficient energy delivery directly to microwave-absorbing materials through molecular interactions with the electric field component. This minimises prolonged heat-up periods, thermal gradients, and energy loss commonly associated with conventional heating methods (Mutyala et al., 2010; Robinson et al., 2010b).

Many works have reported the use of microwave-absorbing materials as additives, susceptors, or catalysts to enhance the heating of solids for the removal of organic contaminants (Apul et al., 2016b; Krouzek et al., 2018; Sivagami et al., 2019). Nevertheless, others have focussed their investigations on the non-catalytic microwave heating that utilises the inherent soil moisture as a susceptor (Ogunniran et al., 2017; Robinson et al., 2014). Sivagami et al. (2019) argue that moisture alone acts as a poor absorber of microwaves as such, susceptors like graphite are necessary to achieve higher temperatures. However, Robinson et al. (2014) showed that temperatures >250°C can be reached upon heating the bound water within soils containing hydrophilic minerals and is sufficient to vaporise lighter hydrocarbons and thermally decompose some heavier ones.

Catalytic additives of metallic oxides (MnO_2, Cu_2O etc.), and carbonaceous materials like activated carbon and graphene fibres are excellent microwave absorbers due to their favourable dielectric properties that enable them to convert microwave energy to thermal energy (Apul et al., 2016b; Li et al., 2009). Although carbon fibres are environmentally friendly, there exist secondary pollution concerns from the addition of metallic catalysts to soils (Li et al., 2009). Furthermore, using high microwave-absorbing carbonaceous materials as susceptors could result in uncontrollable temperatures during heating that may lead to thermal runaway or arcing causing damage to equipment. A safer approach would be to first explore the microwave-absorbing bodies inherent in the contaminated soil matrix as susceptors to drive forward the removal of contaminants before considering the utilisation of external susceptors.

Most of the works carried out on microwave remediation of contaminated soils are limited to lab or bench scale application, however, this process has also been demonstrated both in-situ and ex-situ at a pilot scale by some authors. While in-situ remediation plants comprise microwave generation, transmission and off-gas capture and treatment systems, the continuous ex-situ system makes additional provisions for material handling and transport (Falciglia et al., 2018b; Buttress et al., 2016). For example, Buttress et al. (2016) developed an ex-situ pilot scale continuous microwave process system for treating hydrocarbon-contaminated soils (Figure 3-11).

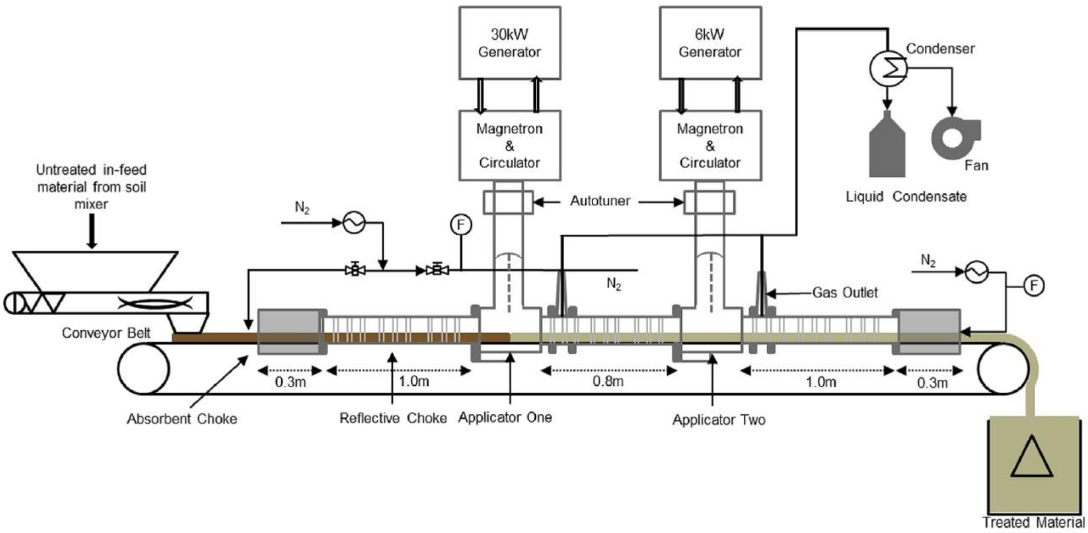


Figure 3-11: Schematic diagram of a pilot scale ex-situ continuous microwave processing system (Buttress et al., 2016)

The system consists of a trough-shaped basalt-fibre conveyor belt, measuring 300 mm wide, which moves soil fed by a screw feeder at a rate of 150 kg/hr into two microwave transverse wave E-field applicators. These applicators are designed with a self-cancelling reflection step and are arranged in series. A nitrogen purge gas, supplied at a rate of 20 m^3/h, is used to inert the system, and remove steam and organic vapours from the applicator. These are then extracted by a fan and condensed using a shell and tube heat exchanger cooled with water. The depth of the soil bed, maintained at 3 cm, is controlled by adjusting the speed of the conveyor belt in relation to the screw feeder. Krouzek et al. (2018) designed an in-situ microwave process system for subsurface soil remediation. It comprises microwaves at 2.45 GHz guided by a 6 kW generator placed in an air conditioning case to an unsaturated soil zone with the help of a constructed application well. The air emission control system consists of a condenser tube heat exchanger and an activated carbon adsorber whereas the contaminated air is extracted using a vacuum pump connecting the microwave application well and additional extraction wells as shown in Figure 3-12.

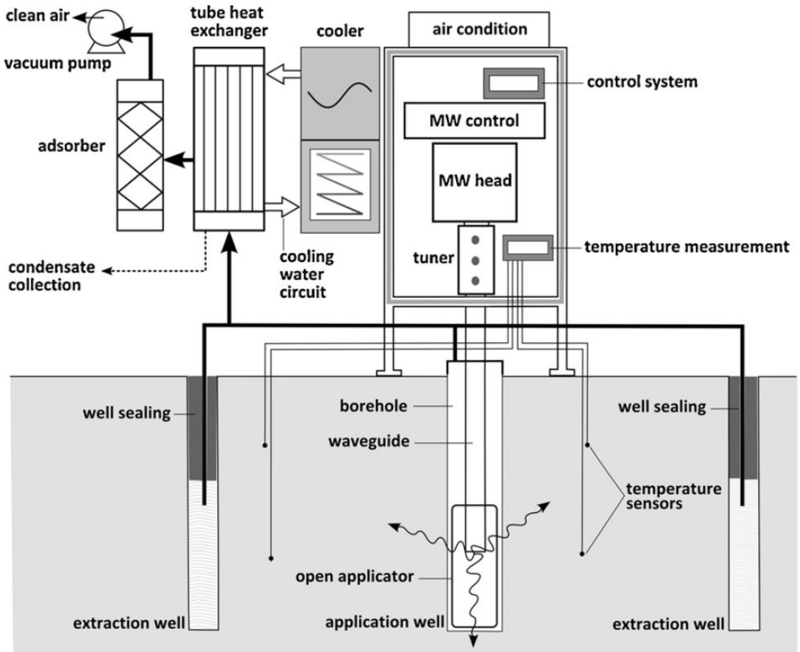


Figure 3-12: Schematic diagram for the pilot scale in-situ microwave soil remediation (Krouzek et al., 2018)

The temperature distribution was measured using thermocouples or optical fibre sensors placed at different depths within the monitoring boreholes. The depth of the applicator well is up to 1.8 metres and a heating radius of up to 1 metre. Table 3-3 summarises some selected applications of microwave heating, ranging from

Table 3-3: Applications of microwave heating for the remediation of hydrocarbon-contaminated solid materials

Author	Target contaminant	Equipment type	Process conditions for optimum contaminant removal efficiencies							Results	
			Moisture content (%)	Heating time (min)	Particle size (mm)	Applied power (kW)	Heating temp. (˚C)	Additives/ Solvents	Bed depth	Key finding(s)	Removal efficiency (%)
Lab/Bench scale applications											
Sivagami et al. (2019)	TPH from heavy fuel (furnace oil) contaminated soil	Ex-situ domestic MW oven (30 g contaminated soil per batch treatment)	4.9	60	0.61	0.45–0.6	>160	2.5 wt% spent graphite waste	-	Graphite enhances the desorption of C_{12}-C_{29} hydrocarbons	88-91
Falciglia et al. (2017)	PAH from artificially contaminated sandy soil	Ex-situ batch MW cavity reactor (20 g soil per treatment used)	10	18-60	75-200 µm	1	200-208	none	-	PAH polarity influences temperature achieved in MW heating and removal kinetics	75-80 (Total PAH removed)
Apul et al. (2016b)	TPH from artificially contaminated soils with crude oil	Ex-situ MW household oven (5 g per batch treatment)	18.7	1	≤4.76 reported elsewhere Apul et al. (2016a)	1	190	Graphene, multi-walled carbon nanotube and nanofiber (~5wt%)	-	Order of TPH removal rate: carbonaceous nanomaterials > macro-scale carbonaceous additives > no additives.	82
Serrano and Gallego (2006)	Aliphatic hydrocarbon (C_9-C_{27} + pristane + phytane) from artificially contaminated soils with diesel fuel	Ex-situ, closed vessel domestic MW (0.1-1 g per treatment)	3.5, 5	5	<2	0.425	-	3 mL n-hexane for 0.1-1 g soil	-	MW-assisted solvent extraction is a fast and inexpensive alternative to soxhlet extraction	80-90
Pilot scale/Commercial prototype											
Krouzek et al. (2018)	TPH, PAH, PCB, HCH and HCB, Naphthalene in contaminated soil/debris	5 L capacity stirred-batch ex-situ MW thermal desorber (reactor). *Purge gas*: N_2 at 6-9 L/min	~20	260-400	≤10	6 kW, 2.45 GHz (Industrial MW generator)	320-380 (max. temp. at reactor wall)	Iron particles	-	Without the use of a tuner in the unit, reflected power was <10% of applied MW power	96-100

	TPH and HCH from sandy soil polluted with light hydrocarbons and heavy oil spill in concrete	MW mobile device for in-situ soil surface heating (0.6*0.4 m irradiation area, 0.5-1 m^2/d capacity). *Purge gas*: Air	10	360	-	6 kW, 2.45 GHz industrial MW generator	100-260	Carbon fibres on specially designed MW applicator	20-50 cm	Only efficient for processing contaminated soil surfaces to a bed depth of 20-50 cm at 0.5-1 m^2/d	78-81
	TPH in diesel-contaminated soils from historical fuel handling	In-situ MW heating of subsurface soil using application well (1 m long steel applicator). *Purge gas*: Air	-	6 weeks	-	3-4 kW for 6 weeks, 4,000 kWh, 2.45 GHz used.	80-200 (Max. subsoil temp.)	-	1-1.5 m depth, 0.3-0.4 m heating radius;	Efficient contaminant removal was limited to a 0.5 m radius of the MW applicator well	80-83*
	TPH in heavy oil-contaminated soils from metalworking industrial site	In-situ MW heating using a 2 m long application well	-	5 weeks	-	6 kW for 5 weeks, 8,550 kWh, 2.45 GHz used	90-100 (subsoil temp.)		1 m depth, 0.5 m radius		87-89*
Buttress et al. (2016)	Hydrocarbons (PAH, BTEX) and from soils collected from an industrially contaminated site	Continuous MW process system. Single applicator (150 kg/h throughput). *Purge gas:* N_2 at 20 m^3/h	8.37-16.05	4	As received	15[a], 22.5[b]	-	None	30 mm	75% organic removal is possible using 2 process steps in series but limited to the amount of power that can be safely delivered to soil material	60-75
Chien (2012)	C_6-C_9, C_{10}-C_{40} and BTEX from soils contaminated with petroleum from a storage tank leak	In-situ MW heating of subsurface soil using a 4 m long antenna (Full-scale field study)	7.76-22.20	210	≤1	2	-	None	0.6-3.6 m depth, 0.4–1 m heating radius	Petroleum hydrocarbons were not effectively removed at 3.4-3.6 m depth and 1 m heating radius	46-100 (BTEX); 24-100 (C_6-C_9); 76-100 (C_{10}-C_{40})
Robinson et al. (2010b)	Petroleum hydrocarbons from oil-contaminated drill cuttings	Single cavity continuous MW process system (500 kg/h). *Purge gas:* N_2	6-12	7-20	As received	15	-	None	30-55 mm	Achieved <1 wt% residual oil levels for discharging drill cuttings using continuous MW processing	98.5

[a] Single microwave (MW) applicator, [b]Two single MW applicators in series, TPH- Total Petroleum Hydrocarbons, PAH- Polycyclic Aromatic Hydrocarbons, HCH- Hexachlorocyclohexane, HCB- Hexachlorobenzene, BTEX- Benzene-Toluene-Ethylenebenzene-Xylene, *estimated removal efficiency from reported results varying with soil depth and heating radius.

laboratory to pilot scale operations aimed at understanding the interaction between contaminated solids and microwave energy which could inform onward development to full-scale applications. From Table 3-3, up to 80 - 90% contaminant removal (e.g. TPH and PAH) were achieved at the laboratory scales. Various authors demonstrated that the microwave heating system could be scaled up to pilot and commercial prototypes for both in-situ and ex-situ applications while maintaining these contaminant removal yields. In some cases, up to ~100% yields were achieved at the pilot scale (Chien, 2012; Robinson et al., 2010b; Krouzek et al., 2018). However, some limitations need to be addressed for this technology to be fully scaled up for commercial application in soil remediation. These challenges are discussed in the following Section 3.8.

3.8. Challenges and Opportunities for Advancing Microwave Heating Systems for Soil Remediation

Despite different research contributions on the application of microwave heating for soil remediation, most microwave systems are limited to a pilot scale treatment or commercial prototypes, and no definitive application has successfully evolved into a full-scale commercial or an everyday real-life one (Mutyala et al., 2010; Krouzek et al., 2018). This is because of the lack of sufficient data from pilot demonstration systems (Buttress et al., 2016). As a result, more understanding from fundamental studies of process design and conditions is needed to overcome the limitations encountered in previous pilot scale demonstrations which would serve as a basis for scaling up into full-scale application. For example, thermal runaway and arcing are a significant limitation in microwave heating (Buttress et al., 2016). The former occurs when an increase in temperature within the soil material changes the process conditions in a way that causes an uncontrollable increase in temperature. High temperatures during microwave heating can cause the decomposition and formation of high microwave-absorbing by-products that are a major contributor to thermal runaway. Generally, thermal runaway degenerates into arcing potentially leading to severe degradation of the heated material and damage to the equipment (Meredith, 1998). It results in very high localised temperatures that can damage the microwave and material handling system as well as the breakdown of the electric field (Buttress et al., 2016).

Other challenges from pilot studies on the remediation of oil-contaminated solid materials exist. Robinson et al. (2010b) combined electromagnetic design and bulk material handling to produce a continuous microwave process system aimed at treating 500 kg/h of contaminated drill cuttings. However, there is a need to establish the boundaries for a continuous treatment system that examines the impact of microwave power, throughput, oil and mineral contents on the levels of oil removed and the quality of recovered oil. Buttress et al. (2016) who addressed some of these issues encountered a limitation in system robustness due to arcing and unsustainability of operation at power levels >15 kW while processing hydrocarbon-contaminated soils at 150 kg/h using a 30 kW capacity single applicator. Although power input distribution using two identical applicators in series was employed by varying the power level in each microwave applicator to a maximum of 22.5 kW (i.e., 15 in applicator 1 and 7.5 kW in 2), it achieved 75% removal efficiency. However, it was 20-30% less energy efficient than the single applicator which achieved 60% removal. Overcoming arcing without trading off decontamination efficiency would require a process strategy that safely and reliably delivers high power whilst maintaining system robustness (Buttress et al., 2016).

The semi-pilot batch microwave thermal desorber developed by Krouzek et al. (2018) achieved a high hydrocarbon removing efficiency of ≥96% and demonstrated low energy loss compared with conventionally heated ones (with power consumption 3 times higher). However, it was achieved at a retention time of 260 - 400 minutes far above the 20 - 40 minutes typical material retention time requirement for industrial microwave processing (Krouzek et al., 2018).

Additionally, inefficient mixing of soils by the anchor stirrer was observed (especially clay soils with moisture content >20%). For a successful industrial-scale operation, a rotary kiln desorber or conveyor belt system could be a more efficient alternative (Krouzek et al., 2018). Furthermore, their in-situ subsurface microwave heating for Total Petroleum Hydrocarbons removal revealed that efficient heating-up of bulk subsurface soil was limited to 0.4 - 0.5 m soil layer around the application well as such, 1 m spacing between them for remediation setup would be a very dense and expensive strategy. Scaling-up for full application would require the implementation of an efficient network of modular systems of several microwave wells (each containing a subsurface open-applicator or antenna), arranged to deploy microwave energy powered by an individual generator to effectively heat subsurface soil and release VOCs to a combine extraction and emission control system (Krouzek et al., 2018; Chien, 2012).

In conclusion, it is imperative to address these limitations to effectively implement microwave processing systems for large-scale commercial use in soil remediation. Additional data is required to enhance our understanding of the interaction between microwave energy and contaminated soils, particularly, regarding overcoming the challenges of thermal runaway and arcing, areas that have not been extensively explored in existing literature. This is essential for ensuring the process safety of microwave heating systems during soil treatment. Furthermore, there is currently a lack of systematic comparison of important factors like soil type and contamination type across comparable remediation systems which is an important consideration for choosing an effective remediation strategy.

3.9. Aim and Objectives

This research aims to carry out a robust and systematic technology evaluation of selected remediation technologies for the removal of Total Petroleum Hydrocarbons (TPH) from soils. To achieve this, the following specific objectives were used.

i. Evaluate existing remediation technology solutions based on efficiency, environmental impact and sustainability, safety, treatment time, cost, and suitability for removing Total Petroleum Hydrocarbons from soils.
ii. Study the textures and contaminant variations in typical Niger Delta contaminated soils and other selected soil materials to understand their relationship with the effectiveness of the microwave remediation process.
iii. Study the dielectric properties of the contaminated soils within the thermal remediation temperature range to understand and link these properties to their interaction with microwave energy.
iv. Optimise oil removal from contaminated soils over microwave heating time, specific energy, and temperature, and overcome the limitations of thermal runaway.
v. Use the findings from objectives (ii), (iii) and (iv) to re-evaluate the initial technology selection decision.

CHAPTER 4

4. MATERIALS AND METHODS

In Chapter 4, the reagents and the petroleum hydrocarbon-contaminated solid[3] materials used in this work are discussed. The sample preparation procedures and the methodologies used to characterise the materials are outlined. The chapter explains why these methods were selected and the measures taken to ensure that the results collected are reliable and reproducible. Furthermore, the remediation technology approaches used, which include microwave and conventional heating systems are discussed. Finally, the procedures of the various microwave heating configurations explored (i.e. dry microwave heating, wet microwave heating, and microwave heating using the liquid inert system) were established.

4.1. Reagents and Materials

4.1.1. Reagents used in this study

The key reagents used in this study which are also discussed in detail under relevant experimental procedures are shown in Table 4-1.

4.1.2. Contaminated Solid Materials Used

Four petroleum hydrocarbons contaminated solid materials were used in this study namely, road planings (tarmac scalpings), filter cake, Bodo soils, and K-Dere soils. While road planings are waste bituminous road scraping products from resurfaced roads and highways that are rich in polycyclic aromatic hydrocarbons, the filter cake is primarily a fine-grained clay-based waste material from soil washing remediation processes that contains various pollutants including total petroleum hydrocarbons. For this work, road planings were received from Park Grange Road, Sheffield, United Kingdom, while the filter cake materials were received from Biogenie's soil treatment facility at Redhill, South London, United Kingdom.

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[3] The term 'solid' material was used instead of 'soil' because road planings (tarmac scalpings) and filter cake are generally not considered soils even though filter cake is similar to clay materials.

Table 4-1: Reagents used for experimentation

Reagents	Specification	Experimental activity
Dichloromethane	Sigma-Aldrich, puriss. P.a., ACS reagent ISO, ≥99.9% (GC)	Soxhlet extraction, fractionation, GC-MS, and asphaltene precipitation
Methanol	Fisher Chemical, certified AR for analysis	Soxhlet extraction, and fractionation
n-Heptane	Fisher Thermo Scientific Chemicals, HPLC, ~95%	Asphaltene precipitation
n-Hexane	Fisher Chemical, n-hexane fraction from petroleum	Liquid inert microwave heating and fractionation
Ethylene glycol (Ethane-1,2-diol)	Fisher Chemical, ethanediol, extra pure, SLR, ≥99%	Wet microwave heating (as susceptor)
Toluene	Fisher Chemical, HPLC grade, ≥99.8%	Dean Stark – moisture content determination
Silica gel	Sigma-Aldrich, high-purity grade (Davisil grade 636), pore size 60 Å, 35-60 mesh particle size	Fractionation
Silica gel	Sigma-Aldrich, silica gel, high-purity grade (7734), pore size 60 Å, 70-230 mesh	Fractionation
Aluminum oxide (Alumina)	Sigma-Aldrich, activated basic, Brockmann I, ~150 mesh size, 58 Å pore size.	Fractionation

In contrast, Bodo and K-Dere soils were collected from Nigeria's Niger Delta i.e. the petroleum contaminated sites at St. Patrick waterside, Bodo, Nigeria, and Nupene, K-Dere, Nigeria, respectively as shown in Figure 2-3. The road planings and filter cake materials from the UK were chosen and used for the establishment of experimental methods as well as to understand how microwave energy interacts with a wider range of oil contaminated solid materials since they represent typical petroleum hydrocarbon contaminated materials. The established experimental methods were then applied to the contaminated soils from the Niger Delta, and the results were compared to give a more robust understanding of the effect of microwave remediation technology on a range of contaminated solid materials.

These contaminated solids were selected to cover a wide range of solid materials (i.e., fine materials such as filter cake to coarse materials such as planings), particle sizes (<2 mm to >10 mm sizes) as well as a wider level of moisture contents (3.0 ± 0.001 to 52.1 ± 0.36%), and oil contamination range (0.88 ± 0.1 to 10.40 ± 0.15%w/w, wet basis). Figure 4-1 shows the petroleum hydrocarbons impacted soils used for this study as received from sites.

Road planings

Filter cake (Beaker ID: 10.7 cm)

Bodo soils

K-Dere soils

Figure 4-1: Contaminated solid materials used

4.2. Contaminated Solids Sample Characterisation

Before undertaking sample characterisation, the contaminated solid materials as received from sites were gently mixed with the aid of a hand shovel to ensure homogeneity of the materials and to minimise errors during analyses. This mixing technique was adopted to prevent (or reduce) the alteration of sample properties that could arise while using mechanically automated mixing methods. A few biomass materials (i.e., wood and root chunks) were contained in the samples, especially in filter cake, Bodo and K-Dere soils. These were handpicked and separated from the soil materials before processing.

After mixing, the solid samples were then divided into smaller quantities for analyses and remediation experiments using the riffling sampling procedure (for larger soil quantities) followed by the cone and quarter sampling procedure for smaller samples ≤30 g (Schumacher et al., 1990; Campos-M and Campos-C, 2017). However, because of the sticky nature of the filter cake, these sampling techniques were unsuitable. As a result, samples were collected randomly from different positions within the bulk filter cake sample after thorough mixing. This ensured a true representation of the bulk sample during each analysis and remediation experiment. The following analyses and microwave processing experiments were carried out on each contaminated solid material.

4.2.1. Dielectric properties measurement

Many techniques exist for the measurement of dielectric properties the most common ones being the cavity perturbation technique, the open-ended probe technique, the waveguide and coaxial transmission line method, and the free-space transmission technique. The open-ended probe technique covers a broad range of frequencies but has poor accuracy in measuring low-loss materials compared with the cavity perturbation technique; the free space technique is difficult to use at low frequencies and requires a large structure and amount of sample; the waveguide technique is easy but has some limitations for high-temperature measurements and difficulty in sample preparation above ~6 GHz (Adam, 2017; Hallikainen et al., 1985). In this work, the cavity perturbation technique was used to measure the dielectric properties of the contaminated soils at the frequency of interest (910 MHz and 2,470 MHz). This technique was used because of its high accuracy and suitability for measuring low dielectric loss materials and can take high-temperature readings of up to 1,000°C (Robinson et al., 2009b; Robinson et al., 2014; Adam, 2017; Zhang et al., 2018).

The perturbation cavity equipment (Figure 4-2) comprises a cylindrical copper cavity connected to an Agilent Technologies E5062A vector network analyser (VNA) which generates and transmits microwave signals to the cavity enabling the measurement of the resonant frequency and quality (Q) factor of the cavity.

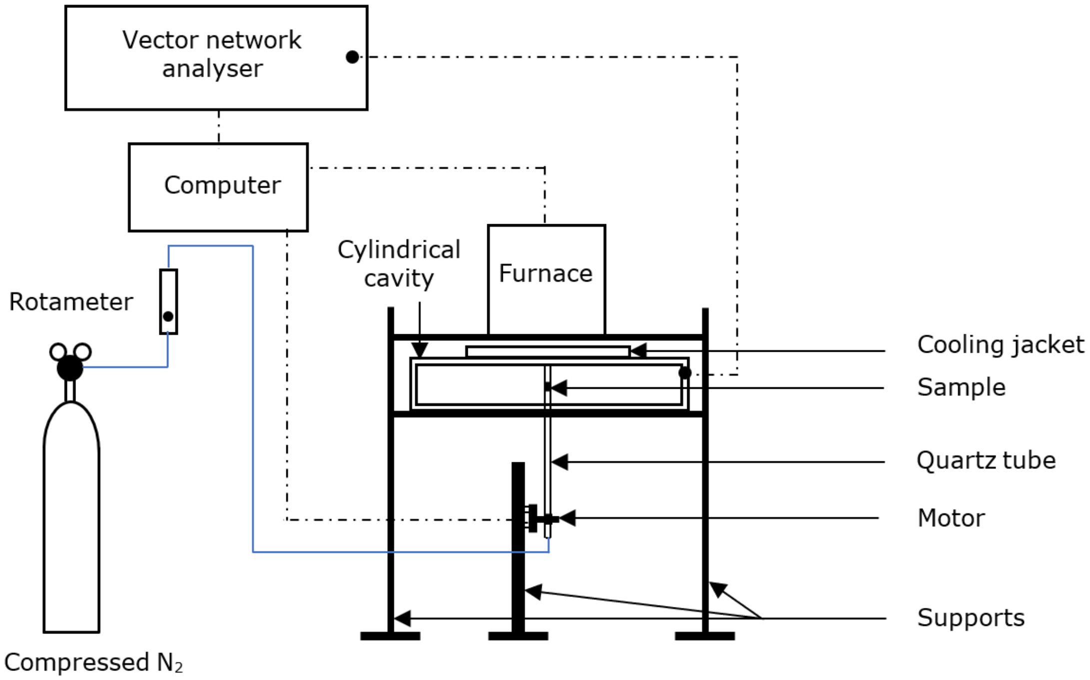

Figure 4-2: A schematic diagram of the cavity perturbation technique for dielectric measurement

The Q factor represents the ratio of the energy stored to that dissipated in the cavity (Adam, 2017). This is connected to a computer equipped with software to record and store the results. A transparent 4 mm (internal diameter) quartz tube with high thermal resistance and very low loss factor was used as a sample holder for the contaminated soils. Dielectric measurements were carried out with and without creating an inert nitrogen environment within the quartz tube and the results were compared.

Measurements were carried out in the cavity over a temperature range of 20°C - 750°C by calculating the frequency shifts and Q-factor with an empty quartz sample holder and subsequently upon inserting the contaminated soil into the cavity. Simple perturbation Equations 4-1 and 4-2 were then used to calculate the dielectric constant (ε'), and loss factor (ε'') of the soil sample (Adam, 2017; Zhang et al., 2018; Smith et al., 2010).

$$\varepsilon' = 1 + 2J_1^2(x_{1,m})\frac{f_o - f_1}{f_o}\frac{V_c}{V_s} \qquad 4\text{-}1$$

$$\varepsilon'' = J_1^2(x_{1,m})\left(\frac{1}{Q_1} - \frac{1}{Q_o}\right)\frac{V_c}{V_s} \qquad 4\text{-}2$$

f_o and f_1 represent the resonant frequencies before and after the quartz sample holder is loaded respectively; Q_o and Q_1 are the quality factors of the empty and loaded quartz sample holder respectively; V_c and V_s represent the cavity and sample volumes respectively, while $J_1(x_{1,m})$ is the second order of the first kind root of the Bessel function.

This experiment was repeated 3-4 times, and the average result and standard deviation[4] were reported using error bars. For dielectric measurements carried out under an inert environment, a quartz tube opened at both ends was used and the sample was supported by a ceramic fibre wool bed. The lower end of the quartz tube was connected to a tube linked to a gas cylinder which supplies nitrogen (N_2) at a rate of 7.5 cc/min [5]. A detailed description of this test procedure is reported by Zhang et al. (2018). However, it should be noted that the dielectric properties of the contaminated solid materials measured in this work are the effective properties of the samples and not their intrinsic properties because of the presence of air within the mixture during measurements.

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[4] The standard deviation (SD) of a data set collected from repeating a particular experiment multiple times under the same experimental conditions is calculated using, $SD = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(x_i - \mu)^2}$. N = total number of experiments conducted under the same conditions, μ = mean value of this data set, and x_i = ith value of the data set. SD is represented by error bars or indicated after a "±" symbol in a result.

[5] For filter cake, N_2 flow was introduced only after heating the sample to 200°C when its moisture and ethylene glycol contents were removed, and cake pores are opened to allow for N_2 flow. This approach allowed the study of dielectric properties under inert environment at higher temperatures (>200°C). Note that, introducing N_2 at the beginning of the experiment creates pressure build up with time below the sample bed that pushes the sample out of the tube during measurements.

Additionally, since a reference tube was used as a sample holder during dielectric measurements, the following measures were taken to ensure that the measured frequency shifts were solely attributed to the sample and not the sample and reference tube. A reference tube made of quartz was used, as the dielectric constant (ε′) and dielectric loss (ε″) of quartz does not change significantly with temperature over the studied range (i.e. up to 700°C) (Baker-Fales et al., 2023; Yang et al., 2011; Jones, 2005). This choice of material ensured that the reference tube would not significantly affect the frequency shift and quality factor, thus minimising interference with the measurements. Also, a thin-walled reference quartz tube (1 mm) was used to minimise the impact of the tube on the field configuration and any perturbation caused by the tube. Furthermore, the shift in central frequency and Q-factor used in calculating ε′ and ε″ was properly quantified by measuring the resonant frequency of the cavity containing the tube and sample relative to that containing the empty tube at room temperature (Zhang et al., 2018; Smith et al., 2010). Finally, consistency was maintained by using the same reference tube for empty measurements and when the sample was loaded to ensure comparability and repeatability of the results.

4.2.2. Oil content determination

The oil content (extractable organic matter) from the contaminated soils was determined using soxhlet extraction (Uguna et al., 2012; Meredith et al., 2020). This technique was used because it allows the immediate measurement of the oil content after the contaminated materials are processed using microwave heating, furthermore, other analyses could also be carried out in parallel. Dichloromethane-

Methanol (93:7 v/v) solvent mixture was used for extracting about 10 – 30 g of contaminated soils for 24 hours as shown in Figure 4-3.

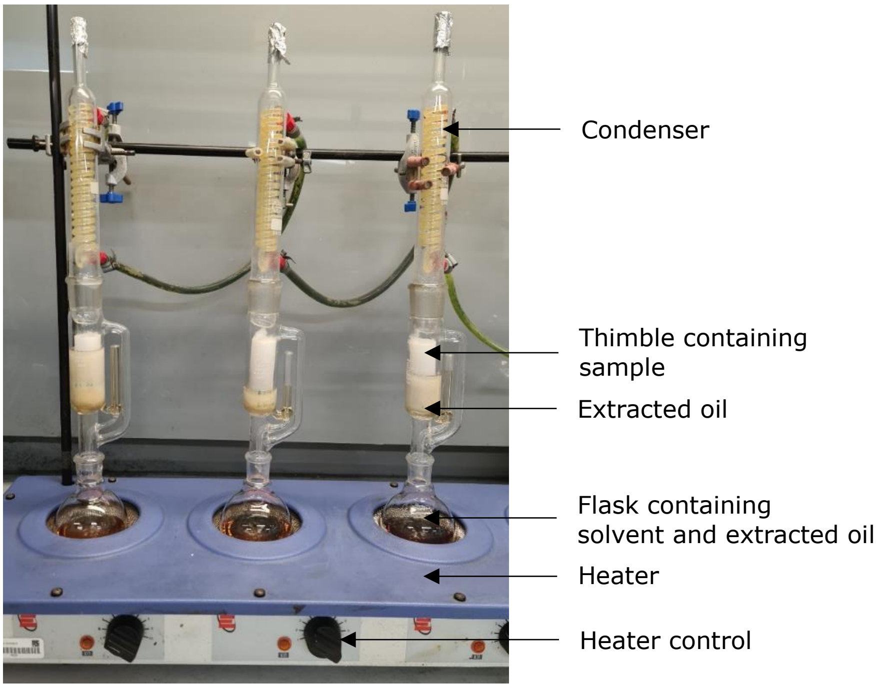

Figure 4-3: Oil determination setup using soxhlet extraction

Methanol and dichloromethane (DCM) solvent mixture enables the extraction of both polar and nonpolar hydrocarbon contents of the soil respectively. The oil-solvent mixture was then separated using a vacuum rotary evaporator set at 30°C and 400 mbar. Dichloromethane was further used to recover the oil from the 250 mL flask (with the aid of a pipette) and then transferred into pre-weighed glass vials and allowed the dry to constant weight. The mass of the glass vial was then subtracted from the total mass of the vial containing oil after drying to determine the extracted oil mass. The vials were stored in a refrigerator at a temperature of -20°C for further analysis. The mass of oil extracted was then used for calculating the soils' oil content on a wet basis as shown in Equation 4-3.

$$Oil\ content\ (w/w\,\%) = \left(\frac{mass\ of\ extracted\ oil}{mass\ of\ soil\ used}\right) * 100 \qquad 4\text{-}3$$

The average oil content and standard deviation from three experimental repeats were reported.

For filter cake, the sample was air dried in a fume hood before oil content determination using soxhlet extraction. This is because preliminary experiments showed that the wet filter cake does not allow the percolation of the Dichloromethane-Methanol solvent into the material during extraction due to its clayey nature (that is muddy and sticky), instead, the solvent only extracts the hydrocarbons at the surface of the sample and via channelling thus bypasses some of the trapped hydrocarbon phase. However, after air drying, it was easy to extract the hydrocarbons because the filter cake became loose due to the moisture removed thereby creating pores within the filter cake that allows the penetration of the solvent during soxhlet extraction. This was also the case after remediation using microwave heating.

This procedure was also carried out for the treated soils and the percentage of oil contents before and after soil treatment was used to calculate the percentage of oil removed from contaminated soils as well as the residual oil in soils using Equations 4-4 and 4-5 respectively.

$$Oil\ removal\ (w/w\%) = \left(\frac{Initial\ oil\ content\ -\ oil\ content\ after\ treatment}{Initial\ oil\ content}\right) * 100 \qquad 4\text{-}4$$

$$Residual\ oil\ in\ soil\ (w/w\%) = 100 - Oil\ removal \qquad 4\text{-}5$$

4.2.3. Moisture content determination

The soil’s moisture content was measured using the Dean Stark method (ASTM-D95-13, 2018). 8 mL receiver (trap) capacity was used for measuring moisture contents before soil treatment while the 2 mL receiver capacity was used afterwards as it enables the measurement of smaller amounts of moisture expected for treated soils due to the loss of water during heat treatment. 20-30 g of the solid sample before treatment (or lesser grams after treatment) were mixed with 100 mL of toluene in a 250 mL flask and the experimental setup was assembled as illustrated in Figure 4-4[6].

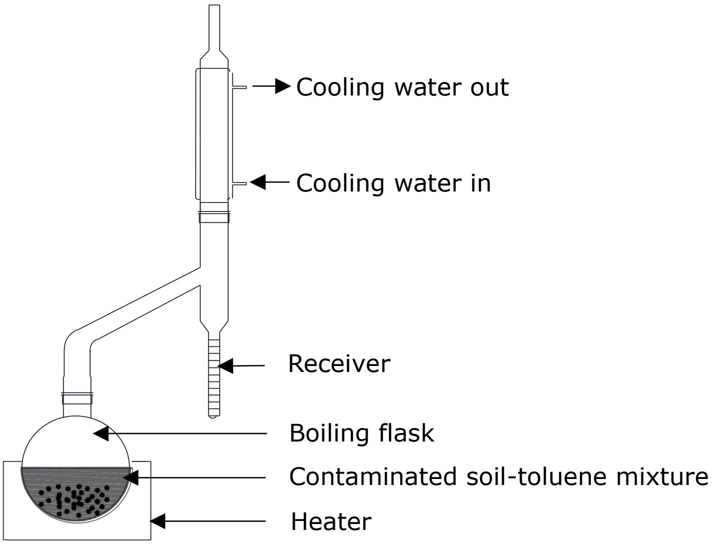

Figure 4-4: Schematic diagram of Dean-Stark setup for moisture content measurement

Upon the application of heat, the boiling rate was adjusted to give an average distillation rate of 40 drops per minute. After 24 hrs when the volume of water remained constant for 5 minutes and no water was visible in any part of the apparatus except the cold trap, the heater was turned off and the setup was allowed to cool. A glass rod was used to dislodge any drops of water adhering to the walls of the cold trap into the water layer. The volume of water reading in the receiver (trap) was then taken and used for soil moisture content calculation (Equation 4-6).

$$Water\ content, \%(V/m) = \frac{(Vol.\ of\ water\ in\ trap, mL) - \left(Water\ in\ solvent\ blank^{7}, mL\right)}{Mass\ of\ soil\ sample, g} \qquad 4\text{-}6$$

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[6] For filter cake, smaller individual chunks (summing up to the total mass of sample used) were transferred into the toluene solvent. This made the penetration of the solvent across the sample possible thus allowed the washing out and subsequent evaporation (during heating) and condensation (upon cooling) of the moisture into the receiver for moisture content measurements. This was not the case when a lump of filter cake was used.

[7] Toluene solvent, which was used as blank had ~ 0% water content.

Average results from three experimental repeats were reported on a dry basis after conversion from a wet basis.

4.2.4. Density and porosity measurements

Soil samples were dried in an oven at 105°C for 24 hours before the bulk density and porosity measurements were taken. The skeletal or true density of the soil sample was determined using the Micromeritics Accupyc 1330 gas pycnometer. This was then used together with the bulk density of the material calculated from the volume occupied by 80 g of contaminated soil within a 100 mL measuring cylinder to determine the porosity of the soil (Equations 4-7 and 4-8).

$$\text{Bulk density } (\rho_b) = \frac{Massof\ soil\ (m)}{Volume\ occupied\ by\ soil\ (v)} \tag{4-7}$$

$$Porosity\ (P) = 1 - \frac{Bulk\ density\ (\rho_b)}{Skeletal\ density\ (S_d)} \tag{4-8}$$

4.3. Extractable Organic Matter Preparation and Analyses

Directly injecting the oil extracted from contaminated soils into the Gas Chromatography-Mass Spectrometry (GC-MS) equipment could damage the column due to the presence of asphaltene. Asphaltene is the black friable solid portion of asphalt that is insoluble in low molecular weight saturated alkanes (Branthaver and Huang, 2015). In this work, asphaltenes were removed from the extracted organic matter using the asphaltene precipitation method reported by Meredith et al. (2020). Fractionation was also carried out to separate the oil into aliphatic, aromatic, and polar hydrocarbons (Khairy et al., 2023).

4.3.1. Asphaltene precipitation

About 100 - 300 mg of the extractable organic matter (oil) sample was dissolved in 1 mL dichloromethane (DCM) and the mixture dissolved in a 40-fold excess of chilled n-heptane. This was allowed to be gently mixed using a magnetic stirrer for 15 minutes and later centrifuged at 2,500 rpm for 10 minutes when a clear separation between the asphaltene (sediment) and maltene (supernatant) fractions was observed. The supernatant containing the mixture of maltene, n-heptane, and dichloromethane was then decanted into a 250 mL flask and the solvents were removed using the rotary evaporator at 85°C and 200 mbar. This was repeated for the asphaltene fraction until a clear supernatant was observed indicating the total removal of the maltene fractions from the asphaltene. These fractions were transferred into pre-weighed glass vials and allowed to dry to constant weights in the fume hood. Their final masses were then used for calculating the asphaltene and maltene contents of the oil. The asphaltene precipitation procedure is skipped when there is no need to estimate the asphaltene and maltene contents of the oil – in which case the extractable organic fraction was fractionated directly.

4.3.2. Fractionation

To enable the separation of the extracted oil (either maltene or extractable organic fraction - whichever one was used) into aliphatic, aromatic, and polar hydrocarbons using an alumina-silica column chromatography, ~40 mg of the oil was adsorbed onto ~0.70 g trap silica. Alumina and column silica in the ratio 1:3, w/w (i.e., 2 g of alumina to 6 g of silica) were transferred respectively into a 25 mL glass burette column containing hexane solvent to form a bed supported by cleaned cotton wool. The adsorbed oil was then transferred into the prepared alumina-silica column and its tap opened to gently elute the aliphatic hydrocarbons (Figure 4-5).

Afterwards, a hexane-dichloromethane mixture (60:40 v/v) was added to elute the aromatic hydrocarbons and finally, a DCM-Methanol mixture (50:50 v/v) was used to elute polar hydrocarbons as shown in Figure 4-6. The eluted samples in pre-weighed glass vials were allowed to dry in the fume hood to constant weight (by evaporating the solvent) and their final weighs were used for the calculation of aliphatic, aromatics, and polar hydrocarbon contents of the oil. This procedure

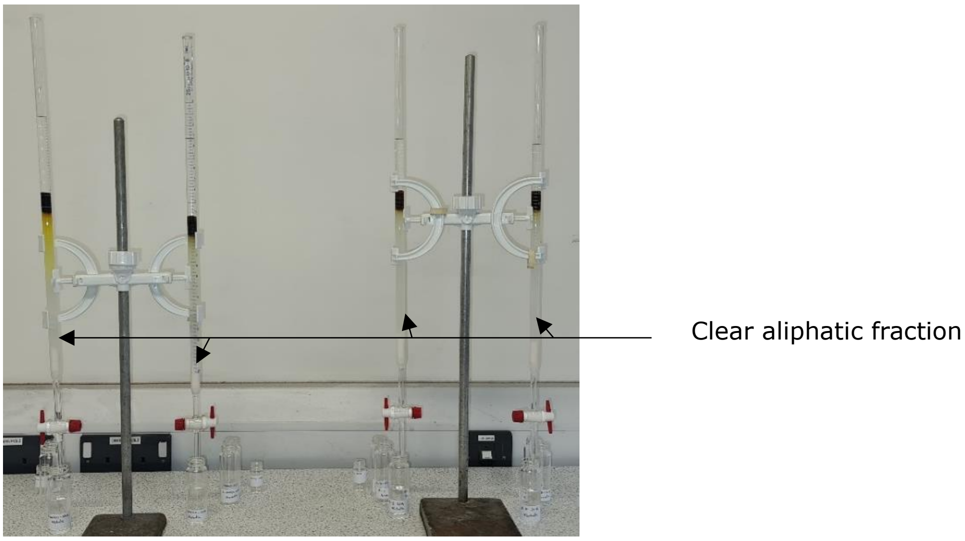

Figure 4-5: Aliphatic hydrocarbon elution

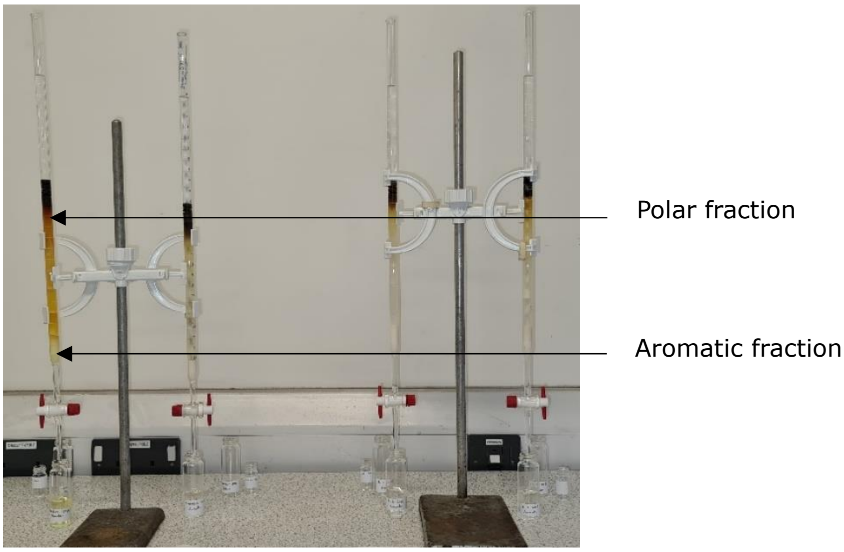

Figure 4-6: Polar and aromatic hydrocarbons

was repeated three times for the contaminated soils and the average value was reported. The soil's total petroleum hydrocarbons were then determined from these fractions using the GC-MS.

4.3.3. Total petroleum hydrocarbons characterisation using Gas Chromatography-Mass Spectrometry (GC-MS)

In this analysis, a method similar to that reported by Khairy et al. (2023) was used because of its suitability for identifying saturates. Aliphatic and aromatic fractions as prepared from the extractable organic matter using fractionation were analysed using an Agilent GC-MS instrument (7890B GC; 5977A MSD) which was fitted with an HP-5MS column (30 m length x 250 μm inner diameter x 0.25 μm film thickness). This analysis was carried out to identify the aliphatic and aromatic hydrocarbons present within the materials and to study their responses to microwave energy. The GC-MS instrument's oven was heated to 50°C and held for 2 min and then to 300°C and held for 20.5 min at a heating rate of 4°C/min. A splitless mode was set for the GC injector and an injection volume of 1 μL was used. Helium carrier gas at 1.2 mL/min (i.e. 39.923 cm/s average velocity) flow rate was used. The scan acquisition mode was used for the GC analysis. A saturated fraction obtained from the Oseberg oil, Norwegian North Sea was used as standard alongside a DCM blank. Prior to running the prepared hydrocarbon fractions on the GC-MS instrument, the DCM blank and standard were run to ensure that the instrument was working correctly. This was also repeated after running half of the total number of prepared samples.

To identify the different peaks from the GC analysis, the peak results were compared with the peaks from the Oseberg standard and other peaks reported by Peters et al. (2005). Additionally, the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) analyses of each soil material before remediation, and their Particle Size Distribution were determined by an external contractor (ALS Laboratories UK Limited)[8]. While the PSD was carried out using ALS's internal method (TM008), the TPHCWG analyses were done using their TM089 (by GC-FID for determining Gasoline Range Hydrocarbons by Headspace) and TM414 (by

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[8] ALS laboratories is accredited to the Monitoring Certification Scheme (MCERT) by the Environment Agency for analysing sand, clay and loam/topsoil, or any of these materials - whether derived from naturally occurring soil profiles or from fill/made ground, as long as these materials constitute a major part of the sample. However, other coarse granular materials such as concrete, gravel and brick are not accredited if they comprise a major part of the sample. These assure regulators, industry and the public of the quality of their environmental data analyses.

GCxGC-FID for determining Speciated Extractable Petroleum Hydrocarbons in Soils). These results were used to understand the petroleum-hydrocarbon contamination range within each contaminated material.

4.4. Microwave Heating Experiment

A single-mode cavity was employed for the remediation of contaminated soils over a range of applied powers and heating times at a 2.45 GHz operating frequency. This was used instead of a multi-mode cavity (e.g. domestic ovens) because multimode cavities are characterised by non-homogeneity of heating and are unsuitable for conducting repeatable soil decontamination experiments because of their random electric field pattern, low power density, cyclical power application and their failure to measure reflected power (Buttress et al., 2016; Robinson et al., 2009b). The desired heating conditions were set for each experiment using the control panel of the 2 kW generator used. Microwaves at this frequency were transmitted to the cavity using standard WR340 waveguides and E-bends. Connected to the waveguide (in between the microwave generator and load i.e. quartz reactor containing the contaminated soils) was a three-stub automatic tuner (S-TEAM) used for impedance matching to minimise reflected power. Although temperature measurements in microwave systems are challenging and often rely on the use of an infrared thermometer that can only read the surface temperature of a material or a fibre optic which is fragile (Buttress et al., 2016), an Optris infrared thermometer (OPTCTLT15CB8) was however used for measuring the surface temperature at the reactor walls containing the heated soil matrix to give an idea of its temperature during microwave heating. This was fitted into the E-bend. The input, absorbed and reflected power data with time during microwave heating were collected using the HomeSoft software for homer control and data logging.

During microwave heating, minimising reflected power to maximise absorbed power is key to the effective and efficient heating of materials such as oil-contaminated soils. This is made possible through power analysis and impedance matching with the help of a tuner. The tuner measures the phase and magnitude of the reflection coefficient alongside power and frequency and uses these data to adjust the position of the stubs for matching (Adam, 2017).

To establish suitable tuning options for the decontamination of these soil materials, an automatic three-stub tuner (with adjustable pistons) is connected to a computer comprising software for tuner control and data logging. The software tuner control allows for various tuning options during microwave heating. This could either be done by manually tuning the tuner using the step tuning (ST) option or the autotuning (AT) option. Step tuning allows for the adjustment of the tuner once at the start of microwave heating to minimise reflected power whereas, autotuning keeps adjusting the tuner's three-stubs throughout the heating time to achieve the same goal. For the sake of this experiment, a third tuning option referred to as step tuning at drop intervals (STDI) was introduced during microwave heating. This involves step tuning at the beginning of the experiment and at any other time when the absorbed power was observed to drop by more than 20%. Trial runs for road planings at power levels of interest (i.e., 0.4, 0.6, 0.8, 1, and 1.2 kW) were carried out in the first instance to establish the optimum three-stubs' setting position (in mm) that minimises reflected power. These settings were then inputted into the tuner control software as the first tuner setting positions at those power levels in subsequent microwave heating of road planings. This is to minimise the time loss often encountered at the start of the microwave heating process when the tuner adjusts to get the best tuning positions. This approach was also used for establishing the optimum three-stub setting position for the processing of contaminated filter cake, Bodo soil and K-Dere soil.

In this work, three microwave heating configurations were studied and compared. The goal is to explore the possibility of increasing oil removal from contaminated soils and to overcome the problem of thermal runaway during heating. These technology configurations were designated as, dry microwave heating, wet microwave heating, and microwave heating using the liquid inert system.

4.4.1. Dry microwave heating system

The dry microwave heating which served as the basis for this study involves heating the contaminated soils as received from sites without the addition of any microwave susceptor. A schematic diagram of the experimental setup is shown in Figure 4-7.

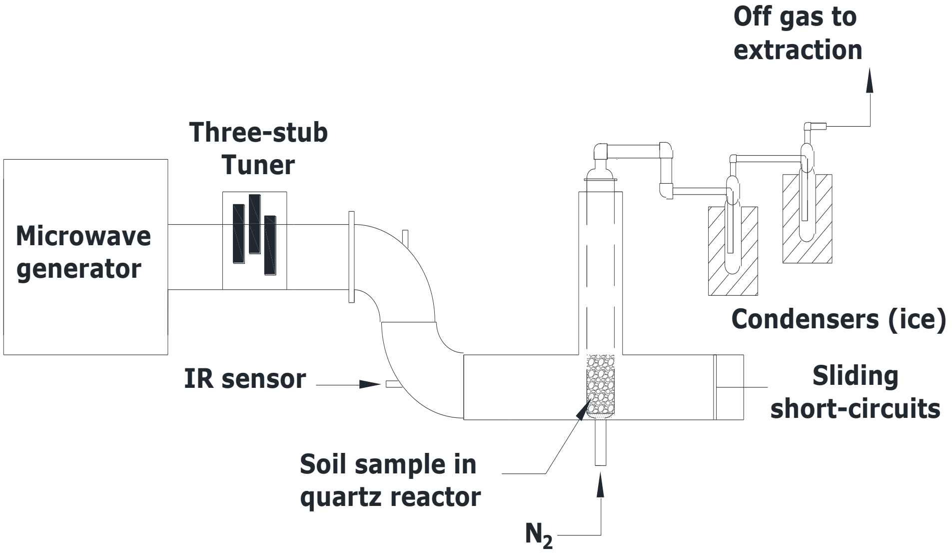

Figure 4-7: Schematic diagram of dry microwave heating of contaminated soils

In this method, 20-30 g of contaminated soil was placed in a quartz reactor (38 mm O/D x 2 mm wall thickness) for each test. This mass range of the sample was chosen to ensure that the sample height does not exceed ~4.3 cm above which part of the material will not be hit by microwaves due to the design of the waveguide. Ceramic fibre wool was used as a bed to support the sample inside the reactor due to its porous nature that allows for the flow of nitrogen (N_2) through the soil to create an inert environment that assists the removal of volatiles released during heating[9]. These vapours leave the top of the reactor and then pass through a series of condensers to aid the recovery of the condensable oil. The non-condensable gases exit the system through the fume-hood. N_2 gas was passed through the system at a constant rate of 1 L/min[10] and allowed for a minimum period of 2 minutes to purge the system before starting the microwave power.

At the end of each experiment, the system was allowed to cool, and the treated soil was collected for water and moisture content analyses. The glassware was then flushed with acetone to recover the oil removed from the soils which were then collected in glass vials and stored in the refrigerator at -20°C for further analyses after drying to constant weight in the fume-hood. Note that the recovered oil was not used in calculating the percentage of oil removed instead, the oil contents before and after soil treatment using soxhlet extraction were used as discussed in Section 4.2.2. The specific energy input as a function of power and time was calculated using Equation 4-9.

$$Specific\ energy\ \left(\frac{J}{g}\right) = \frac{Power\ absorbed\ (W) \times heating\ time\ (s)}{mass\ of\ sample\ (g)} \qquad 4\text{-}9$$

The error bars reported with results represent the standard deviation from three experimental repeats.

4.4.2. Wet microwave heating system

In the wet microwave heating, contaminated soils were wetted with 5 wt% ethylene glycol which serves as a microwave susceptor because of its high

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[9] Care was taken to allow room for nitrogen flow within the quartz reactor while loading the filter cake. This was ensured by loading smaller individual chunks (which when combined, sum up to the total mass of the sample required for an experiment) that leave gaps for nitrogen flow through (or at the sides) of the sample during the experiment.

[10] 1 L/min N_2 flowrate was established from preliminary runs as the suitable flowrate that prevents the drying of soil moisture when creating an inert atmosphere before microwave heating, minimises the cooling of soils during microwave heating (since N_2 is supplied at atmospheric temperature), and effectively allows the sweeping of vapours generated during heating.

dielectric loss factor similar to those of water (12 for ethylene glycol and 13 for water measured at 25°C and 2.5 GHz)(Meredith, 1998). 5 wt% ethylene glycol was used as this was established from preliminary experiments to be the concentration sufficient for the contaminated soil to absorb without ethylene glycol leakage from the soil matrix during heating. More so, ethylene glycol (b.p. 197°C) has a higher boiling point than water (b.p. 100°C) which meant that this could potentially drive forward oil removal even after the inherent soil moisture is removed at 100°C.

For each experiment, contaminated soil was mixed with ethylene glycol in a beaker at a ratio of 95/5 wt% (soil/ethylene glycol). 20 g of this mixture was loaded into the reactor and the experiment was carried out using the procedure outline for the dry microwave heating in Section 4.4.1. The time gap between loading and starting the experiment is minimised to ≤3 minutes after the required N_2 inflow is achieved to prevent solvent leakage through the glass wool under gravity.

4.4.3. Microwave heating using the inert liquid system

For the inerted liquid heating system, the experiment was carried out by heating the contaminated soil in a solvent that is loss-less to microwaves. Hexane was used as the solvent because it is microwave-transparent (Martinez-Guerra et al., 2014). Additionally, n-hexane is cheap and one of the most available microwave transparent solvents. A microwave-transparent or loss-less solvent allows for selectively heating the contaminated soil matrix and not the solvent itself even though the heat generated within the system is then transferred to the solvent by conduction and convection. The objective is to prevent or reduce thermal runaway encountered during the dry and wet microwave heating experiments, especially at powers >800 W.

However, it is important to note that, microwave transparent solvents are non-polar which implies that they would dissolve some aliphatic and aromatic hydrocarbons present in the contaminated soil during processing. As a result, the amount of oil removed would be the combined effect of both microwave heating and oil extraction by the solvent. The amount of oil (extractable organic matter) removed by microwave heating was determined by first estimating the amount of oil removed by the solvent alone upon mixing the contaminated soil with hexane at ambient temperature over the average time the contaminated soil remains in the solvent during a typical microwave heating process using the inert liquid system. This is then subtracted from the total oil removed by the combined effect of the solvent and microwave heating to determine the amount removed using microwave irradiation of the soils.

In this method, 10 g of contaminated soil was immersed into a reactor containing 100 mL hexane and then heated with microwaves[11]. The reactor is fitted with an overhead condenser to allow the reflux of vaporised hexane into the reactor during heating as shown in Figure 4-8.

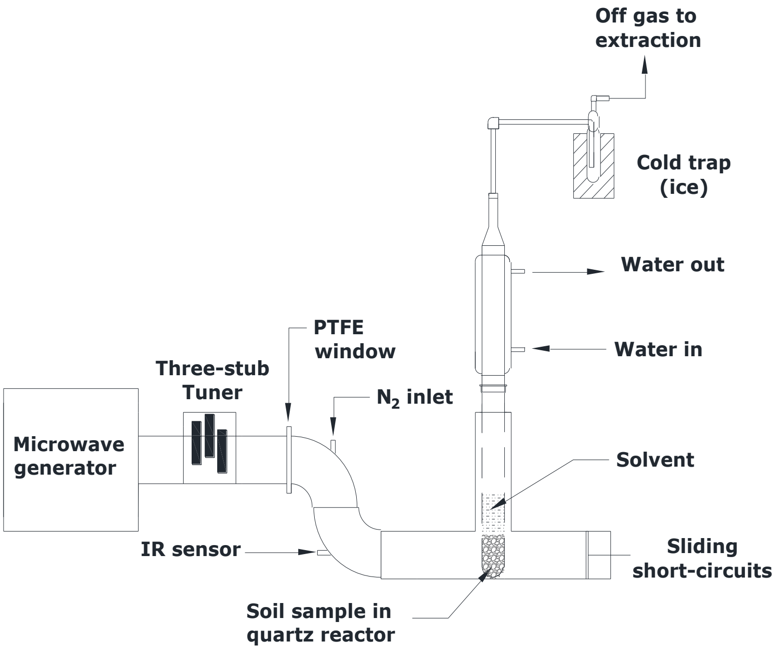

Figure 4-8: Schematic experimental setup for MW heating using the liquid inert system

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[11] 10 mL hexane per 1g of contaminated soil mass was used. Hexane was measured using a measuring cylinder, and the quartz reactor used is domed at one end and has 38 mm O/D x 2 mm wall thickness.

A nitrogenous environment in the waveguides and cavity - but not inside the heating system (reactor) - was used to ensure minimal risk of heated solvent and oil compounds reacting with oxygen in the surrounding air in the event of any breakage of glassware during heating. A polytetrafluoroethylene (PTFE) window was installed in the waveguide to prevent the flow of N_2 and other vapours toward the generator (Adam, 2017).

4.5. Conventional Heating Experiment

The objective of using conventional heating (thermal desorption) for soil remediation is to estimate and compare the energy required for achieving the same oil removal as obtained using microwave heating. Estimation of the energy consumed during conventional heating was carried out using the method reported by Elmatic-Ltd (2024) and Li et al. (2018). The conventional heating setup used for this experiment as shown in Figure 4-9 consists of a Carbolite electric tube furnace MTF 12/25/250, with a maximum power and heating temperature of 0.7 kW and 1 200°C respectively.

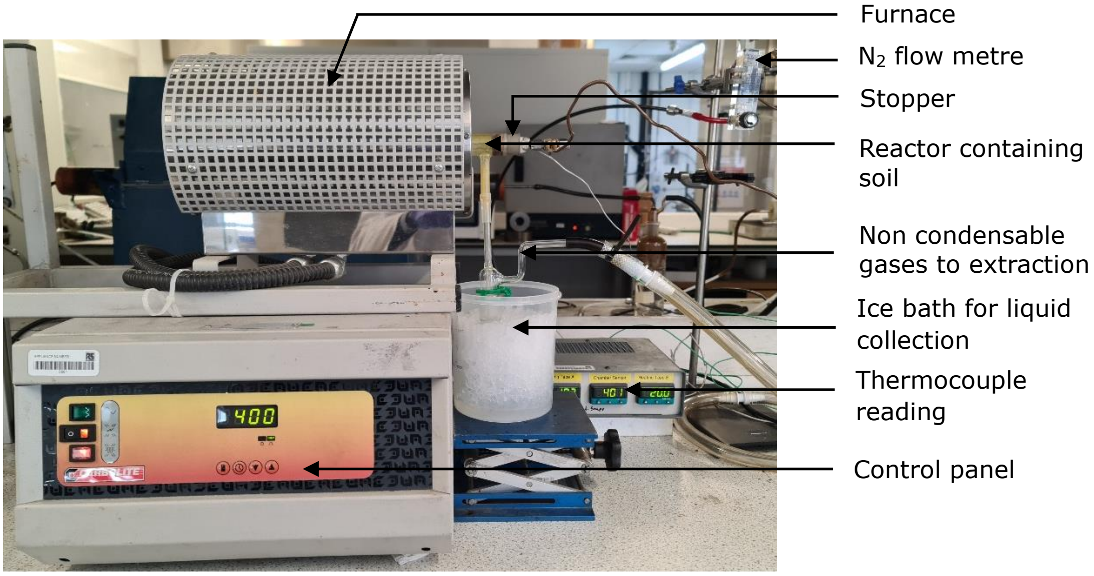

Figure 4-9: Soil remediation using conventional heating (thermal desorption)

The horizontal furnace connected to the controller has a 25 mm and 300 mm work tube bore diameter and length respectively. 20 g of contaminated soil as used during microwave heating was loaded into a tubular quartz reactor (domed at one end) with a 20 mm internal diameter, 1.5 mm wall thickness, and a length of 300 mm. A stopper fitted with a purge gas inlet and a thermocouple (inserted up to the middle of the loaded tube to monitor the temperature inside the tube) was used to seal the quartz tube before inserting it axially into the horizontal tube furnace. Nitrogen purge gas was set at a flow rate of 1 L/min, the same as that used during microwave heating[12]. The furnace was set to a constant heating rate of 20°C/min estimated from the general rule of thumb equation reported by Carbolite (2016), based on the quartz reactor's internal diameter (mm) as shown in Equation 4-10.

$$Max\ heating\ rate\ (°C/min) = 400/internal\ dimater(mm) \qquad 4\text{-}10$$

In this experiment, the tube furnace containing the loaded sample was heated initially to a constant temperature of 400°C and at various holding time ranges between 5–180 minutes to establish the holding time for subsequent experiments and to study the effect of holding time on oil removal. For subsequent experiments, the established holding time of 30 minutes was kept constant and the heating temperature was then varied within a range of 200 – 700°C - covering Low, medium, and high-temperature thermal desorption ranges (Wang et al., 2023; Zhao et al., 2019). The vapours generated during heating are purged by the carrier gas and the condensable oil is collected in a condenser while the non-condensable gases are sent into the extraction system.

After each experiment, the reactor and its content were allowed to cool, and the treated soils were collected in a sealed bag and extracted to determine the amount of oil removed as discussed in Section 4.2.2.

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[12] The same sample mass and gas flow rate as established for microwave heating were used in conventional heating to allow room for comparison.

CHAPTER 5

5. MICROWAVE DRY HEATING OF CONTAMINATED SOLIDS

Understanding the interaction between microwave energy and hydrocarbon-contaminated soils is vital for successfully designing and developing any microwave processing system for soil remediation. This includes understanding the properties of the soil material and the nature of the contamination as well as establishing the contaminant removal mechanisms during microwave heating. These would determine how the contaminated soils would behave upon irradiation with microwaves and could be leveraged to enhance hydrocarbon removal which is essential for process development. In this chapter, the petroleum hydrocarbon-contaminated solid materials, namely road planings, filter cake, Bodo soils, and K-Dere soils, were characterised and treated using microwave 'dry' heating under various processing conditions. The chapter further explores the behaviour of these materials under these conditions to understand the oil removal mechanism during heating. The term 'dry' heating refers to the microwave treatment of polluted solid materials as received from the sites without the addition of any solvent or microwave susceptors like ethylene glycol.

5.1. Physicochemical Properties of Contaminated Solid Materials

The properties of the contaminated solid materials used in this study are outlined in Table 5-1.

Table 5-1: Physicochemical properties of hydrocarbon-contaminated solids

Property	Road planings	Filter cake	Bodo soil	K- Dere soil
Moisture content (%v/m)[a]	7.3 ± 0.45	52.1 ± 0.36	14.2 ± 2.2	3.0 ± 0.001
Oil content (%w/w)[b]	2.90 ± 0.14	10.40 ± 0.15	1.30 ± 0.10	0.88 ± 0.10
Bulk density (g/cm^3)	1.43 ± 0.03	0.71 ± 0.01	1.11 ± 0.01	1.52 ± 0.04
Porosity	0.47 ± 0.01	0.64 ± 0.01	0.56 ± 0.01	0.42 ± 0.01

[a] wet basis, [b] Extractable organic matter - wet basis, values after "±" represent the standard deviation from three repeated measurements

Filter cake and road planings were found to have higher oil contamination (heavy hydrocarbon contamination of 10.4 wt% and 2.9 wt% respectively) as compared with Bodo and K-Dere soils (light hydrocarbon contamination of 1.3 wt% and 0.88 wt% respectively). The standard deviations obtained from three repeated measurements for oil and moisture contents, bulk density, and porosity of the contaminated materials were low, which is an indication that the materials were properly homogenised before processing. Thus, it is believed that subsequent experiments and analyses are a true representation of the bulk soil matrix. The TPH CWG organic range and their concentrations in the various contaminated solids as determined by ALS Laboratories UK (refer to Section 4.3.3) are presented in Table 5-2.

Table 5-2: Total Petroleum Hydrocarbons analysis of contaminated materials

TPH CWG organics range	Road planings	Filter cake	Bodo soil	K-Dere soil	Boiling point (°C)
Aliphatic (mg/kg)					
>C5 - C6	0.01	0.15	<0.01	0.01	36.1 – 68.7
>C6 - C8	0.03	1.10	0.04	0.01	>68.7 – 125.6
>C8 - C10	0.03	12.00	0.05	0.02	>125.6 – 174.1
>C10 - C12	5.00	685.00	5.57	4.74	>174.1 – 216.3
>C12 - C16	36.30	2,850.00	189.00	278.00	>216.3 – 286.9
>C16 - C21	38.40	6,940.00	1,120.00	1,560.00	>286.9 – 356.5
>C21 - C35	293.00	15,700.00	80.90	1,080.00	>359.0 – 490.0
>C35 - C44	640.00	2,510.00	38.90	180.00	>490.0 – 547.6
Aromatics (mg/kg)					
>EC5 - EC7	<0.01	<0.01	<0.01	<0.01	80.1[a]
>EC7 - EC8	<0.01	<0.01	<0.01	<0.01	110.6[b]
>EC8 - EC10	0.02	8.00	0.03	0.01	136.0[c]
>EC10 - EC12	<5.00	364.00	<1.00	1.34	218.0[d]
>EC12 - EC16	44.40	1,010.00	131.00	121.00	279.0[e]
>EC16 - EC21	723.00	917.00	510.00	148.00	404.0[f]
>EC21 - EC35	2,440.00	951.00	3,150.00	1,360.00	495.0[g]
>EC40 - EC44	70.30	11.10	85.30	33.10	>495.0
>EC35 - EC44	255.00	32.20	306.00	88.50	

TPH CWG: Total Petroleum Hydrocarbon Criteria Working Group, EC: Equivalent Carbon number (for n-alkanes, carbon number is same as EC number), Gasoline range: C5-C10 and EC5 – EC10, Boiling points of typical constituents of potential concern (EC) (CL:AIRE, 2017): [a] Benzene (EC 6.5), [b] Toluene (EC 7.6), [c] Ethylbenzene (EC 8.5), [d] Naphthalene (EC 11.7), [e] Acenaphthene (EC 15.5), [f] Pyrene (EC 20.8), [g] benzo[a]pyrene (EC 31.3)

The equivalent carbon number (EC) indicates the retention time of the gas chromatographic separation that separates hydrocarbon compounds based on their boiling points (b.p.) (CL:AIRE, 2017). For example, Benzene with b.p. of 80°C has an EC of ~6.5 because it exhibits a retention time between those of n-hexane and n-heptane with carbon numbers and boiling points of 6 and 69°C (n-hexane), and 7 and 98°C (n-heptane) respectively. About 91% of road planings are aliphatic and aromatic hydrocarbons within the range >C21 – C44 and >EC16 – EC35 respectively, while 88% of the filter cake is contaminated with majorly >C16 – C44 (aliphatic) and >EC12 – EC35 (aromatics). Bodo soil has 90% of its aliphatic and aromatic petroleum hydrocarbon concentrations within >C12 – C21 and >EC16 – EC35 respectively, whereas K-Dere soil has 86% aliphatic and aromatics ranging between >C16 – C35 and >EC16 – EC35 respectively. This implies that remediating these soils using thermal desorption would require temperatures around the boiling points of these contaminant ranges i.e. about 359 – 547°C (road planings), 287 - 547°C (filter cake), 216 - 495°C (Bodo soil), and 287 - 495°C (K-Dere soil). However, if other contaminant removal mechanisms like steam stripping or steam distillations dominate the heating process, then contaminants are likely to be removed below their boiling points. This is discussed in detail in Section 5.3.3.

In Figure 5-1, the oil-contaminated material classification was carried out based on their particle size fractions; clay (≤0.002 mm), silt (>0.002 to ≤0.063 mm), sand (>0.063 to ≤2 mm) and gravel (>2 to ≤63 mm) (BS-EN-ISO-14688-1, 2018). Bodo soil, K-Dere soil, and filter cake were fitted in the texture triangle as sand, sandy loam, and clay respectively, as they have a composition of 89% sand, 11% silt+clay (Bodo soil), 81% sand, 13% silt+clay, and 6% gravel (K-Dere soil), and 85% clay+silt, 13% sand, and 2% gravel (Filter cake). Road planings could not fit into the soil texture triangle as it was predominantly gravel (62% gravel, 29% sand, and <10% silt+clay).

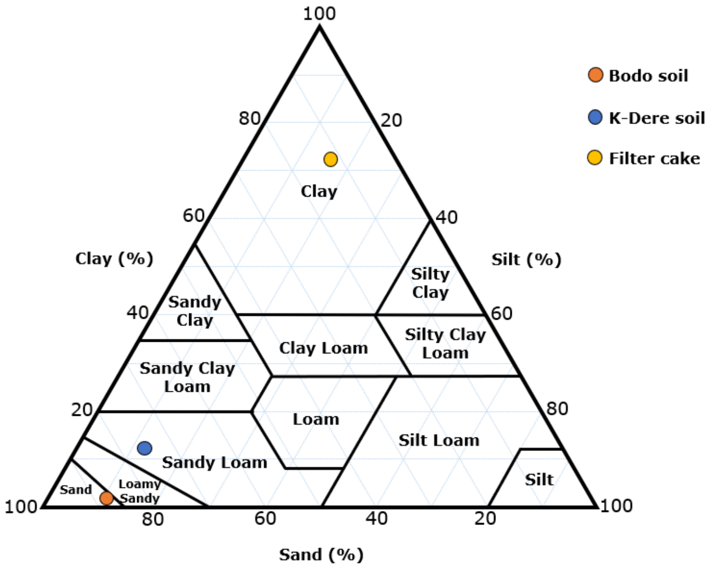

Figure 5-1: Soil texture triangle showing the classification of the hydrocarbon-contaminated solids. 62% of road plainings is classified as gravel and is excluded

Robinson et al. (2014) reported that clayey soil materials contain hydrophilic minerals that indicate the presence of interlayer moisture (bound water) within their structure apart from the free water on their surfaces and within their pores and capillaries. The filter cake material is clayey (with 85% of its particle size ≤0.063 mm) and has a higher moisture content (52.1%) when compared with the other materials, which is likely due to the contribution of its inherent hydrophilic minerals. Additionally, its 0.64 porosity indicates that 64% of its total volume consists of pore spaces that are available for water to fill thus explaining its high moisture content of 52.1%. K-Dere soil had the least moisture content (3%) due to its lower porosity (0.42) when compared with the other materials. Overall, the moisture contents of the hydrocarbon-contaminated solids were directly proportional to their porosities and inversely proportional to their bulk densities as shown in Table 5-1. This agrees with the findings of Oleszczuk and Truba (2013) and Khater (2012) who studied the relationship between moisture content, porosity and bulk density of peat soil layers and composts respectively.

These properties are important during microwave heating because the moisture content and bulk density of a material could depend on its porosity (presence of voids) which can influence its dielectric properties that are calculated on a volumetric basis. Additionally, pore space is known to influence fluid transport within soil materials (Nimmo, 2013) and could explain how contaminants are removed during microwave heating. Robinson et al. (2010b) showed that at higher bulk densities of drill cuttings containing 10% moisture, fewer air voids exist compared with lower densities hence more drill cuttings are contained within the same volume resulting in higher dielectric constant and loss factors. Although this is the case when the bulk density of a material at constant moisture is varied, it is however not expected to apply when comparing the bulk densities of different materials containing different moisture contents as used in this work. This is because moisture is expected to also contribute significantly to the dielectric properties of the materials and is further discussed in Section 5.2. Therefore, at room temperature, the dielectric constant and loss factors of filter cake and Bodo soil are expected to be higher than those of road planings and K-Dere soil because of their high moisture contents. Since variations in the dielectric properties of material with moisture content and bulk density pose a very significant challenge when designing and scaling up a continuous microwave processing system, blending the polluted soils with already remediated dry materials can maintain a consistent moisture content and bulk density (Robinson et al., 2010b).

The heavy oil phase within the contaminated soil material is a poor microwave absorber, therefore the combination of the water content and the clayey nature of the filter cake material could favour microwave heating in the filter cake compared with the other materials with larger particle sizes and lower moisture content like K-Dere soil (with 81% of particles within >0.063 to ≤2 and contains 3% moisture). Additionally, since bound water has lower mobility compared to surface water, the bound water within the filter cake material could allow for the microwave heating of this material beyond 100°C unlike road planings, Bodo and K-Dere soils which have predominantly surface water that would be easily evaporated at this temperature due to their larger particle and pore sizes. From previous studies (Robinson et al., 2014), the mass transfer limitations of the bound water within the filter cake's micropores and capillaries can lead to pressure build-up and the superheating of the material during microwave irradiation, thereby enabling more removal of petroleum hydrocarbons from the material.

5.2. Dielectric Properties of Contaminated Solids

How a material interacts or behaves under an electromagnetic field can be explained by its dielectric properties i.e., its dielectric constant (ε'), loss factor (ε'') and loss tangent (also referred to as dissipation factor, $\tan\delta = \varepsilon''/\varepsilon'$). ε' explains how easily the material could be polarised and store electromagnetic energy, ε'' shows its ability to convert energy into heat, while tan δ measures the efficiency of this energy conversion (Adam et al., 2021). The ability of a material to absorb microwaves is directly proportional to its loss factor.

The dielectric properties of the hydrocarbon-contaminated solid materials used in this work (measured at room temperature and 2.47 GHz frequency) were compared with other dry and wet soil materials. Additionally, the dielectric properties of other materials used as susceptors to enhance microwave heating (such as ethylene glycol and water), and as loss-less materials and solvents (such as quartz and hexane), were also presented as shown in Figure 5-2.

From Figure 5-2, good microwave absorbers like water and ethylene glycol have better dielectric properties when compared with the contaminated solids under study as well as other soil materials. Water contributed to the dielectric properties of the studied hydrocarbon-contaminated solid materials at room temperature because their dielectric constants were directly proportional to their moisture contents Figure 5-3.

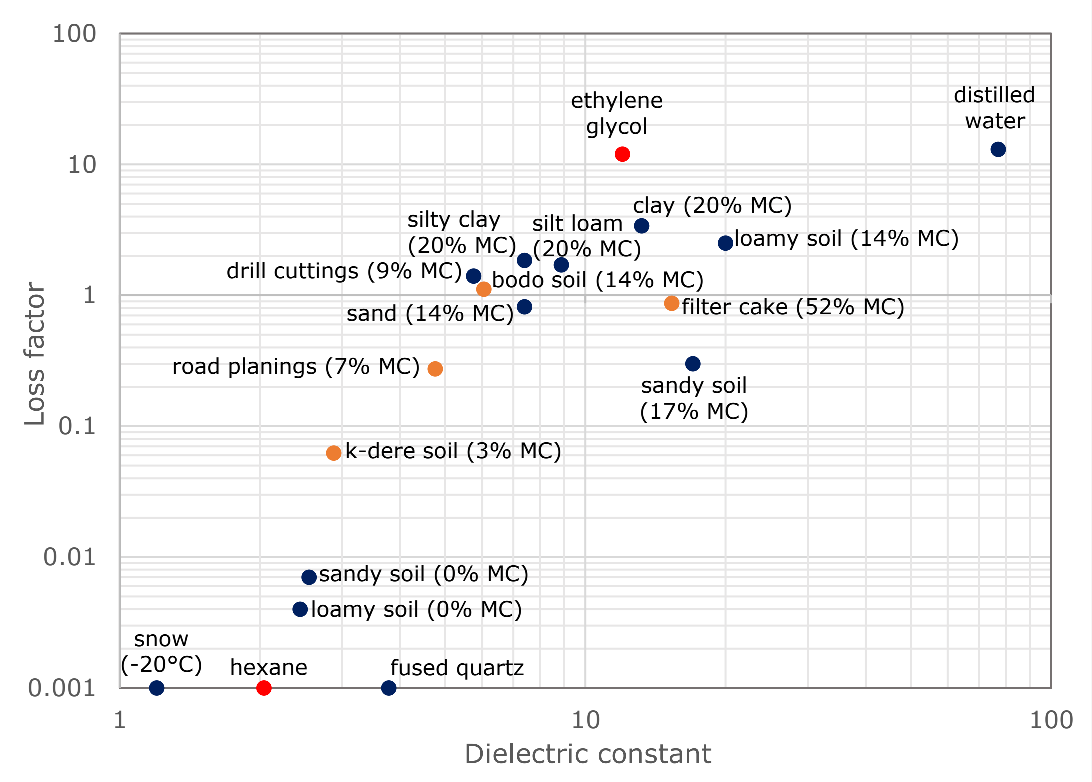

Figure 5-2: Dielectric properties of the studied contaminated solids at room temperature (20-25°C) and 2.47 GHz compared with the dielectric properties of other materials under similar conditions (Adam, 2017; Hallikainen et al., 1985; Meredith, 1998; Robinson et al., 2010b; Robinson et al., 2012; Palta et al., 2022). The moisture content (MC) of the contaminated materials studied is reported on a wet basis

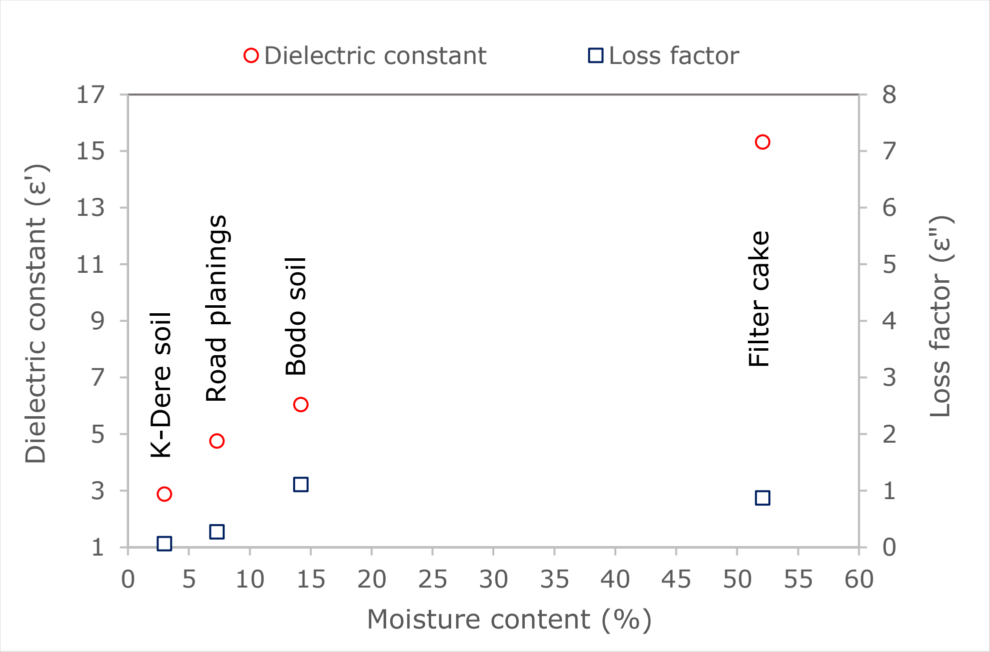

Figure 5-3: Dielectric properties of hydrocarbon contaminated solids under various moisture contents (in wet basis) at ~20˚C and 2.47 GHz

Dry soil materials e.g. sandy and loamy soils (with 0% MC) had lower dielectric constants and loss factors when compared with similar materials with inherent moisture (see Figure 5-2). At room temperature, higher dielectric constants (ε') and loss factors (ε'') were observed in Bodo soils ($\varepsilon' = 6.05,\ \varepsilon'' = 1.11$) and filter cake ($\varepsilon' = 15.32,\ \varepsilon'' = 0.87$) whereas, K-Dere ($\varepsilon' = 2.88,\ \varepsilon'' = 0.06$) and road planings ($\varepsilon' = 4.76,\ \varepsilon'' = 0.27$) had lower dielectric constants and loss factors. The dielectric loss factors of Bodo soil, filter cake and road planings indicate that these materials are expected to readily absorb microwave energy when irradiated with suitable field intensities compared with K-Dere soil. This is because, although some materials with loss factors below 0.1 could absorb microwave energy and be readily heated especially at high electric field intensities (when high power levels are used), it has been established that for a given temperature and frequency, soil materials with dielectric loss factor >0.1 will readily absorb microwave energy (Robinson et al., 2009b; Buttress et al., 2016; Meredith, 1998). Loss-less materials like hexane and fused quartz have very low dielectric properties (dielectric loss <0.001) compared with the studied materials (Adam, 2017; Meredith, 1998). Ethylene glycol ($\varepsilon' = 12,\ \varepsilon'' = 12$) on the other hand, is a very good microwave absorber similar to distilled water ($\varepsilon' = 77,\ \varepsilon'' = 13$). In comparison, heavy oils typically have loss factors between 0.004 and 0.015 at room temperature (Zhang et al., 2018) and are not expected to contribute significantly to microwave heating during soil remediation. Thus, in this work, a quartz reactor was used as a sample holder to support the soil samples during heating in microwave cavities, while hexane was used to create an inert system for microwave heating. Furthermore, ethylene glycol was utilised as a microwave susceptor in the wet microwave heating system. The wet and inert liquid microwave heating systems are discussed in Chapter 6.

A comparison of the dielectric properties of soils with different textures (Figure 5-4) shows that, for soils with a similar texture at a given moisture content and frequency, the dielectric constant (ε’) increases with sand content.

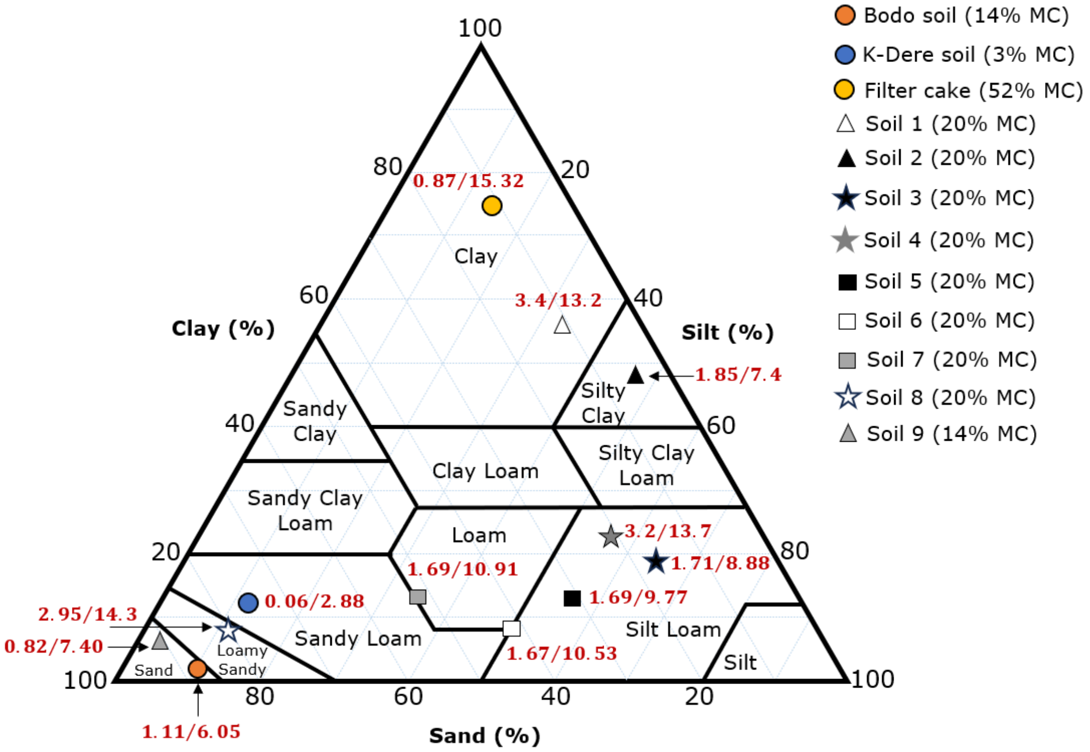

Figure 5-4: Soil texture triangle comparing the loss tangent (ε”/ε’) of the studied materials with other soils at 20-25°C, 2.47 GHz, and various moisture contents (MC). Road plainings is excluded because it contains 62% gravel (Hallikainen et al., 1985; Palta et al., 2022; Robinson et al., 2012)

For example, at 14% moisture, the ε’ of the Bodo soil (89% sand) and soil 9 (>90% sand) are 6.05 and 7.40 respectively. However, this is not the case with an increase in moisture contents (MC) as the ε’ of Bodo and soil 9 was much lower than that observed in soil 8 (14.3 at 20% MC) even though it had lesser sand content of 80%. Similarly, K-Dere soil has a higher sand content (81% at 3% MC) when compared with soil 8 (52% sand at 20% MC), however, its dielectric constant is lesser. This can be attributed to the variation in their moisture contents because water is known to improve the dielectric properties of soils as previously discussed (refer to Figure 5-2). Additionally, this is likely the reason why the clayey filter cake with 52% MC has the highest ε’ among the soils compared. Thus, moisture content was the key contributing factor to the dielectric properties. Hallikainen et al. (1985) who studied the dielectric properties of soils with different textures (refer to soils 3, 5, 6 and 7 in Figure 5-4) between 1.4 and 18 GHz, found that at any given moisture content and at all frequencies, ε′ is roughly proportional to its sand content but inversely proportional to its clay content. Palta et al. (2022) also observed that, under the same conditions, ε′ is higher in sandy soil and least in clay soils (see soil 1, 4, and 8 in Figure 5-4). Both authors also reported an increase in ε′ with increasing moisture content at the same frequency and temperature. Although Palta et al. (2022) reported an increase in ε″ of soils with increasing clay content at all frequencies for the same temperature and moisture content, this is however not the case for the loss factors (ε″) of the materials studied in this work as their behaviour with soil texture was rather different and more complicated as they followed no particular trend with respect to their clay or sand contents. Hallikainen et al. (1985) observed the complex behaviour of ε″ with soil texture and showed that at a lower frequency of 1.4 GHz, the loss factor (ε″) increased with clay content however, ε″ was independent of soil texture between 4.0 and 6 GHz but decreased with clay content at ≥ 8 GHz.

5.2.1. Variation of dielectric properties of contaminated solids with temperature

During microwave heating, the power absorbed by a material is directly proportional to its dielectric loss factor and the square of its electric field strength (refer to Equation 3-3). The dielectric loss factor generally indicates the ability of a material to be heated upon irradiation with a microwave field - the higher these properties are the better the materials are heated (Buttress et al., 2016; Robinson et al., 2010a). The result from the dielectric property measurements of contaminated road planings, filter cake, Bodo soils and K-Dere soils are shown in Figure 5-5.

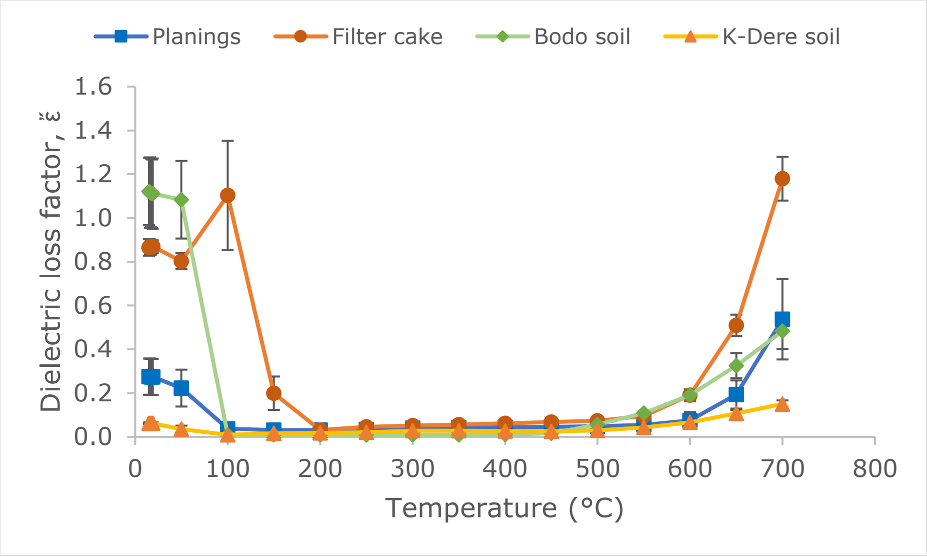

Figure 5-5: Dielectric loss of hydrocarbon-contaminated solids with temperature at 2.47 GHz with nitrogen (N_2) supplied at 7.5 cc/min. For the filter cake, N_2 was only introduced after 200ºC when moisture was removed, and the cake's pores were opened to allow free N_2 flow

Dielectric losses with peak values of 0.27±0.08, 1.10±0.25, 1.12±0.15, and 0.06±0.004 were observed for road planings, filter cake, Bodo soil, and K-Dere soil respectively at temperatures ≤100°C. Unlike the other soil materials, K-Dere soil had a peak loss factor below 0.1. This indicates that the microwave heating of this material might be challenging leading to a low hydrocarbon removal unless a high electric field intensity from a high-power level is used within a safe operating limit.

The drop and sudden increase in the loss factor of filter cake between 50°C and 100°C can be attributed to the decrease in filter cake's free water with increasing temperatures from 20°C to 50°C, after which the bound water within its hydrated clay minerals start to contribute to the loss factors beyond 50°C and ≤100°C. Palta et al. (2022) attributed the increase in the value of the loss factor between 5 and 75°C to bound water molecules and thermal agitations. Robinson et al. (2014), who observed an increase in the loss factor of low-grade oil sands between 20°C and 80°C, attributed a 0.18 peak loss factor (out of 0.3) as the contribution of the material's interlayer water from its hydrophilic clay minerals comprising predominantly kaolinite[13]. The interlayer water contributed to the loss factor of the material and the high temperatures >300°C achieved when free and surface water is removed at around 100°C.

With decreasing water phase at 100°C, the loss factors of road planings, Bodo soil and K-Dere soil dropped to 0.037±0.014, 0.009±0.001, and 0.009±0.004 respectively. This is because these materials are predominantly gravel, sand, and sand-loam respectively, thus their high dielectric properties at room temperature were largely contributed by their mobile surface water that is easily evaporated at 100°C leading to low dielectric properties. This was not the case for filter cake as it only recorded its minimum loss factor (0.031±0.004) at ~200°C due to the presence and contribution of bound water within its hydrophilic minerals that play an important role in sustaining the high dielectric properties even after its surface water is evaporated. Oil removal during microwave heating beyond 100°C is expected in filter cake since the evaporation of its bound water would require temperatures >100°C. The loss factors of all the contaminated solids remained far below 0.1 with no significant change up to ~500°C. Within these low dielectric loss regions and temperatures, very little microwave energy can be absorbed by the contaminated materials, as such, there is little expectation for microwave heating to occur.

The relatively high dielectric losses of the contaminated materials at temperatures up to 100°C when compared with those between 100°C and 500°C can be explained by the water phase present in the materials (Table 5-1). Filter cake and Bodo soil, which had higher moisture contents, recorded higher dielectric loss factors when compared with materials with lower moisture contents like road planings and K-Dere soil. These results show that the selective microwave heating and conversion of their water phases to steam will occur and will act as a mass

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[13] A 0.18 loss factor was obtained after extracting the free water phase of the low-grade oil sand by Soxhlet extraction and drying at 150°C.

transfer media that would potentially lead to hydrocarbon removal either via steam stripping, steam distillation, entrainment, or the combination of two or more of these mechanisms. Beyond 100°C, the mass transfer limitations of the bound water within the filter cake's micropores and capillaries can lead to pressure build-up and the superheating of the material during microwave irradiation, thereby enabling more removal of petroleum hydrocarbons from the material (Robinson et al., 2014).

At temperatures ≥500°C, an increase in the loss factors of all the materials were observed. This began gradually and then rapidly to a maximum dielectric loss factor of 0.54±0.18 (road planings), 1.18±0.10 (filter cake), and 0.48±0.08 (Bodo soil) at 700°C respectively. However, the increase in the dielectric loss of K-Dere soil remained gradual up to a maximum value of 0.15±0.02 at 700°C respectively. This agrees with the findings of Robinson et al. (2014) and Robinson et al. (2009b) who reported a sharp increase in loss factors of oil sands and heavy hydrocarbon-contaminated soils to values ≥0.3 and ≥0.4 respectively at temperatures ≥500°C. The increment in loss factor at high temperatures is attributed to the decomposition of the organic contaminants leading to the formation of carbonaceous deposits which are strong microwave absorbers (Robinson et al., 2009b; Robinson et al., 2014; Robinson et al., 2012). This sharp increment in the loss factors of road planings, filter cake and Bodo soil could result in thermal runaway during the dry microwave heating which could cause instability in process conditions within the heated matrix and lead to an uncontrollable increment in temperature. However, this might not be the case for K-Dere soils - even if it were, the effect would be very little because only a gradual increment in the dielectric properties of this material was observed at >500°C.

Additionally, it was observed that the dielectric properties resulting from the formation of these carbonaceous compounds were higher for materials with higher oil contents, e.g. at 700°C filter cake (10.4 wt%) > road planings (2.9 wt%) >

Bodo soil (1.3 wt%) > K-Dere soil (0.88 wt%). Similar findings were reported by Robinson et al. (2014) for oil sand materials with a high oil content of 20.4 wt% versus that with a lower oil content of 7.1 wt% at ≥600°C. Therefore, materials that are heavily contaminated with petroleum hydrocarbons might favour the formation of more carbonaceous compounds at high temperatures when compared with those with low hydrocarbon contamination.

To verify the different behaviour in dielectric properties observed for the contaminated materials with increasing temperature, and to further confirm the contribution of hydrocarbons to the formation of carbonaceous materials at higher temperatures, the dielectric properties of road planings were also measured after the hydrocarbon phase and the free water within the contaminated soils was removed using soxhlet extraction followed by drying at room temperature, and the results were compared in Figure 5-6.

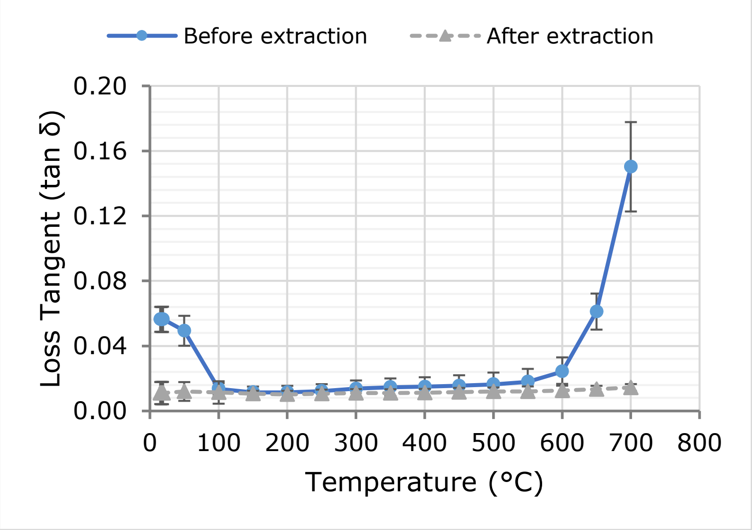

Figure 5-6: Dielectric properties of Road planings at 2.47 GHz before and after oil extraction. Nitrogen flow was only introduced at 7.5 cc/min for the experiment carried out before the planings were extracted

At temperatures <100°C, the difference in the loss tangent of the contaminated and extracted road planings is attributed to the presence of the water phase in the contaminated material before extraction. This is confirmed by the difference in behaviour observed after the free water from road planings was removed - as a loss tangent of ≤0.01 was observed throughout the experiment. However, above 100°C when the free water phase of the planings was removed via evaporation, similar results for the two materials with insignificant differences were obtained up until temperatures ≥400°C, when carbonaceous materials in the contaminated materials began to form. At these temperatures, the loss tangent increased gradually and then rapidly at temperatures beyond 550°C. However, this is not the case in the extracted road planings. This confirms that the hydrocarbon phase of oil-contaminated materials is responsible for the formation of carbonaceous materials (char) that lead to higher dielectric properties at higher temperatures ≥400°C.

5.2.2. Effect of the use of nitrogen purge gas on dielectric properties

To understand the effect of the use of nitrogen purge gas on dielectric properties, the dielectric properties of road planings were also measured without the supply of nitrogen. This is significant as the passage of dry nitrogen through the soil bed might displace soil moisture, potentially influencing the dielectric properties of the materials, given that moisture significantly contributes to these properties. The findings of this investigation were compared with the results obtained when nitrogen was supplied as shown in Figure 5-7.

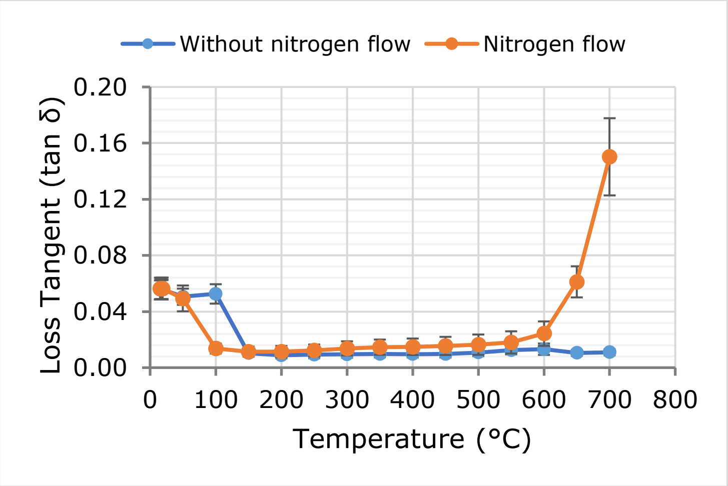

Figure 5-7: Dielectric properties of road planings at 2.47 GHz without and with the use of nitrogen at a flow rate of 7.5 cc/min as a purge gas

Not using nitrogen implies that oxygen-containing air was present in the system and, as such allows room for combustion to take place with increasing temperature[14]. The variation in dielectric properties at 100°C suggests the contribution of the purge gas in removing free water (via drying) within the soil matrix in addition to the ongoing moisture evaporation during microwave heating. This resulted in a drop in loss tangent when nitrogen purge gas was used. At 150°C, the loss tangents for both experiments were similar (<0.02) since free water had been evaporated from the soils. However, with further increments in temperature beyond 200°C, variations in the loss tangents with and without the use of nitrogen were observed. These variations increased gradually with increasing temperature and then rapidly at temperatures ≥600°C. This is likely because the use of nitrogen prevents the combustion of hydrocarbons within the system. As a result, the carbonaceous materials formed at higher temperatures remain in the system thus explaining the higher dielectric loss recorded unlike when not using nitrogen where the carbonaceous materials are combusted in the process leading to lower dielectric loss.

5.2.3. Comparison of the Dielectric Properties of Hydrocarbon Contaminated Solids at Industrial Microwave Heating Frequencies

The dielectric constants and loss factors of dielectric materials vary significantly with changes in microwave frequency (Nelson and Trabelsi, 2012). Since the relationship between the frequency and dielectric properties of materials depends on the loss mechanism(s) involved (Adam, 2017), comparing these properties at different frequencies could help in the identification of the dominant loss mechanism during heating. For non-magnetic materials like soils, the common mechanisms could either be via dipolar polarisation, conduction (or ionic) loss or

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[14] Nitrogen was originally used for the dielectric measurements to mimic the microwave heating system that requires the use of nitrogen to purge volatiles and oxygen from the system, thus prevent combustion and ensure the safety of the system during the processing of hydrocarbon impacted soils.

a combination of both - referred to as interfacial polarisation (Gude et al., 2013; Mishra and Sharma, 2016; Zhang et al., 2018).

While dipolar loss mechanisms are common and more dominant in dielectric materials (absorbers like water, and polar solvents) where dipoles are generated when the materials interact with microwaves, the conductive loss mechanism is dominant in semi-conductors, salt solutions and carbon materials. Figure 5-8, Figure 5-9, Figure 5-10, and Figure 5-11 show the plots of the loss factors of road planings, filter cake, Bodo soil and K-Dere soils respectively with increasing temperatures at key industrial frequencies of 910 and 2,470 MHz with their starting moisture contents given on a wet basis.

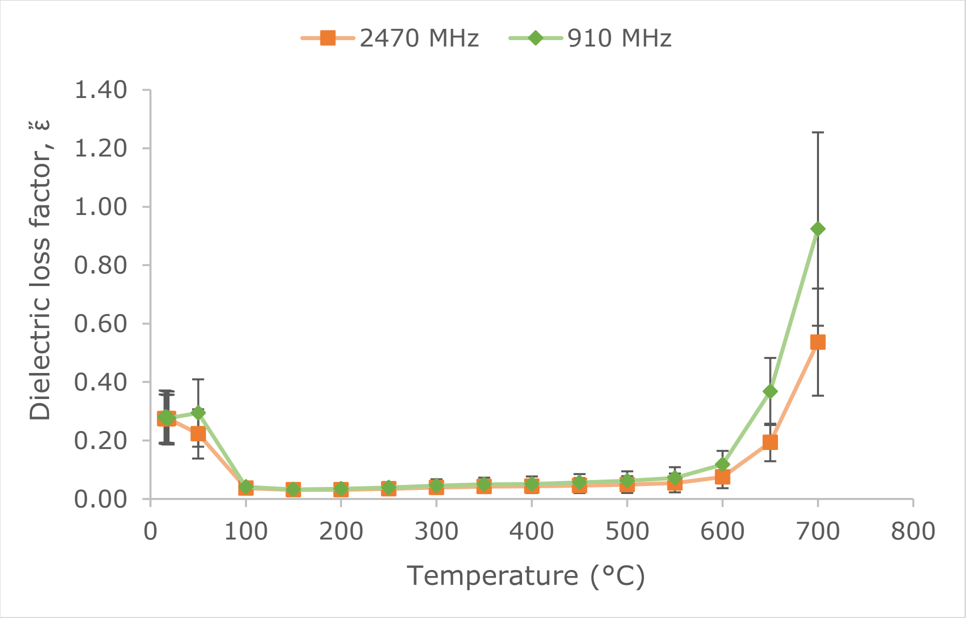


Figure 5-8: Dielectric properties of road planings at 910 and 2,470 MHz with N_2 flow at 7.5 cc/min. The starting moisture content is 7.3±0.45%

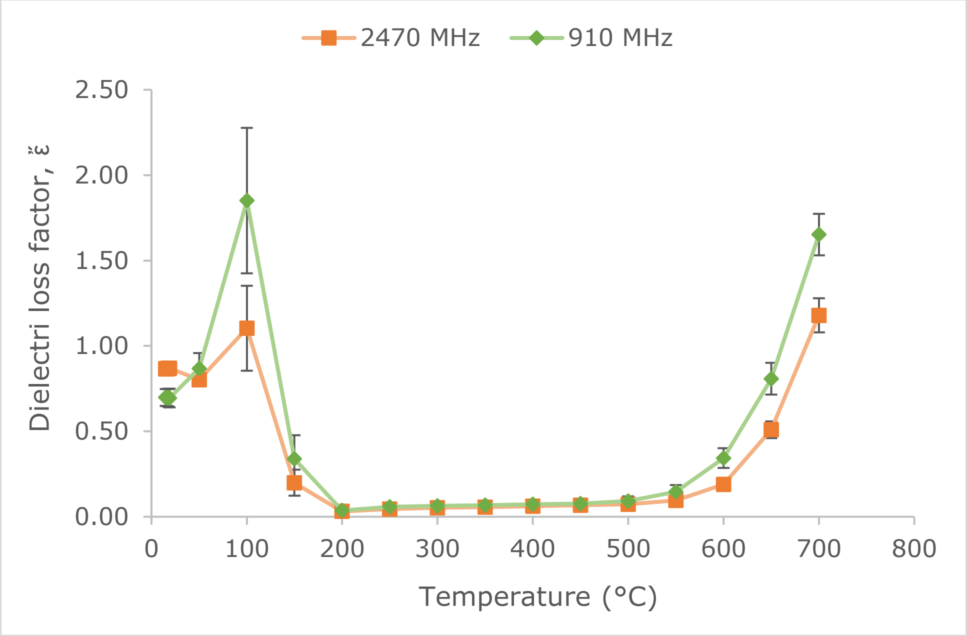


Figure 5-9: Dielectric properties of Filter cake at 910 and 2,470 MHz with N_2 flow at 7.5 cc/min. N_2 was only introduced after 200ºC when moisture was removed, and the cake's pores were opened to allow free N_2 flow. The starting moisture content is 52.1±0.36%

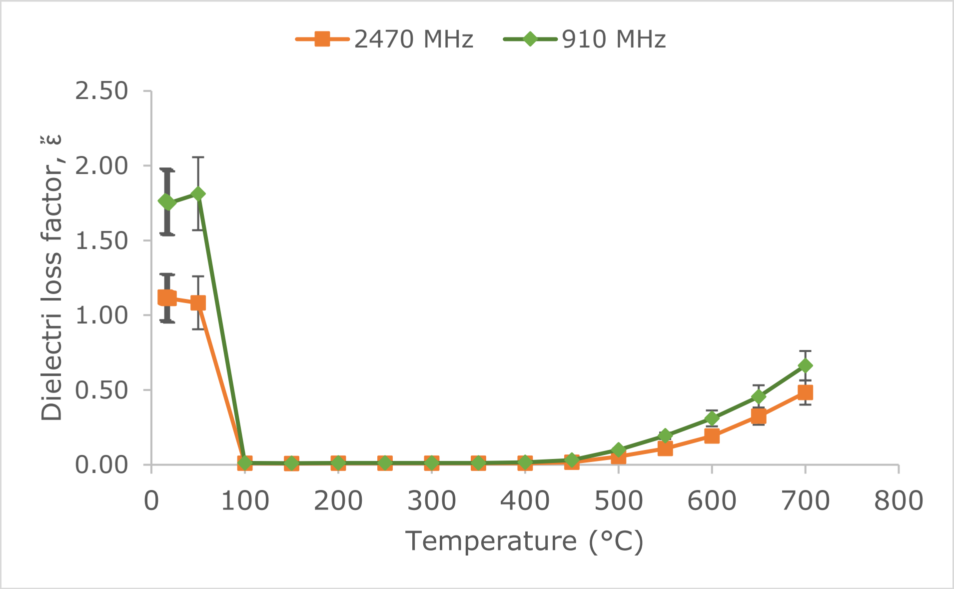


Figure 5-10: Dielectric properties of Bodo soils at 910 and 2,470 MHz with N_2 flow at 7.5 cc/min. The starting moisture content is 14.2±2.2%

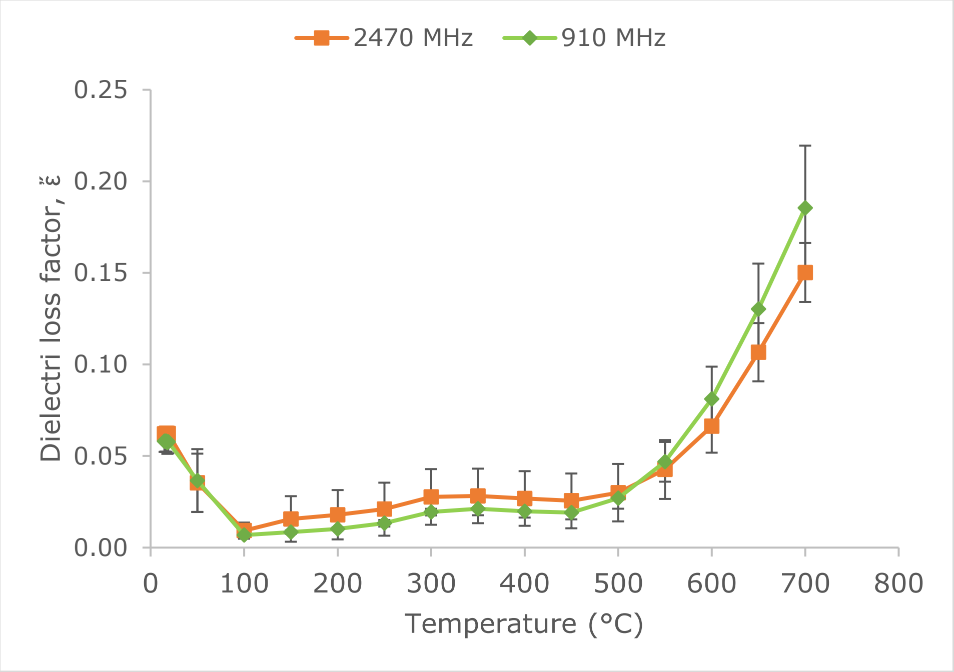


Figure 5-11: Dielectric properties of K-Dere soils at 910 and 2,470 MHz with N_2 flow at 7.5 cc/min. The starting moisture content is 3.0±0.001%

During the drying stages i.e. at temperatures below 100°C (for road planings and Bodo soil), and at under 200°C (for filter cake) when water is not completely removed, the peak loss factors of the contaminated soils at 2,470 MHz were lower than those at 910 MHz. Road planings, filter cake and Bodo soil respectively recorded ε" up to 0.27, 1.10, and 1.12 at 2,470 MHz, and up to 0.29, 1.85, and 1.81 at 910 MHz. The higher loss factors observed at the lower frequency (i.e. 910 MHz) compared with those of 2,470 MHz can be explained as follows. Soil minerals are known to contain inherent salts (Hallikainen et al., 1985; Curtis et al., 1995; Rengasamy, 2016). When these salts dissolve in soil moisture, they form soil liquids of salts. This aqueous salt solution has an increased loss factor compared with that of both individual solid salt and distilled water (Meredith, 1998; Adam, 2017). When the soil material is irradiated with an electric field, the ions within the liquid of salts travel via the soil's pore spaces oscillating back and forth thus creating an electric current that faces internal resistance from the collisions of the charged species. This resistance generates heat due to ionic conductivity. Ionic conductivity is known to be the dominant loss mechanism in moist heterogeneous materials at low frequencies (Curtis et al., 1995; Hallikainen et al., 1985). This explains the higher peak loss factors observed in road planings, filter cake and Bodo soil at 910 MHz compared to those at 2,470 MHz. However, K-Dere soils behaved slightly differently at temperatures below 100°C. The difference between its loss factors at 2,470 and 910 MHZ were insignificant. This can be attributed to its lower moisture content (3%) compared with those of the other materials whose moisture contents are between 7 and 52%. The low soil moisture made it rather difficult for the dissolution and formation of aqueous salts leading to an insignificant difference in its loss factors at the two frequencies. If the moisture content of K-dree soil is increased to improve its heating ability, it would be expected that the more dominant loss mechanism would also be the ionic conductivity as observed in the other materials.

However, the presence of soil moisture indicates that the dipolar mechanism would also play a role in heat generation during microwave heating of the soils. While the presence of soil moisture suggests the contribution of the dipolar loss mechanism within the drying stage since water is polar, the conductive loss mechanism has a stronger effect when compared to the dipolar loss mechanism in terms of heat generation (Anwar et al., 2011; Shakoor, 2023). This is because of the high mobility of ions (e.g. in salt species) that generates heat due to friction between them, a stronger interaction with the electric field that results in a more effective heat generation, and their temperature-dependent effects (i.e. ion mobility increases with increased temperature) thus enhances heat production.

However, at temperatures >100°C and <450°C (for road planings, Bodo soil and K-Dere soil), and at >200°C and <500°C (for filter cake), when soil water/moisture is completely removed from the solids as explained by the drop in dielectric properties to low loss factors, very negligible heating of soil materials is expected to occur when exposed to an electric field. Starting at temperatures around ≥450°C when carbonaceous materials begin to form (i.e. the char formation stages), the loss factors recorded for all the contaminated soils at 910 MHz are higher than those obtained at a higher frequency of 2,470 MHz. At 910 and 2,470 MHz, their peak loss factors were 0.92 and 0.54 (road planings), 1.65 and 1.18 (filter cake), 0.66 and 0.48 (Bodo soil), and 0.19 and 0.15 (K-Dere soils) respectively.

This increase in loss factors can be attributed to the carbonaceous materials formed at the char formation stages. These materials are very good microwave absorbers as previously shown in Figure 5-6. Additionally, carbon materials such as graphene and the solid carbon-rich decomposition by-products are known to promote the conductive loss mechanism thus resulting in making the soil materials more microwave-susceptible (Robinson et al., 2012; Qin et al., 2022). Therefore between ≥450°C and 700°C, the conductive loss mechanism is believed to be the dominant heating loss mechanism in road planigns, filter cake, Bodo and K-Dere soils due to the presence of carbonaceous materials.

5.3. Remediation Using Microwave Dry Heating

5.3.1. Establishing the suitable microwave generator tuning option and positions

To establish the suitable tuning options during the decontamination of these materials, the step tuning, autotuning and step tuning at drop intervals options were examined during the microwave processing of 30 g of road planings at 0.8 kW and 1 kW power levels using a 2 kW generator for 60 seconds. These power levels were chosen to allow for comparison as preliminary experimental results revealed that the 2 kW generator's Homer auto-tuner used does not autotune at low power levels (≤0.4 kW) because it was calibrated to work only in the range of 0.6 - 60 kW. The result from this comparison is presented in Table 5-3.

Table 5-3: Comparison of microwave heating of 30 g of road plainings for 60 s using single tuning, step tuning at drop intervals and auto-tuning at 2.45 GHz. Results are reported on a dry basis

Power (W)	800							1,000								
Tuning type	Step tuning	Auto tuning			Step tuning at drop intervals			Step tuning			Auto tuning			Step tuning at drop intervals		
Run	1	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
Time attained during MW heating (s)	64	33	42	36	64	60	64	63	64	63	23	18	31	63	64	52
Specific energy input (kJ/g)	0.26	0.39	0.52	0.42	0.76	0.67	0.69	0.25	0.25	0.27	0.32	0.29	0.41	0.97	1.00	0.73
Oil content before MW heating (%w/w)	3.18 ± 0.2	3.18 ± 0.2			3.18 ± 0.2			3.18 ± 0.2			3.18 ± 0.2			3.18 ± 0.2		
Oil content after MW heating (%w/w)	3.30	2.61	2.02	1.63	2.29	2.47	2.56	3.07	2.85	3.11	2.93	3.03	2.87	2.37	2.04	2.16
Oil removal (%w/w)	-	17.92	36.40	48.87	28.20	22.41	19.70	3.42	10.34	2.22	7.78	4.93	9.95	25.43	35.79	32.08
Average oil removal (%w/w)	-	34.4 ± 12.7			23.4 ± 3.5			5.3 ± 3.6			7.6 ± 2.1			31.1 ± 4.3		
Average specific energy input (kJ/g)	0.30	0.44 ± 0.05			0.71 ± 0.04			0.26 ± 0.01			0.34 ± 0.05			0.90 ± 0.12		
Observations	No visible oil removal. Experiments reached the desired completion time.	Visible oil removal. Experiments did not reach completion time due to thermal runaway.			Visible oil removal. Experiments reached the desired completion time.			No visible oil removal. Experiments reached the desired completion time.			Visible oil removal. Experiments did not reach completion time due to thermal runaway.			Visible oil removal. Experiments reached the desired completion time.		

Table 5-3 compared step tuning, auto-tuning, and step tuning at drop intervals based on their ability to remove oil from the soil, meet desired remediation time during processing, and the reproducibility of their results. Firstly, the microwave heating of road planings using autotuning and step tuning at drop intervals showed visible oil removal leaving behind condensed oil stains on glassware walls and cold traps at 800 and 1,000 W power levels. However, this was not the case for step tuning, as no visible oil removal was observed. This was validated by the low oil removal yield of ≤5.3±3.6 wt% (obtained at 800 W and 1,000 W) when using step tuning, and higher oil yields of 7.6±2.1 (for 800 W) and 34.4±12.7 wt% (for 1,000 W) obtained when using autotuning, and 23.4±3.5 wt% (for 800 W) and 31.1±4.3 wt% (for 1,000 W) obtained while using step tuning at drop intervals.

Secondly, for achieving the set microwave processing time of 60 s, step tuning and step tuning at drop intervals met the desired processing time, unlike autotuning. This is because the continuous adjustment and refocusing of the microwave power by the Homer autotuner on an identified microwave absorbing phase within the soil matrix led to hotspots and changes within the soil matrix that resulted in an uncontrollable increase in temperature - a phenomenon called thermal runaway. This led to the instability of the system and compromised process safety; as a result, the experiment was terminated before the set processing time. All the experiments conducted using auto-tuning did not achieve the set processing time as they were terminated halfway because of thermal runaway (see Table 5-3). Although step tuning achieved the desired microwave heating time of 60 s without encountering any thermal runaway, this tuning option was not carried further for the processing of contaminated soils since it showed a low potential for achieving a high oil removal yield during microwave processing. Based on the time attained during microwave heating, the step tuning at drop intervals worked effectively, allowing room to process the road planings up to the desired heating period (60 s) with a lower risk of encountering thermal runaway when compared with auto-tuning. Autotuning was observed to be unstable, resulting in thermal runaway and thus could only achieve a heating time of ≤42 seconds for 800 W and ≤31 seconds for 1,000 W instead of the desired 60 s.

Lastly, the error bars for oil removal and specific energy inputs from the experimental repeats were higher in autotuning compared with those of step tuning at drop intervals (especially at a higher energy input) as shown in Figure 5-12.

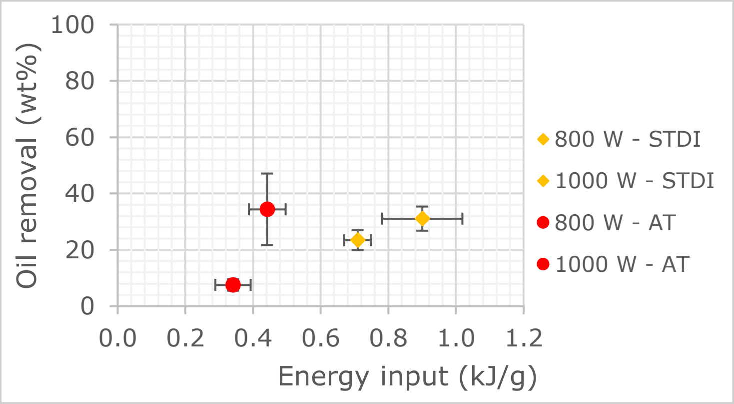


Figure 5-12: Comparison of the microwave heating of 30 g of road plainings using Auto-tuning (AT) and Step Tuning at Drop Intervals (STDI) at 2.47 GHz. Error bars represent the standard deviation from three measurements

Although autotuning achieved a higher oil removal yield of 34.4±12.7 wt% at a lesser energy input of 0.44 kJ/g as compared with step tuning at drop intervals, the latter gave more reproducible results and did achieve a similar oil removal yield of 31.1±4.3 wt% at 0.9 kJ/g. As a result, the step tuning at drop intervals was adopted for the subsequent set of experiments to optimise the experimental conditions.

5.3.2. Scoping - choice of powers

In addition to establishing suitable tuning positions and options, suitable microwave operating input powers for the decontamination of the soils were investigated. During these preliminary experiments, microwave heating between 400 and 800 W powers were found to be more stable as it reduced the risk of thermal runaway compared to powers above 800 W. However, powers below 400

W were observed during experiments to be insufficient to drive forward oil removal.

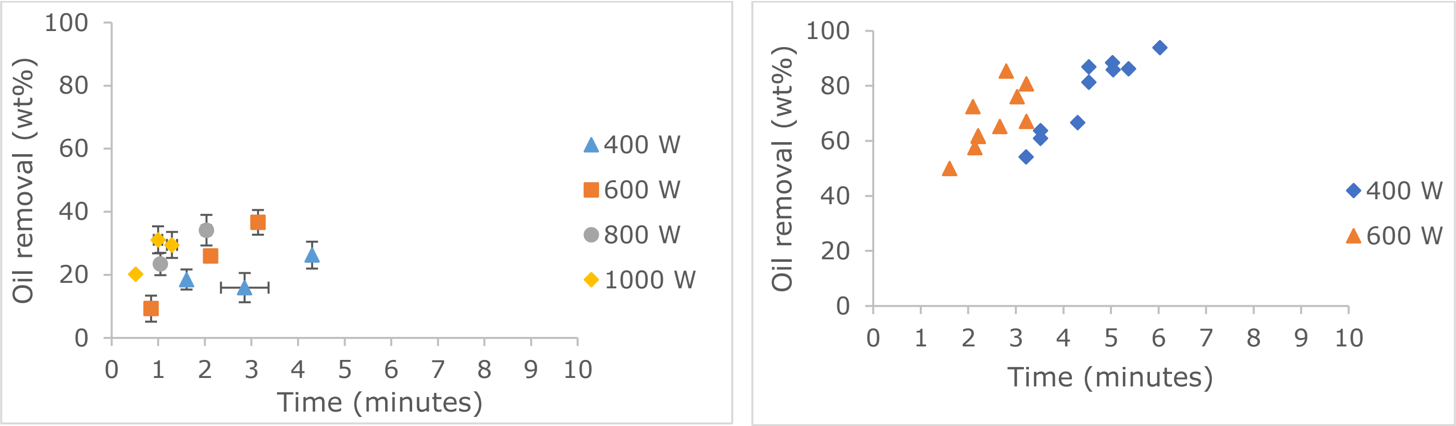
5.3.3. Optimisation of microwave dry heating process conditions

To understand the interaction between microwave energy and contaminated soils, 20 to 30 g of contaminated road planings, filter cake, Bodo soil and K-Dere soils were irradiated by a 2 kW generator at a frequency of 2.45 GHz using different power levels within 0.4 and 1 kW over various heating times up to 10 minutes.

5.3.3.1. Effect of heating time and power levels on oil removal

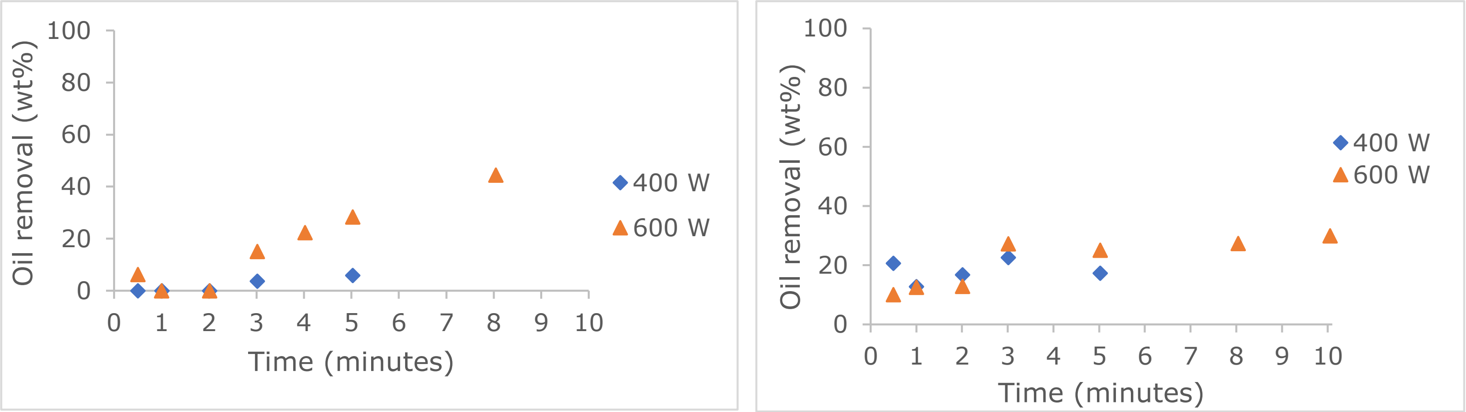
Figure 5-13 shows the results of the investigation of the effect of microwave processing time and power levels on oil removal yield. Oil removal up to 94 wt% at 6 minutes, 37 wt% at 3 minutes, 44 wt% at 8 minutes, and 30 wt% at 10 minutes were achieved in filter cake, road planings, Bodo and K-Dere soils respectively. The rate of oil removal was more rapid in filter cake than in other materials like K-Dere where oil removal was observed to be gradual. For example, at 3 minutes of microwave processing, up to 76% oil removal was achieved in filter cake, whereas, only about 37%, 15%, and 27% were achieved in road planings, Bodo and K-Dere soils respectively.

This trend is expected for filter cake due to not only its high moisture content (~52%) but also the presence and contribution of the bound water within its hydrophilic clay layers which enable achieving high heating temperatures during microwave heating – since soil moisture is the primary microwave-absorbing phase within the material. This behaviour is confirmed by the high dielectric loss factor observed for filter cake discussed in Section 5.2.1 (see Figure 5-5). Although Bodo soil has a high moisture content of ~14% and recorded a high loss factor like those of filter cake at <200°C, its oil removal rate was not rapid and was also lower than those in filter cake. This is because the material is sandy, containing



(a) Road planings

(b) Filter cake



(c) Bodo soil

(d) K-Dere soil

Figure 5-13: Effect of heating time and power levels on oil removal during the microwave dry heating of 20 g of contaminated solids at 2.45 GHz and 1 L/min N_2 flow. For road planings, 30 g was used instead. Results are reported on a dry basis. Error bars were not used in Figure 5-13 (b), (c), and (d) as each result represents a single data point i.e. no experimental repeats were conducted mostly free water (rather than bound water) which is easily evaporated especially since sandy soils pose insignificant mass transfer limitations to the escaping generated steam (refer to Section 3.5) and thus cannot sustain microwave heating for a longer time. This means that the temperature required for significant oil removal isn't reached (see Section 5.3.3.3) and the steam velocities are too low to cause steam stripping or physical entrainment. As its moisture content rapidly decreases with microwave heating time, so also its dielectric loss factors at ≤200°C (see Figure 5-5) resulting in a decrease in the power absorbed with time. The sandy-loam K-Dere soil had low loss factors from its low moisture content that resulted in the least oil removal yield with time. Overall, particle size and moisture content had a major influence on the oil removal yields across the contaminated materials with time; smaller particle sizes and higher moisture contents (contributed by hydrated clay minerals) favoured oil removal with time in filter cake.

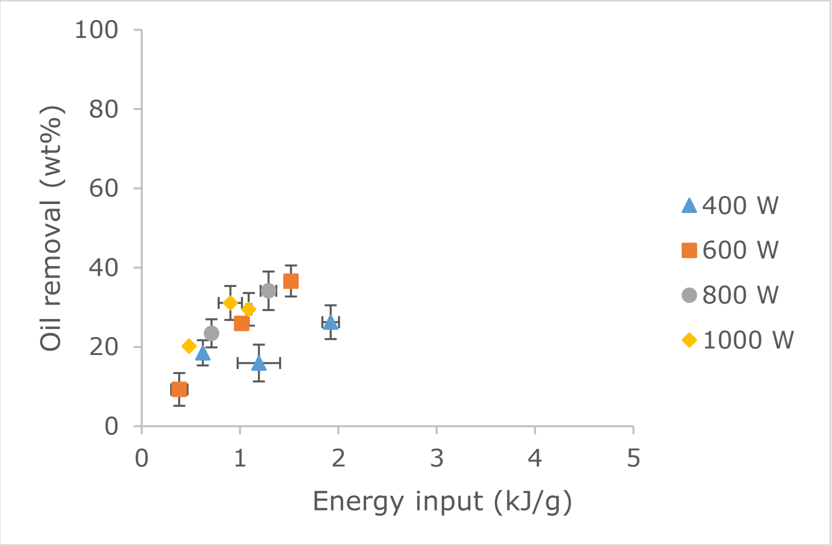
Additionally, it was observed that microwave processing time reduces with applied power. Higher oil removals were recorded at higher input power levels than those at lower input powers for an equivalent processing time. For example, in Figure 5-13(a), at ~1 minute of the microwave processing of road plainings, the oil removal when using 1 kW power was 31 wt% which is greater than those obtained when using 0.6 kW (9 wt%) and 0.8 kW (23 wt%). This was also the case while processing filter cake, Bodo and K-Dere soils over various heating times e.g., at ~3 minutes (Figure 5-13 (b), (c), and (d)). However, the effect of power level was most pronounced in filter cake and least in K-Dere soils due to the variation in particle size and moisture content of the materials i.e. filter cake had fine particles and high moisture content, which enhanced microwave heating when compared with K-Dere soil. Additionally, the smaller pore size of the filter cake limits the mass transfer of steam through its micropores and capillaries when its inherent water phase is rapidly heated at high power. This mass transfer limitation promotes high velocities as the steam forces its way out of the pores and in the process removes the hydrocarbon phase predominantly via the steam stripping mechanism (Ogunniran et al., 2017). However, physical entrainment of contaminants from the high-velocity steam is likely to have occurred too. Unlike in filter cake, the larger pore sizes associated with coarser soils like the Bodo and K-Dere soils have less mass transfer limitation effect, as a result, only low-velocity steam is generated from the boiling and evaporation of their water-oil phase, in the process, the hydrocarbon contamination is removed via the steam distillation mechanism.

In all the contaminated materials processed, shorter heating times at a high power level achieved comparable oil removal yields as those achieved under a longer time at a low power level - indicating that at higher powers, microwave heating is more efficient at an equivalent processing time. Other authors also reported this phenomenon (Robinson et al., 2014; Ogunniran et al., 2017). Ogunniran et al. (2017) processed oil-contaminated sandstone-based and shale-based drill cuttings over a range of power levels (1 – 5 kW) and attributed the phenomenon to the steam stripping mechanism. The authors showed that this dominant contaminant removal mechanism was caused when high power input levels result in high power densities that promote high steam velocities that increase the hydrocarbon removal yield via evaporative mass transfer.

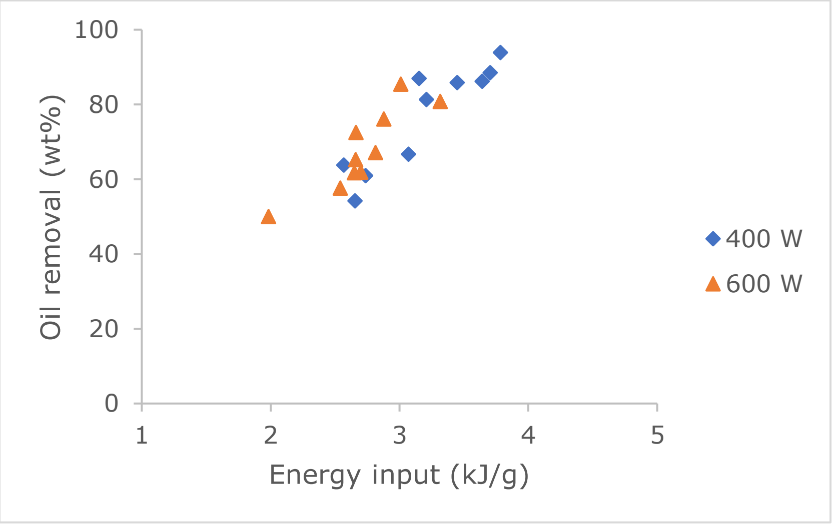
Overall, oil removal generally increased with increasing microwave dry-heating time across all applied input power levels upon irradiation of the oil-contaminated materials using a single-mode cavity (Figure 5-13). However, a few outliers within the trends were observed e.g. there was lower oil removal in road planings at 3 minutes compared to 2 minutes using 400 W (Figure 5-13(a)). Although this decrease is not significant when considering the error bars, it, however, indicates that the challenge of repeatability of results under microwave dry heating is not completely irradicated.

5.3.3.2. Effect of energy input and power levels on oil removal

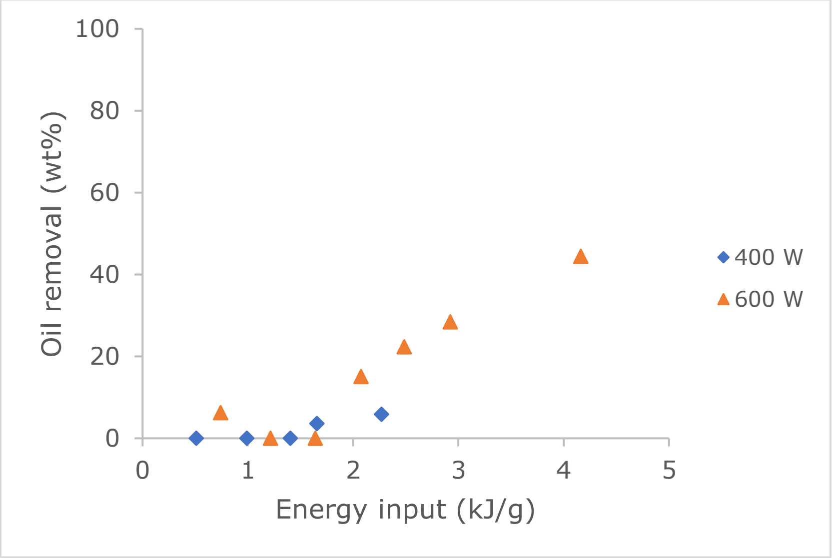
The specific energy input during microwave heating is key to understanding the actual interaction of microwave energy with contaminated soils. This is because it expresses the absorbed microwave power over the heating period since part of the input power is not absorbed by the materials during microwave heating and is therefore reflected. The specific energy input also adjusts for the effect of heating time and soil mass used (refer to Equation 4-9). The results showing the effect of specific energy input on oil removal yield are shown in Figure 5-14.



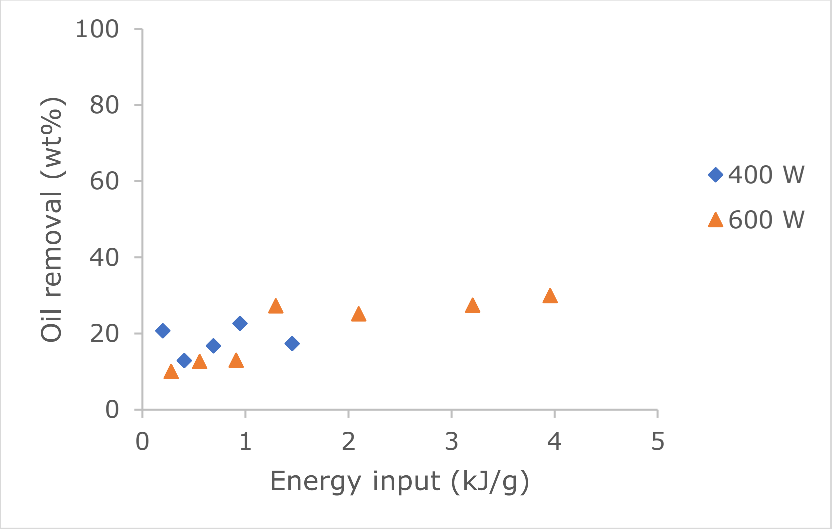
(a) Road planings



(b) Filter cake



(c) Bodo soil



(d) K-Dere soil

Figure 5-14: Effect of energy input and power levels on oil removal during the microwave heating of 20 g of contaminated solids at 2.45 GHz and 1L/min N2 flow. For road planings, 30 g was used instead. Results are reported on a dry basis. Error bars were not used in Figure 5-14 (b), (c), and (d) as each result represents a single data point i.e. no experimental repeats were conducted

The data presented in Figure 5-14, reveals that as specific energy input increased, a corresponding increase in oil removal yield was observed for all the contaminated materials with the highest oil removal recorded in filter cake (94 wt% achieved at 3.8 kJ/g). Additionally, oil removal achieved was up to 37% at 1.5 kJ/g (road planings), 44% at 4.2 kJ/g (Bodo soil), and 30% at 4 kJ/g (K-Dere soil). The high oil removal in filter cake was expected because this material is clayey and hydrated clay layers play an important role as revealed by its high dielectric loss even at temperatures ≥100°C and <200°C discussed in Section

5.2.1. This enabled the absorption of more microwave energy by the water phase trapped within its pores thus generating steam in situ within these pores and capillaries. The high-pressure steam makes the removal of petroleum hydrocarbons from the pores and capillaries of the soil possible via steam stripping as it escapes. Unlike the filter cake material, K-Dere soils had the lowest oil removal yield with increasing specific energy input (i.e., 30 wt% at 4 kJ/g). This is likely because K-Dere soil is predominantly a sandy soil material and has the least dielectric properties compared with the other materials due to its low moisture content which indicates its poor ability to absorb microwave energy and due to its relatively large particle size when compared with the filter cake material that allows the steam generated in-situ during heating to easily escape. When this happens, no apparent increment in oil removal yield was recorded for K-Dere soils beyond 1.3 kJ/g as shown in Figure 5-14 (d). A similar behaviour was observed in road planings which are predominantly gravels, however, this was not the case for Bodo soils and filter cake which had higher moisture content and smaller particle sizes.

Similar to the effect of heating time and power levels discussed in Section 5.3.3.1, at a particular energy input, better oil removal yields were achieved when processing road planings and Bodo soils at higher power levels than when processing them at lower power levels. Although increasing the specific energy input during the microwave heating of Bodo soil beyond 2.3 kJ/g at 400 W was not explored due to the low oil removal yields observed, more oil removal yield is expected at higher energy input but are likely to be below those of 600 W at an equivalent energy input (see Figure 5-14 (c)). This implies that, for the scale-up of this processing system, high-power microwave systems will yield higher oil removal and allow higher throughputs of road planings and Bodo soils than the low-power systems at an equivalent specific energy input (Robinson et al., 2014). This would not be the case for filter cake and K-Dere soils as they exhibited no clear effect of power levels on oil removal yields at an equivalent specific energy input.

Overall, the comparison of the highest oil removal yields recorded in the four contaminated materials is in the order: filter cake (94%) > Bodo soil (44%) > road planings (37%) > K-Dere soils (30%). This agrees with the order of their peak recorded dielectric losses (ε'') below 200°C, which is filter cake (1.1) ≈ Bodo soil (1.1) > road planings (0.3) > K-Dere soils (0.06). Although filter cake and Bodo soil recorded similar peak dielectric properties, more oil was removed from the filter cake because, unlike Bodo soil, its high bound water and smaller particle size (being a clayey material) allowed high dielectric properties even beyond 100°C when its surface water is evaporated (see Figure 5-5).

5.3.3.3. Effect of temperature on oil removal

The temperature at the external walls of the quartz reactor containing the heated soil material was measured for each experiment using an IR thermometer. The results represent the maximum recorded temperature attained during each experiment. Although there exist some limitations in these temperature measurements as they represent the temperature at the wall perpendicular to the IR thermometer (which might not necessarily be the actual temperature of the bulk material during processing), they were however sufficient to draw some key conclusions regarding the range of temperatures reached since the actual maximum temperatures reached by the bulk materials during microwave processing were expected to be slightly higher than those obtained at the walls. Figure 5-15 and Figure 5-16 show the effect of temperature on oil removal yield at 0.6 and 0.4 kW respectively, while Figure 5-17 shows the variation in temperature with specific energy input at 0.4 kW[15] (Results are reported on a dry basis).

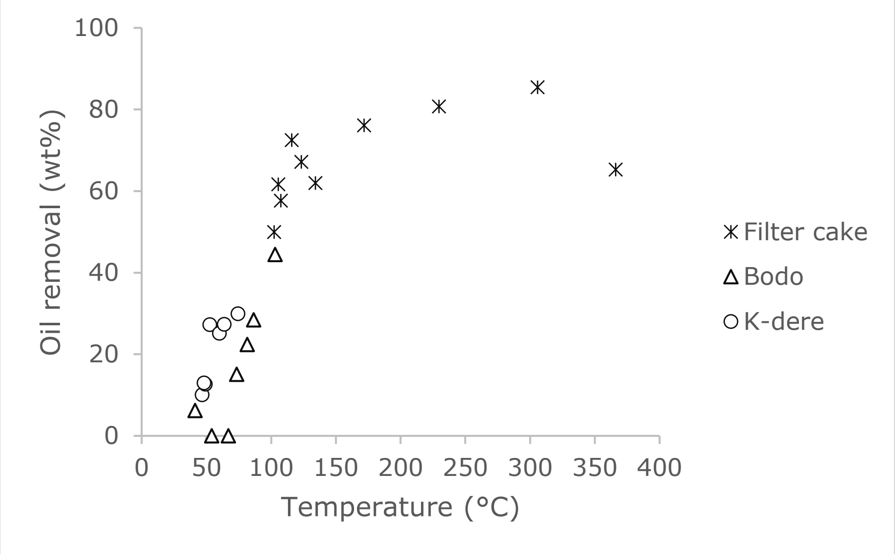


Figure 5-15: Effect of temperature on oil removal during the microwave dry heating of 20-30 g of contaminated solids using 0.6 kW, 2.45 GHz, and 1L/min N_2 flow. Results represent the temperatures at the walls of the reactor containing the heated materials

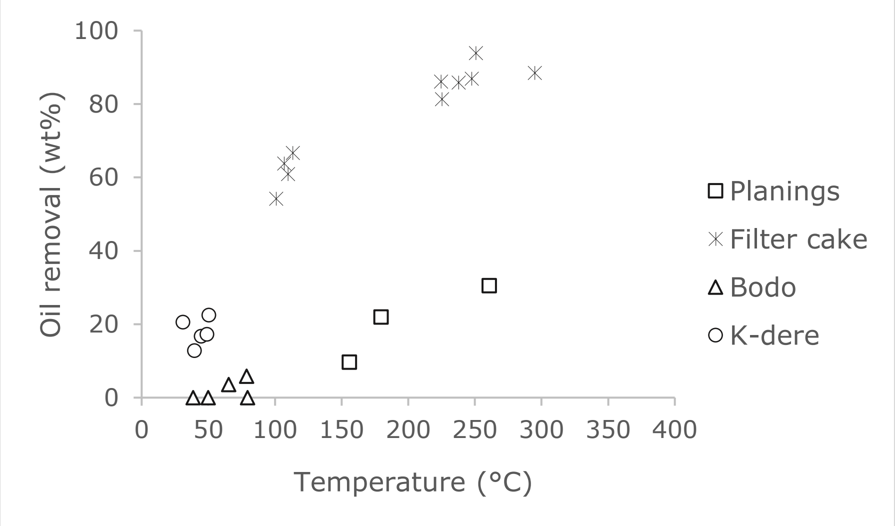


Figure 5-16: Effect of temperature on oil removal during the microwave dry heating of 20-30 g of contaminated solids using 0.4 kW, 2.45 GHz, and 1L/min N_2 flow. Results represent the temperatures at the walls of the reactor containing the heated materials

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[15] No temperature measurements were carried out during the dry heating of road planings using 0.6 kW, and only a few points were measured when using 0.4 kW. This was because the IR thermometer was not yet installed when most of the experiments for road planings were conducted. However, the results obtained are sufficient to draw the desired conclusions.

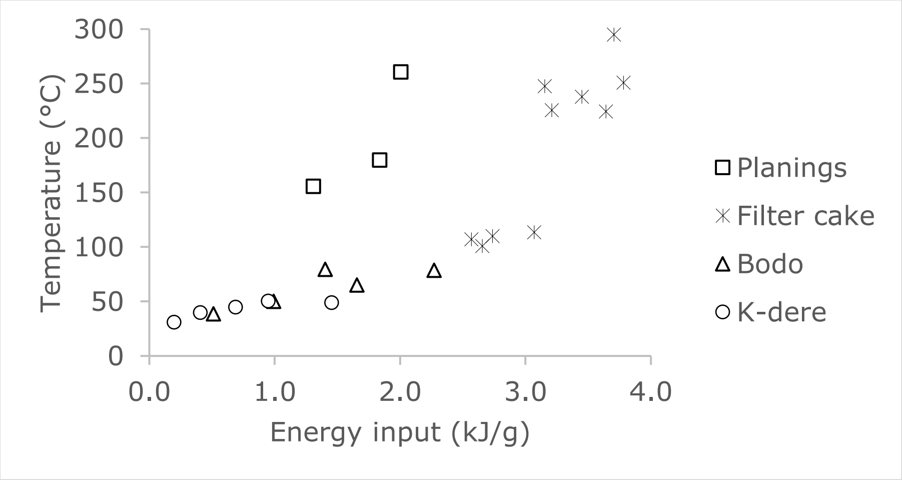


Figure 5-17: Temperature variation with specific energy input during microwave processing of 20-30 g hydrocarbon-contaminated materials using 0.4 kW and 2.45 GHz. Results represent the temperatures at the walls of the reactor containing the heated materials

Bodo soil and K-Dere soils were observed to heat to only temperatures approximately ≤100°C while processing them using both 0.6 kW and 0.4 kW input powers. This is the maximum attainable temperature expected for these materials when the free water on the surfaces, pores, and capillaries of their soil grains are selectively heated by microwaves. However, the temperatures reached were insufficient to effect high oil removal as they are composed of majorly >C12 – C21, >EC16 - EC35 (Bodo soil), and >C12 – C35, >EC16 - EC35 (K-Dere soil) which would require ≥216.3°C to be removed via thermal desorption (see Table 5-2). The heat generated is transferred within the bulk material by conduction before the water phase is completely vaporised. This achieved an oil removal yield of up to 44% using 0.6 kW input power at ~100°C for Bodo soil, and 30% at ~74°C for K-Dere soil (as observed in Figure 5-15). Much lower temperatures i.e. ~79°C and ~50°C respectively for Bodo and K-Dere soils were reached when irradiated at a lower input power of 0.4 kW leading to lower oil removal efficiencies (Figure 5-16 and Figure 5-17).

Filter cake behaved differently as it was able to heat beyond 100°C due to the presence of bound water within its clay minerals which has reduced mobility that allows it to be properly heated beyond this temperature achieving a much higher bulk material temperature that enhanced its oil removal via steam stripping.

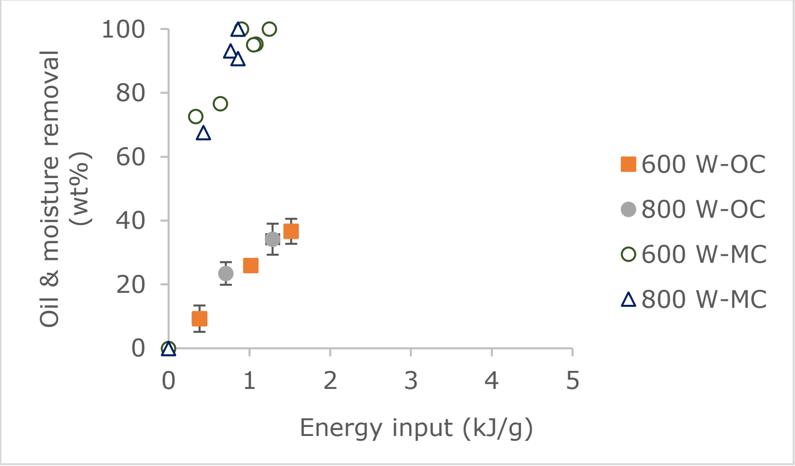
Additionally, since large soil particles are associated with larger pore sizes when compared with those of small particles (Nimmo, 2013), the difference in the maximum recorded temperature can be explained by the poor heat transfer coefficient of the sandy Bodo and K-Dere soils due to their low water content and larger air pore size when compared with the clayey filter cake. This resulted in a slower rate of heat transferred to the reactor walls where the temperature is recorded by the IR thermometer.

In Figure 5-16 and Figure 5-17, the oil removal cluster around 100°C and between 2.7 – 3.1 kJ/g can be attributed to the vaporisation of the surface water within the pores and capillaries of the filter cake which was only able to remove <70% oil. The cluster between 225°C and 295°C at 3.2 – 3.8 kJ/g can be attributed to the stripping of its bound water, which achieved a much higher oil removal yield of >80%. About 88% of the hydrocarbon composition in filter cake falls within the aliphatic and aromatic range of >C16 - C44 and >EC12 - EC44 respectively and have boiling points of >279 – 547.6°C (see Table 5-2). However, up to 94% of oil was removed at recorded temperatures of ≤295°C. This high oil removal yield at much lower boiling points can be attributed to the contribution of steam stripping rather than thermal desorption. At a high input power of 0.6 kW, temperatures above 300°C were achieved as observed in Figure 5-15. Although road planings also recorded temperatures up to 260°C only about 30% oil removal was achieved. This is because road planings are majorly contaminated with heavy oil within >C21-C44 (aliphatic) and >EC16-EC35 (aromatics) which are predominantly bituminous/asphalts (containing PAHs). These contaminants would require a very high temperature of about >359°C - 547.6°C to be removed when using thermal desorption (see Table 5-2). Additionally, compared with filter cake, road planings were observed to have larger pore space (that allows steam to easily escape) and do not contain clay minerals that can help enhance the pressure built up and subsequent removal of its heavy oil at temperatures below their boiling points via steam stripping.

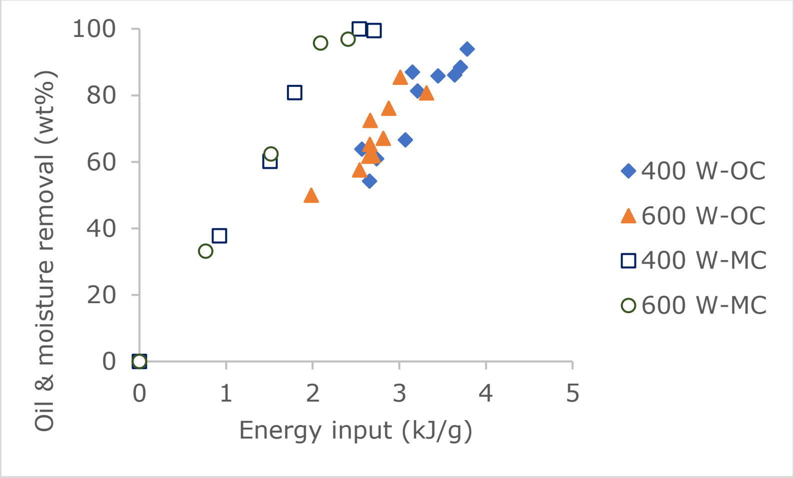
5.3.3.4. Effect of energy input and power levels on water and oil removal mechanism

Since the hydrocarbon contamination phase within these materials are generally poor microwave absorbers, understanding the role of soil moisture (water) in the oil removal process is vital because water is the predominant microwave absorbing phase in the hydrocarbon contaminated road planings, filter cake, Bodo soil and K-Dere soil materials. Figure 5-18 shows the variation of water and oil removal efficiencies with changes in energy input and power.

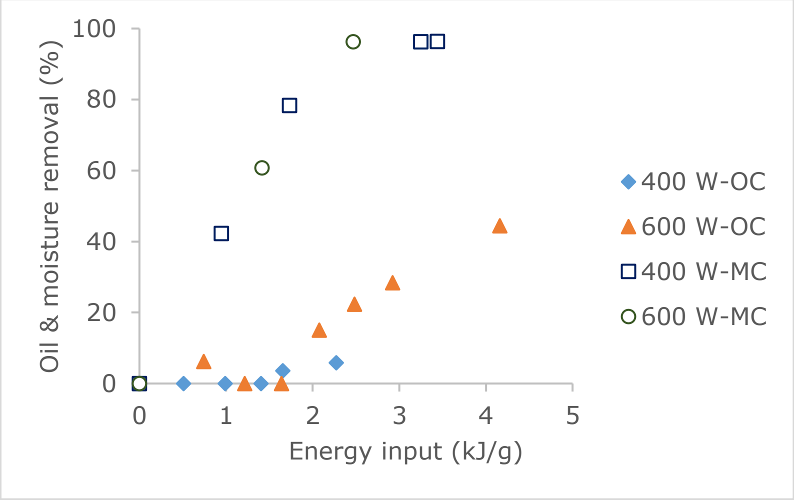
From Figure 5-18, water removal increased significantly (for all the contaminated materials) with increasing energy input until ~90% of the water was removed. This removal was achieved at about 0.9, 2.0, 2.0 and 0.4 kJ/g for planings, filter cake, Bodo and K-Dere soils respectively. However, the variation in the water content was negligible at higher energy inputs when ≥90% water was removed. Contrary to the behaviour observed for oil removal as previously shown in Figure 5-14, power levels (at a constant energy input) seem not to affect water removal in road planings (i.e. at 600 and 800 W), and at 400 and 600 W for filter cake and



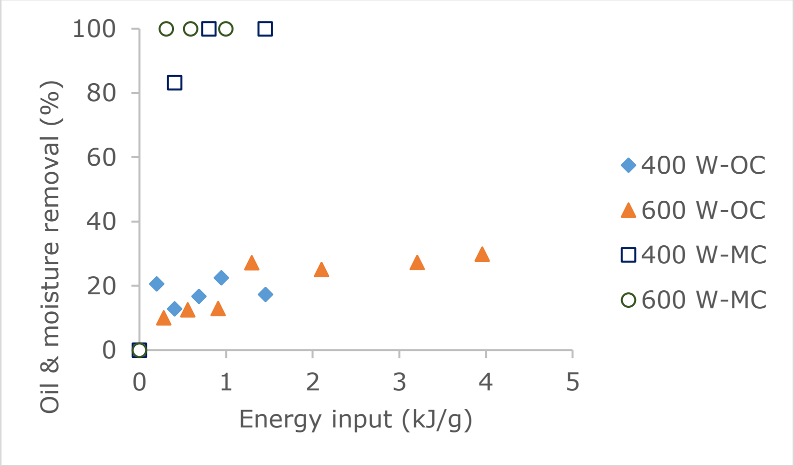
(a) Planings



(b) Filter cake



(c) Bodo



(d) K-Dere

Figure 5-18: Moisture and oil removal during microwave heating of 20-30 g of contaminated materials at 2.45 GHz and 1L/min N_2 flow. Starting moisture content (MC) and oil contents (OC) are planings (7.3±0.45, 2.9±0.14), filter cake (52.1±0.36, 10.4±0.15), Bodo soil (14.2±2.2, 1.30±0.1), and K-Dere soils (3.0±0.001, 0.88±0.1) respectively on a wet basis. Error bars were not used in all moisture content results as well as the oil content results in Figure 5-18 (b), (c), and (d) as each result represents a single data point i.e. no experimental repeats were conducted

Bodo soils. However, more water was removed at 600 W compared with that at 400 W in K-Dere soil at a specific energy input <0.1 kJ/g.

When the first ~80% of the water content of the contaminated materials was removed, only about 23%, <50%, 15% and 13% of oil removal yields were achieved for road planings, filter cake, Bodo and K-Dere soils respectively. Higher oil removal yields were only reached when >90% of the water content was removed. The water phase in road planings, Bodo and K-Dere soils are thought to consist of free water located at the surfaces of their large particle-sized grains (which are predominantly gravels, sand, and sand-loam respectively) and interstitially within their large pore sizes. During microwave heating, the free water phase is selectively heated and easily boils and vaporises from the surface and pores of the soil grains when it exerts its full vapour pressure at 100°C. This temperature is far below the temperature requirement to effect significant oil removal. As it vaporises, oil removal is thought to likely be by steam distillation due to the large pore size of these coarse materials that results in a low-velocity steam generation. The generated steam in coarse materials is insufficient to cause steam stripping compared with fine soil that has smaller pore sizes. This accounts for the low oil removal of <45% recorded in these materials.

However, for clayey materials which comprise both free and bound water, Robinson et al. (2014) reported that when their surface water is vaporised to steam during microwave heating, their bound water (which has reduced mobility and does not exert its full vapour pressure) will be present within the hydrophilic mineral matter and can be heated to temperatures ≥250°C which is sufficient to vaporise light hydrocarbons or even decompose some heavy ones. This was the case for filter cake material (which is clayey), as temperatures above 250°C were achieved leading to the removal of up to ~94% oil even after >99% of its moisture content (free water) was removed (see Figure 5-15, Figure 5-17 and Figure 5-18(b)).

5.4. Conclusions

The dielectric properties of the contaminated soils studied were very significant in understanding how road planings, filter cake, Bodo and K-Dere soils would interact with an electric field during microwave processing. Although both dipolar (due to the presence of soil water) and ionic/conductive loss mechanisms played a role in heat generation at the drying stage (i.e. between 20 and <200°C), the ionic/conductive loss is thought to be the more dominant loss mechanism at these stages due to the presence of ionic salt solutions in the soils. It is also the dominant loss mechanism at the char formation stage (i.e. ≥450 to 700°C when water is evaporated) due to the carbonaceous materials formed. Soil moisture and texture contributed significantly to the dielectric properties of these soils as well as the temperatures reached during heating.

The microwave dry heating of filter cake material was promising, as oil removal >90% was achieved. However, road planings, Bodo and K-Dere soils only achieved oil removal yields of <50%. The clayey texture of filter cake that comprises bound water played an important role in allowing the achievement of temperatures beyond 250°C thus creating a high-pressure build-up that supports hydrocarbon removal via the steam stripping mechanism. However, the likely contaminant removal mechanism in the coarse soils (road planings, Bodo and K-Dere soils) is the steam distillation (co-distillation) mechanism due to the low mass transfer limitation effect and their inability to reach thermal desorption temperatures during microwave heating. Chapter 6 explores ways to enhance and improve upon the oil removal yields of these materials, especially road planings, Bodo and K-Dere soils. Furthermore, it seeks to improve the stability of the heating system and enhance process safety.

CHAPTER 6

6. IMPROVING OIL REMOVAL EFFICIENCY AND OVERCOMING THERMAL RUNAWAY

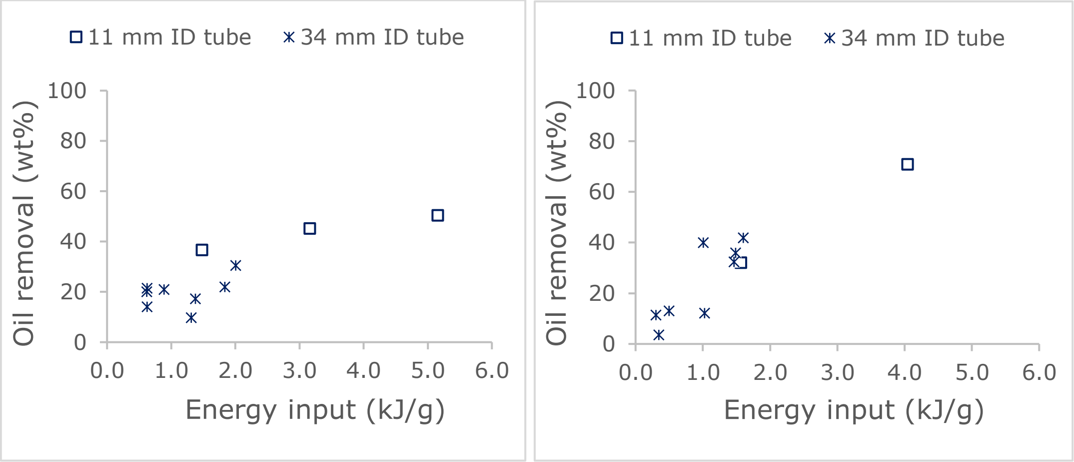
In Chapter 5, the remediation of petroleum-contaminated solid materials was explored using microwave "dry" heating. Up to 94%, 37%, 44% and 30% oil removal yields were achieved in filter cake, road planings, Bodo and K-Dere soils respectively. Although the result obtained for filter cake was promising, other materials did not fare as well. In light of this, Chapter 6 delves into alternative methods, including the use of a wet microwave heating system that involves wetting the oil-contaminated soils with ethylene glycol which has a higher boiling point (197°C) and is more thermally stable than water. Higher processing temperatures can be achieved in the process which could improve oil removal yields. The chapter also identifies thermal runaway as a major limitation to a successful microwave remediation of hydrocarbon-contaminated solids which often presents a barrier in moving this technology to full-scale commercial application. It addresses this challenge by exploring the use of an inert liquid system which immerses the contaminated soil materials into a microwave lossless solvent during processing.

6.1. Improving Oil Removal Efficiency

6.1.1. Varying the reactor diameter during microwave dry heating

When microwaves are applied to a dielectric material, the intensity and density of the electric field decrease exponentially as the waves penetrate the material (Adam, 2017; Robinson et al., 2012). Hence, enhancing power density could be achieved by reducing the volume of soil processed and increasing power input. This could be accomplished by reducing the internal diameter of the quartz tube from the previously used 34 mm (see Sections 4.4 and 5.3) while maintaining a packing height of ≤43 mm to ensure exposure of the material to microwaves.

These adjustments could potentially lead to higher power density. To improve the oil removal yield when processing contaminated road planings with the microwave dry heating system, this hypothesis was tested using an 11 mm ID quartz tube, and the results are presented in Figure 6-1.



a) 400 W b) 600 W

Figure 6-1: Effect of internal tube diameter on oil removal during the dry microwave heating of road planings at 1 L/min N_2 flow. 30 g of material was used in the 34 mm tube diameter while 7.2±0.7 g was used in the 11 mm tube. Results are reported on a dry basis

More oil removal was achieved when remediating road planings at 400 W using the 11 mm ID tube compared with the 34 mm ID tube. For example, at ~1.4 kJ/g, ~37% oil removal was achieved using the 11 mm tube whereas only about 17% was achieved in the 34 mm tube. This increment in oil removal could be attributed to the reduction in the sample size from 30 g to ~7.2 g due to the reduction in tube diameter. Ogunniran et al. (2017) found that in microwave heating of drill cuttings, decreasing the sample bed cross-sectional area by half doubled the steam velocity and increased the mass transfer coefficient by a factor of 2.48. This led to more oil removal, which could also have contributed to the increased oil yield in Fig 6-1a. However, this was not the case while heating the same material using 600 W, as the change was insignificant. At ~1.6 kJ/g, oil removal of ~32% and ~31% were observed in the 11 mm and 34 mm tubes respectively. This insignificant difference is likely due to the increase in the applied power to 600 W which in turn increased the power density due to an increase in its electric field intensity (Ogunniran et al., 2017). This increase in power density was sufficient to enhance the velocity of steam generated and drove oil removal in both tubes despite the differences in the sample volume unlike what was observed when using 400 W.

Although an increase in oil removal yields up to 50% (at 400 W) and 71% (at 600 W) were achieved while using the 11 mm tube, the difference in oil removal is not expected to be much if the dry heating of road planings using the 34 mm tube were continued up to similar energy input to those achieved in the 11 mm tube (especially at 600 W). This is because the oil removal within the conditions studied was observed to increase with increasing energy input and can be represented by Equations 6-1 and 6-2 for 400 W and 600 W respectively.

$$y = 7.9405x + 12.403, \quad R^2 = 0.7033 \tag{6-1}$$

$$y = 17.626x + 3.484, \quad R^2 = 0.7415 \tag{6-2}$$

Where x, y, and R^2 represent energy input (kJ/g), oil removal (%), and the coefficient of determination respectively. This behaviour may vary with other materials because of their different texture and composition; however, due to limitations of thermal runaway encountered while processing road planings, this was not explored further.

The implication of reducing sample volume on large-scale soil remediation without compromising processing throughput would mean using (for example) a conveyor belt system for continuous ex-situ microwave remediation of the contaminated materials. However, to achieve similar oil removal yields to those obtained in this work, the sample bed depth on the conveyor belt must be minimised to <4.3 cm to ensure good microwave penetration. For example, Buttress et al. (2016) developed a continuous microwave processing system that processed 150 kg/h of contaminated soil. The authors controlled the soil bed depth on a conveyor belt to 3 cm and achieved up to 75% oil removal by using two processing steps arranged in series. Additionally, Robinson et al. (2010b) who scaled up a continuous microwave remediation system capable of treating up to 500 kg/h of drill cuttings maintained a bed depth of 3 - 5 cm on a conveyor belt and achieved >98% oil removal using 15 kW.

6.1.2. Wet microwave heating

The use of microwave susceptors to enhance oil removal efficiencies during microwave heating is common (Krouzek et al., 2018; Sivagami et al., 2019; Apul et al., 2016b). In this work, the studied contaminated materials were wetted with 5 wt% ethylene glycol as discussed in Section 4.4.2. Ethylene glycol was used because of its high dielectric loss factor of 12 (at room temperature and 2.5 GHz) similar to that of water, 13, but has the advantage of a higher boiling point of 197^{o}C compared with water (i.e., 100^{o}C). This implies that wetting the contaminated solids with ethylene glycol could improve the heating of the materials at temperatures below 100^{o}C and extend their heating beyond 100^{o}C when their water phases are evaporated. As shown in Chapter 5, contaminant removal by steam stripping or entrainment mechanism is unlikely in coarser materials like sandy soils thus, there is a need to enhance the thermal desorption and steam distillation mechanisms within such materials. Overall, the use of ethylene glycol could potentially improve oil removal during the remediation of the various materials via thermal desorption, steam or ethylene glycol distillation, steam stripping, entrainment, or the combination of one or more of these mechanisms as discussed later in Section 6.1.2.2.

6.1.2.1. Dielectric properties of contaminated solids wetted with ethylene glycol

The dielectric properties of the wetted oil-contaminated road planings, filter cake, Bodo and K-Dere soils were measured as shown in Figure 6-2.

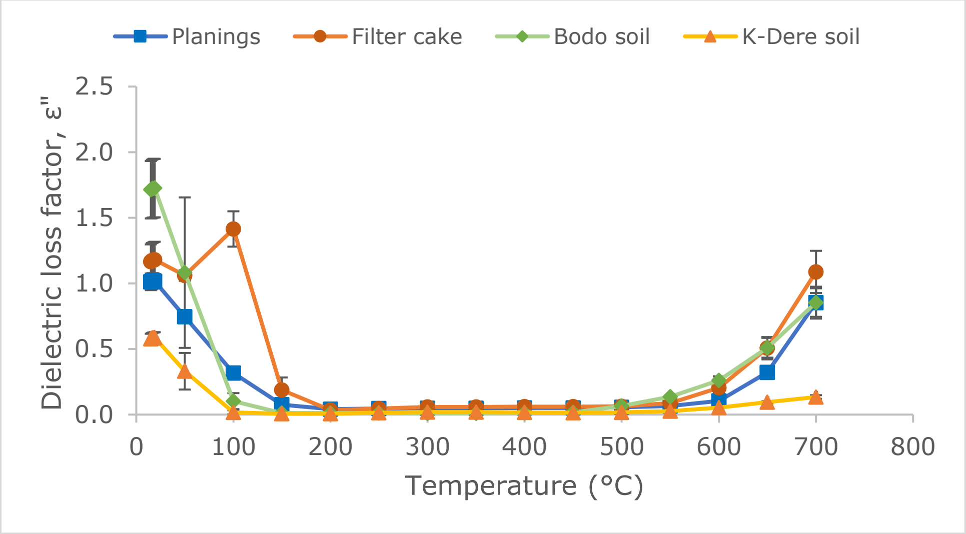


Figure 6-2: Dielectric loss of hydrocarbon-contaminated solids (wetted with 5 wt% ethylene glycol) with temperature. Nitrogen (N_2) was supplied at 7.5 cc/min. For filter cake, N_2 was only introduced after 200°C when its moisture was removed, and cake pores were opened to allow free N_2 flow. Error bars represent the standard deviation of three to four measurements

At temperatures below 200°C, the loss factors of the materials reached the following peak values; road planings (1.02±0.06), filter cake (1.41±0.14), Bodo soils (1.73±0.22), and K-Dere soils (0.59±0.04). These high dielectric properties are a result of the combined effect of ethylene glycol (b.p. ~197°C) and water within the material's matrix, and they indicate the likelihood that these materials will be readily heated when irradiated with microwaves at these temperatures. The increase in the loss factor of filter cake at about 100°C is attributed to the contribution of the bound water within its hydrated clay minerals as discussed in Section 5.2.1. Beyond 200°C and up to ~550°C for road planings, filter cake and K-Dere soil, and ~450°C for Bodo soil, their loss factors were found to drop significantly below 0.07 (road planings), 0.1 (filter cake), 0.02 (Bodo soil), and 0.03 (K-Dere soil), as a result, there is little expectation for these materials to be heated upon irradiation with microwave energy. Subsequently, at temperatures between ~500°C and 700°C when the hydrocarbon phase decomposes and forms carbonaceous deposits, high loss factors up to 0.85±0.12 (road planings), 1.09+0.16 (filter cake), and 0.85±0.11 (Bodo soil) were obtained respectively, which were similar to those observed for these materials at temperatures <200°C and could be attributed to the contribution of the good microwave absorbing carbonaceous materials formed. The loss factors of these materials are expected to further increase with temperatures above 700°C.

Like the behaviour observed in the dielectric properties of these materials before wetting them with ethylene glycol, a gradual increment followed by a sharp increase in the loss tangents and loss factors were observed in road planings, filter cake and Bodo soil beyond 500°C, indicating the likelihood of the occurrence of thermal runaway during microwave heating. However, only a gradual increment and low peak values of loss factor (0.13±0.01) were observed in K-Dere soil at these temperatures. This indicates a lesser likelihood for a thermal runaway to occur in this material.

To understand the effect of ethylene glycol on the oil-contaminated materials, their loss tangents before and after wetting them with ethylene glycol were compared (see Figure 6-3 and Figure 6-4).

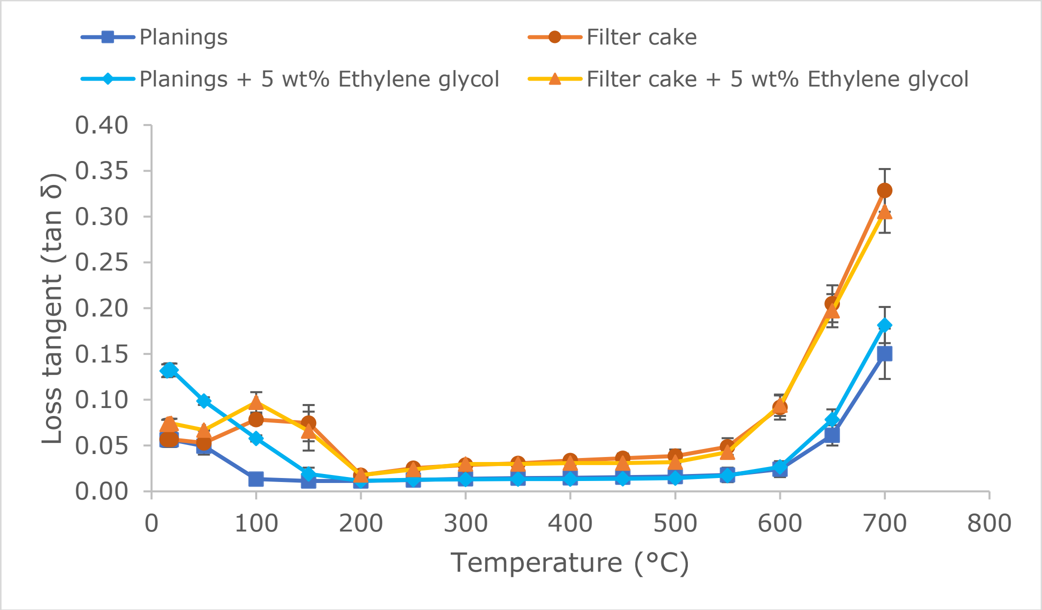


Figure 6-3: Loss tangent comparison for road planings and filter cake before and after wetting them with 5 wt% ethylene glycol. Nitrogen was supplied at 7.5 cc/min. For filter cake, N_2 was only introduced after 200°C when its moisture was removed, and cake pores were opened to allow free N_2 flow

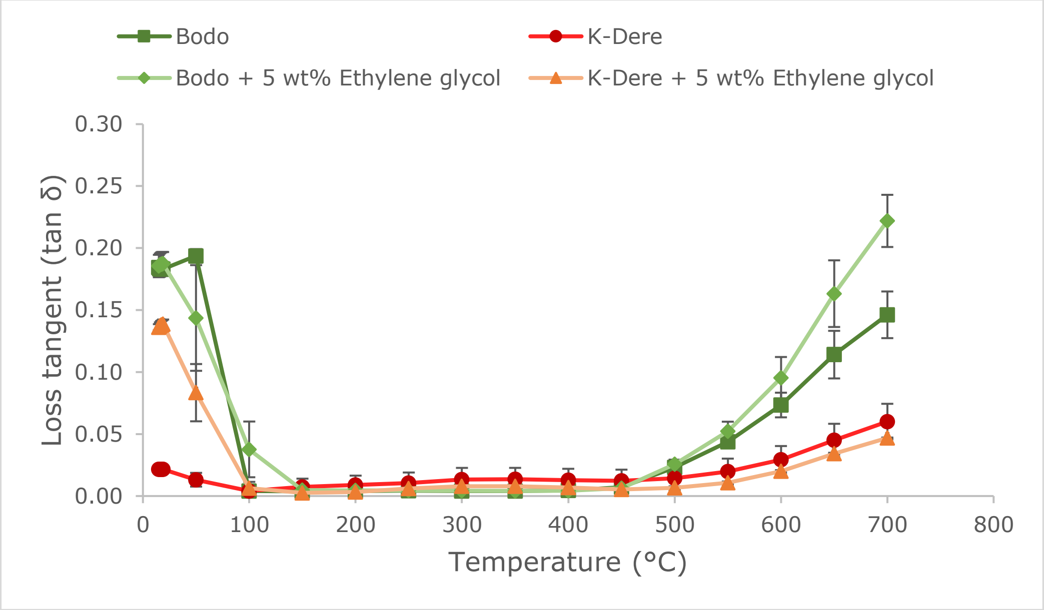


Figure 6-4: Loss tangent comparison for Bodo and K-Dere contaminated soils before and after wetting them with 5 wt% ethylene glycol. Nitrogen (N_2) was supplied at 7.5 cc/min

Generally, an increase in the loss tangents of the contaminated materials wetted with ethylene glycol at temperatures below 100°C was observed when compared with those without ethylene glycol. This change was more significant in road planings, filter cake and K-Dere soils unlike in Bodo soil. For example, at 50°C, the loss tangent increased from 0.05±0.01 to 0.10±0.004, 0.05±0.002 to 0.07±0.001, and 0.013±0.006 to 0.08±0.02 for road planings, filter cake and K-Dere soils respectively. The increment can be attributed to the presence of ethylene glycol susceptor in the soil materials. Although there was an insignificant difference between the loss tangent of Bodo soil at 50°C, a change from 0.004±0.001 to 0.04±0.02 was observed at 100°C. Significant increments were also recorded for road planings and filter cake materials at 100°C. For example, after wetting road planings with ethylene glycol, its loss tangent increased from 0.01±0.004 to 0.06±0.003. However, this was not the case for K-Dere soil as there was no difference between the loss tangents of its wetted and dry samples at 100°C. The change in the dielectric properties of road planings and Bodo soils even when their moisture contents were evaporated at 100°C confirms the contribution of ethylene glycol susceptor (b.p. of 197°C) and suggests that the heating of these materials is likely to be sustained beyond 100°C.

However, unlike in filter cake, it was observed that even at temperatures below the boiling point of ethylene glycol (197°C), the loss tangents of wetted K-Dere and Bodo soils dropped to similar levels to those of their unwetted (dry) materials i.e. ≤0.006 at 100°C (K-Dere soil), and ≤0.005 at 150°C (Bodo soils). This unexpected behaviour which could lead to the poor heating of these materials at these temperatures during microwave processing is likely because of the larger particle and pore sizes of these coarse materials comprising predominantly sand (Bodo soil) and sandy-loam (K-Dere soil), which allows easy evaporation of the ethylene glycol at these temperatures especially since dry nitrogen is also being passed through the sample bed as purge gas. Road planings also have a large particle size because they are predominantly gravel. As a result, it also experienced a significant decrease in its loss tangent to values ≤0.02 at 150°C even after being wetted with 5% ethylene glycol. However, when compared with the dry road planings, its loss tangent increased from 0.01±0.004 to 0.02±0.007 at this temperature. Furthermore, a more detailed observation of its loss factor (see Figure 6-5) showed an increase from 0.03±0.01 to 0.08±0.03 at 150°C when wetted with ethylene glycol which could make a significant increase in its ability to heat during microwave processing leading to more oil removal.

Filter cake however maintained high loss tangent and loss factors even at temperatures ≥150°C and below ~200°C which could be associated with the combined effect of its bound water as extensively discussed in Section 5.2.1 and the contribution of ethylene glycol up until 197°C when they are evaporated. At temperatures >200°C (beyond the boiling point of ethylene glycol), similar behaviours in dielectric properties were observed for all the oil-contaminated materials in both wetted and dry samples. This is because the ethylene glycol is evaporated from these materials at these temperatures and their loss tangents and loss factors were consistently low up to temperatures starting from ~500°C.

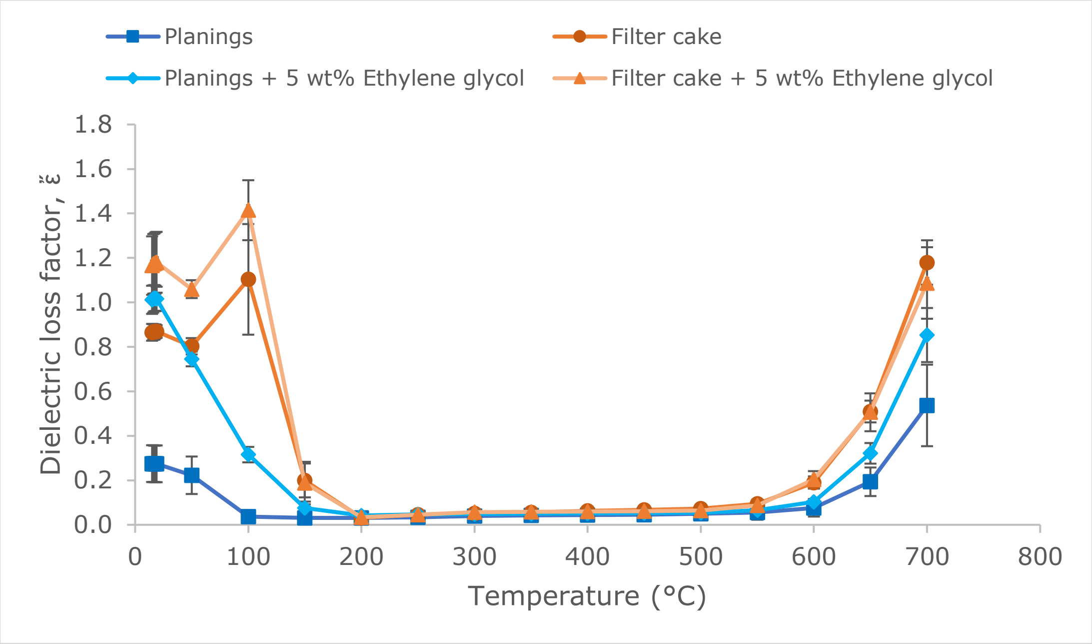


Figure 6-5: Loss factor comparison for road planings and filter cake before and after wetting them with 5 wt% ethylene glycol. Nitrogen was supplied at 7.5 cc/min. For filter cake, N_2 was only introduced after 200°C when its moisture was removed, and cake pores were opened to allow a free N_2 flow

At these very low dielectric properties, there is less expectation for the materials to heat. However, at temperatures ≥550°C these properties were observed to increase due to the formation of carbonaceous materials which are good microwave absorbers and thus pose a possible risk of encountering thermal runaway when processing the contaminated materials.

Therefore, from the dielectric properties of the contaminated materials discussed, the microwave heating temperature region when processing the material is expected to extend beyond 100°C but up to ≤150°C for wetted road planings unlike in dry road planings. In the case of filter cake materials, the microwave heating temperature region is also expected to extend beyond 100°C but ≤197°C, however, the behaviour in filter cake might not necessarily be linked to the presence of ethylene glycol susceptor but its bound water, as there was an insignificant difference in the dielectric properties for its wetted and dry materials between 100°C and 200°C. For K-Dere soil, no extension in the heating region beyond 100°C is expected even with the presence of ethylene glycol. This is because its dielectric properties between ≥100°C and <200°C remained alike before and after being wetted with ethylene glycol. At these temperatures, a similar behaviour to that observed in K-Dere soil is expected for Bodo soil because the change in its dielectric properties was insignificant and might not be sufficient to improve oil removal.

It is worth noting that, the inability of some of the contaminated materials to have a significant increase in their dielectric properties up to temperatures close to the boiling point of ethylene glycol could also be associated with the presence of soil moisture. This is because ethylene glycol is water-soluble, and it's probable that the two substances have mixed, thereby reducing the boiling point of the ethylene glycol, and consequently diminishing its overall efficiency.

6.1.2.2. Microwave processing of oil-contaminated solids wetted with ethylene glycol

A comparison of the results obtained while processing the oil-contaminated road planings and filter cake materials before and after wetting them with 5% ethylene glycol are presented in Figure 6-6 and Figure 6-7 respectively.

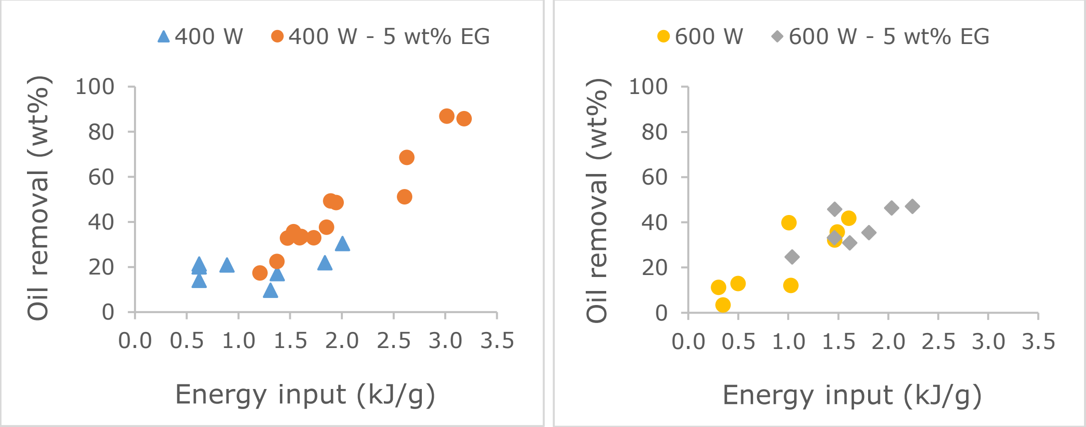


Figure 6-6: Comparison of the oil removal efficiencies of the microwave processing of 30 g of road planings before and after wetting with 5 wt% ethylene glycol (EG) at 1 L/min N_2 flow. Results are reported on a dry basis

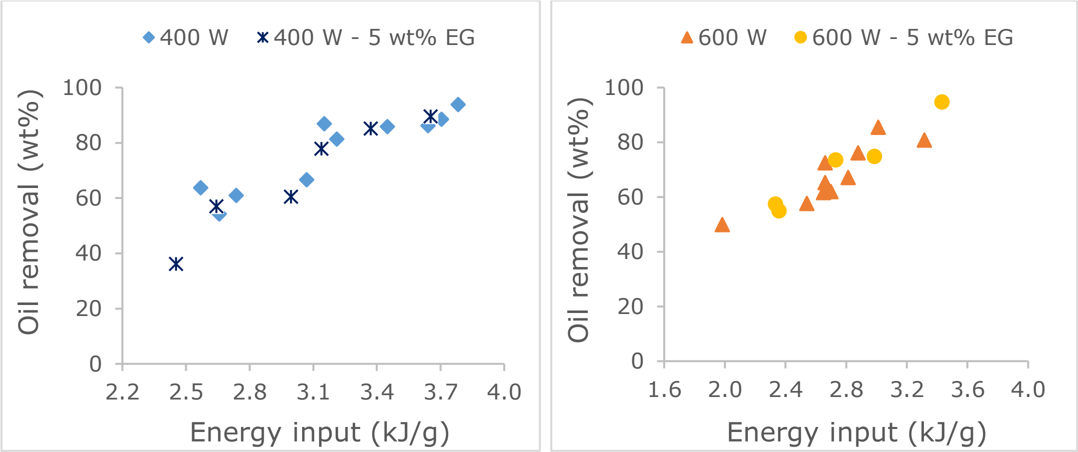


Figure 6-7: Comparison of the oil removal efficiencies of the microwave processing of 20 g of filter cake before and after wetting with 5 wt% ethylene glycol (EG) at 1 L/min N_2 flow. Results are reported on a dry basis

While processing road planings at 400 W, it was observed that the oil removal yield for the wetted road planings significantly increased from a maximum recorded value of ~31% achieved during dry microwave processing to ~87% in the wet heating system (see Figure 6-6). Additionally, wetting the material with ethylene glycol made it possible to further heat this material at higher energy inputs up to ~3 kJ/g compared with the ~2 kJ/g observed in the dry microwave heating system. Similarly, oil removal increased from a maximum recorded value of ~42% at 1.6 kJ/g (in dry heating) to ~47% at 2.2 kJ/g (in the wet system) while processing road planings at 600 W. This improvement in the oil removal yield of road planings (when wetted with ethylene glycol) is expected and can be linked to the increase in its dielectric loss factor and loss tangent observed at temperatures below 200°C as previously discussed in Section 6.1.2.1. Ethylene glycol made it possible for the heating of road planings to continue at temperatures beyond 100°C and ≤197°C after its moisture content was evaporated leading to a higher oil removal when compared with those processed under a dry microwave heating system. The oil removal in the wetted road planings beyond 100°C and up to 197°C can be attributed to steam distillation (co-distillation) of ethylene glycol and oil contamination that are immiscible and the thermal desorption of some of the hydrocarbon phase with lower or similar boiling points.

Furthermore, for the same energy input, it was observed that at 400 W, more oil removal was recorded in the wet road planings (with ethylene glycol) compared with its dry material (without ethylene glycol). For example, at ~2 kJ/g energy input, the oil removal recorded for the dry and wet road planings were 31% and 49% respectively. There was however no clear difference in the oil removal yields recorded at any given energy input for the wet and dry road planings while processing them at 600 W. This is likely because the microwave processing of road planings at 400 W is limited in its ability to sufficiently drive forward oil removal without requiring a susceptor as generally observed for lower powers during experimentation (refer to Section 5.3.2 for details), however, 600 W was sufficient to also drive forward oil removal in the dry heating process even before the material's water phase was evaporated. In the wet microwave processing of road planings, similar oil removal yields to those observed at 400 W are expected at 600 W when the energy input is increased beyond the ~2.2 kJ/g studied. Although this was not explored, the results obtained were sufficient to draw the desired conclusions regarding the effect of ethylene glycol on the decontamination of the material.

The behaviour observed while processing road planings was not the case for filter cake material as there was no significant change in its oil removal yield even after wetting the material with ethylene glycol susceptor. For example, at ~3.7 kJ/g energy input and 400 W, the oil removal yield recorded during the microwave processing of filter cake under the dry and wet system conditions are ~88.5% and 89.5% respectively (see Figure 6-7). A similar behaviour was also observed for filter cake at 600 W. Wetting this material with ethylene glycol had an insignificant effect on the overall oil removal because unlike in road planings which is characterised by large particle sizes (predominantly gravel) that allow for good mixing of the sample with ethylene glycol, the fine clayey and muddy filter cake material has much smaller particle sizes that resulted in the poor mixing and penetration of ethylene glycol into the material. As a result, its effect is only limited to the surfaces of the material rather than its pores and capillaries.

This behaviour was anticipated in filter cake because the change in its loss factors and loss tangents between 100°C and <200°C before and after being wetted with ethylene glycol were insignificant (refer to Section 6.1.2.1), indicating that oil removal within these temperatures is not expected to improve upon mixing the material with the susceptor. Therefore, oil removal in filter cake at temperatures exceeding 100°C can be chiefly attributed to the dominant contribution of the bound water within its hydrated clay layers (rather than ethylene glycol) that are converted into steam during microwave heating which ultimately results in the steam stripping of the hydrocarbon phase within the material. However, the high temperatures generated during this process which were above the boiling point of ethylene glycol as previously discussed in Section 5.3.3.3 also led to the vaporisation of this susceptor from the material.

While processing Bodo and K-Dere soils under the wet microwave heating system, it was observed during experiments that although oil removal occurred, the specific energy input was however insufficient to strip off all the ethylene glycol contained in the soil materials. Only temperatures below 197°C (the boiling point of ethylene glycol) were recorded i.e. a maximum recorded temperature of 145.1°C and 105.2°C for K-Dere and Bodo soils respectively. Although the actual soil bed temperature is more likely to be higher than the maximum temperature recorded at the walls of the reactor during the experiment, it is not expected to reach the boiling point of ethylene glycol as the difference between the recorded temperature and the boiling point of ethylene glycol was between 52 and 92°C. Figure 6-8 compares the oil removed while processing Bodo soil under dry and wet microwave heating systems at 600 W.

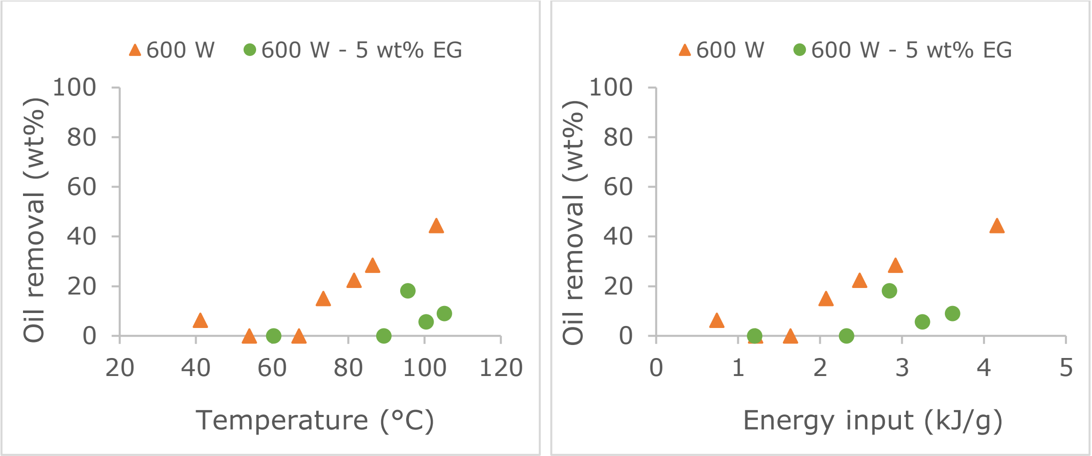


Figure 6-8: Comparison of the oil removal efficiencies of the microwave processing of 20 g of Bodo soil before and after wetting with 5 wt% ethylene glycol (EG) at 600 W, and 1 L/min N_2 flow. Results are reported on a dry basis

It is expected from the increase in the loss tangent of Bodo soil observed when wetted with ethylene glycol as previously shown in Figure 6-4, that at ~100°C, more soil heating would occur and could potentially lead to more oil removal compared with those of its dry material. However, this is not the case as the oil removed significantly dropped from ~44% recorded during dry processing to ~9% in the wet processing system (see Figure 6-8). Additionally, after extracting the treated soil to determine its oil content using soxhlet extraction, layers of ethylene glycol were observed within the oil phase thus confirming that not all the ethylene glycol was removed from the soil during remediation. This added to the overall mass of the extracted oil and led to the low oil removal yields calculated for the wetted materials. The practical difficulty in measuring only the amount of oil removed during the remediation of Bodo and K-Dere soils under the wet microwave heating system resulted in no further experiments for these soils.

The response of the aliphatic and aromatic fractions (refer to Table 5-2) to microwave heating was observed after the extractable organic matter of road planings was analysed before and after remediation using Gas Chromatography-Mass Spectrometry (GC-MS). The result in Figure 6-9 shows a reduction in the normal alkanes (especially below n-C_{20}) after microwave irradiation using 3.02 kJ/g of energy while Figure 6-10 shows the complete elimination of the lower molecular weight PAHs i.e. acenaphthylene, acenaphthene, fluorene and anthracene, and a reduction in the higher molecular weight ones like fluoranthene and pyrene upon irradiation with 2.24 kJ/g.

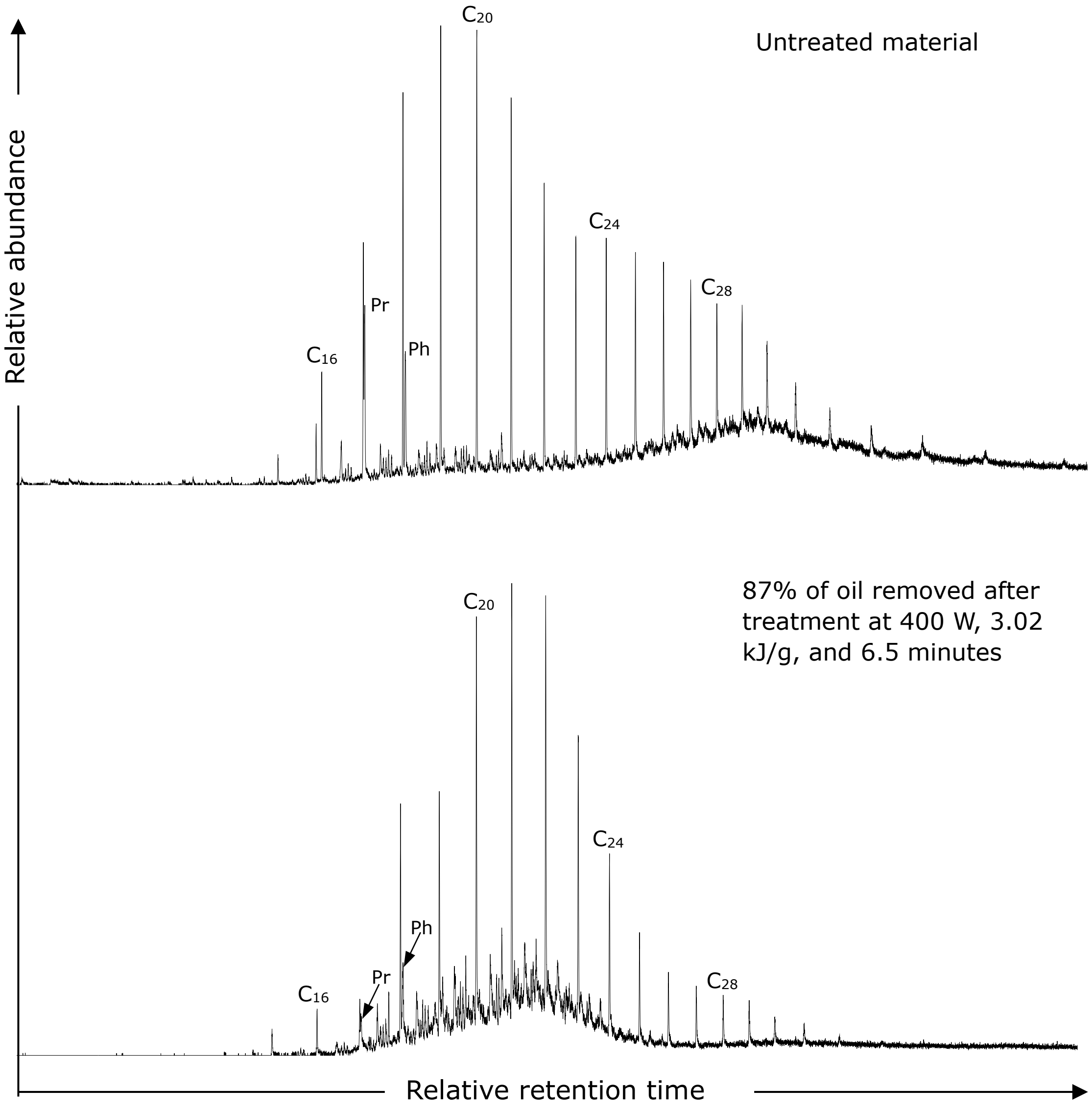


Figure 6-9: Gas chromatograms (GC) for the aliphatic fractions of extracted road planings before and after remediation using wet microwave heating. Where Pr: Pristane, Ph: Phytane, Cn: normal alkane

However, not all the n-alkanes and PAHs were removed from road planings since only 87% and 47% of the oil were successfully removed from the material.

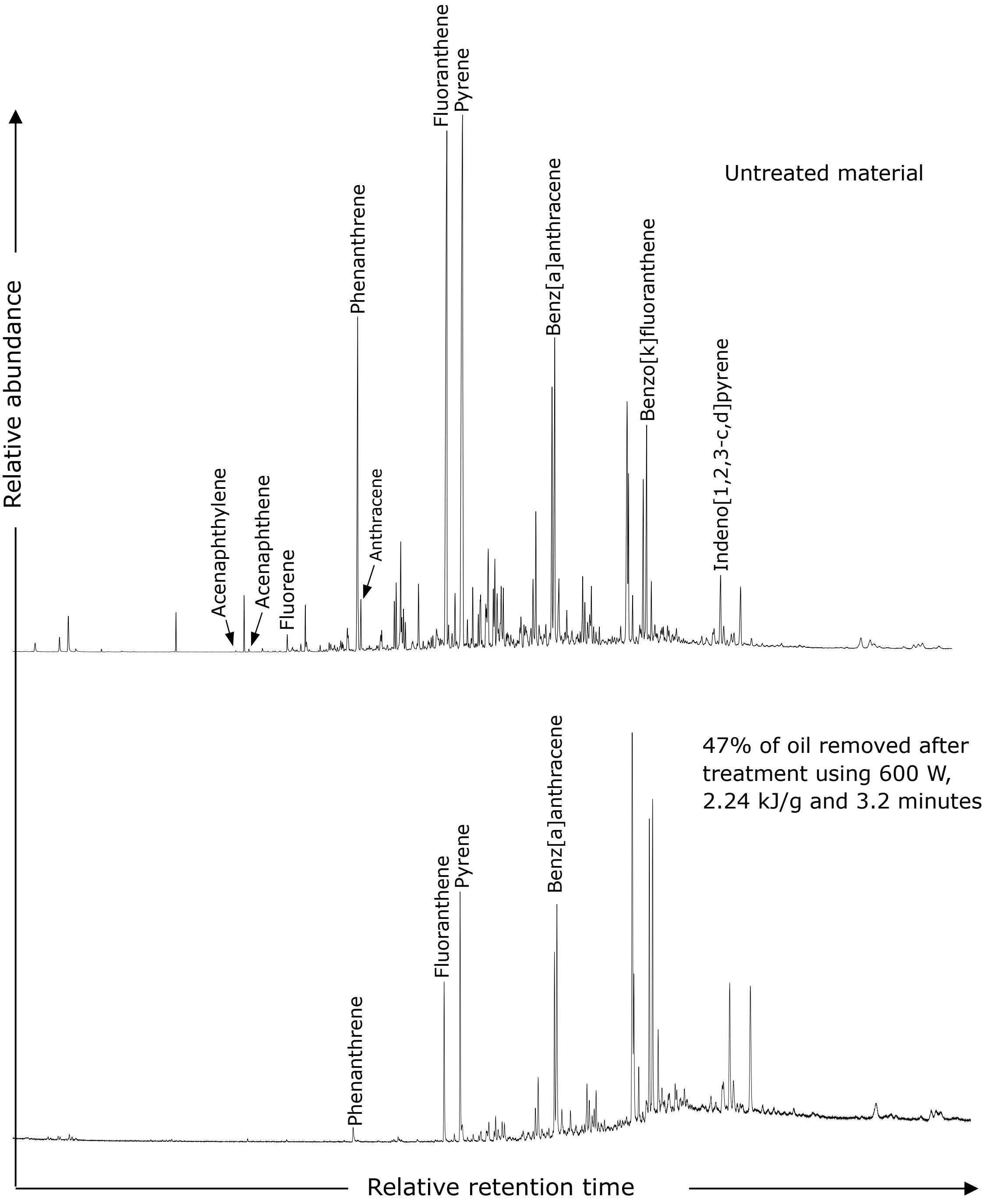


Figure 6-10: Total Ion Chromatogram (TIC) for the aromatic fraction of road planings before and after remediation using the wet microwave heating system

In conclusion, using a wet microwave heating system had no significant improvement to the 94% oil removal recorded in filter cake during remediation while using the dry microwave heating system. However, it significantly improved the oil removal yield in road planings to 87%. The effect of the wet heating system could not be estimated for Bodo and K-Dere soils due to the difficulty encountered caused by residual ethylene glycol susceptor in the materials.

6.2. Challenges encountered during MW heating of soil samples – Thermal runaway

The use of dry and wet microwave heating systems for the remediation of the contaminated soils achieved oil removals in all soil materials, especially in filter cake and road planings which recorded up to ≥87% oil removal. However, achieving such high oil removal was sometimes accompanied by a compromise on process safety due to thermal runaway. This was expected because of the dielectric behaviour of these materials at temperatures beginning from ~450°C as discussed previously (see Sections 5.2.1 and 6.1.2.1). At these temperatures, carbonaceous materials begin to form due to the decomposition of the petroleum hydrocarbons phase within these materials. Carbonaceous materials are good microwave absorbers. As a result, during microwave heating, they readily absorb microwave energy and create hotspots within the soil materials resulting in sudden increasing temperatures which then leads to changes in the process conditions in a way that causes an uncontrollable rise in temperature called thermal runaway. Thermal runaway is easily identified as it is characterised by a sharp increase in the power absorbed by the material and can result in the termination of the experiment to prevent damage to the equipment as shown in Figure 6-11.

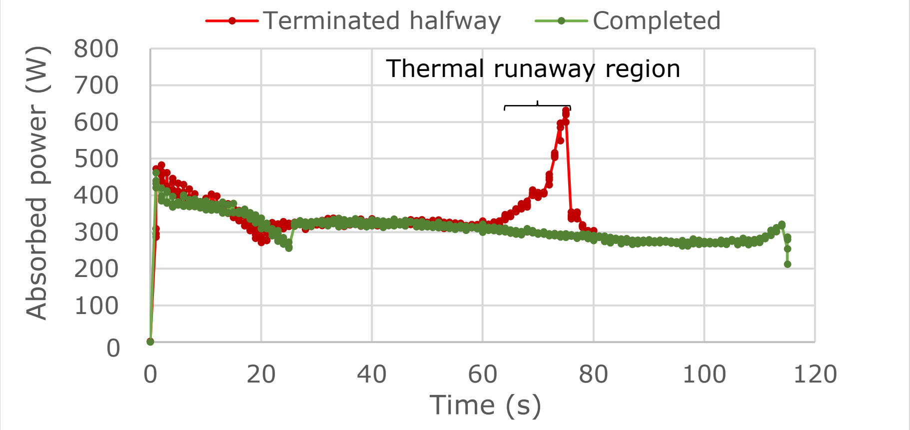
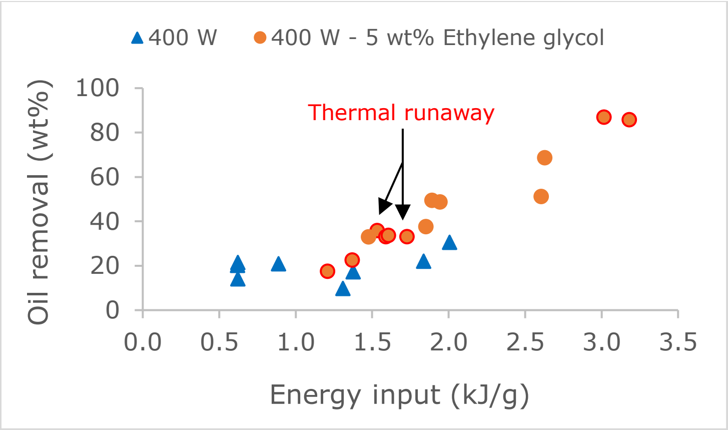
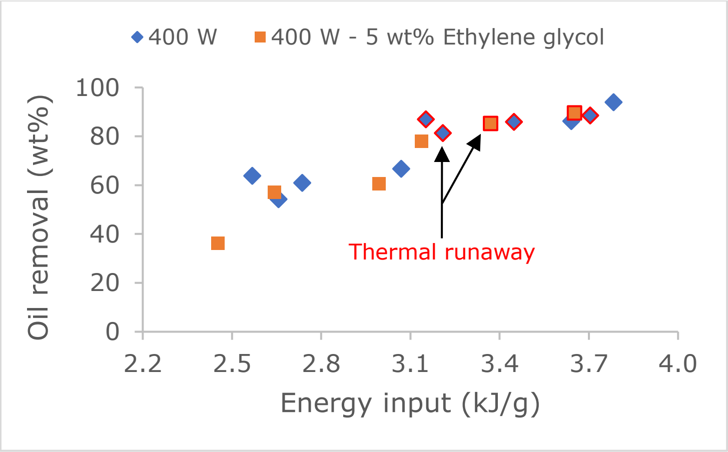


Figure 6-11: Thermal runaway during the dry microwave processing of 30 g of road planings at 800 W

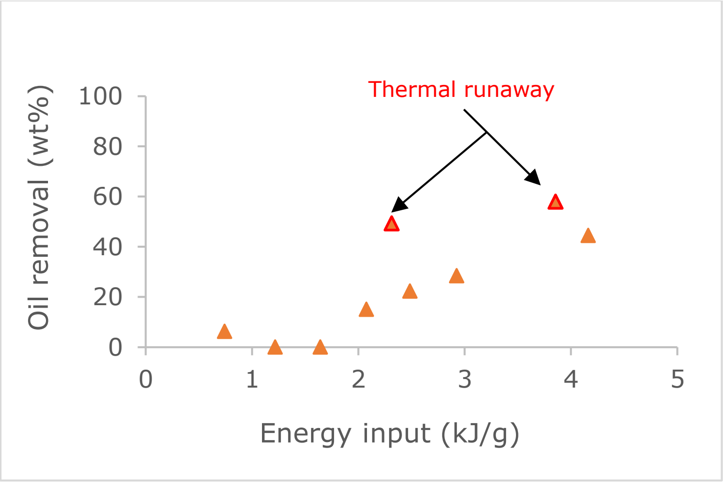
Figure 6-12 shows the results of the oil removal yields that were achieved during thermal runaway while remediating the hydrocarbon-contaminated road planings, filter cake and Bodo soil using microwave heating.



a) Road planings, 30 g



b) Filter cake, 20 g



c) Bodo soil, 20 g, 600 W

Figure 6-12: Thermal runaway encountered while processing contaminated soil materials under 1 L/min N_2 flow

Although thermal runaway also occurred at some low oil removal yields (e.g. at <35% in road planings), it was mostly encountered at high oil removal yields i.e. >85% in road planings, >80% in filter cake, and >49% in Bodo soil. No thermal runaway was encountered while processing K-Dere soils even at an energy input of 4 kJ/g achieved in 10 minutes. This agrees with the dielectric properties discussed in Sections 5.2.1 and 6.1.2.1, which indicated a very low likelihood for a thermal runaway to occur in K-Dere soil at high temperatures ≥450°C because only a gradual increment and low peak values of loss tangent and loss factors were observed. However, since there was an increase in the dielectric properties of this material at temperatures ≥450°C, there still exists the possibility of the occurrence of a thermal runaway at energy inputs beyond what was reached in these experiments. K-Dere soil was not processed beyond 4 kJ/g as its oil removal was observed to plateau with no significant change between 1.3 kJ/g and 4 kJ/g (see Figure 5-13).

When thermal runaways were encountered, hot spots were formed and were sometimes accompanied by a glow of visible light emanating from the overheating of the materials due to the very high temperatures reached. When this occurs, it compromises process safety during microwave heating by causing severe degradation of the heated material (vitrification of soil in this case) and damage to the equipment holding it (e.g. quartz reactor), thus limiting the effectiveness of the remediation technique. This often results in the termination of the experiment before the set completion time to prevent further damage. Additionally, in materials like Filter cake, rather than leveraging on the steam stripping mechanism at temperatures exceeding 100°C to get rid of petroleum hydrocarbons (below their boiling points), the oil removal mechanism during thermal runaway is predominantly attributed to thermal desorption due to the high temperatures reached in the process. Figure 6-13 and Figure 6-14 respectively show the impact of a thermal runaway on the remediated solid materials and the quartz tube during microwave heating.

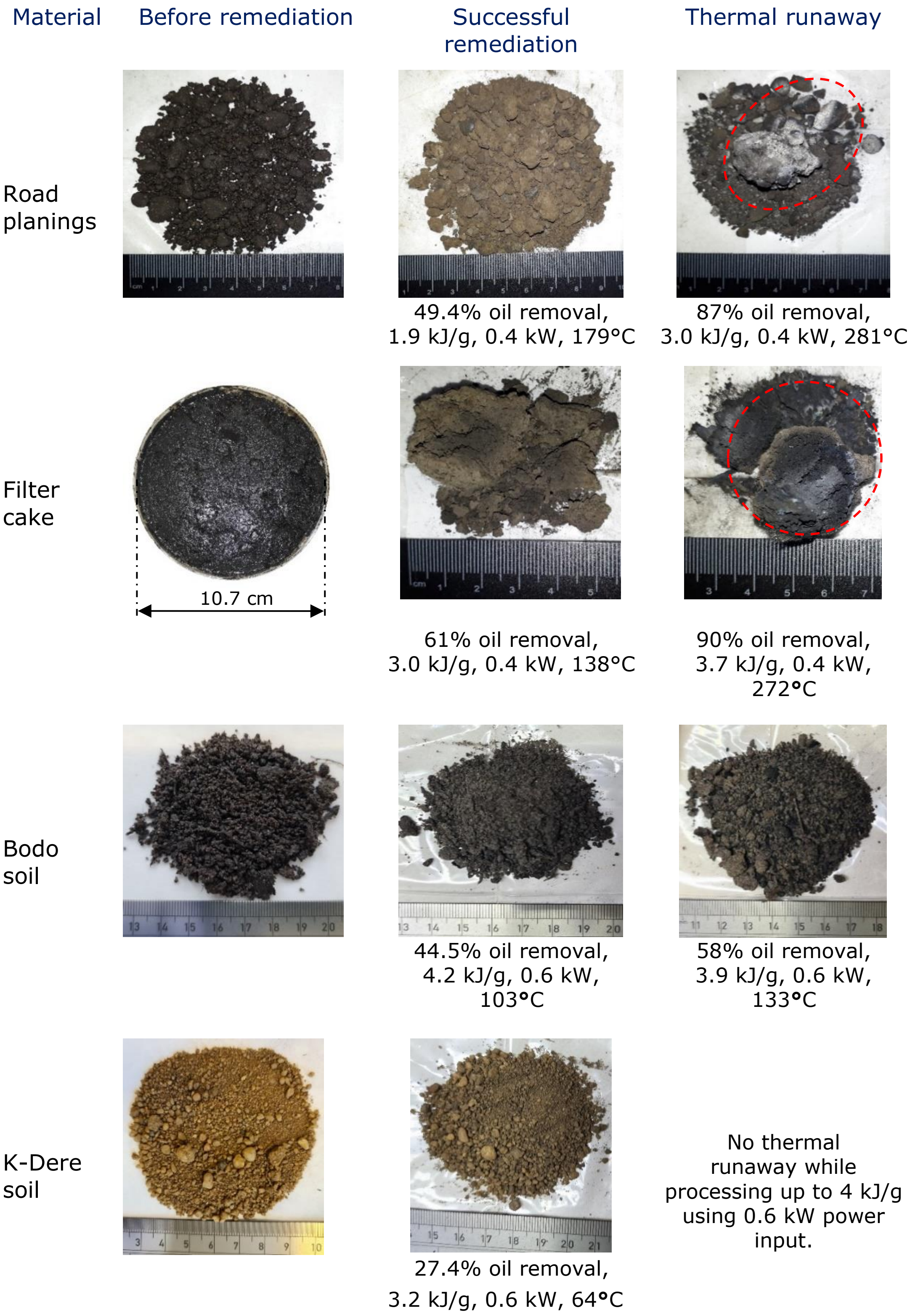
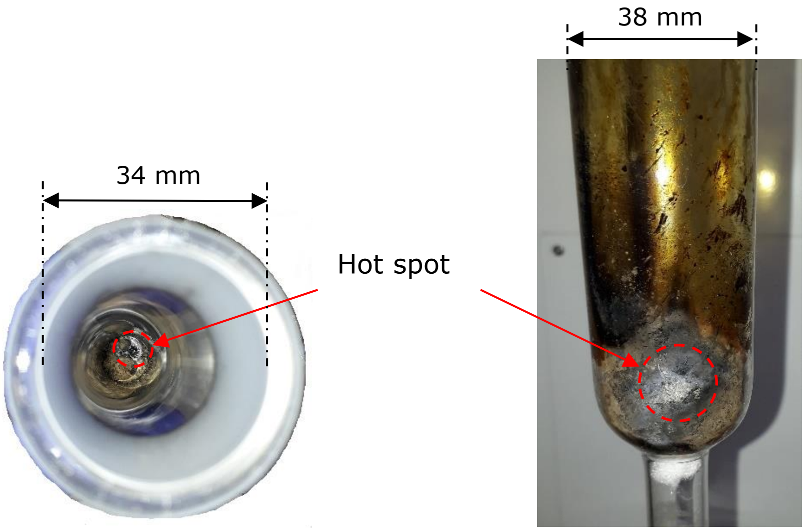
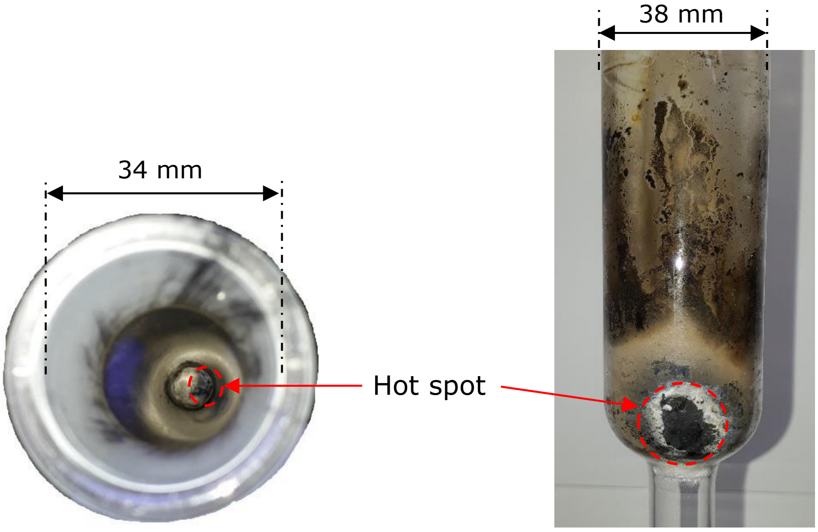


Figure 6-13: A comparison of successfully remediated soil materials with those affected by thermal runaway. Microwave heating was carried out under 1 L/min N_2 flow. Highlighted regions represent hot spots during thermal runaway



a) Road planings



b) Filter cake

Figure 6-14: Effect of thermal runaway during microwave processing of hydrocarbon-contaminated materials

In Figure 6-13, unlike in Bodo soil which showed no obvious physical degradation of the soil, the impact of thermal runaway is rather obvious in road planings and filter cake materials. Furthermore, when the carbonaceous materials formed during processing stuck to the reactor wall creating hot spots during thermal runaway, it resulted in damage to the quartz reactors as shown in Figure 6-14. Overall, it was observed that the impact of thermal runaway on the materials and equipment was little or none when processing contaminated Bodo and K-Dere soils but was rather high while processing road planings and filter cake.

Therefore, the challenge of thermal runaway must be dealt with to prevent the degradation of contaminated materials and the damage of equipment during microwave heating. Furthermore, this would help to better understand the impact of longer microwave heating times and higher energy input on oil removal yield. To achieve these, microwave heating using the inert liquid system was explored.

6.3. Microwave Heating Using Inert Liquid System - Hexane

The inert liquid system involves immersing the contaminated soils into a lossless liquid – in this case, hexane. This solvent allows the selective irradiation of the soil material without interference. However, as discussed in Section 4.4.3, non-polar solvents like hexane are known to also dissolve some aliphatic and aromatic hydrocarbon fractions as a result, control experiments were conducted to estimate the amount of oil removed by the effect of hexane alone to determine the amount removed due to microwave heating.

6.3.1. Effect of heating time and power levels on oil removal

The effect of heating time during microwave processing using the inert liquid system was studied and the results of these experiments are presented in Figure 6-15[16]. For three of the contaminated materials, microwave heating had little effect compared with the control, but for Bodo soil, it had a big effect. In terms of their combined effects on oil removal, the following behaviours were observed in the contaminated materials. With increasing microwave heating time, little increase in oil removal was observed in road planings. For example, at 500 W, oil removal increased from 34% at 2.5 minutes to 40% at 15 minutes. However, at 400 W and 600 W, there was no significant change in oil removal with time once

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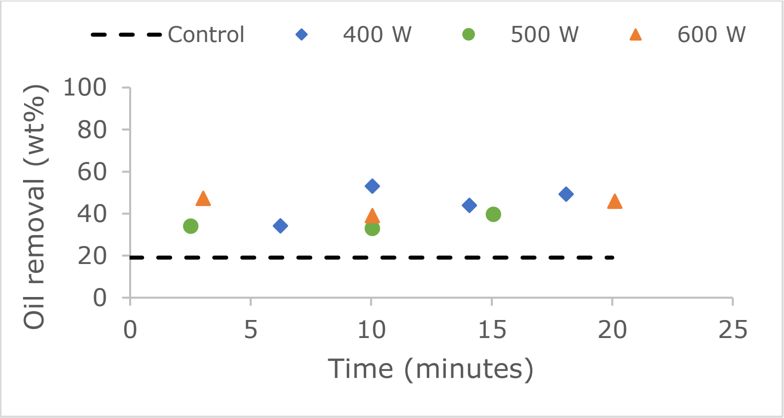
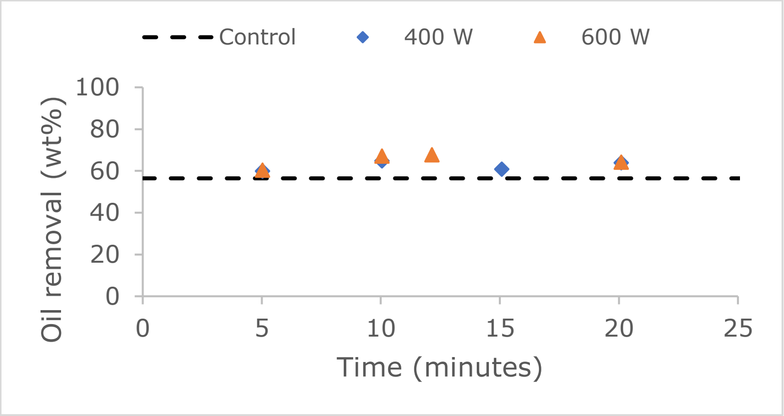
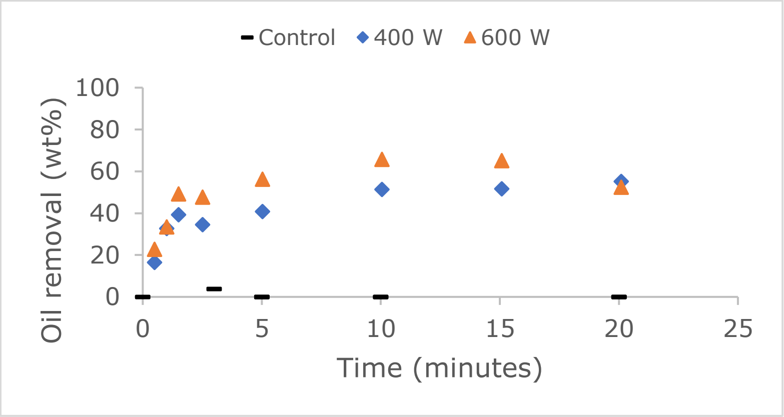
[16] For road planings and filter cake materials, the control experiment represents an average of three experiments conducted at room temperature for 40 minutes – the time the sample spends in hexane from loading to separation during a typical microwave experiment. For all the materials, the reactor was fitted with an overhead condenser to allow the reflux of vaporised hexane during heating.



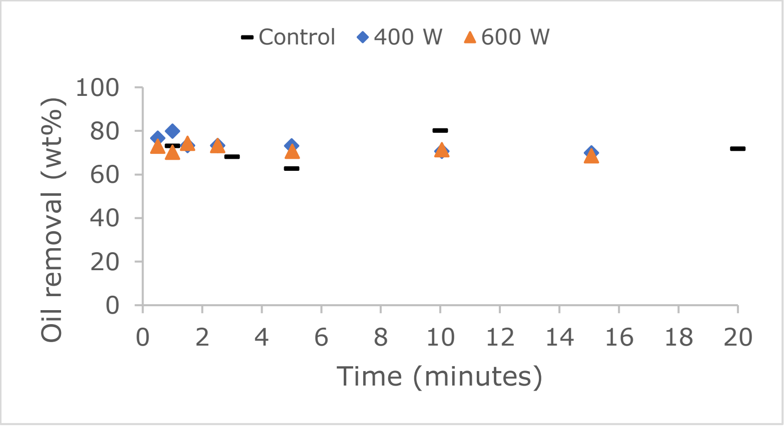
a) Road planings



b) Filter cake



c) Bodo soil



d) K-Dere soil

Figure 6-15: Effect of time on the microwave heating of 10 g of contaminated soils in 100 mL hexane. Control experiments represent the results when the soil materials were immersed in hexane at room temperature without microwave heating the peak yield values of 53% (in 10 minutes) and 47% (in 3 minutes) were reached respectively. Similar behaviour was observed in filter cake as oil removal increased respectively from 60% to a maximum of 68% between 5 and 12 minutes, after which there was no further increment.

In Bodo soil, oil removal increased from 17% at 0.5 minutes to a maximum of 55% after 20 minutes at 400 W. In comparison, more oil was removed from Bodo soils at a shorter time using 600 W than when 400 W was used. For example, at 600 W, oil removal increased from 23% at 0.5 minutes to a maximum of 66% in 10 minutes for Bodo soil which was half the time required to achieve 55% at 400 W. In K-Dere soils, a maximum oil removal of 80% at 1 minute was achieved and no further significant change was observed beyond this time. Although running more experiments below 5 minutes for road planings and filter cake would have given a clearer behaviour of oil removal with time as shown in Bodo and K-Dere soils, this was not explored because the goal of investigating the inert liquid system was to overcome thermal runaway while achieving the maximum possible oil removal from the materials.

It is important to note that the oil removal results presented in Figure 6-15 for all the materials are from the combined contribution of hexane and microwave heating. Although a maximum oil removal of 53% (road planings), 67% (Filter cake), 66% (Bodo soil) and 80% (K-Dere soil) was achieved, the contribution of microwave heating in these peak yields was more significant in Bodo soil. Apart from Bodo soils, the contribution of hexane in decontaminating these materials (without heating effects) was more than that from microwave heating. The low oil content (3.0%) and sandy nature of K-Dere soil made it easier for hexane to wash off 72% of the hydrocarbon contamination within the material within 1 minute without microwave heating. Apart from Bodo soil, it is very likely that heating the contaminated material in hexane using conventional heating could achieve the same results observed for road planings, filter cake and K-Dere soils under the microwave-inert liquid system.

The microwave heating of the contaminated materials beyond the heating times achieved while using the dry and wet microwave heating systems was made possible with the use of the inert liquid system and at the same time overcoming thermal runaway. Within the heating period studied in this work, microwave heating times of up to 20 minutes in road planings, filter cake and Bodo soil, and 15 minutes in K-Dere soil were achieved whereas, only a maximum of ≤8 minutes for the dry heating of road planings, filter cake and Bodo soil, and ≤6.5 minutes for the wet heating of road planings and filter cake were achieved without the occurrence of thermal runaway[17].

6.3.2. Effect of energy input and power levels on oil removal

The effect of energy input between 400 and 600 W are presented in Figure 6-16. As energy input increased, an increment in oil removal was observed in road planings, filter cake and Bodo soils. This increment in oil removal was observed to increase from 34% at 2.5 kJ/g to a maximum of 53 kJ/g in road planings, and from 60% at 6.4 kJ/g to 68% at 15 kJ/g in filter cake. In Bodo soils, oil removal increased from 17% at ~1 kJ/g to a maximum of 66% at 15 kJ/g. However, in K-Dere soil, the effect of energy input on oil removal was low as most of the oil contamination removed up to a peak value of 80% at 0.7 kJ//g was because of the contribution of hexane rather than microwave heating. While the power level made no significant difference in the oil removed from road planings, filter cake and K-Dere soil, it had a significant effect on Bodo soil as the amount of oil removed while using 400 W was less than those observed at 600 W. For example, at ~23 kJ/g, the oil removed while using 400 W was 52% whereas it was 65% at

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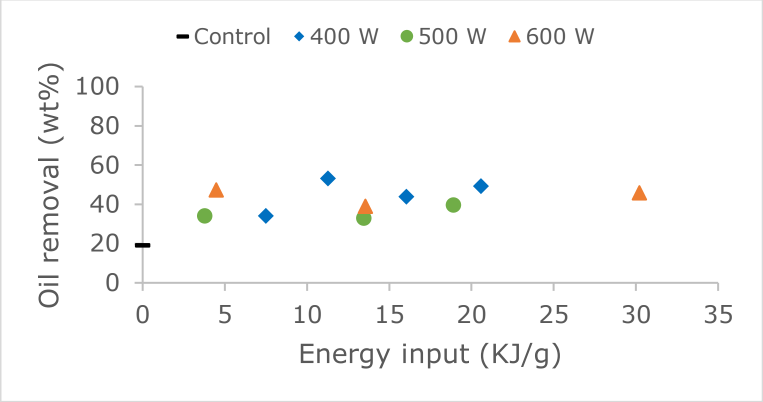
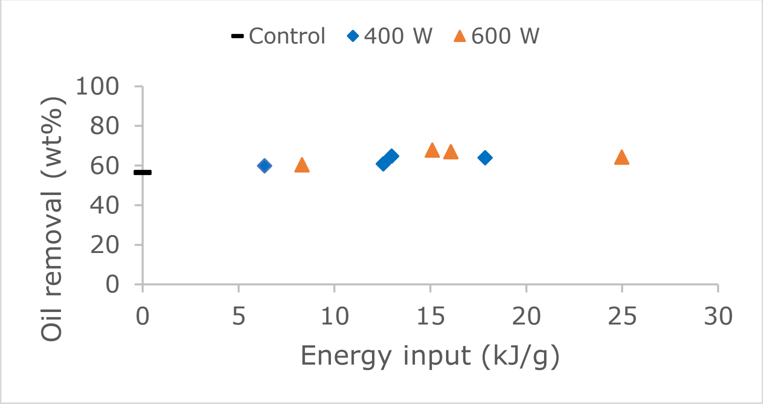
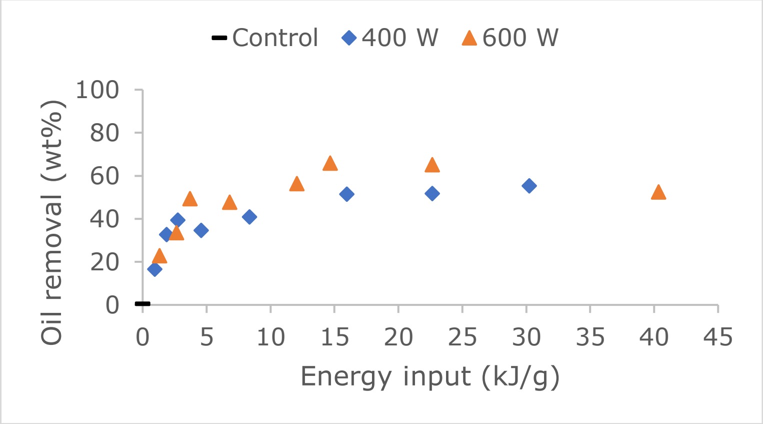
[17] K-dere soil was not included since no thermal runaway was encountered during the dry heating of this material. Also, Bodo and K-dere soils were not included in the wet heating experiment as they were not explored further using the wet system as discussed in Section 6.1.2.2.



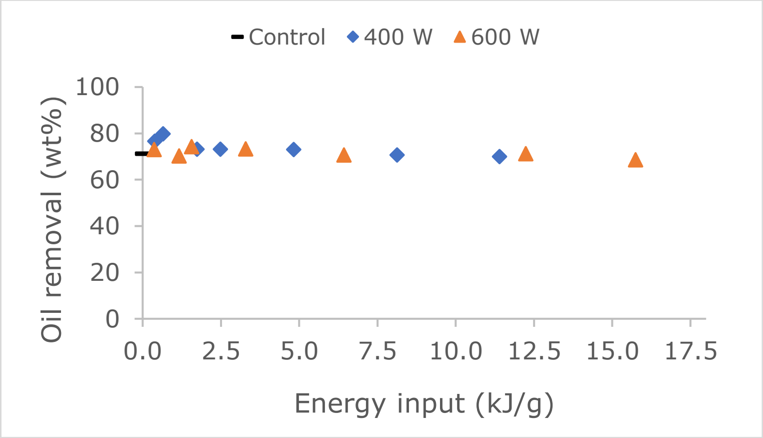
a) Road planings



b) Filter cake



c) Bodo soils



d) K-Dere soils

Figure 6-16: Effect of energy input on the microwave heating of 10 g of contaminated soils in 100 mL hexane. The control experiment represents the average results when the soil materials were immersed in hexane at room temperature without microwave heating

600 W power input. This indicates that for the processing of Bodo soil using the inert liquid system, more oil removal can be achieved for the same energy input using a higher forward power compared with lower ones.

The microwave heating of the contaminated materials using an inert liquid encountered no thermal runaway limitations while processing them up to energy inputs of 30 kJ/g, 25 kJ/g, 40 kJ/g and 16 kJ/g in road planings, filter cake, Bodo soil and K-Dere soil. This was because, when the material is heated with microwave energy, some of the heat generated from the core of the materials dissipates into hexane thus preventing the overheating of the material observed in dry and wet heating systems. The continuous reflux of the system maintains the temperature around the heated soil material up to the boiling point of hexane (~69^{o}C). However, this comes with a trade-off as more energy input is required to remediate the soil materials to achieve high oil removal yields like those obtained using the dry and wet microwave heating systems. Apart from the contribution of microwave energy in removing oils from the materials, the rise in the temperature of the lossless solvent also enhances the soil washing which results in further oil removal. Figure 6-17 shows a visual look at oil removal with time and energy input during microwave heating using the inert liquid system.

Unlike road planings, filter cake and Bodo soil that had a clear hexane solution when the contaminated materials were immersed in the solvent before microwave irradiation, K-Dere soils behaved differently as some of the oil within the soil material was observed to have been washed off by the solvent. This was indicated by the yellowish colour known to signify the presence of aromatic fractions within crude oil-containing materials and could also contain saturates (aliphatic) that are clear or colourless (Gharbi et al., 2018). More than 70% of the oil was removed in K-Dere soil within 1 minute without microwave heating as confirmed by the controlled experiment presented in Figure 6-15 (d). Once the peak oil removal of 77% in K-Dere soil was achieved during microwave heating at 0.4 kJ/g for 0.5

minutes, no further change in colour was observed. Figure 6-18 shows the GC-MS analysis of the hydrocarbon liquid collected during the inert liquid treatment of K-Dere and Bodo soils after hexane was evaporated. This confirms the oil removed

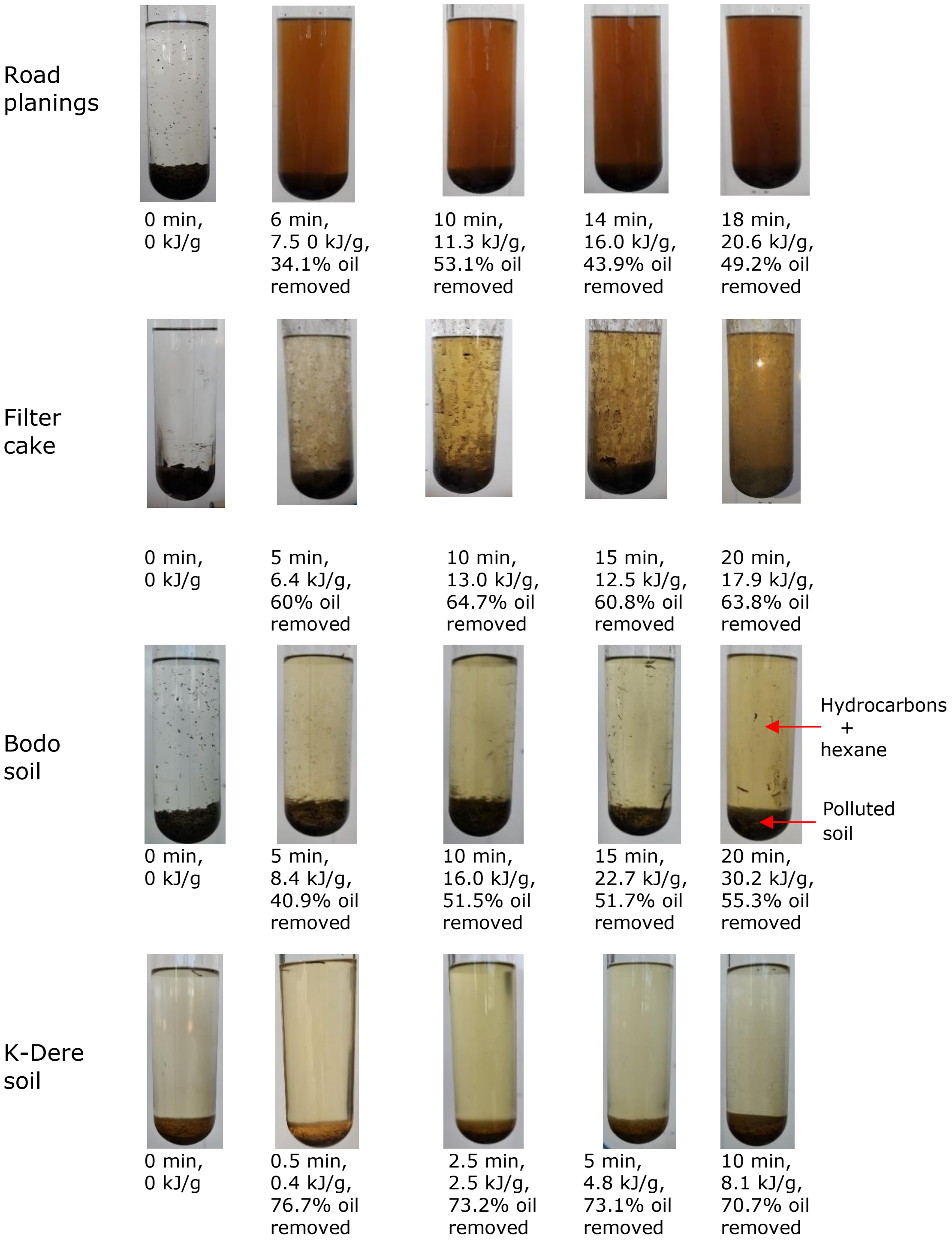


Figure 6-17: Microwave heating of 10 g of oil-contaminated materials immersed in 100 mL hexane at 400 W. The internal diameter of the quartz reactor is 34 mm

from the materials due to the presence of the hydrocarbon contamination recovered especially below nC_{20}.

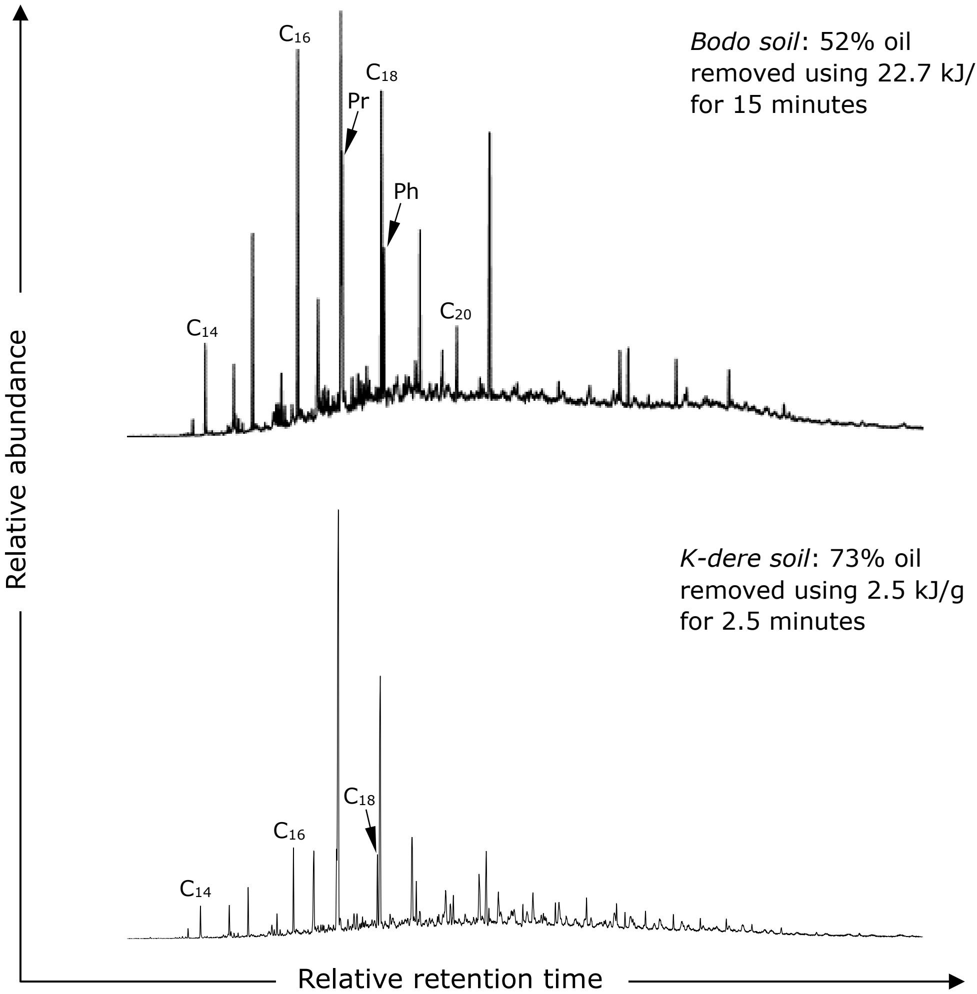


Figure 6-18: Gas chromatograms (GC) for the aliphatic fractions of the hydrocarbon liquid collected during the inert liquid microwave treatment of Bodo and K-Dere soils at 400 W. Where Pr: Pristane, Ph: Phytane, Cn: normal alkane

With increasing oil removal in filter cake and Bodo soil, the yellowish colour became more obvious confirming the removal of more oil fractions. This colour change was however dark brown in road planings indicating the presence of the combination of resins and asphaltenes since road planings are known to contain heavier ends of crude oil fractions like tars (refer to Table 5-2). This was confirmed by the asphaltene precipitation and fractionation results shown for the extracted oil in soils before remediation in Table 6-1.

Table 6-1: Extractable organic matter composition

Property	Road planings	Filter cake
Oil content, (%w/w) - *dry basis*	2.9 ± 0.14	10.4 ± 0.15
Maltene (%w/w)	74.9 ± 1.4	88.8
Aliphatic hydrocarbon	15.5 ± 0.7	56.0
Aromatic hydrocarbon	33.8 ± 0.6	8.5
Polar hydrocarbon	50.6 ± 0.8	35.3
Asphaltene (%w/w)	25.1 ± 1.4	11.2

6.4. Conclusions

Microwave heating using the inert liquid system enabled the overcoming of thermal runaway encountered while remediating oil-contaminated materials using the dry and wet microwave heating systems. Additionally, this heating system increased the amount of oil removed during the dry heating of road planings, Bodo and K-Dere soils i.e. from 37% to 53% in road planings, from 44% to 66% in Bodo soil, and from 30% to 80% in K-Dere soil. However, these increases in oil removal yields were because of the combined effect of microwave heating and the inert liquid (hexane). Unlike in other materials, a drop in the oil removal yield was recorded in filter cake from ~94% (in the dry and wet heating systems) to 68% when using this heating system. A detailed comparison of the various approaches used in remediating the contaminated soil materials is discussed in Chapter 7 to understand the merits and demerits of various approaches for removing petroleum hydrocarbons from soil materials.

CHAPTER 7

7. THERMAL TECHNOLOGY EVALUATION

In previous Chapters, the remediation of petroleum-contaminated solid materials using the microwave heating system was discussed extensively. Three technology configurations were explored for this purpose, namely the dry microwave heating system that processes the materials without modification, the wet microwave heating system that involves wetting the contaminated solid materials with ethylene glycol susceptor before processing, and the microwave heating using an inert liquid system that remediates the contaminated materials after immersing them in a lossless liquid (in this case, hexane). Since the most mature and widely used thermal technology for the remediation of solid materials contaminated with petroleum hydrocarbons is the conventional heating system using thermal desorption (Wang et al., 2021; Zhao et al., 2019), this chapter undertook a few experiments using the thermal desorption technology from low to high temperatures to serve as a basis for comparison to the microwave heating system. This is to ascertain the merits, and the demerits of the microwave heating systems used in this work. Additionally, the chapter re-evaluates the initial technology selection decision matrix carried out in Chapter 3 and outlines some recommendations as to what approach is considered suitable for decontaminating road planings, filter cake, Bodo and K-Dere soils which could also extend to other materials with similar properties.

7.1. Conventional Heating System

The effect of sample holding time on oil removal was studied for road planings at 400°C - which is considered as medium temperature thermal desorption (MTTD) (Wang et al., 2023), and at a heating rate of 20°C/min. The oil removal after conventional heating was estimated as discussed in Section 4.2.2, and the result presented in Figure 7-1.

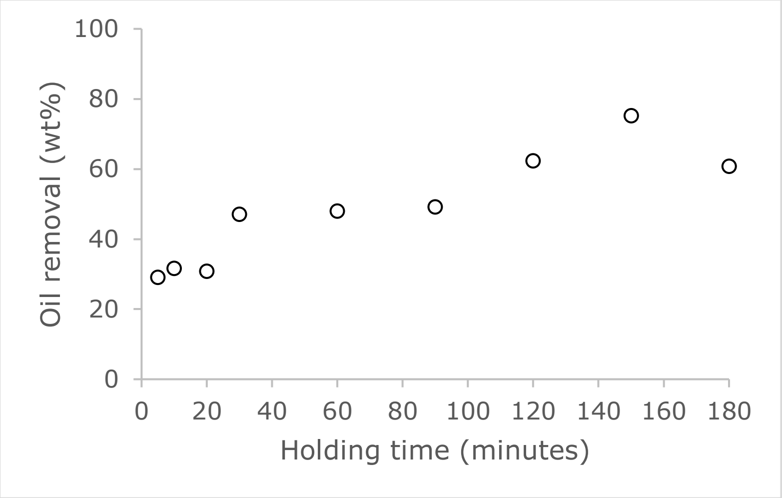


Figure 7-1: Effect of holding time on oil removal during the thermal desorption of 20 g of road planings at 400°C using a 20°C/min heating rate and 1 L/min N2 flow

An increase in the sample holding time resulted in a corresponding increase in oil removal achieving up to ~75% of oil removal yield at 2.5 hrs. 400°C was sufficient to volatise the heavy oil contamination in road planings thus achieving up to 75% oil removal, however, it was only possible at a longer holding time of up to 150 minutes. Overall, increasing holding time led to a corresponding increase in oil removal.

The study of the effect of temperature on the decontamination of road planings at a 30-minute holding time is presented in Figure 7-2.

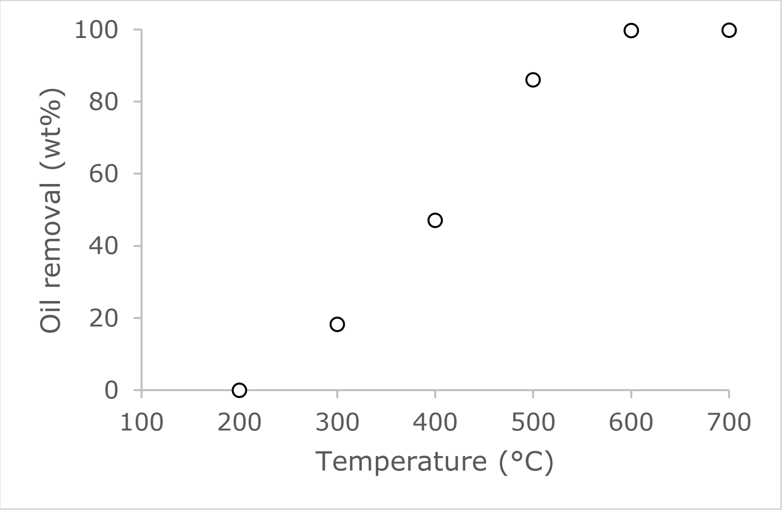


Figure 7-2: Effect of temperature on oil removal during the thermal desorption of 20 g of Road planings at 20°C/min heating rate, 1 L/min N2 flow, and 30 minutes holding time

The rate of oil removal in road planings increased rapidly from ~0% at 200°C to 86% at 500°C, and then slowly beyond 500°C up until 600°C where it plateaus – achieving 99.7% of oil removal. It was observed that for low-temperature thermal desorption (LTTD) i.e. at 200°C, no oil removal was achieved. This is likely because road planings comprises heavy oil contamination from its bituminous/tar composition (see Section 5.1) that would require higher temperatures than those of LTTD to be volatilised. Between 300 - 400°C i.e., medium temperature thermal desorption (MTTD), <50% of oil was removed from the material. However, high-temperature thermal desorption (i.e. at temperatures ≥500°C) achieved most of the oil removal within the set holding time of 30 minutes, as the volatility of heavy oil was readily increased at these temperatures leading to very high oil removal up to 99.8%.

A comparison of the thermal desorption of filter cake, Bodo soil and K-Dere soil at a few temperatures (Figure 7-3), showed that, unlike Bodo soil and road planings that achieved no significant oil removal at 200°C, K-Dere soil recorded up to 24% signifying that the material consists of some light hydrocarbon contamination that is easily volatilised at temperatures ≤200°C.

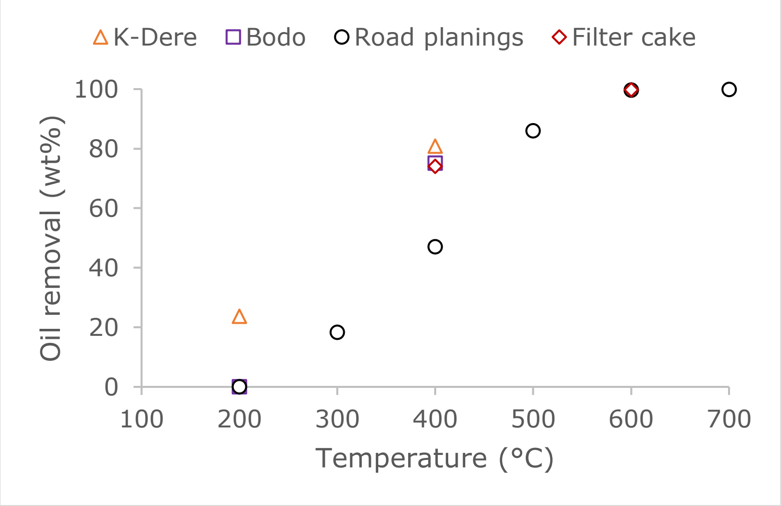


Figure 7-3: Comparison of the thermal desorption of 20 g of contaminated solids at 20°C/min heating rate, 1 L/min N_2 flow, and 30-minute holding time

At 400°C, 74%, 75% and 81% oil removal yields were achieved in filter cake, Bodo soil and K-Dere soil respectively which were greater than (by at least 27%) what was achieved in road planings at the same temperature. This confirms that the oil contamination within these materials is not comprised of heavy bituminous ends like those in road planings. Similar to what was achieved in road planings at 600°C, Filter cake achieved up to 99.8% oil removal indicating that this temperature is sufficient to desorb most if not all the oil contamination within all the materials.

However, it can be seen in Figure 7-4 that, as oil removal increased with increasing temperature, the material's physical structure was also damaged, especially at ≥600°C for road planings and filter cake - which is also expected for Bodo and K-Dere soils if treated at such temperatures. This has the potential to impact the end use of the soil material after processing especially for sensitive applications like agricultural purposes. This is because, unlike in microwave heating, thermal desorption raises the temperature of the soils to or greater than the boiling points of the contaminants before the soils can be decontaminated, and in the process, it compromises the soil’s characteristics thus limiting its re-use. For example, Zhao et al. (2019) reported that high-temperature thermal desorption will destroy soil structure, volatilise and pyrolyze soil organic matter and the carbonate in soil minerals. Additionally, O'Brien et al. (2018) showed a rapid deterioration in soil organic matter, an increase in soil pH, alteration in soil nutrients, collapse of soil mineralogy, and particle size distribution when heated at >450^{o}C for 30 min, causing diminished plant and microbial biomass production. Furthermore, Vidonish et al. (2016a) found a pH increment from 7.2 to 11.1 and 7.7 to 11.9 respectively upon remediating two heavy hydrocarbon-polluted soils (by crude oil) at 650^{o}C via conventional heating by incineration, and pH increase is known to inhibit plant tolerance, root and leaf growth and cation exchange capacity (Troeh and Thompson, 1993). Therefore, since land reclamation requires that these deteriorated soil characteristics be addressed, this has the potential to increase the cost of thermal desorption since these issues must be taken into account while considering the overall land reclamation cost (O'Brien et al., 2018).

Figure 7-4: Thermal desorption of 20 g of hydrocarbon-contaminated materials at 30 minutes holding time. 1 L/min N_2 flow was used as a purge gas

7.2. Microwave and Conventional Heating Systems Compared

The energy requirement of a thermal remediation plant is an important parameter that should be considered from the process economics point of view. This is because it would potentially impact the overall cost of remediation. For example, a thermal remediation unit that consumes high energy would potentially lead to a higher remediation cost, unlike a process that requires less energy. The total energy required to power a thermal remediation system for the decontamination of the soil materials comprises the energy required to heat the material as well as the energy required to compensate for heat losses to the system and the environment during processing. While the pre and post-processing steps for remediating petroleum-contaminated soil using both microwave dry heating and conventional heating systems are alike, the key differentiation lies in the heating process. This section will therefore focus on comparing these systems.

7.2.1. Energy requirement for microwave heating

The microwave energy requirement to heat the contaminated soil material (E) is estimated using Equation 7-1,

$$E = \sum_{i=1}^{n-1} (\frac{P_i + P_{i+1}}{2})(t_{i+1} - t_i) \qquad 7\text{-}1$$

Where P_i (kW) and t_i (s) are the power absorbed by the contaminated materials and the heating time respectively recorded during the entire microwave processing time via the HomeSoft software for Homer data logging.

Additionally, although hexane is a lossless solvent and does not absorb microwave energy during microwave irradiation of the contaminated soils using the inert liquid system, energy from the heated soil is however lost to hexane by conduction during processing. Similarly, energy is also lost to the nitrogen purge gas in the dry and wet microwave heating systems. These need to be accounted for as part of the energy consumed in the process.

To estimate the energy losses to hexane and nitrogen, the parameters in Table 7-1 and Table 7-2 were used in Equation 7-2 and 7-3.

Table 7-1: Parameters for the estimation of heat loss using an inert liquid system. 100 mL of hexane was used (NIST, 2023)

Parameters	Values
Ambient temperature, T_1 (K)	273
Boiling point (bp) of hexane, T_2 (K)	342
Specific heat of hexane, C_h (kJ/kg.K)	2.252
Latent heat of hexane at bp (69°C), L_h (kJ/kg)	335.68
Density of hexane at 20°C, ρ_h (kg/m^3)	659.38
Volume of hexane used, V_h (m^3)	1×10^{-4}

Table 7-2: Parameters for the estimation of heat loss to nitrogen purge gas using the wet and dry microwave heating systems (NIST, 2023)

Parameter	Road planings		Filter cake		Bodo soil	K-Dere soil
	MDH	MWH	MDH	MWH	MDH	MDH
Heating time, t (s)	186	390	324	300	480	480
Temperature, T_1 (K)	293	293	293	293	293	293
T_2 (K)	455	625	498	501	376	347
Density (ρ) of N_2 at T_2, ρ (kg/m^3)	0.7498	0.5458	0.6850	0.6809	0.9074	0.9833
Density (ρ) of N_2 at T_1, (kg/m^3)	1.1648					
Specific heat of N_2, c_{N2} (kJ/kg.K)	1.0413					
N_2 flowrate, F_r (m^3/s)	1.6×10^{-5}					

MDH: Microwave dry heating, MWH: Microwave wet heating

The heat loss to hexane via conduction (E_h),

$$E_h = \rho_h V_h C_h (T_2 - T_1) + \rho_h V_h L_h \qquad 7\text{-}2$$

Heat loss to N_2 purge gas (E_N) is estimated as,

$$E_N = (F_r \rho_{average\ at\ T1,T2}) C_{N2} (T_2 - T_1) t \qquad 7\text{-}3$$

7.2.2. Energy requirement for conventional heating

The energy required to heat the contaminated soil material using thermal desorption is estimated using the parameters presented in Table 7-3.

Table 7-3: Energy calculation parameters for the remediation of contaminated soil using thermal desorption. 20 g of soil (*m_s*) was used (NIST, 2023; Elmatic-Ltd, 2024; Li et al., 2018; Perry and Green, 2007; Shanghai Zhuqing New Materials Technology Co., 2024)

Parameter		Road planings	Filter cake	Bodo soil	K-Dere soil
Heating time,	*Temperature rise,* t_1 (s)	25 x 60	19 x 60	19 x 60	11 x 60
	Holding time, t_2 (s)	30 x 60	30 x 60	30 x 60	30 x 60
Temperature*:*	*Ambient*, T_1 (K)	293	293	293	293
	Final, T_2 (K)	773	673	673	673
Specific heat, c_s (kJ/kg.K)		0.9211 (asphalt)	0.9378 (clay)	0.7997 (sand)	0.7997 (sand)
Density of N_2 at T_2, ρ (kg/m^3)		0.4414	0.5069	0.5069	0.5069
Density of N_2 at T_1, ρ (kg/m^3)		1.1648			
Specific heat of N_2, c_{N2} (kJ/kg.K)		1.0413			
N_2 flowrate, F_r (m^3/s)		1.6×10^{-5}			
Latent heat of water, L_w (kJ/kg)		2257			
Latent heat of petroleum oil, L_o (kJ/kg)		577			
Specific heat of quartz, c_q (kJ/kg.K)		0.7118			
Mass of quartz reactor, m_q (kg)		0.0716			
Outer surface area of furnace, A (m^2)		0.177			
Furnace heating rate, r (K/s)		0.3			
Typical energy density of recovered oil, E_d (kJ/kg)		46020			
Thickness of furnace insulation, W (m)		0.125			
Thermal conductivity of furnace insulation i.e. for the refractory ceramic fibre at T_2, K (W/m.K)		0.13	0.10	0.10	0.10
Heat transfer coefficient, U = K/W, (W/m^2.K)		1.0	0.80	0.80	0.80
Radiation loss factor at T_2, R_L (kW/m^2) - Estimated		0.7	0.6	0.6	0.6

Where the,

Energy absorbed by the soil material at temperature rise (E_1),

$$E_1 = m_s C_s (T_2 - T_1) + m_w L_w + m_o L_o \tag{7-4}$$

Energy absorbed by the quartz reactor at temperature rise (E_2),

$$E_2 = m_q C_q (T_2 - T_1) \tag{7-5}$$

Heat loss from the furnace surface during the temperature rise (E_3),

$$E_3 = \frac{AR_L}{2} . t_1 \tag{7-6}$$

Equation 7-6 is divided by 2 because the average surface losses during the heat-up period (temperature rise) are approximately half the steady losses at the final operating temperature (Elmatic-Ltd, 2024).

Heat loss to nitrogen purge gas at temperature rise (E_4) and at holding time (E_5),

$$E_4 = (F_r \rho_{aver.\ at\ T1,T2}) t_1 C_{N2} (T_2 - T_1) \tag{7-7}$$

$$E_5 = (F_r \rho_{aver.\ at\ T1,T2}) t_2 C_{N2} (T_2 - T_1) \tag{7-8}$$

Heat loss from the furnace surface at constant temperature (E_6),

$$E_6 = UA(T_2 - T_1) t_2 \tag{7-9}$$

The total energy requirement for the remediation of contaminated soils (E),

$$E = E_1 + E_2 + E_3 + E_4 + E_5 + E_6 \tag{7-10}$$

If all the oil removed from the soil is recovered, the energy that could be produced from the oil (E_r) based on its typical energy density (E_d) can be estimated by,

$$E_r = m_s R E_d \tag{7-11}$$

Table 7-4 compares the estimated energy requirement results during the remediation of contaminated soil materials using microwave and conventional heating.

Table 7-4: Comparison of various technologies for the remediation of contaminated soils at some selected oil removal yield

Parameter\Material	Road planings				Filter cake				Bodo soil			K-Dere soil		
	TD	MDH	MWH	MIL	TD	MDH	MWH	MIL	TD	MDH	MIL	TD	MDH	MIL
Oil removed yield (%)	86	37	86	53	74	86	85	68	75	44	66	81	30	73
Soil mass used, m_s (g)	20	30	30	10	20	20	20	10	20	20	10	20	20	10
Recovered oil, *R* based on yield (%)	2.49	1.07	2.49	1.54	7.70	8.94	8.94	7.07	0.98	0.57	0.86	0.71	0.26	0.64
Soil mass reduction after processing (%)	10.2	9.1	21.9	7.9	58.3	63	63.1	59.7	15.7	19.1	14.5	3.1	3.7	5.9
Input power (kW)	0.7	0.6	0.4	0.6	0.7	0.4	0.4	0.6	0.7	0.6	0.6	0.7	0.6	0.6
Temperature (°C)	500^a	182^*	352^b	65^c	400^a	225^b	228^b	76^c	400^a	103^b	66^c	400^a	74^b	60^c
Time (minutes)	55.0	3.1	6.5	10.0	49.0	5.4	5.0	12.1	49.0	8.0	10.0	41.0	10.0	2.5
Energy absorbed by polluted soil, E_1 (kJ)	12.5	46	95	113	31.8	73	68	151	12.6	83	146	7.5	79	32
Energy absorbed by reactor, E_2 (kJ)	24.4	Negligible [d]			19.4	Negligible [d]			19.4	Negligible [d]		19.4	Negligible [d]	
Heat loss via furnace surface at temperature rise, E_3 (kJ)	92.8				60.5				60.5			35		
Heat loss to N_2 purge gas at temperature rise, E_4 (kJ)	9.6	0.4	1.4		6.0	1.0	1.0		6.0	0.7		3.5	0.5	
Heat loss to N_2 purge gas at holding temperature, E_5 (kJ)	11.6				9.5				9.5			9.5		
Heat loss via furnace surface at holding temperature, E_6 (kJ)	152.7				96.7				96.7			96.7		
Heat loss to hexane E_h (kJ)				29.4				29.4			29.4			29.4
Total energy consumption, *E* (kJ)	304	46	96	142	224	74	69	180	205	84	175	172	80	61
Energy from recovered oil, E_r (kJ)	23	10	23	14	71	82	82	65	9	5	8	7	2	6

Oil contents of materials before processing, road planings (2.9%), filter cake (10.4%), Bodo soil (1.30%), and K-Dere soil (0.88%). [a] Measured soil temperature, [b] Maximum temperature recorded at reactor walls, [c] Maximum recorded temperature at reactor walls (reactor contains hexane and contaminated soil mixture). Estimated from temperatures of similar % oil removal yield for MWH. TD: Thermal desorption, MDH: Microwave dry heating, MWH: Microwave wet heating, MIL: Microwave inert liquid heating. [d] Energy absorbed by quartz reactors is negligible as they are transparent to microwaves.

In road planings, the energy required to achieve ~86% oil removal using thermal desorption and microwave wet heating systems were compared. Results from Table 7-4 revealed that 304 kJ (thermal desorption) and 96 kJ (microwave wet heating) are required to achieve the same oil removal efficiency. This is a 68% drop in the energy consumed when the microwave wet heating system was used. Similarly, in filter cake, less energy i.e. 74 kJ and 69 kJ were required to achieve ~86% oil removal in microwave dry heating and microwave wet heating systems respectively when compared to the energy required to achieve 74% oil removal in thermal desorption (224 kJ). While the microwave heating systems require lesser energy (about one-third) to achieve oil removal yields similar to those of thermal desorption, the microwave dry heating was observed to require ~7% more energy than the wet heating system when remediating filter cake. Additionally, in filter cake, less energy (~27 kJ) was required to achieve about 86% oil removal than those required in road planings when using the same microwave wet heating system.

The high energy consumed in thermal desorption can be explained by the longer heating time and high temperatures required to achieve the desired oil removal yield. While only about 5-7 minutes was needed to achieve ~86% oil removal from road planings and filter cake materials using microwave heating, >49 minutes was needed to achieve a similar yield in thermal desorption. The longer heating time observed in thermal desorption during soil remediation allowed for more energy losses to the system and the environment via the furnace's outer surface as well as the nitrogen purge gas.

Among the microwave heating technologies explored, soil remediation using the microwave inert liquid system required the most energy. For example, the energy required to achieve 66% oil removal in Bodo soil is twice the energy required to achieve a lesser oil removal of 44% using the microwave dry heating system. This is however not the case in K-Dere soils as 73% of oil removal was achieved in <3 minutes largely due to the contribution of hexane in washing off the oil contamination rather than the effect of microwave heating thus requiring about 61 kJ energy when compared with the 80 kJ observed in the dry microwave heating.

Overall, it could be said that the energy requirement for the thermal technologies investigated is in the order of thermal desorption > microwave inert liquid heating > microwave dry heating > microwave wet heating. This agrees with the findings of Falciglia and Vagliasindi (2014) who investigated the microwave irradiation of diesel-contaminated soil containing 0, 8 and 12% moisture and showed that microwave heating when compared with conventional ex-situ thermal desorption could significantly decrease the energy required to remediate hydrocarbon-polluted soils and could further be reduced by 25% for soils that are moisturised. Furthermore, Robinson et al. (2009a) found that the remediation of oil-polluted drill cuttings using a continuous pilot-scale microwave treatment process required more than three times less energy than those required when using a conventional heating system by thermal desorption and can be as little as one-fifth of the energy requirement in conventional heating systems (Robinson et al., 2014). It is important to note that the actual energy requirements of all of the scale-up processes will be different to these small batch processes. In general, they will all be lower because the heat losses will be less (especially in the TD process). However, the estimated energy requirements in this work are a useful starting point for comparison rather than an absolute number.

A similar trend is expected in terms of the associated remediation costs of these technologies, which could place microwave heating at an advantage because of the inherent moisture contents of the materials investigated especially filter cake (Table 5-1). This is because the specific energy cost associated with the microwave remediation of soils contaminated with hydrocarbon concentrations >1,500 mg/kg is estimated at 30 - 220 €/tonne, and an average reduction from about 25 - 70

€/tonne could further be achieved for moisturised soils (Falciglia and Vagliasindi, 2014). In another study involving the treatment of sandy, silty and clayey diesel-polluted soils, Falciglia and Vagliasindi (2016) calculated the cost of remediations as 20 – 160 €/tonne with lower energy requirement observed for soils with 10 and 12% moisture contents. Additionally, for ~150 kWh/tonne minimum energy requirement for the microwave remediation of hydrocarbon-contaminated soils, an energy cost of about 18 - 27 €/tonne and 14 £/tonne were estimated for a modelling study on full-scale in-situ remediation and a pilot study on an ex-situ treatment using a continuous conveyor belt processing respectively (Falciglia et al., 2018a; Falciglia et al., 2018b; Buttress et al., 2016). The disparities in these energy costs can be attributed to the variations in soil type/texture, moisture content and contaminant concentration (Falciglia and Vagliasindi, 2016; Zhao et al., 2019). Nonetheless, the expenses associated with this approach are considerably lower compared to the standard cost range of 200-400 €/tonne for fuel utilised in the ex-situ thermal desorption of hydrocarbon-contaminated soils through the rotary kiln system (Falciglia and Vagliasindi, 2014). The overall cost of thermal desorption can reach as high as approximately 560 US$/tonne (US-EPA, 2001; Falciglia and Vagliasindi, 2015). Therefore, the microwave heating system could be a more cost-effective alternative to other conventional heating systems like thermal desorption and incineration.

In Figure 7-5, it can be seen that for all the remediation of contaminated soils using thermal desorption as outlined in Table 7-4, most of the energy requirement within the system is targeted at compensating for the energy losses during material processing rather than for heating the contaminated materials. For example, only about 4%, 14%, 6% and 5% of the total energy consumed within the system would be required to heat the contaminated road planings, filter cake, Bodo soil and K-Dere soil respectively to achieve the specified oil removal yields. However, for the various microwave heating configurations, most of the energy consumed is targeted at heating the materials directly. The high loss of energy observed in conventional heating compared with microwave heating could be attributed to the selective heating (via radiation energy) in microwave systems that makes it possible to target the soil material directly without requiring additional energy to heat the entire system.

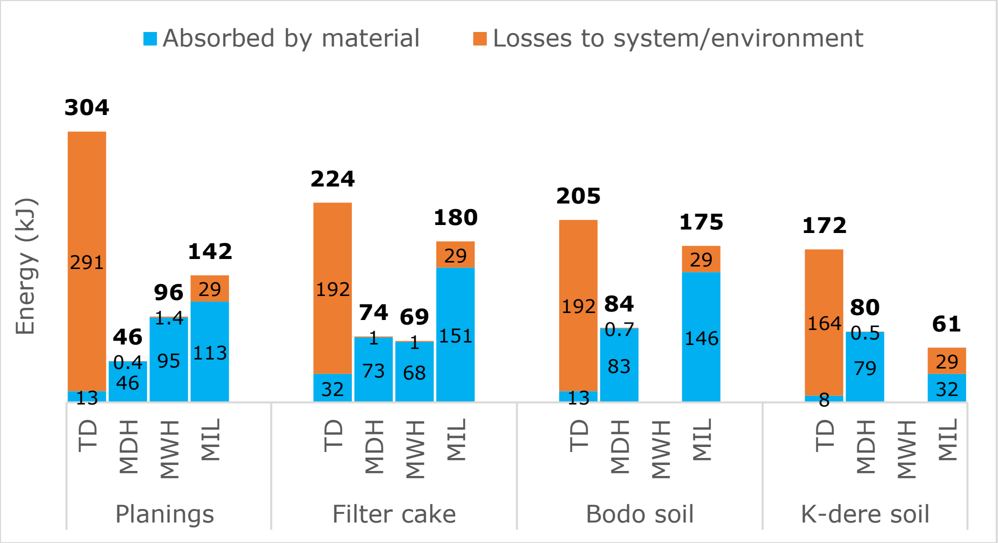


Figure 7-5: Comparison of energy absorbed and energy losses at some selected oil removal yields using various remediation methods. TD: Thermal desorption, MDH: Microwave dry heating, MWH: Microwave wet heating, MIL: Microwave inert liquid heating

This selective heating is not possible in thermal desorption because the heat transfer mechanism is largely via conduction and convection. This means that energy is first required to heat the entire system to the set temperature (usually above the boiling points of the target contaminants), and in the process, heat is then transferred to the material which in turn results in the decontamination of the materials.

Additionally, in Figure 7-6, more energy could potentially be produced from materials with higher oil content such those of filter cake if all the oil from the removal yield is successfully recovered.

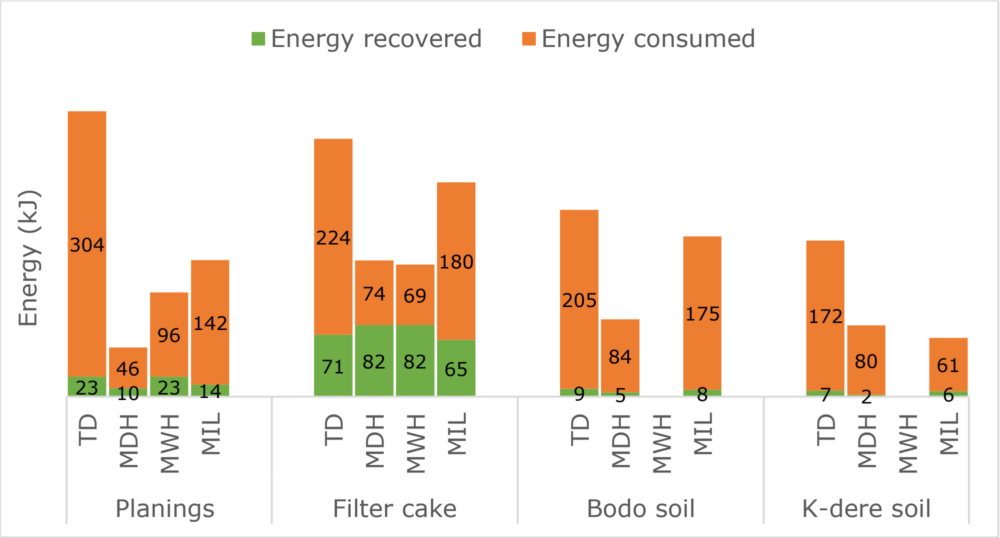


Figure 7-6: Comparison of energy absorbed, and energy that could be produced if all the oil removed from each soil at various yields is recovered. TD: Thermal desorption, MDH: Microwave dry heating, MWH: Microwave wet heating, MIL: Microwave inert liquid heating

For example, at around 74 - 86% oil removal using thermal desorption, the energy that could potentially be produced if all the oil removed is recovered is ~8% for road planings, ~4% for Bodo and K-Dere soils, and ~32% for filter cake in relation to the total energy consumed while processing each material. However, it is ~24% in road planings, and 119% in filter cake when using the microwave-wet heating system. This increment observed in microwave heating can be linked to the lower energy losses that contribute largely to the total energy consumed during the conventional heating system by thermal desorption. In both instances, the energy that could potentially be produced from filter cake's recovered oil was higher than those obtained for other materials because of its high level of oil contamination of 10.4% compared with the 2.9%, 1.3% and 0.88% in road planings, Bodo and K-Dere soils respectively.

7.2.3. Environmental requirement

The ability of a technology to remediate contaminated soils and make them fit for purpose is important. Sometimes soil guideline values are set as limits to ensure that the treated soil material is fit for purpose or disposal. A comparison of the performance of the thermal technologies against the Environmental Guidelines and Standards for the Petroleum Industry in Nigeria (EGASPIN) is shown in Figure

7-7, Figure 7-8, and Figure 7-9 - only technologies and contaminated materials that met the guideline values are included therefore, the results from the microwave dry heating system were excluded because they didn't reach the treatment limits.

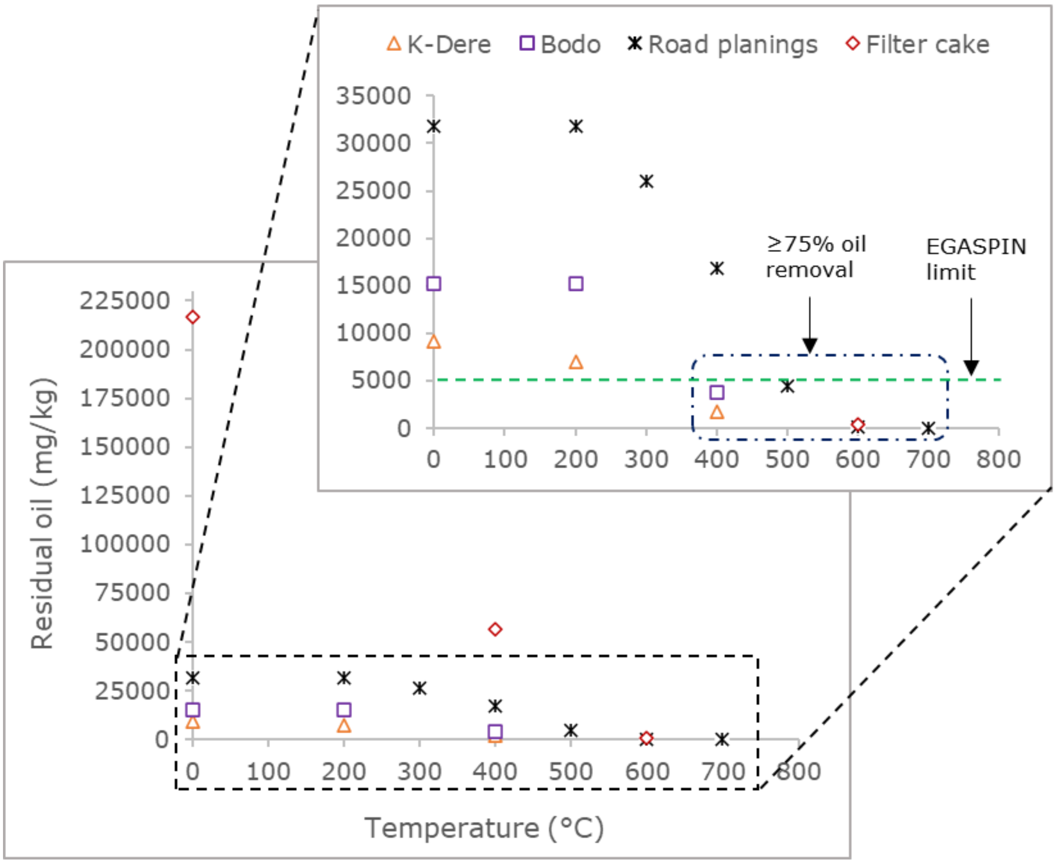


Figure 7-7: Thermal desorption of petroleum-contaminated soils. Results are reported on a dry basis

From Figure 7-7, the use of thermal desorption reduced the concentration of petroleum hydrocarbons from all the soil materials to the <5,000 mg/kg guideline stipulated by EGASPIN. This indicates that the use of conventional heating by thermal desorption effectively remediated the soil materials to the required guideline values. Materials which require high temperatures to desorb their heavy oil contamination like road planings and filter cake could not be remediated below 5,000 mg/kg at temperatures ≤400°C, however, this temperature was sufficient

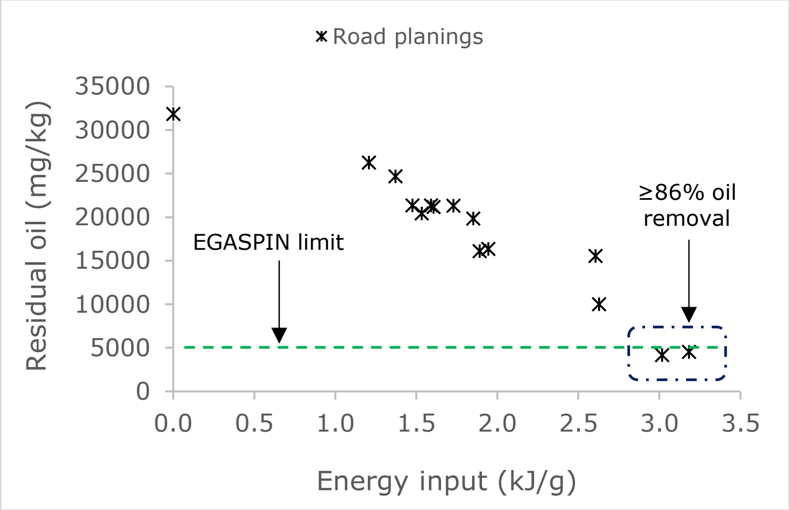


Figure 7-8: Remediation of road planings using the microwave-wet heating system at 400 W. 5 wt% ethylene glycol was used. Results are reported on a dry basis

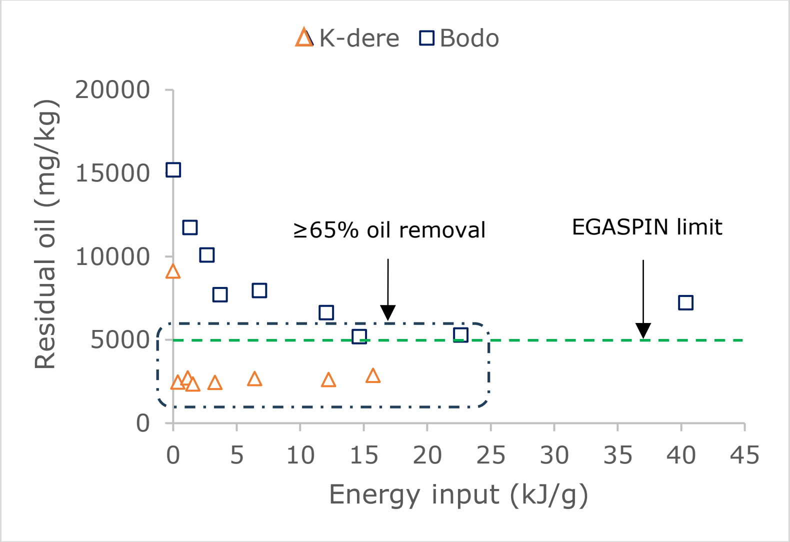


Figure 7-9: Remediation of 10 g of K-Dere and Bodo soils using the microwave inert liquid heating system at 600 W. 100 mL of hexane was used. Results are reported on a dry basis

to volatilise the hydrocarbons from soil materials containing lower oil contamination like Bodo and K-Dere soils.

Unlike in the dry microwave heating which was unable to remove the hydrocarbon contamination from the various materials to acceptable EGASPIN limits, only road planings achieved the guideline values at around ≥86% oil removal using the wet microwave heating system. Filter cake could not meet this requirement despite achieving up to ~94% under dry heating, and ~95% under wet heating which could be because of its high oil contamination when compared with the other materials. Nonetheless, it is important to note that, unlike countries like Nigeria, the United Kingdom - where the road planings and filter cake samples were collected - does not operate on specific soil limit values for soil contaminants, as such, remediation is site-specific, and considers whether soil contamination poses a significant risk to human health and/or the environment. Remediation action is only necessary when there are unacceptable risks to health or the environment, taking into consideration the current land use and its environmental setting (Cole and Jeffries, 2009). This implies that reducing the oil concentration in materials like filter cake by 94% could be sufficient and make them better suited for other useful purposes or disposal in landfills.

The inert liquid microwave heating system favoured the decontamination of K-Dere and Bodo soils to concentrations within the EGASPIN guideline values. However, this was achieved at a high energy input compared to the wet microwave heating system. For example, ~3.0 kJ/g of specific energy was required to reduce the oil contamination of road planings below 5,000 mg/kg, however, ≥15 kJ/g was required in Bodo soils without the risk of thermal runaway. This implies that achieving set environmental limit values might require some trade-offs in terms of energy requirements and associated costs. Unlike Bodo and K-Dere soils, this was not the case for road planings and filter cake as only <70% oil removal was achieved which did not meet the ≤5,000 mg/kg limit. This is likely because the heavy oil contamination in these materials could not easily be washed off by hexane from the materials unlike in the case of light hydrocarbons comprising aliphatic/saturates.

Therefore, in terms of meeting environmental guideline values, thermal desorption was a more efficient thermal remediation solution irrespective of the type of material and the concentration of contaminants. In addition to this technology, the microwave wet heating system was also suitable for remediating road planings while the inert liquid system was better suited for the Niger Delta soils (Bodo and K-Dere). However, a more sustainable solution would not only consider the efficiency of oil removal but also future soil usage and other techno-economic considerations to be a robust solution.

7.3. Re-evaluation of Initial Technology Selection Decision

In Chapter 3, a decision matrix was developed to choose the remediation technology option with the best potential to address petroleum-based land contamination problems based on remediation efficiency, speed, environmental impact, cost, and suitability for total petroleum hydrocarbon removal. Ex-situ microwave heating and ex-situ thermal desorption were selected and considered for further study. Three ex-situ technology configurations for microwave heating namely, the dry, wet, and inert liquid microwave heating systems were investigated and compared with the ex-situ conventional heating by thermal desorption.

Overall, the interaction of these technologies with the four contaminated materials i.e. road planings, filter cake, Bodo and K-Dere soils showed that more oil removal is obtainable when thermal desorption is used. However, this heating system requires a longer remediation time to achieve similar oil removal yields as those seen during the microwave heating experiments, especially while using the dry and wet heating systems, resulting in higher energy requirements. However, from the point of safety and system performance, no thermal runaways were seen in the conventional heating system unlike in the dry and wet microwave heating systems. This means that for these microwave systems to be robust, a process would have to be designed taking thermal runaway into account (e.g. in the design of the electromagnetic field) alongside proper hazard studies. It should be noted that the higher temperatures required in conventional heating systems could pose safety issues. The inert liquid system compared well with thermal desorption because it overcame the thermal runaways observed in the other microwave heating systems. However, there is a need to properly manage the hot flammable solvents used as inerting medium. The liquid inert system, however, requires higher energy input compared to dry and wet microwave processing, as some of the heat is lost to hexane in the process.

In terms of post-remediation use of soil materials, thermal desorption at high temperatures >500°C as well as microwave heating (when thermal runaway was encountered resulting in high temperatures) may destroy the soil materials. However, the impact on road planings and filter cake was considered lesser when compared with the Bodo and K-Dere soils. This is because, unlike Bodo and K-Dere soils, road planings were originally used as road finishings whereas the filter cake is a waste product from the soil washing remediation process that would go to landfills. When successfully remediated, road planings and filter cake materials could be used for soil stabilization purposes, construction or backfill applications rather than for agricultural purposes. Aside from removing the oil from filter cake material, a mass reduction of this material of up to 63% was observed in microwave dry and wet heating processes and up to 58% in thermal desorption as shown in Table 7-4. This implies that a high reduction in this waste-contaminated material is also achieved in addition to the oil products that could be recovered from the process.

Therefore, to compare the suitability of the application of the various thermal remediation techniques investigated, a technology decision matrix that took into consideration the pros and cons of each technology when applied to each contaminated material was developed to re-evaluate the performances of these techniques against the hydrocarbon-contaminated materials. The comparison of these technologies as discussed in Section 7.2 was used as the basis for rating these technologies and the result of this re-evaluation is presented in Table 7-5 and Table 7-6.

Table 7-5: Technology decision matrix for the re-evaluation of the decontamination of Road planings and Filter cake

Criterion		Road planings								Filter cake							
		TD		MDH		MWH		MIL		TD		MDH		MWH		MIL	
	Weight (%)	Rating	Score	Rating	Score	Rating	Score	Rating	Score	Rating	Score	Rating	Score	Rating	Score	Rating	Score
Remediation efficiency	20	5	1.0	2	0.4	4	0.8	3	0.6	5	1.0	4	0.8	4	0.8	3	0.6
Low energy requirement	15	1	0.2	5	1.0	5	1.0	3	0.6	1	0.2	5	1.0	5	1.0	3	0.6
Low impact on environment/soils	20	3	0.6	3	0.6	2	0.4	2	0.4	3	0.6	3	0.6	2	0.4	2	0.4
Safety considerations	20	5	1.0	2	0.4	2	0.4	4	0.8	5	1.0	2	0.4	2	0.4	4	0.8
Speed of remediation	10	1	0.2	5	1.0	5	1.0	3	0.6	1	0.2	5	1.0	5	1.0	3	0.6
Suitability for soil application	15	5	1.0	2	0.6	4	0.8	3	0.6	5	1.0	5	1.0	2	0.4	3	0.6
Total score	100		4.0		4.0		4.4		3.6		4.0		4.8		4.0		3.6
Rank		2		2		1		4		2		1		2		4	
Recommendation		Maybe		Maybe		Yes		No		Maybe		Yes		Maybe		No	

TD: Thermal desorption, MDH: Microwave dry heating, MWH: Microwave wet heating, MIL: Microwave inert liquid heating

Rating: 1 - Poor, 2 - Fair, 3 - Good, 4 - Very good, 5 – Excellent

$\text{Total score} = \sum_{i=1}^{n} \text{Rating}_i \text{ x } \%\text{Weight}_i$

The scoring system is based on the qualitative and quantitative assessment of the experimental results obtained, comparing various technology configurations as extensively discussed in Section 7.2.

Table 7-6: Technology decision matrix for the re-evaluation of the decontamination of Bodo and K-Dere soils

Criterion		Bodo soil						K-Dere soil					
		TD		MDH		MIL		TD		MDH		MIL	
	Weight (%)	Rating	Score	Rating	Score	Rating	Score	Rating	Score	Rating	Score	Rating	Score
Remediation efficiency	20	5	1.0	2	0.4	3	0.6	5	1.0	2	0.4	4	0.8
Low energy requirement	15	1	0.2	5	1.0	3	0.6	1	0.2	5	1.0	5	1.0
Low impact on environment/soils	20	2	0.4	3	0.6	2	0.4	2	0.4	3	0.6	2	0.4
Safety considerations	20	5	1.0	3	0.6	4	0.8	5	1.0	3	0.6	4	0.8
Speed of remediation	10	1	0.2	3	0.6	3	0.6	2	0.4	3	0.6	4	0.8
Suitability for soil application	15	5	1.0	2	0.4	3	0.6	5	1.0	2	0.4	4	0.8
Total score	100		3.80		3.60		3.60		4.00		3.60		4.60
Rank		1		2		2		2		3		1	
Recommendation		Yes		No		Maybe		Maybe		No		Yes	

TD: Thermal desorption, MDH: Microwave dry heating, MIL: Microwave inert liquid heating

Rating: 1 - Poor, 2 - Fair, 3 - Good, 4 - Very good, 5 – Excellent

$\text{Total score} = \sum_{i=1}^{n} \text{Rating}_i \text{ x } \%\text{Weight}_i$

The scoring system is based on the qualitative and quantitative assessment of the experimental results, comparing various technology configurations as extensively discussed in Section 7.2.

7.4. Conclusions

In general, for the remediation of road planings and filter cake materials, microwave wet heating and microwave dry heating performed best respectively. This is coupled with the fact that they achieved high oil removal yields over a short time thus consuming less energy which would potentially reduce the remediation cost when compared to thermal desorption. Additionally, oil contamination was removed at a much lower temperature of about ≤352°C (road planings) and 225°C (filter cake) when compared to thermal desorption at ≥500°C for both materials. This implies that microwave heating may likely reduce the impact of the heating process on decontamination of these and other similar materials and would increase their potential for re-use for different applications including more sensitive applications like agriculture. Therefore, a more sustainable, cost-effective and efficient thermal remediation technology should be the one that uses the lowest effective temperature to reduce contaminant concentration whilst minimising soil damage or decomposition or its ability to function (Vidonish et al., 2016b; O'Brien et al., 2018). The drawback of the microwave heating techniques remains the safe processing of the materials. However, since road planings and filter cake were originally for non-agricultural use, the impact on the materials in terms of post-remediation usage would be less even when thermal runaway occurs. Improving the system's robustness/performance would require experienced microwave engineers embedded in a multidisciplinary team of chemical engineers, electrical engineers, material handling specialists etc. to design a safe and effective microwave process.

Thermal desorption performed best on Bodo soils whereas the inert liquid heating system was best for K-Dere soil. This is because, unlike the microwave dry and wet heating systems, which performed less well on the sandy Bodo soil, thermal desorption achieved high oil removal in Bodo soil and may also be considered for K-Dere soil where it also performed well. This agrees with the findings of Vidonish et al. (2016b) who recommended that high-temperature technologies might be well suited for sandy soils due to their quartz composition which makes them thermally stable when compared with other soil types. Additionally, Robinson et al. (2014), who studied the microwave heating of high-grade oil sands, showed that they were not amenable to microwave heating unless the oil sands contained hydrophilic clay minerals that make them susceptible to microwave as observed in the low-grade oil sands studied. The inert liquid system was very suitable for the K-Dere soil as it relied more on the interaction between hexane and the soil material via soil washing rather than microwave heating. The decontamination of this material was made easy because K-Dere soil is sandy, and commercially available soil washing systems are known to be suitable for soil materials that do not contain a substantial proportion of organic matter or clay (Nathanail and Bardos, 2004). Although thermal desorption had the overall best performance for Bodo soil, the inert liquid system performed well for Bodo soil as it did for K-Dere soils as its oil content was easily washed from the sandy material by hexane.

CHAPTER 8

8. CONCLUSIONS AND RECOMMENDATIONS

8.1. CONCLUSIONS

In a quest to preserve and protect human health, wildlife, and the environment, from the adverse impact of land contamination from petroleum hydrocarbons, this research set out to conduct a robust and systematic technology evaluation of selected remediation technologies for the removal of Total Petroleum Hydrocarbons (TPH) from soils. To achieve this, five objectives were investigated in depth from which the following conclusions can be drawn.

8.1.1. Technology Selection Decision

The remediation technology decision matrix conducted on five major remediation technology classifications based on important criteria peculiar to Nigeria's Niger Delta contaminated site characteristics showed thermal methods as a viable technology with the best potential to contribute towards addressing this problem. It scored 3.77 ahead of physicochemical methods (3.53) because of its suitability and effectiveness for removing high concentrations of petroleum hydrocarbons from a wide range of soil types over a short time. Furthermore, ex-situ microwave heating (3.46), and ex-situ thermal desorption (3.21) emerged as the leading technologies from a detailed investigation and screening of nine thermal remediation approaches. These technologies were taken further for investigation and comparison towards a final re-evaluation of the initial remediation technology selection decision. Four selected contaminated soils i.e. road planings, filter cake, Bodo and K-Dere soils were used for this purpose.

8.1.2. Effect of soil texture and contaminant types on microwave remediation

In terms of soil texture, an investigation into the selected contaminated materials showed that they fit into the texture triangle as predominantly sandy (Bodo soil), sandy-loam (K-Dere soil), and clayey (filter cake). However, road planings could not fit into the texture triangle as it was 62% gravel. Their moisture contents were in the order filter cake > Bodo soil > road planings > K-Dere soil and were directly proportional to their porosities and inversely proportional to their bulk densities. They are a function of their porosities as they were directly proportional to their porosities and inversely proportional to their bulk densities. It was concluded that the interlayer moisture from hydrophilic minerals in clay materials contributed to the high moisture content in filter cake thus influencing their high dielectric constant and loss factors required for dielectric heating in microwaves.

About 91% of road planings comprise aliphatic and aromatics within the range >C21 – C44 and >EC16 – EC35 respectively, while 88% of filter cake consist of >C16 – C44 (aliphatic) and >EC12 – EC35 (aromatics). Bodo soil has 90% of its petroleum hydrocarbon concentrations within >C12 – C21 and >EC16 – EC35, whereas K-Dere soil has 86% between >C16 – C35 and >EC16 – EC35. Remediating these soils using conventional heating by thermal desorption would require temperatures around the boiling points of these contaminants i.e. 359 – 547°C (road planings), 287 - 547°C (filter cake), 216 - 495°C (Bodo soil), and 287 - 495°C (K-Dere soil). It was concluded that high contaminant removal yields at much lower temperatures are only achievable in microwave heating if other contaminant removal mechanisms like steam stripping or steam distillations play a significant role.

8.1.3. Dielectric properties studies

Soil moisture and texture contributed significantly to the dielectric properties and the temperatures reached during heating. Road planings, filter cake, Bodo, and K-Dere soils achieved peak loss factors of 0.27±0.08, 1.10±0.25, 1.12±0.15, and 0.06±0.004 respectively at temperatures ≤100°C. It was concluded that the microwave heating of the sandy loam K-Dere soil would be challenging leading to low hydrocarbon removal due to its low loss factor. Loss factors decreased with the decreasing water phase and dropped significantly when completely removed. Unlike the other materials whose loss factors were minimum at 100°C, filter cake was minimum at ~200°C due to the contribution of its bound water and indicated that hydrocarbon removal beyond 100°C would occur. The sharp increase in the loss factors of road planings, filter cake, and Bodo soils at ≥500°C was attributed to the formation of microwave-absorbing carbonaceous materials from the decomposition of organic contaminants. Thus, thermal runaway during microwave heating was likely to occur. There was however only a gradual increase in the loss factors of K-Dere soil at these temperatures, and it was less likely that thermal runaway would occur.

Both dipolar (due to the presence of soil moisture) and ionic/conductive loss mechanisms played a role in the dielectric loss between 20 and <200°C (drying stage). However, the ionic/conductive loss is thought to be more dominant at these temperatures due to the presence of ionic salt solutions. It was also the dominant loss mechanism between ≥450 and 700°C (char formation stage) due to the formation of carbonaceous materials.

8.1.4. Microwave heating and overcoming thermal runaway

Oil removal up to 94% (at 3.8 kJ/g and 6 minutes), 37% (at 1.5 kJ/g and 3 minutes), 44% (at 4.2 kJ/g and 8 minutes), and 30% (at 4 kJ/g and 10 minutes) were achieved for filter cake, road planings, Bodo and K-Dere soils respectively using the dry microwave heating system. Hydrated clay layers of filter cake influenced the achievement of temperatures beyond 250°C generating steam in situ that created a high-pressure build-up from the mass transfer limitation effect within its small pore sizes. This supported hydrocarbon removal via the steam stripping mechanism. The contaminant removal mechanism in the coarser road planings, Bodo and K-Dere soils is the steam distillation (co-distillation) mechanism due to the low mass transfer limitation effect and the inability of soils to reach thermal desorption temperatures during microwave heating. At an equivalent specific energy input, more oil is removed from road planings and Bodo soils at 600 W compared with 400 W. However, power levels did not affect filter cake and K-Dere soil. For the scale-up of this processing system, high-power microwave systems will yield higher oil removal and allow higher throughputs of road planings and Bodo soils.

Using ethylene glycol in the wet microwave heating system significantly improved the oil removal yield in road planings to 87% by increasing its heating beyond 100°C and ≤197°C. Its effect on filter cake was however insignificant. Thermal runaway was a major challenge limiting the processing of the materials at longer heating times and high energy input. This degraded road planings and filter cake and caused equipment damage during the dry and wet microwave heating. It was found that remediating the contaminated soils using the inert liquid system overcame the challenge of thermal runaway. It also increased oil removal in road planings, Bodo and K-Dere soils compared to their dry microwave heating however, it came with a trade-off as higher specific energy inputs were required. This increase results from the combined effect of microwave heating and the liquid extraction by hexane.

8.1.5. Re-evaluation of initial technology selection decision

Overall, the remediation of road planings and filter cake were best achieved using microwave wet and microwave dry heating systems respectively. They achieved high oil removal yields over a short time, consumed less energy and would potentially reduce the overall remediation cost compared with thermal desorption. Furthermore, contaminant removal was achieved at much lower temperatures when compared with thermal desorption. This would reduce the impact of the heating process on these materials and enhance their reuse post-remediation. However, unlike thermal desorption which reduced contaminant concentrations of all the materials to below the acceptable Environmental Guidelines and Standards for the Petroleum Industry in Nigeria (EGASPIN) of ≤5,000 mg/kg, the wet microwave heating only achieved these guideline values in road planings at ≥86% oil removal. Both dry and wet microwave heating systems could not meet this requirement in filter cake despite achieving oil removals up to ~94% under dry heating, and ~95% under wet heating. This was attributed to its high oil contamination compared with the other materials.

It was concluded that in Bodo soils, thermal desorption performed best whereas the inert liquid heating system was best for K-Dere soil. Unlike the dry and wet microwave heating systems which performed less well on the sandy Bodo soil, thermal desorption achieved high oil removal in Bodo soil and can be considered for K-Dere soil where it also performed well. Similarly, the microwave inert liquid system performed well for Bodo soil as it did for K-Dere soils and reduced the hydrocarbon contamination of these soils to acceptable concentrations within the EGASPIN guideline values.

8.2. RECOMMENDATIONS FOR FUTURE WORK

Future research aimed at enhancing the understanding of the microwave heating configurations used in this study as well as overcoming some of the limitations encountered could prioritise the following for field trials and the scale-up of this technology:

1. Conducting a comprehensive analysis and investigation of the quality of the recovered oil from all the contaminated materials studied under different microwave technology configurations and processing conditions. This would help improve our understanding and establish the suitability of each microwave technology configuration for the selective removal of specific hydrocarbon contaminants. Additionally, quantifying the aliphatic and aromatic hydrocarbons present in the materials after microwave treatment would provide detailed information on not just the types of hydrocarbons present (as shown from the hydrocarbon identification data

obtained using the GC-MS) but also their concentrations and how these vary with changes in the process conditions of the thermal remediation approaches used in this work. This will enable the optimisation of the remediation of targeted hydrocarbons (e.g. PAHs) and monitor the effectiveness of the remediation over time.

2. The wet microwave heating system used in this work was limited to the processing of only filter cake and road planings because of the practical difficulty encountered in measuring the amount of oil removed when remediating the Niger Delta soils (Bodo and K-Dere soils) due to the presence of ethylene glycol in the treated soils. Further study to quantify the inherent ethylene glycol using the GC-MS could enable the determination of the actual amount of oil removed during the wet microwave processing of Bodo and K-Dere soils.
3. Further studies on the numerical modelling of the electromagnetic field distribution within the microwave applicators during heating using COMSOL Multiphysics® would be beneficial in further understanding the impact of microwaves on the various contaminated materials studied. This approach will allow for the prediction of the electromagnetic field distribution, ensuring uniform heating within the materials thus minimising hotspots that potentially result in thermal runaway. It would also help to optimise the design of the microwave applicator to achieve the desired heating pattern and efficiency, especially for field trials and the scaleup of this technology.
4. Lastly, modelling the velocities of the steam generated during the microwave heating of each contaminated material would help understand the contribution of each contaminant removal mechanism to the overall contaminant removal.

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