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New Microwave Technology for the Treatment of Drill Cuttings

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Above all, I give thanks to God for how far He has brought us.

Dedicated to Caroline & Nuna

Abstract

The focus of this thesis was to investigate the limitations of the new microwave susceptor technology. The technology offers promising opportunities in the treatment of oil contaminated drill cuttings to meet OSPAR and oil companies on the Norwegian Continental Shelf's standards. The concept relies on increasing process temperature to enhance oil separation by the use of highly volatile organic compounds. The organic compounds are polar, absorb microwave radiation and are not soluble in oil. Significant amount of energy is saved during the process due to the rapid heating of the susceptor, oil and high vapour pressure contribution from the oil as a result of the increased process temperature.

Drill cuttings were successfully treated to discharge limits of less than 1% by weight. It is shown that enhancing parameters, such as reducing amount of water, bed depth, adequate susceptor dousing and retention time, result in better oil separation.

Susceptor decomposition as a function of microwave heating and the effect of water on decomposition was investigated in this study. Selected susceptors, MEG and TEG, showed signs of decomposition, even when mixed with different proportions of water and subjected to microwave irradiation. MEG, however, showed little signs of degradation when added to drill cuttings and recycled ten times. TEG on the other hand showed significant signs of degradation after one cycle. The tests showed that water reduced process temperature but did not prevent decomposition.

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Abbreviations

AP	Alkylphenols
Bp	Boiling point
BAT	Best Available Technique
BET	Best Environmental Practices
DEG	Diethylene Glycol
DPG	Dipropylene Glycol
EC	European Commission
EM	Electromagnetic
EMS	Electromagnetic Spectrum
IRIS	International Research Institute of Stavanger
MPG	Monopropylene Glycol
MEG	Monoethylene Glycol
NEA	Norwegian Environment Agency
NOROG	Norwegian Oil and Gas Association
NCS	Norwegian Continental Shelves
OBM	Oil Based Mud
OCDC	Oil Contaminated Drill Cuttings
OOC	Oil on Cuttings
OSPAR	Convention for the Protection of the Marine Environment of the North East Atlantic
PAH	Polyaromatic Hydrocarbons
PLONOR	Pose Little Or No Risk
ROC	Retained Oil on Cuttings
RPM	Rounds Per Minute
SBM	Synthetic Based Mud
TBT	Theoretical Boiling Point Temperature
TCC	Thermochemical Cuttings Cleaner
TEG	Triethylene Glycol
T	Temperature
TWT	Travelling Wave Tube
Vol	Volume
WBM	Water Based Mud
WOC	Water On Cuttings
Wt%	Percent by weight

PART 1-BACKGROUND

1 Introduction

1.1 Background of Research

Drilling activities for the exploration and production of oil and natural gas requires the use of drilling fluids, also known as “drilling mud”. Mud is continuously pumped into the well through a hollow drill string during the drilling process, and returns to the surface through the annulus (Ball et al., 2012). As it returns, it lifts the crushed formation also known as drill cuttings to the surface. Shakers, hydrocyclones or centrifuges are used to separate the drill cuttings from the mud before they are recycled. Mud, which stick to the drill cuttings and cannot be recycled are considered as drilling waste.

The type of mud used depends on the formation. Consequently, Water-Based Mud (WBM), Synthetic-Based Mud (SBM) and Oil-Based Mud (OBM) are used to match well conditions for smooth operations. Until about two decades ago, drilling waste was directly discharged to sea, resulting in large cutting piles around platforms and destruction of local ecosystems (Ormeloh, 2014). Mud is made from chemicals with potential environmental impacts, which have generated strict environmental regulations in recent times. OBMs are classified as hazardous substances and must be treated before discharge into the open environment.

OSPAR regulations require that strict laws are upheld to ensure environmental integrity in the North Sea. Offshore operations raise concerns for marine ecosystems, hence regulations have been established to protect marine life. For instance, the offshore strategy requires collection of data on the use and discharge of chemicals used offshore, emissions to air, spills and discharges of oil and radioactive substances. The Offshore Industry Committee (OIC) is responsible for the collection of the data at all installations which include, the use and discharge of drilling fluids and cuttings, discharges of oil in produced water and chemicals used and discharged offshore. This information is published annually in the OSPAR reports with reference to data on discharges from 1984 (OSPAR, 2016). OSPAR recommends 1% retained oil on cuttings (ROC). This is also the limit set in Norway. North Sea cuttings typically contain about 15% oil (Robinson et al., 2010) and must be treated to meet regulatory limits before discharge. Current practices offshore include slurrification for reinjection or skip and ship to shore. There are however, concerns about transporting cuttings onshore (mainly cost and safety issues). These concerns make offshore treatment an attractive alternative.

The Thermochemical Cuttings Cleaner (TCC) was tested on the Martin Linge platform and reported to have met regulatory requirements of less than 1% oil on cutting (OOC). Specifically, between 0.04-0.10 % by weight of dry cuttings (Ormeloh, 2014). This was below the standard set by OSPAR. The Norwegian Environment Agency (NEA) permitted the operator (TOTAL) to use it, setting a standard for 0.05 % OOC. However, continuous environmental monitoring showed that the TCC could not meet the criteria of 0.05% by weight that was set by the NEA (NOROG, 2016). TWMA Norge AS, a TCC operator in Norway gave reasons for not meeting the requirements at the time and remain positive about its use offshore. There is information that Statoil has applied for permit to allow the use of the TCC on Johan Sverdrup and other platforms in Norway (NEA, 2016) . If this information is reliable, then probably the initial criteria set by the NEA has been adjusted or the TCC meets the criteria. That notwithstanding, the TCC remains the current Best Available Technique (BAT) for treating OBM contaminated cuttings both onshore and offshore.

There are various challenges associated with the transportation of drill cuttings onshore for treatment (Shang et al., 2006); 1). Safety issues with regards to crane lifts, 2) high energy usage in transportation and processing, 3) bad weather conditions do not allow for crane movements and other activities for transporting cuttings onshore. This may result in halting of drilling activities once the buffer capacity is reached. The development of offshore cuttings treatment methods will reduce these challenges in the oil and gas industry.

Since most oil rigs in the North Sea were not originally designed to have cuttings treatment systems, retrofitting is required to carry such systems. This implies that off-shore treatment systems must be integrated into existing infrastructure of platforms. This is a challenging task due to large foot prints required by these systems. The need for suitable alternatives is imminent. Even though, slurrification and re-injection into dedicated wells have been used in recent times, issues of leakage and resurfacing have made the method less attractive. Microwave processing of drill cuttings has been identified as a potential method to meet regulatory requirements, small foot print, cost reduction and addressing safety concerns offshore (George et al., 1994, Pereira, 2012, Robinson et al., 2008). A pilot continuous operation microwave system has proved that it is capable of treating cuttings at 500kg/h to meet discharge limits of 1% (Robinson et al., 2010). Although it has been tested on a pilot base, there is further research into making it industrially feasible.

1.2 Problem Formulation

The limitations of the TCC and other treatment methods offshore in terms of cost, large footprints and weight, maintainability, safety, and treatment capacity is the motivation for continuous research into alternative methods for treating oil contaminated drill cuttings (OCDC). Norwegian Technology AS has developed a new concept within microwave treatment for OCDC. The concept relies on increasing process temperature to enhance oil separation, while simultaneously decreasing the energy consumptions. This is achieved by dousing cuttings with highly volatile chemicals, called **susceptors,** before irradiating it with microwaves. Susceptors and oil are distilled off, leaving the solid treated to legislation requirements. The chemicals have lower enthalpies of vaporization than water, which is part of the reason for high energy efficiency. The other reason is the increased process temperature that allow for enhanced oil separation. Less susceptor is therefore required in order to achieve high separation degree.

There are many parameters that need to be investigated with this new technology, such as: oil separation degree as a function of alternating variables, the effect of water on the chemicals, decomposition, and effect of decomposition of the chemicals on oil separation. These parameters were investigated in this thesis, as a continuation of previous studies conducted by Norwegian Technology AS.

1.3 Objectives of the Thesis

The goal of this thesis is to investigate the limiting factors of using susceptors in microwave treatment of OCDC. This will be achieved using both theoretical analysis and experiments in the laboratory. The following steps were carried out to achieve the main objective:

1. Reviewing information available on microwave radiation for cuttings treatment.
2. Investigating susceptor properties in respect to decomposition and susceptor recovery:
    a. Investigate susceptor decomposition as a function of heating in a microwave oven
    b. Recycling times for MEG in respect to decomposition
    c. Evaluate the susceptor properties as a function of water contamination
3. Alternate parameters and variables to increase oil separation:
    a. Alternate process setup to increase oil separation. This includes testing a mixed system, and alternate nitrogen dosage point
    b. Evaluate the effect of increased dosage
4. Determining the most suitable susceptor dousing method for a scale up

1.4 Collaboration with Industry

This thesis is being carried out in collaboration with *Norwegian Technology AS*. The company provides onsite and offsite waste water treatment facilities in diverse industrial sectors. They achieve this by designing and building specific equipment to suit a specific need. Their focus is to provide environmental solutions by offering technologies that are: robust, easy to operate and maintain. Their equipment is built to have high treatment capacity and low footprint and weight for both onshore and offshore installations. With sustainable development as a hallmark, they build systems that are compact and use environmentally friendly chemicals.

The company is developing an integrated waste management system to handle waste from the oil and gas industry. The use of microwave heating with environmentally friendly chemicals to treat waste products is a major part of this development. The birth of a full industrial microwave processing unit will be a breakthrough in the company's development.

1.5 Novelty of the Research

The use of microwaves for synthesis is known in various industries. Its use for the treatment of OCDC has also been studied and a pilot system, tested by Robinson et al., at the University of Nottingham, UK. According to available knowledge, the process can reduce OOC to < 1 wt %.

Previous studies have used water as the absorbing medium. However, a most recent study by Norwegian Technology AS, has proven that certain organic compounds can be used instead of water. The benefits of using these compounds are that they require far less energy than is needed when water is used. They also ensure a high process temperature needed to vaporize base oil contained in drill cuttings. As mentioned earlier, the vaporized oil contributes a higher vapour pressure than water. This translates to tremendous cost savings to the operator in addition to meeting environmental requirements.

2 Drilling Process and Waste Production

2.1 Drilling Process

In the oil and gas industry, wells are drilled into the earth with an oil rig with varying components, essentially a drill bit. The process is called rotary drilling. The drill bit is situated at the bottom of a drill string which consists of several heavy hollow pipes that exert pressure on the bit as it cuts through the formation. The cuttings are lifted to the surface by circulating drilling fluid down the string to push them up the annular (Bourgoyne et al., 1986). The diameter of the well may vary from 30-5 inches (OCD, 2010) decreasing with depth.

After drilling, a casing is built in by placing a steel pipe in the hole before it is cemented into position. This is to ensure that the hole does not collapse. Figure 1 shows a schematic of a drilling rig. Prior to casing, many effects of friction and wellbore conditions such as varying temperatures and pressures must be overcome. This is achieved using drilling fluids. They are used for but not limited to (OCD, 2010); 1) cool and lubricate the drill bit, 2) transport cuttings to the surface, 3) maintain well pressure, 4) cool the formation, 5) seal permeable formations encountered while drilling, 6) transmit hydraulic energy to download tools and the bit, 7) regulate the chemical and physical characteristics of the mixture arriving at the drilling rig, 8) provide information to drillers about what is happening downhole as they monitor flowrate, pressure and composition of the drill fluid.

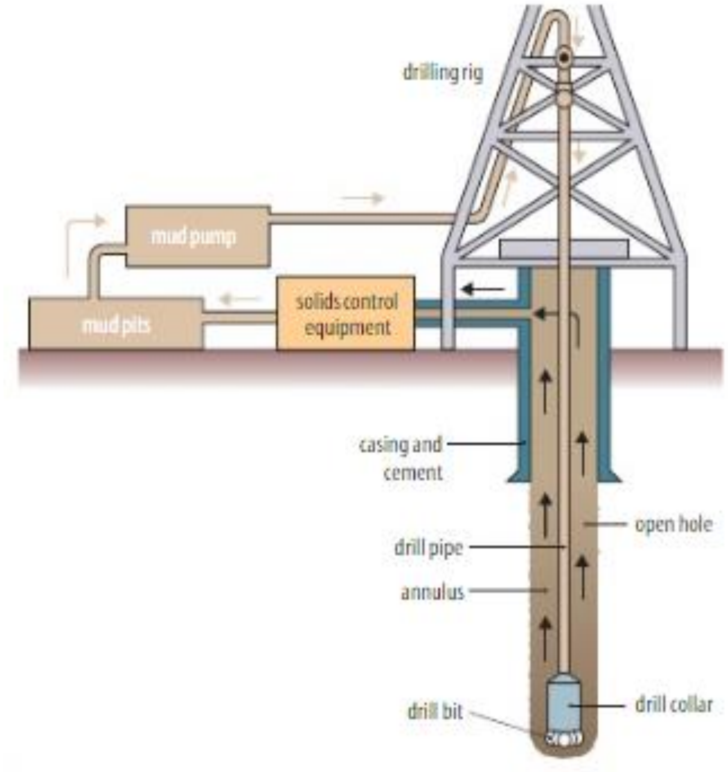

Figure 1: Schematic of a drilling rig with a mud circulation system (IPIECA, 2009)

2.2 Drilling Waste Types

The quest for hydrocarbons requires the removal of huge amounts of waste streams which can be harmful to the environment. These include drill cuttings, used drilling fluids (mud), produced water and slop. Slop is formed when drilling fluids, wash water from daily cleaning operations or rain runoff become contaminated with drill fluid components (Mueller et al., 2013). Mud is any liquid mixtures and gaseous fluids and mixtures of fluids and solids used to drill boreholes into the earth (Schlumberger, 2017). The mud lifts the cuttings to the surface. Muds are designed based on the conditions of the wellbore and can be oil based, water based or made with synthetic materials. SBMs are high performance drilling fluids made from synthetic materials. These materials vary from vegetable esters, poly alpha olefins, synthetic paraffins, ethers and linear alkyl benzene.

The discharge of mud contaminated drill cuttings from offshore petroleum industry on the Norwegian Continental Shelf (NCS) was the main source of oil hydrocarbon entering the marine environment in the mid-1990s (Bakke et al., 2013). Reiersen et. al, reported that the average annual discharge of OOC to the NCS was 1940 tons from (1981-1986) (Reiersen et al., 1989). It was also estimated in 1995, that 150 million barrels of drilling waste generated from onshore wells in the United States of America (USA)(Veil, 2002). These discharges have environmental and health implications.

Toxicity tests have been conducted over the years to study the impact of drilling waste on continental shelf ecosystems. For instance, reports indicate that caged cod and blue mussels near discharge outlets accumulated Alkylphenols (AP) and polyaromatic hydrocarbons (PAH). These chemicals may disturb reproductive functions, and affect several chemical, biochemical, and genetic biomarkers. In the same vein, WBM can affect biomarkers in filter feeding bivalves, and cause increased sediment oxygen consumption and mortality in benthic fauna (Bakke et al., 2013). These concerns have resulted in the establishment of laws to govern how various waste streams associated with drilling for hydrocarbons should be treated. The treatment of drilling waste depends on their composition and a lot more on cost and safety factors as well as local environmental regulations. Figure 2 shows the amount of OBM cuttings produced on the NCS over the years.

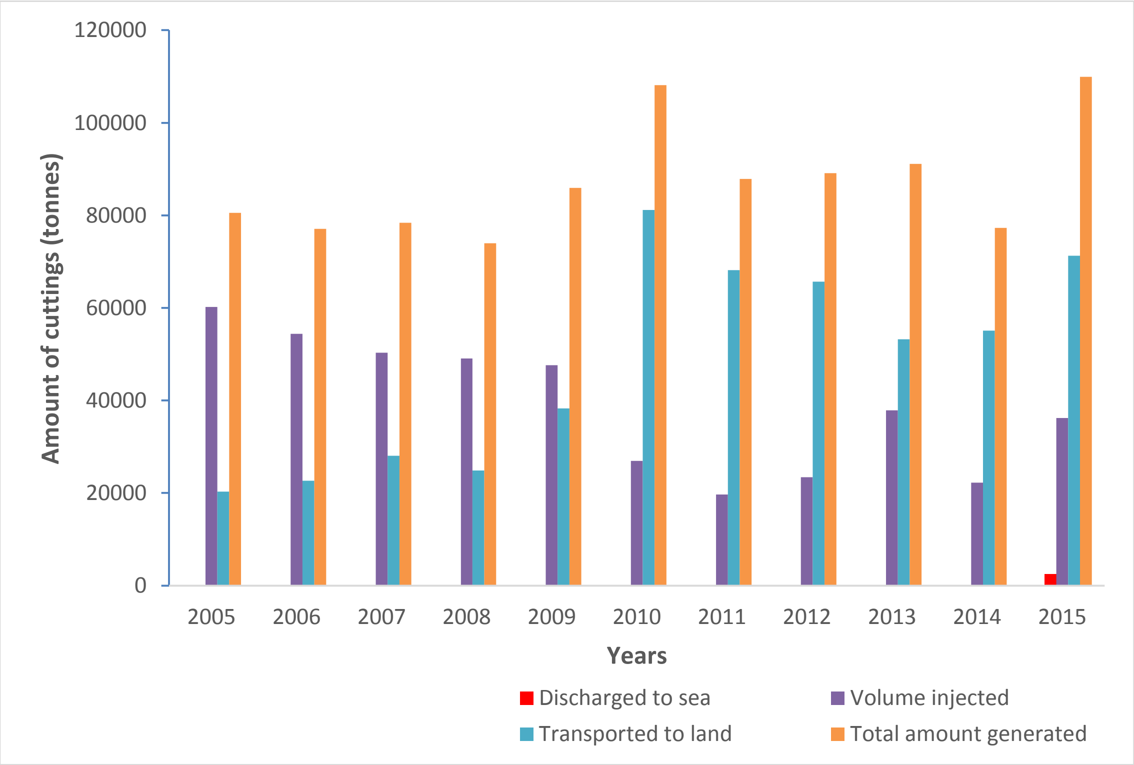

Figure 2: Amount of OBM produced on the NCS. Data extracted from NOROG Report 2016

2.3 Drill Cuttings Treatment Methods

Drill cuttings have hazardous components that must be treated to meet statutory environmental requirements before discharge. Thus, various methods are used, with some preferred than others due to cost and environmental requirements of the location. Some of the methods listed by Cripps et al., 1998 include: thermal treatment, reinjection techniques, retrieval technology, mechanical dredging, and bioremediation.

2.3.1 Thermal Treatment

2.3.1.1 *Thermomechanical Cuttings Cleaner (TCC) and Operating Principle*

The constituents of liquid mixtures can be separated by the process of distillation and evaporation. This is applied to drill cuttings in a thermal desorption process called: **thermo-mechanical cuttings cleaning (TCC)**. In this case, the drill cuttings are subject to distillation so that the water and oil are boiled off. The technology was developed by THERMTECH AS in Bergen. Its operating principle involves changing kinetic energy from a drive unit into thermal energy. This is achieved by development of friction in a hammer-mill: - it consists of a drive unit which rotates a drive shaft on which hammer arms are attached. Increased rotation of the arms causes the waste fed into the mill to be pressed towards it's inner walls. The mechanical action generates heat because of friction between particles. Temperatures rise to 275-300°C (Paulsen et al., 2003). Once these temperatures are reached, hydrocarbons are removed from the solids to an acceptable disposal limit (<1% OOC cuttings) (Halliburton, 2016, Thermtech, 2016). The vapour generated goes through a cyclone to remove fines, then an oil scrubber before going through the oil and steam condensers. There is also an additional oil/water separation chamber to recover oil and water since some lighter oil will condense with the water (Thermtech, 2016). The remaining powder can then be discharged or used for other suitable purposes. An example of a TCC is depicted in Figure 3.

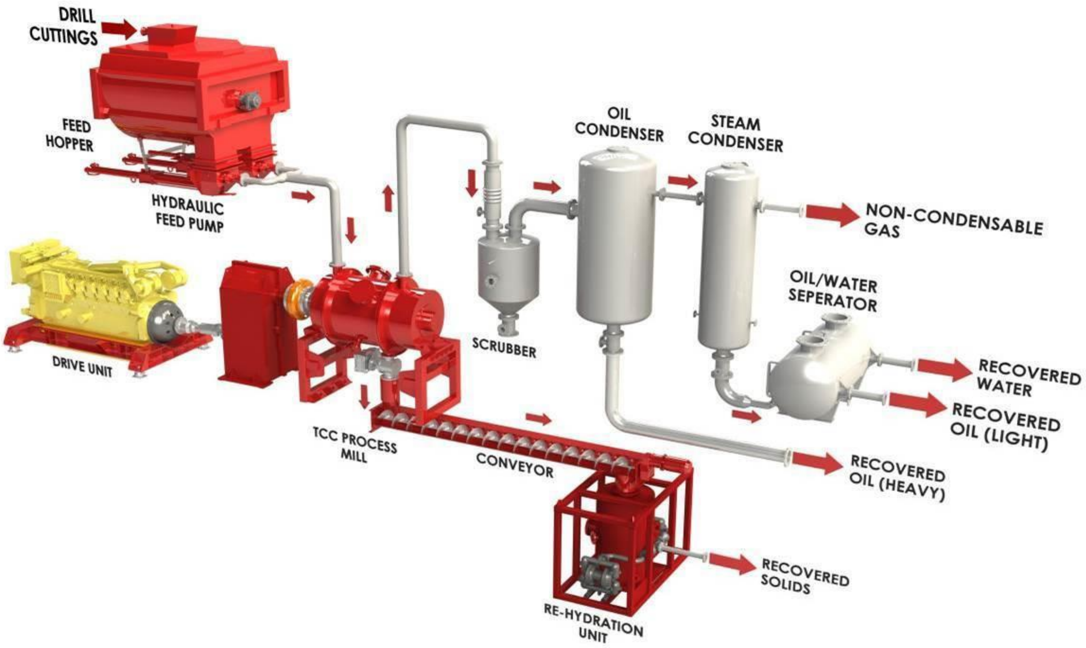

Figure 3: TCC diagram (Halliburton 2016)

Advantages of TCC

- Low overall process temperature compared to rotary kiln
- Direct mechanical heating eliminates the need for large heating surfaces
- Meets regulatory requirements of <1% OOC
- Temperatures do no degrade oil, hence the oil can be reused.

Limitations of TCC

- Requires large footprints (size and weight) which is a constraint offshore
- Hammer mill producing high temperature can crack the oil when the loading of cuttings is not well managed
- A breakdown can lead to high downtime, translating to high operational cost
- Requires constant supervision to control temperatures (HSE issues)
- Since the final solids product is powdery, heavy metals within the powder become available to fish. This can potentially harm the ecosystem
- High cost of equipment.

2.3.1.2 ***Microwave***

Studies have shown that microwave heating can be used to reduce oil contaminated drill cuttings to <1% ROC (Whitford, 2009). It has also been shown that there are significant process engineering benefits in terms of equipment size and more simplified processing steps (Robinson et al., 2009b). This can potentially reduce CAPEX and OPEX.

During microwave processing of OCDC, the cuttings are conditioned in a mixer and fed into a microwave cavity, Figure 4. As mentioned earlier, microwaves are absorbed by susceptors within the pores of the material to be processed. The absorbed microwaves are converted to heat energy. Steam is formed by the susceptor as it absorbs microwaves and converts it to heat. As the steam escapes, it physically entrains the oil. This is how the oil removal mechanism works during treatment of OCDC.

Materials have different characteristics upon interaction with microwaves due to their dielectric properties. Some are transparent to microwaves (materials with low dielectric loss), others are opaque to microwaves (conductors) whilst others absorb microwaves (material with high dielectric loss) (Robinson et al., 2010). These properties allow for selective heating of materials during microwave processing of materials which contain a mixture of absorbers and transparent components. The amount of energy saved due to selective heating is potentially high since the entire matrix of the material does not need to be heated. The process allows the reuse of the recovered fluids in preparing new drilling fluid since their physical properties do not change and the solid residue can be used in construction works (Santos et al., 2014). Dielectric properties are explained further in Chapter 4.

The microwaves are generated in vacuum tubes called magnetrons, although other tubes exist, such as the klystron and the travelling-wave tube. The magnetrons have high efficiency conversion rate from electrical power to microwave at a constant frequency range compared to the others (Meredith, 1998). A full description of the mechanism and operability of the microwave can be found in “Engineers’ Handbook of Industrial Microwave heating” by Roger Meredith, 1998.

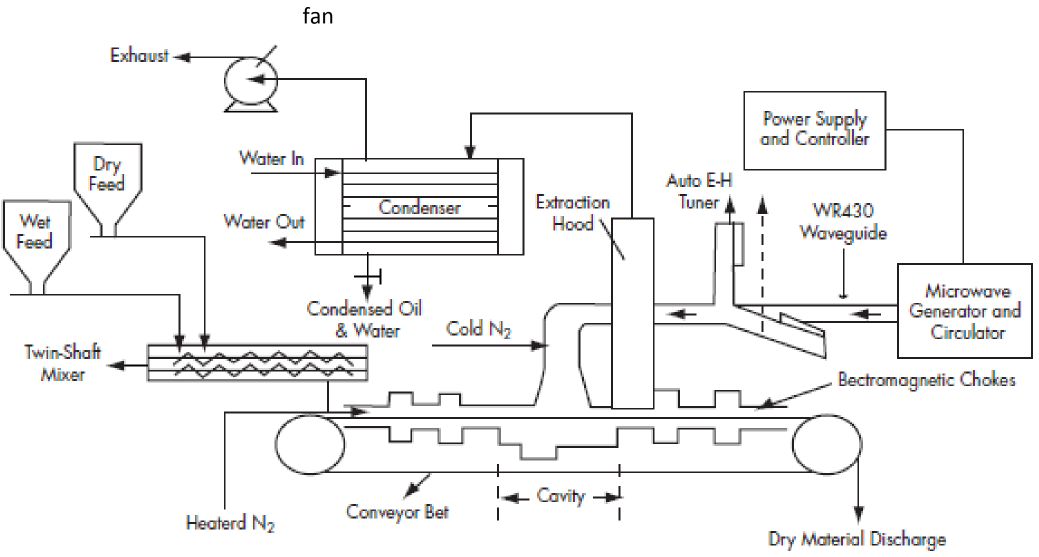

Figure 4: Schematic of a pilot microwave cuttings treatment unit (Robinson et al., 2008, Robinson et al., 2010)

Advantages of Microwave

- Meets regulatory requirements
- Fast reaction processes lead to low energy consumption
- Does not need constant supervision as compared to the TCC
- Good maintainability and less downtime
- Low footprints/deck impact
- Process rate could be very high with good design
- Heavy metals and salts are concentrated in the processed solids
- Faster settling speed due to larger particle size of final product
- Low environmental implications
- Potential good capital expenditure (CAPEX) and less operational expenses (OPEX)

Limitations to Microwave

- Robustness of the technology on an industrial scale is yet to be tested
- Inhomogeneous distribution of microwave energy could affect the efficiency of treatment

2.3.1.3 ***Rotary Kiln***

Rotary kilns are heat exchangers which consist mainly of a long inclined rotating cylinder driven by a direct motor. The cuttings are fed continuously into the upper end of the cylinder (inlet chute) and transported to the discharge chute due to the inclination and rotation of the cylinder. As it moves from one end to the other, hot exhaust gases (1200-1500 ^{o}C) generated by the combustion of fuel dries it at very high temperatures (Liu et al., 2016), Figure 5. Unlike the microwave method that allows for oil recovery, the temperatures are very high in the kiln and cracks the oil beyond reuse. More so, it is a very energy intensive process and not suitable for offshore purposes.

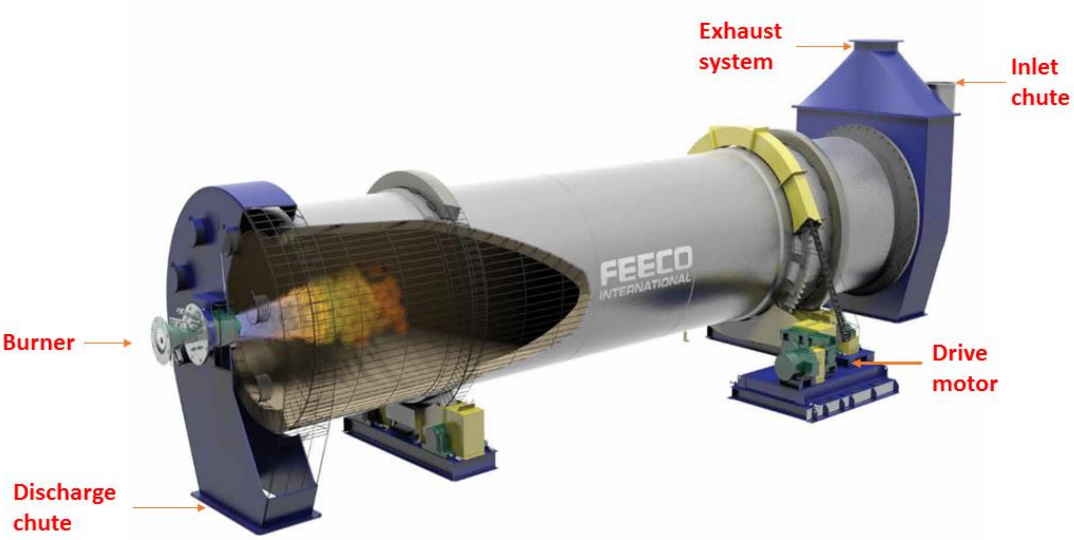

Figure 5: Rotary Kiln (FEECO, 2017)

2.3.1.4 *Biological Treatment of Drill Cuttings*

Biological treatment involves the use of bacterial products to enhance the natural degradation process in a bioreactor. The products are from naturally occurring materials that are capable of degrading toxic organic compounds. Parameters such as temperature, oxygen supply, moisture and nutrient within a reactor are controlled to speed up the decomposition process (Cripps et al., 1998). Bio-surfactants are used to enhance the remediation process. This helps to reduce the surface tension at air–water interface and thereby offering high activity at environmental conditions which translates to good biodegradability and environmental compatibility (Yan et al., 2011). Although landfill bioremediation is practiced in some locations, it has limitations such as: increased risk of leaching, potential waste management issues and increased cost of cleaning of landfills. In addition to these, large footprints (land) are required and the cost of transportation remains high.

2.3.1.5 ***Chemical Washing***

Chemical washing method uses chemicals to remove hydrocarbons from contaminated cuttings. According to Perry and Griffin, two types of chemicals can be used; solvents and surfactants (Perry and Griffin, 2001). The process itself has to do with separation of the cuttings through a series of sieves until the required goal is reached. This process has limitations such as: 1) high cost of chemicals, 2) high volume of water used which require treatment before discharge, 3) large footprints to handle huge volumes.

2.3.1.6 ***Cuttings Dryer***

Cutting dryer is a high-speed centrifuge for maximum separation of drilling fluids (Schlumberger, 2016). The design is a combination of a fine-screen and rotating basket that generates the centrifugal forces (CAPP, 2001). The cuttings are routed from shakers via a conveyor or vacuum transfer system to a dryer, through the top feed inlet and separated inside the dryer. The clean solids get out through the bottom and collected in boxes for further treatment or discharged. The recovered liquid is run through a decanter centrifuge for final clarification, storage or reuse. Optimum conditions will still retain about 5 % residual oil content (ROC) (Gerard and Antle, 2003). This is too high to meet OSPAR regulations for direct discharge. Further treatment is therefore necessary. In regions like the Gulf of Mexico, where discharge limits are 6.9%, the cuttings dryer is still used (Whitford, 2009). Figure 6 describes how the cuttings dryer functions.

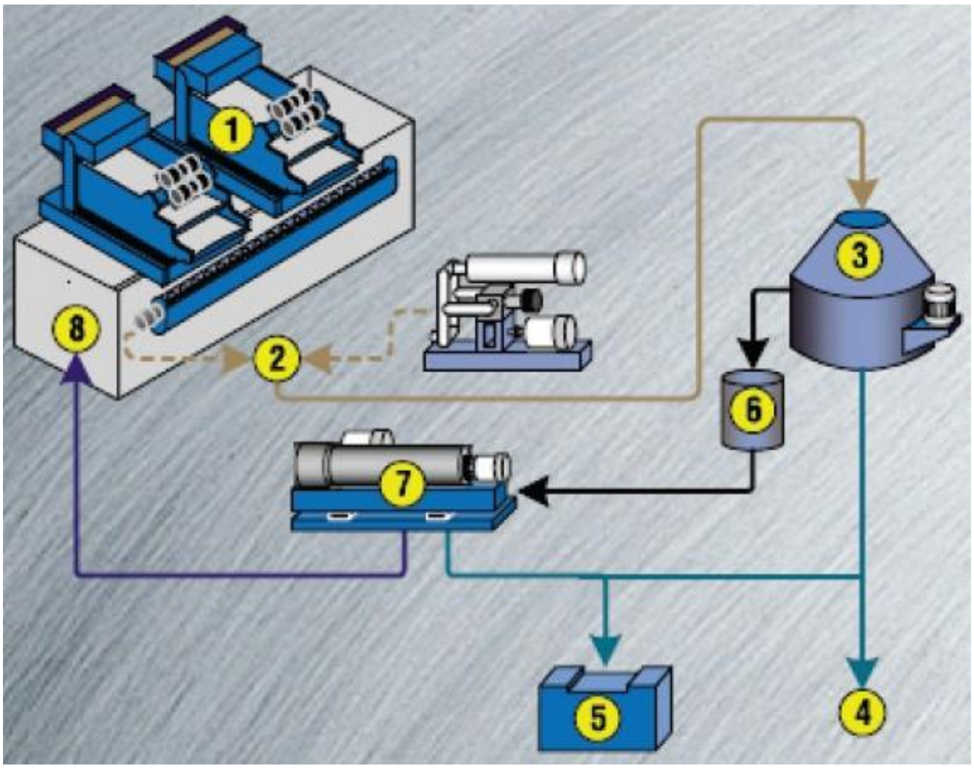

Figure 6: The Vertical Cuttings Dryer (GN, 2017)

1. Solids control equipment
2. Vacuum transfer unit
3. Top feed inlet
4. Discharge overboard
5. Cuttings boxes
6. Liquid collection tanks
7. Decanting centrifuge
8. Storage and reuse

2.3.1.7 ***Decanter Centrifuge***

A decanter centrifuge separates solid materials from liquids in slurry based on buoyancy or settling properties as defined by Stokes Law. It is a continuous process that uses centrifugal forces up to 4000 Gs. Denser solid particles are pressed outwards against a rotating bowl wall and the less dense liquid phase forms a concentric inner layer, when subjected to such high forces. A screw conveyor continuously removes the solid particles whilst the clarified liquid is also removed under pressure in the opposite direction. A variable frequency drive (VFD) is used to automatically adjust the speed of the screw conveyor. These centrifuges are designed specifically to process drilling fluids to the highest environmental standards with high fluid recovery rates (Schlumberger, 2016). They however have low process rates <40g/min (CAPP, 2001). Figure 7 shows a typical decanter centrifuge from Flottweg.

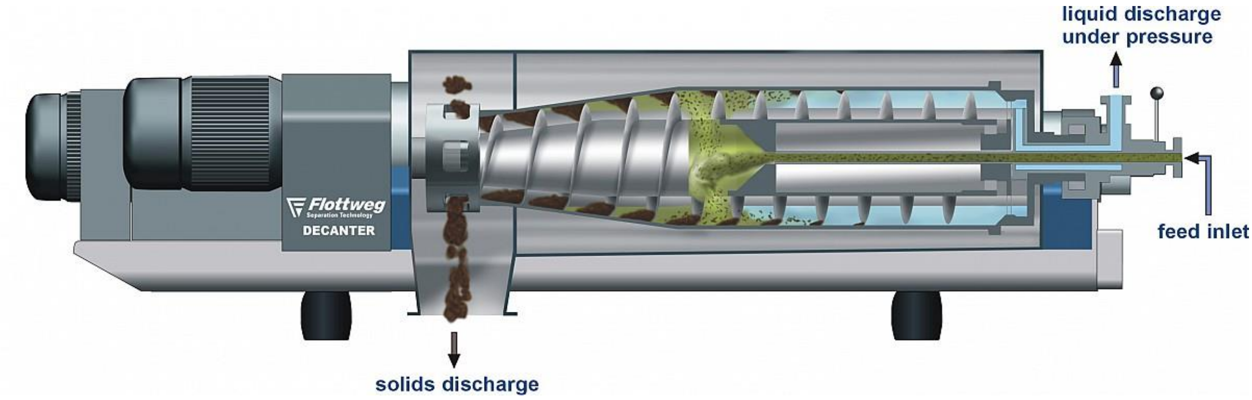

Figure 7: Operating principle of a decanter centrifuge

2.3.1.8 *Cuttings Reinjection (CRI)*

CRI is purported to be an environmentally sound, cost- effective method of zero discharge waste disposal. The cuttings are mixed with sea water to form a stable viscous slurry which is pumped into a dedicated disposal well or through the annulus between casing strings (Minton et al., 2006). Some disadvantages related to this method are:

1. Annuli and casing can be blocked
2. Injection perforations can also be blocked
3. Slurry can migrate through natural fractures or poorly cemented sections of the well back to the surface
4. Fractures can extend to the seabed and subsequently release slurry
5. Significant environmental damage and high remediation cost due to slurry release
6. Heavy fines can be slapped on operators.

Figure 8 shows a simplified schematic of the reinjection process.

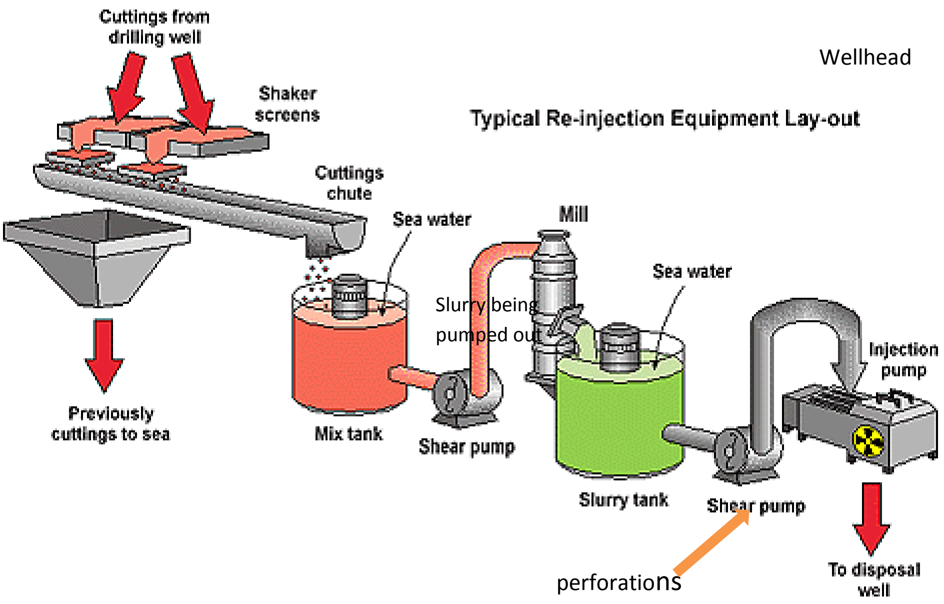

Figure 8::CRI schematic (Gidatec, 2017, Minton et al., 2006)

2.4 Comparison of Treatment Methods

A comparison of the treatment methods described so far shows their advantages and disadvantages. The overarching goals of a BAT offshore are: 1) to reduce health and safety issues to the barest minimum (example, skip and ship), 2) reduce CAPEX and OPEX, 3) satisfy footprints restrictions on the platforms, 4) satisfy environmental regulations, 5) enhance operability and maintainability to reduce downtime, 6) reduce energy consumption and 7) maintain environmental integrity.

Currently, the TCC is the BAT for cuttings treatment in the oil and gas industry. It was permitted to be used on the Martin Linge Platform until continuous monitoring showed that it failed to meet the criteria of 0.05% OOC and 30mg/ L discharge limit on recovered water, set by the Norwegian Environment Agency (NEA) (NOROG, 2016). Apart from that, the TCC is very expensive and requires large footprints on the rig. Although Halliburton boasts of a compact and stackable design, the taken space is significant on the rig. Although it meets the OSPAR criteria of <1% OOC, companies and statutory regulations in Norway set higher standards. The quest is still on for a better system than the TCC.

Microwave steam distillation and susceptor technology has the potential to offset most of the challenges associated with the TCC to meet the goals mentioned earlier. In that, it has the minimal environmental impact compared to the others. In addition to that, it minimizes safety issues associated with crane movement and reduce transport and operational cost offshore. An integrated waste management treatment plant will minimize space requirement on offshore platforms. Although the technology has been tested on a pilot scale, more research is being done on optimizing it to industrial scale.

2.5 Cost of Handling and Treating Cuttings

The cost of handling and treating cutting is influenced by geography of the field. Most of the expenses goes into the logistic involved in transportation from the field to the treatment facility. This varies from one location to the other. A field in Angola or Ghana will not cost the same as a field in Norway. A comparison between cuttings re-injection, offshore and onshore treatment in Norway was conducted by Karlsen in 2013. They demonstrated that offshore treatment would be cheaper than the others (Table 1)

Table 1 Cost of cuttings handling (Karlsen, 2013)

Alternative	**Cost (per ton in NOK)**
Offshore treatment	6500
Onshore treatment	9000
Re-injection	9500

2.6 Legislation for Discharge

The offshore environmental legislation in Europe is guided by the Convention for the Protection of the Marine Environment of the North East Atlantic (OSPAR). This came to birth after member states met in Paris on in September 1992. OSPAR Commission was established as a result of this meeting to oversee the protection and preservation of resources, biodiversity and other environmental aspects of the North-East Atlantic (OSPAR, 2016).

The “polluter-pays principle” and the “precautionary principle” were adapted by OSPAR to work out decisions and recommendations to be adhered to by Norway, UK and other contracting parties (Ormeloh, 2014). The precautionary principle states that whenever there is scientific uncertainty about the likely occurrence of a negative event, precautions should be taken. The polluter pays principle means that the offending party should bear the consequences of pollution and put measures to mitigate the impact of pollution. The commission also requires all contracting parties to apply the principles of best available technique (BAT) and best environmental practice (BEP). BAT is the state of the art technology suited for limiting waste, discharge, and emissions, whilst BEP is a combination of most appropriate environmental control measures and strategies. In relation to drill cuttings the decisions in Table 2 are relevant.

In Norway, the use and discharge of drilling fluids is governed by Norwegian Environmental Agency (NEA) through issuance of discharge permits. The Activities Regulations (PSA, 2016), which govern how activities in the Oil and Gas Industry shall be performed, is used for the evaluation of permit applications. Some relevant sections of the regulations are:

§ 60 Water discharge to sea in any event, shall not have oil content exceed 30 mg oil per litre of water as a weighted average for one calendar month.
§ 68 Cutting and other solids to be discharged should not have oil content exceeding 1 % weight on dry basis.

Table 2: OSPAR Decisions

Decision	Summary
Decision 2000/2	Authorities shall ensure that hazardous substance are substituted. The birth of Harmonized Offshore Notification Format (HOCNF)
Decision 2000/3	Disharge of Organic Phase Fluids (OPF) is prohibited with limits of <1 wt% OOC
Recommendation 2005/2	Phase out all chemicals on the list of priority action due toxicity, bioaccumulation potential by January 1, 2010.
Recommendation 2006/3	Contracting parties should have phased out chemical identified for substitution by January 2017

2.6.1 Other regions

Regulations vary around the world. For instance, in the Gulf of Mexico 6.9 % wet weight limit is set for internal olefin base fluids (SBM), whilst it is set at 9.4 % when the SBM is ester based. The discharge of OBM is prohibited (Whitford, 2009). In Malaysia, there is no limitation for the discharge of WBM, SBM, or OBM (Bernier et al., 2003, Whitford, 2009).

PART 2-THEORY OVERVIEW

3 Mechanism for Microwave Treatment of OCDC Using Susceptor Technology

3.1 Mechanism of Oil and Water Separation From OCDC Using Microwaves

Earlier studies have shown that removal of oil from drill cuttings during microwave processing can be achieved through three mechansms; 1) evaporation using gas such as air or nitrogen, 2) vaporisation or steam distillation and 3) entrainment (Robinson et al., 2009a). Vaporisation is however identified as the main mechanism (Pereira, 2012). Parameters such as density, intial water content and size of particles affect these mechanisms. The effect of using nitrogen gas as a sweep gas in oil removal was investigated by Pereira, 2013 (refer to Figure 9). These results showed that the weight of the sample reduces from 150 to132 g within 2 mins when subjected to MW power of about 700W and 15L/min supply of nitrogen gas. This shows that the use of nitrogen gas alone (without microwave heating) with increased flow rate, did not cause a significant weight change.

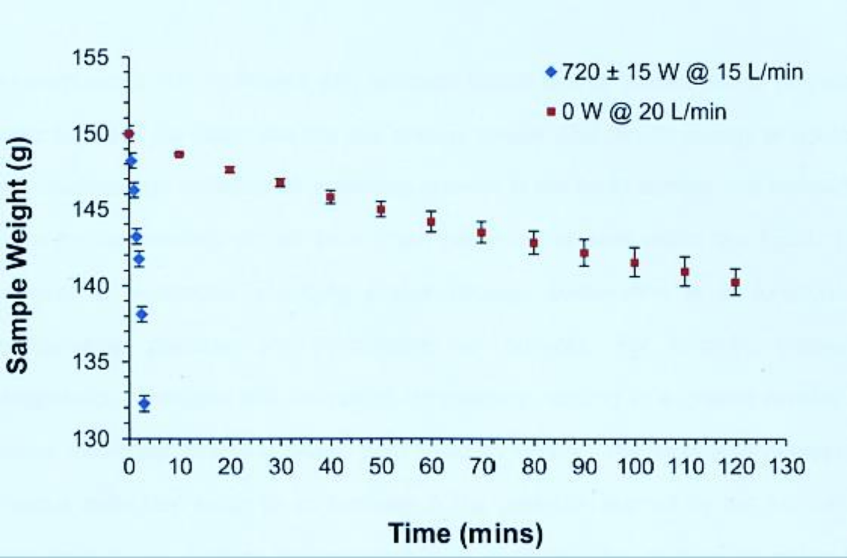

Figure 9: Variation of weight in sample (Pereira, 2012).

3.1.1 The Effect of Density on Oil Removal

There are different ways in which liquids are held in cuttings. The free liquids available on the near surface and surface are easily vaporized but liquids held in a bound state require more energy and time to be removed. Pereira, 2013 investigated this phenomenon and explained that during initial microwave drying, liquids are removed from the surface but in later stages the main limiting factor is how to drive the vapor present within the pores and structures of the cuttings to the surface (Pereira, 2012). In the same vain, when susceptors are being used for oil separation during steam distillation, it can be trapped in these pore structures as shown in Figure 10. This may require more energy, stirring or/and the application of heated nitrogen gas to remove it.

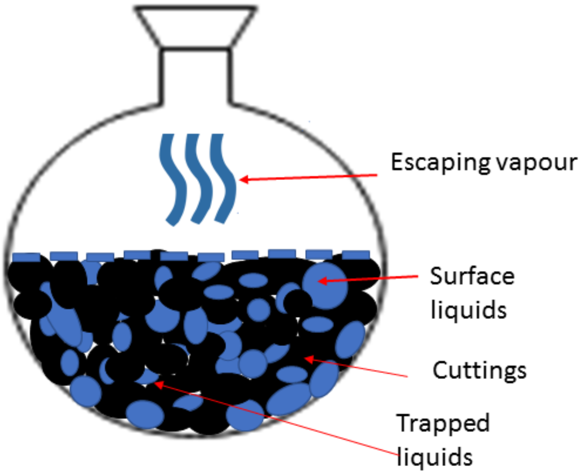

Figure 10: Trapped liquids in treated cuttings

Another reason for liquids being held interstitially is due to density variations of the drill cuttings. Earlier studies have demonstrated that oil removal is better in samples with lower densities and higher pores. This is expected since lower density materials may have larger overall surface areas for contact between the steam and oil in the samples than when the sample is more compact. In this case, some oil will be locked away in the sample bed and become hard to reach by the steam as shown in the graph in Figure 11.

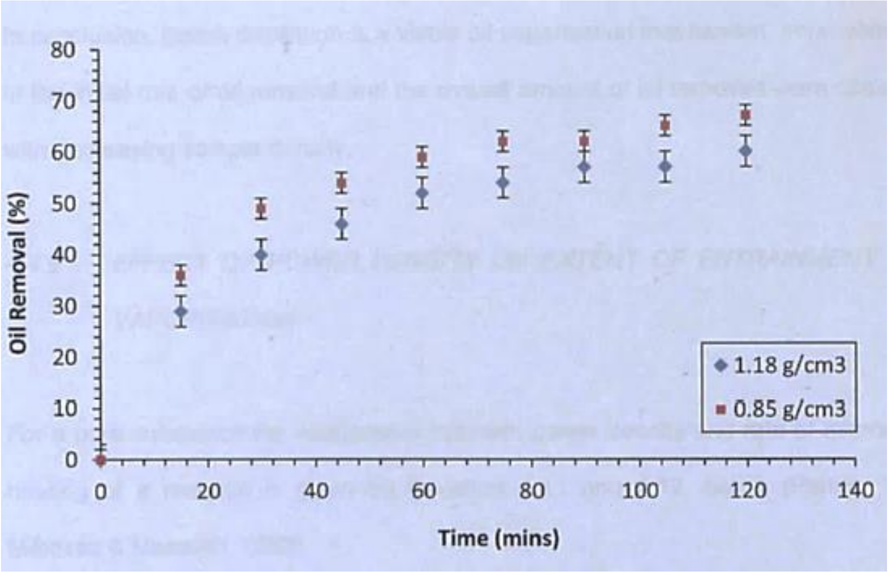

Figure 11: Oil removal from samples with different bulk densities (Pereira, 2012)

It is observed that the amount of oil collected from sample with density of 0.85 g/cm^3 was about 5-10 % more at any time considered during the process as compared to the other sample with density of 1.18 g/ cm^3.

3.1.2 Effect of Particle Size on Oil Removal Process and Energy Requirement

The effect of particle size on the microwave process is primarily due to electric filed distribution in different sample sizes and the effects of mass transfer. Large particles have lower electric field strengths than smaller particles. This results in low heating rates and longer path lengths and resistances to mass transfer (Pereira et al., 2011). Earlier works by Pereira et al, 2011, proved that small aggregate sizes contained more oil than large ones. The reason is the large surface area of small particles which allow for oil to attach to its surface. It is observed in Figure 12 that the oil content in a sample decreases with increased particle size. Per the study, about 15 % energy savings could be achieved with sizes <1 mm. However, it might not be economical to explore this energy savings commercially. The reason being that there is additional cost incurred in getting a bulk handling equipment, footprint and storage (Pereira et al., 2011). This may defeat the purpose of the microwave technology in terms of cost and small footprint requirements.

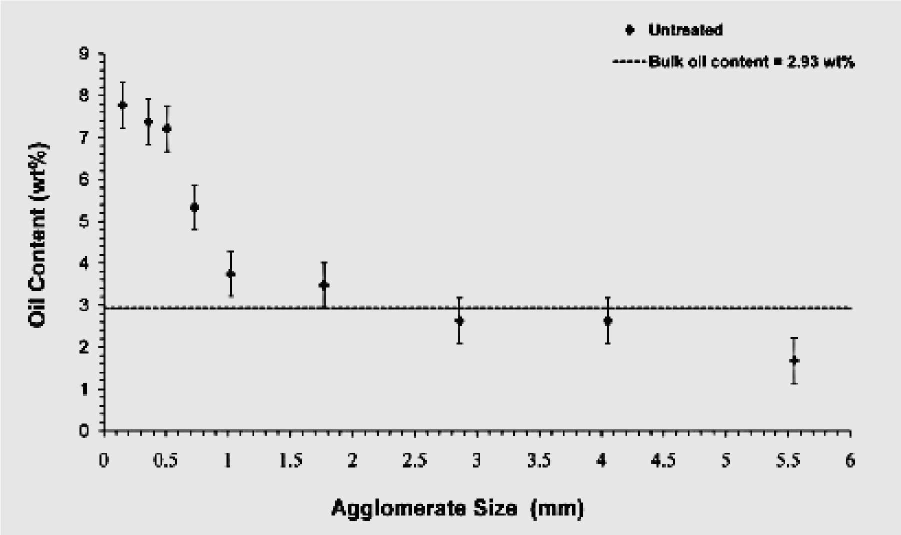

Figure 12: Oil content in untreated sample

3.1.3 Effect of Nitrogen Gas on Microwave Treatment Process

Nitrogen gas maintains inert environment during the treatment and reduces the risk of explosions. It improves the treatment process in two major ways; 1) as a sweep gas it reduces stagnation and increases the concentration gradient between the sample surface and the bulk gas (Pereira, 2012). This implies a stronger driving force and prevention of saturation that can lead to 2) re-condensation. It is important to note however, that adding nitrogen at room temperature will lead to undesired re-condensation (Rossi, 2016).

3.1.4 Effect of Initial Water Content

The study by Shang, et al., 2005 indicated that a minimum amount of water content is critical for oil removal in a sample since the removal process is through entrainment and steam distillation. Going above the minimum amount does not add any benefits but rather require more energy. The same idea applies in the use of organic compounds as susceptors. However, a study in 2016 indicated that water is a limiting factor in microwave steam distillation due to its thermal properties. The strong hydrogen bonds make the enthalpy of vaporization of water very high, requiring more energy. Using organic compounds rather than water leads to significant energy savings since they are highly volatile and require less energy to vaporize.

4 Introduction to Dielectric Heating

4.1 Electromagnetic Theory

James Clerk Maxwell in 1865 developed a scientific theory to explain electromagnetic waves. He demonstrated that electrical and magnetic fields could be coupled together to form electromagnetic waves. His experiments showed that a changing electric field results in a changing magnetic field and vice versa. He also predicted that electric and magnetic fields are perpendicular to each other and perpendicular to the direction of propagation of the wave, Figure 13. These discoveries lead to the famous Maxwell's equations (1) and (2), which are the physical laws that describe electromagnetic fields varying with time (Thostenson and Chou, 1999). They are fundamental to the design and operation of microwave applications.

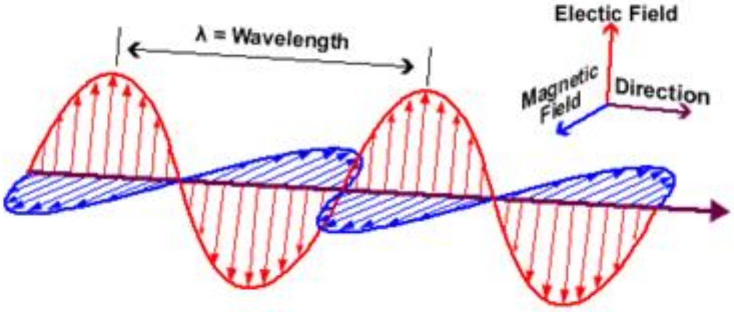

Figure 13: Propagation of electromagnetic wave

$$\nabla \times \mathbf{E} = \frac{\partial \mathbf{B}}{\partial t}, \qquad \nabla . \mathbf{B} = 0 \tag{1}$$

$$\nabla \times \mathbf{H} = \frac{\partial \mathbf{D}}{\partial t} + \mathbf{I}, \qquad \nabla \cdot \mathbf{D} = \rho \tag{2}$$

In equations (1) and (2), **E** is the electric field vector, **H**, the magnetic field vector, **D**, the electric flux density vector, **B**, the magnetic flux density vector **I**, the current density vector, and ρ is the charge density

4.1.1 Microwaves

Microwaves fall between wavelengths from 1 mm to 1 m and corresponding frequencies between 300 MHz and 300 GHz of the electromagnetic spectrum (EMS). This portion also includes frequencies used for radar, television satellite communications and cellular phones (Thostenson and Chou, 1999).

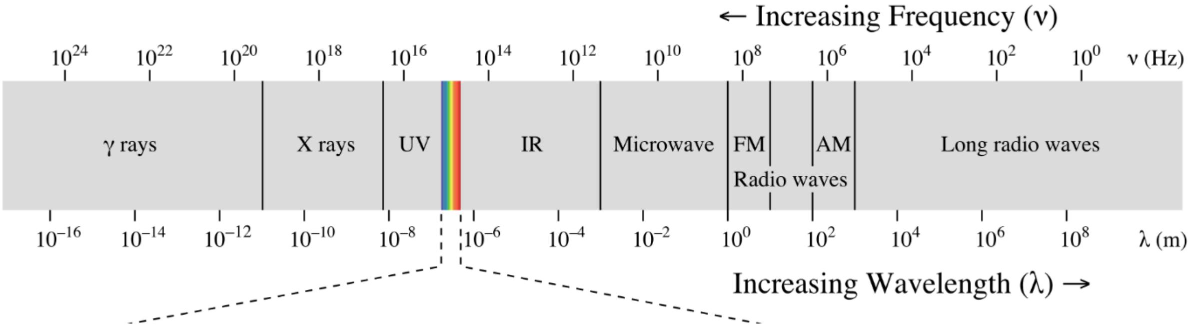

Figure 14: Electromagnetic spectrum

4.1.2 Complex Dielectric Permittivity

Microwaves can be described as a constantly alternating electromagnetic field, applying a series of alternating potentials as it passes through a dielectric material (Pereira, 2012). Absorption of microwave energy by lossy materials is due to dipole polarization. There is a series of re-orientation of charges within the material with collisions, vibrations, and distortion of lattice structure in materials with fix charges. The field reverses with high frequency causing collisions and vibrations which lead to dissipation of the potential energy gained during polarization into heat (Thostenson and Chou, 1999). The ability for materials to polarize is characterized by the so called **relative dielectric permittivity or dielectric constant**, ε', presented in equation 3.

$$\varepsilon' = 1 + \frac{N\alpha_p}{\varepsilon_0} \tag{3}$$

Where α_p is the polarizability of the medium, N is the particles concentration.

Other polarization mechanisms such as electronic, ion (atomic), dipolar and interfacial (Maxwell-Wagner) contribute to what is called the **dielectric loss factor** ε'' (equation 4).

$$\varepsilon'' = \varepsilon''_d + \frac{\sigma}{\varepsilon_0 \omega} \tag{4}$$

Where $\boldsymbol{\varepsilon''_d}$ is the **dielectric loss** due to the dipole polarization and $\boldsymbol{\sigma}$ is the **ionic conductivity**. From equations 1 and 2, the electronic and atomic polarizations can be ignored since they fall mainly at the infrared and optical frequency. The dielectric properties of materials can then be described by combining the two equations to get the **complex dielectric permittivity $\boldsymbol{\dot{\varepsilon}}$,** equation 5. Another term used to compare the dielectric loss of materials is the tangent of loss angle (equation 6). A good microwave absorbing material has tan δ ≥ 0.01 and poor ones have tan δ ≤ 0.01 (Bykov et al., 2001).

$$\dot{\varepsilon} = \varepsilon' - j\varepsilon'' \tag{5}$$

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} \tag{6}$$

It is important to note that both $\acute{\varepsilon}$ and ε'' are affected by frequency, temperature, moisture, and pressure. However, since most microwave applications operate at normal pressure and fixed frequencies, $\dot{\varepsilon}$ mostly depends on temperature and moisture (Komarov, 2012).

The power density inside the material is determined by equation, 7 and the depth of microwave penetration into the dielectric material D_p is given by equation 8.

$$P_d = 2\pi f \varepsilon_0 \varepsilon'' E_i^2 \tag{7}$$

Where P_d is the power dissipation density in Wm^{-3}, f is the frequency in Hz, ε_0 is the permittivity of free space (8.8 x10 $^{-12}$ Fm^{-1}) (Benenson et al., 2001) and E_i represents the internal voltage stress in the dielectric (Vm^{-1}).

$$Dp = \frac{\lambda\sqrt{\varepsilon'}}{2\Pi\varepsilon''} \tag{8}$$

From equation 8 a higher penetration depth is achieved by increasing the wavelength (λ) whilst it will decrease when the dielectric loss factor is increased.

4.1.3 Power Density

The power applied and absorbed by a material determines the amount of energy being dissipated per second. This provides the heating rate during processing of material per given volume, see equation 9. Power density is basically the amount of power transferred per unit volume. In microwave heating, it refers to power that is dissipated into the sample under consideration. The unit of measurement is W/m^3 (Pereira, 2012). Materials with higher dielectric constant and loss have higher power density than those with lower. From equation 7 it can be said that microwave energy absorbed by a dielectric material is proportional to the square of the electric field strength. This information is critical for design of the microwave cavity. It can be designed to have a definite electric field in a relatively small volume, in this case called a single mode cavity. It can also be designed to allow electric fields to cover a much larger volume with less defined field, in this case called a multimode cavity (Robinson et al., 2010). The heating rate of a particular component depends on power density, specific heat capacity and density, equation 9.

$$\frac{\Delta T}{\Delta t} = \frac{2\pi f \varepsilon_0 \varepsilon'' |E|^2}{\rho Cp} \qquad (9)$$

Where T is temperature, t is time C_p is specific heat capacity and ρ is the density of the material

4.2 Thermal Runoff

As described earlier, selective microwave heating is due to the dielectric and thermal properties of materials and the impact of temperature. Thermal runoff is one of the reasons for uneven distribution of heat in lossy materials. It is described as the uncontrolled rise of temperature in a local area in the sample (Komarov, 2012). The rapid increase of the loss factor (ε'') can result in thermal runoff since more energy is absorbed when $\varepsilon''$is higher. The result is overheating and possible damage of a sample in the microwave.

The Figure 15 A and B show how thermal runoff leads to increase in temperature within a sample and subsequent breaking of a glassware during one of the experiments. It is evident in this case that the sample contained a mixture if components with varying dielectric properties. Components with high loss factors must have been concentrated in this location and absorbed a lot of energy. After emptying the reactor, normal clay particles were obtained but the overheated component was pitch black and as hard as a rock. It could not be broken apart easily

(Figure 15 B). No further test was conducted to identify these components and their dielectric properties.

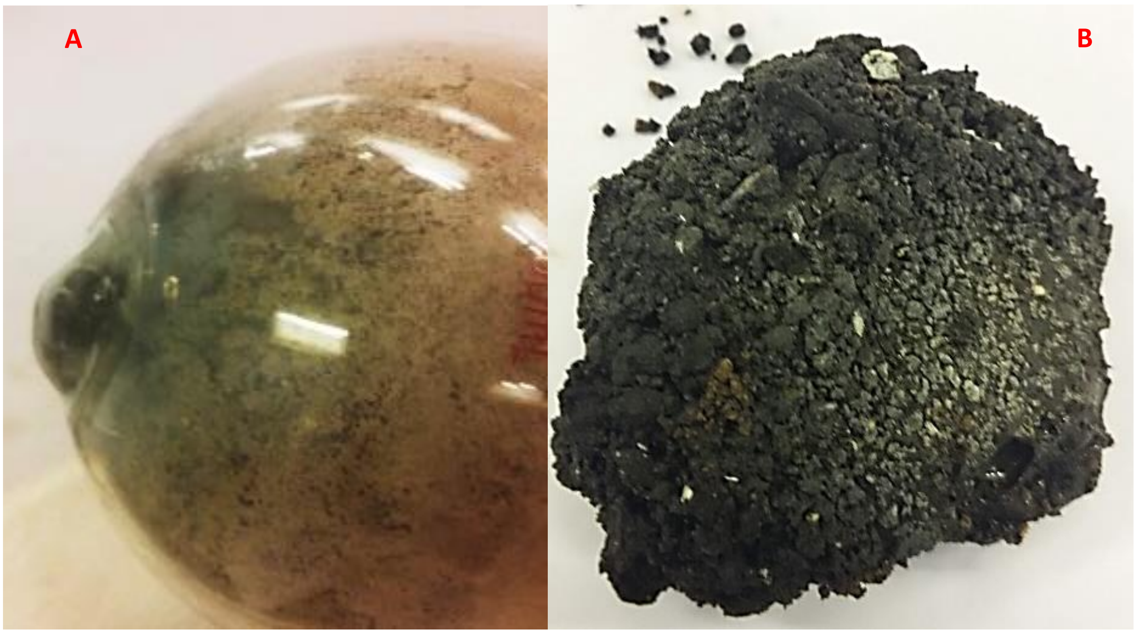

Figure 15: Effect of thermal runoff

A) Thermal runoff caused the round bottom flask to bulge out B) The part of sample that was superheated, formed a very hard material that was strongly bound together

In 'A' a localised area of the sample got overheated and caused the round bottom flask (reactor) to bulge out and break. 'B' is the part of the sample that got overheated

4.3 Microwaves and Arcing

Microwaves bounce around in an enclosed cavity until they are absorbed by a material placed inside the cavity. The interior walls of the cavity are tuned to the frequency of the energy output and anything that interrupts this arrangement can lead to abnormal results called arcing (Gallawa, 1989). The oscillation of the microwaves produces a concentrated electric field at corners or an edge of a metallic object causing the ionization of the surrounding air. The ionized air acts as an electrical conductor (Ross, 2010), allowing electric current to flow. The current can be propelled from the corners or edges and observed as a small bolt of lightning. So long as the energy is being applied, arcing will continue and may cause pitting of surfaces or burn a hole through the cavity wall (Gallawa, 1989).

4.4 Microwave Components and Applicators

A microwave setup includes four main components; 1) microwave generators, 2) transmission components, 3) power supply and 4) microwave heating applicators.

4.4.1 Microwave Generators

Microwaves are generated in vacuum tubes. Three main tubes used are: 1) travelling-wave tubes (TWTs), 2) klystrons and 3) magnetrons. Magnetrons are preferred due to lower manufacturing cost, reliability and high conversion rate from electrical power to microwaves (Meredith, 1998). This is the type commonly used in domestic microwave ovens. It uses resonant cavities to generate electromagnetic waves at fixed frequencies, Figure 16. The anode is at a high potential compared to the cathode which create a potential difference and corresponding electric field. Heating the cathode causes the loosely bound valence electrons to be removed and accelerated towards the anode by the electric field. An external magnet is used to create a magnetic field. The combination of electric and magnetic fields causes an electron cloud to be formed as they are accelerated towards the anode. As electrons pass the resonant cavities, the cavities set up oscillations in the electron cloud, with varying frequencies depending on the size of the cavities. The reader is referred to further literature on generators (Meredith, 1998, Pereira, 2012, Staprans et al., 1973, Tsimring, 2007).

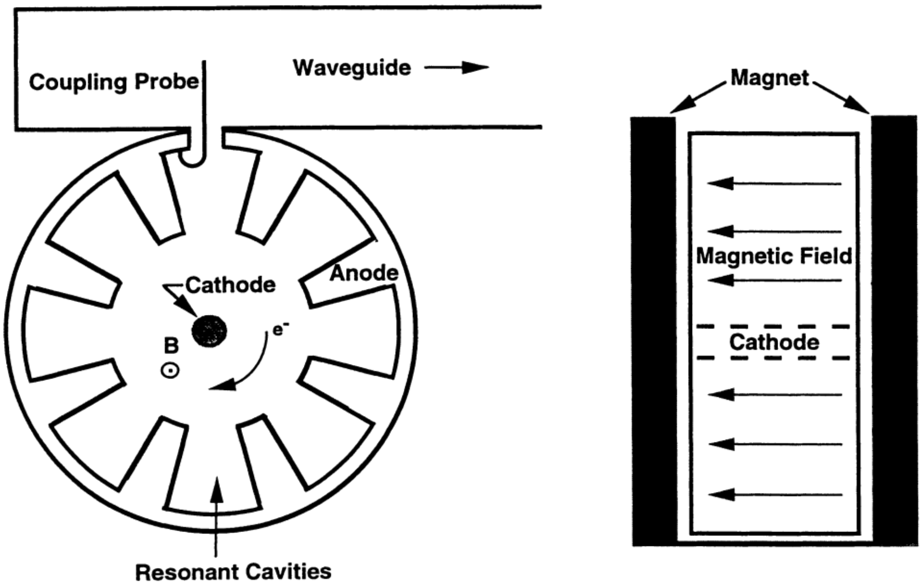

Figure 16: Schematic of a magnetron microwave tube (Thostenson and Chou, 1999).

4.4.2 Transmission Components

Microwaves are transmitted from the generator through cylindrical or rectangular waveguides to the load. When materials that are not good absorbers of electromagnetic energy are heated, a significant amount of the energy is reflected to the source, which can destroy the magnetrons. Circulators are specially designed waveguides used for the protection of the system. They allow power from the magnetron to be directed into the load and redirect reflected power into a dummy load, often water, to prevent damage to the magnetron (Thostenson and Chou, 1999). Tuners are used to maximize energy absorption in the load through impedance matching. A number of tuners are used so that the differences between the impedances of the microwave source can be adjusted (Thostenson and Chou, 1999).

4.4.3 Applicators

These are cavities of specific dimensions that are connected to the generator via the wave guides. They allow energy to be transferred to the load. Different types of applicators exist. However, this study is limited to single mode and multiple mode applicators.

4.4.3.1 *Single-mode Applicators*

Single mode applicators have non-uniform but predictable electric field distributions. The areas of high and low fields are therefore known. This makes it possible to design an applicator to focus microwave field at a given location so it can achieve high power density (Thostenson and Chou, 1999). However, it can yield electric field distribution which falls to zero at the cavity walls by its design (Robinson et al., 2010). From equation 7, $P_d = 2\pi f \varepsilon_0 \varepsilon'' E_i^2$, power density will reach its peak at the center and reduce to zero at the edge of the cavity (Robinson et al., 2010). This implies that there will be enough treatment in some areas than others. To get high and even power densities throughout the cavity, a tunnel applicator with a self-cancelling reflection step may be used. Refer to (Robinson et al., 2010).

Single mode applicators are designed for specific purposes due to the non-uniform fields and limitations due to geometry of materials (Thostenson and Chou, 1999).

4.4.3.2 ***Multi-mode Applicators***

Multi-mode applicators are made to sustain many high order modes simultaneously. The home microwave oven is an example. The presence of different modes results in low peak power density as well as large power density distribution within the cavity (Robinson et al., 2010). However just as with the single mode, local fluctuations in the electromagnetic field result in localized overheating. This is the reason for using turntables in the home oven. The turntables rotate during operation and reduce the effect of multiple hot spots by passing the load through areas of high and low power to achieve average uniformity. The multi-mode applicator is more versatile than the single mode applicator for operations of large scale, batch processing and objects of complex geometry (Thostenson and Chou, 1999).

A multimode cavity MW oven was used in a study, for the treatment of drill cuttings in 2005. The study showed that during the treatment of cuttings, there were dry and wet patches in the sample after treatment. Meaning that heat was not evenly distributed throughout the sample. This was alluded to the uneven electric field distribution within the cavity (Shang et al., 2006). To improve temperature distribution, the sample was conditioned with more water to make it semi-fluid. They also increased the retention time to allow for better conductive heat transfer.

5 The New Microwave Technology from Norwegian Technology AS

The use of the microwave in combination with susceptors is the brainchild of Norwegian Technology AS. This technology offers tremendous benefits for the treatment of OCDC in terms of oil separation at high process temperatures, albeit, using less energy. The system is robust with good maintainability and potentially, less downtime.

In addition to these, the use of susceptor offers high treatment capacity compared to using ordinary microwave method, where water is the main microwave absorbing medium. This is because the chemicals are very volatile with significantly lower enthalpy of vaporization and produce high enough process temperatures, than water. The high process temperatures enable high vapour pressure contribution from the oil, Table 4.

Table 3 and Table 4 compares the effect of process temperature on oil separation for Sipdril and Clarisol when distilled with water and glycerol whilst Figure 17 shows the enthalpies of vaporization for water, MEG and TEG. According to Raoult's and Dalton's Laws, high process temperatures lead to high shared vapour pressures, between the oil and glycerol compared to that of oil and water. This translates to better oil separation, marked by the distillation ratios. There is significant energy efficiency due to the high volatility of these chemicals as evident in Figure 17.

Furthermore, to meet regulatory requirements, a second barrier is needed where adjustments can be made to correct any irregular or unexpected outcome from the treatment process. For instance, if the particles sizes and water content are not optimal for oil separation, or the amount of susceptor is not yielding good results on oil removal, the parameters can be easily adjusted with minimal downtime. The flexibility offered by this technology makes it superior to other drill cuttings treatment methods.

Table 3: Vapor pressure and distillation ratio when distilling with water

Distilled Oil	Theoretical boiling point with Water	Vapor Pressure – mmHg (Oil/Water)	Distillation ratio (ml oil/ml Water)
Sipdril (tridecane)	100	7,3/758	1/9
Clarisol (Hexadecane)	100	0,57/758	1/90

Table 4: The vapor pressure and distillation ratio when distilling with Glycerol

Distilled Oil	Theoretical boiling point with Glycerol	Vapor Pressure – mmHg (Oil/Glycerol)	Distillation ratio (ml oil/ml glycerol)
Sipdril (tridecane)	228	636/125	17/1
Clarisol (Hexadecane)	265	457/300	6/1

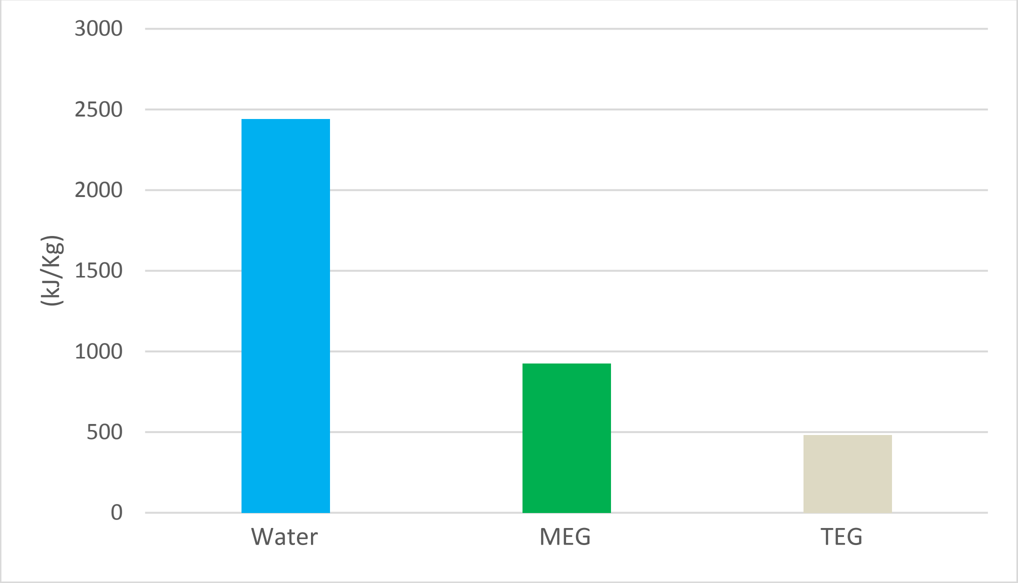

Figure 17: Enthalpies of vaporization for Water, MEG and TEG (Rossi, 2016)

If the assumption is made that the total amount of water is replaced with TEG, then energy consumption is approximately five times less, based on the enthalpy of vaporization. This could be improved further when the laws of Dalton and Raoult's are employed. This is because the oil removal mechanism depends on the combined vapour pressures of oil and susceptor. Assuming that 50 % of TEG is used and the oil supplements its vapour pressure, the energy consumption could drop to approximately 1/10th of what would be consumed if water is used (Rossi, 2016). The energy cost savings, low footprints, reduced weight, and improved treatment capacity provided by this new technology cannot be overemphasized.

The fundamental parameters; gas laws, vapour pressures, distillation and distillation ratios have been discussed in the works of (Rossi, 2016). They are however emphasized in the next sections since they form the backbone of the technology.

5.1 The Theory of Distillation

Distillation is the process of separating components of a liquid mixture by selective evaporation and condensation. The components of the mixture have different boiling point temperatures which is the major advantage of the process. Distillation can lead to total or partial separation of components depending on the margin of the difference between their boiling point temperatures. In the microwave and susceptor technology, water mixes with the susceptor after the first round of treatment since the cuttings always contain water. This means that, the susceptor will have to be recovered. Because the two components are miscible, it is challenging to separate them using simple distillation. Fractional distillation will have to be employed. This is however, energy intensive and the process may cause the susceptor to decompose. It is best to focus efforts to reduce the amount of water in the cuttings before dousing with susceptor.

The relevant parameters that surround the distillation process have been explained in succeeding sections.

5.1.1 Gas Laws

Distillation processes satisfy Raoult's law and Dalton's law of partial pressures. Raoult's Law is very significant to the distillation process since it describes the behavior of ideal miscible liquids. The law states that for ideal miscible liquids the partial vapour pressure of a component in a mixture is equal to the vapour pressure of the pure component at that temperature multiplied by its mole fraction in the mixture. For example, a mixture of liquids, 'A' and 'B' can be written as it is shown in equations 8 - 11:

$$\mathrm{P}_B = X_B \cdot P_B^o \tag{10}$$

$$\mathrm{P}_A = X_A \cdot P_A^o \tag{11}$$

Where:

P_A and P_B are the partial vapour pressures of the components A and B.

X_A = mole fraction of A

X_B = mole fraction of B

The mole fraction for A,

$$X_A = \frac{moles\ of\ A}{total\ number\ of\ moles} \tag{12}$$

The mole fraction for B,

$$\mathrm{X}_B = \frac{moles\ of\ B}{total\ number\ of\ moles} \tag{13}$$

P^o values are the vapour pressures of pure A and B and can be found using Antoine's equation:

$$\log_{10} P_n^0 = A - \frac{B}{C + T} \tag{14}$$

Where:

- $P^o{}_n$ - vapour pressure (mmHg)
- A, B, and C – unit-less constants for the specific components
- T-Temperature (°C)

Total vapour pressure,

$$P_T = P_A + P_B \tag{15}$$

Dalton's law of partial pressures also states that in a mixture of non-reacting gases the total pressure exerted by these gases is equal to the sum of the partial pressures of the individual gases (equation 13).

$$P_{total=} P_1 + P_2 + \cdots + P_{n-1} + P_n \tag{16}$$

5.1.1.1 ***Miscible Liquids***

As mentioned earlier, water mixes with the susceptor during microwave treatment. Oil, on the other hand, is immiscible with either of the two. According Raoult's law, these features play a significant role in steam distillation in terms of their vapour pressure contributions. To throw light on the mechanism involved, these parameters have been explained in detail here.

Illustrations of the exerted pressures of each component in a mixture consisting of 'A' and 'B' miscible liquids are shown in vapour composition diagrams in Figure 19. From Raoult's law, when the mole fraction is increased the partial vapour pressure is increased as well. This is to say that, the partial vapour pressure of ‘A’ at a temperature is proportional to its mole fraction. A plot of partial vapour pressure of ‘A’ against its mole fraction will result in a straight line for ideal mixtures. The same applies to ‘B’, but the mole fraction of ‘B’ falls as ‘A’ increases. So, the line slopes down. The vapour pressure is also higher, which means that the molecules break away more easily on the surface of ‘B’ than they do for ‘A’. That makes component ‘B’ the more volatile liquid. The sum of pressures is illustrated in Figure 20. Further applications of the concept are described in Chapter 7.

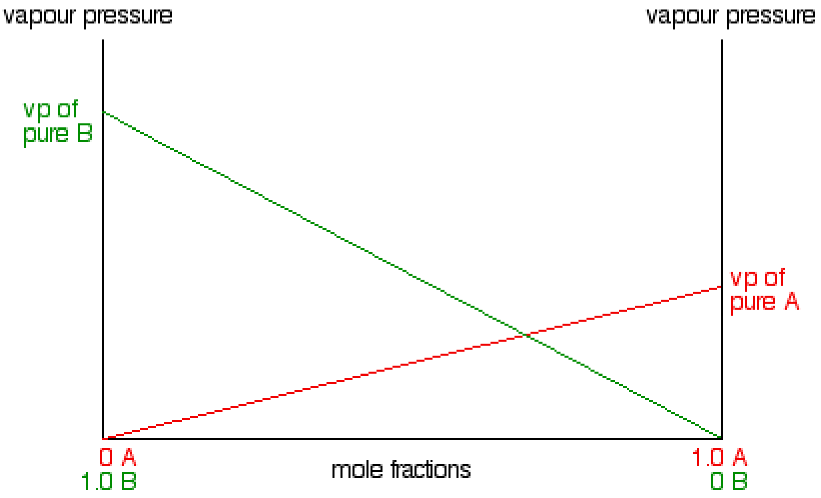

Figure 19: Raoult’s law for vapour pressure of liquids ‘A’ and ‘B’(Clark, 2005)

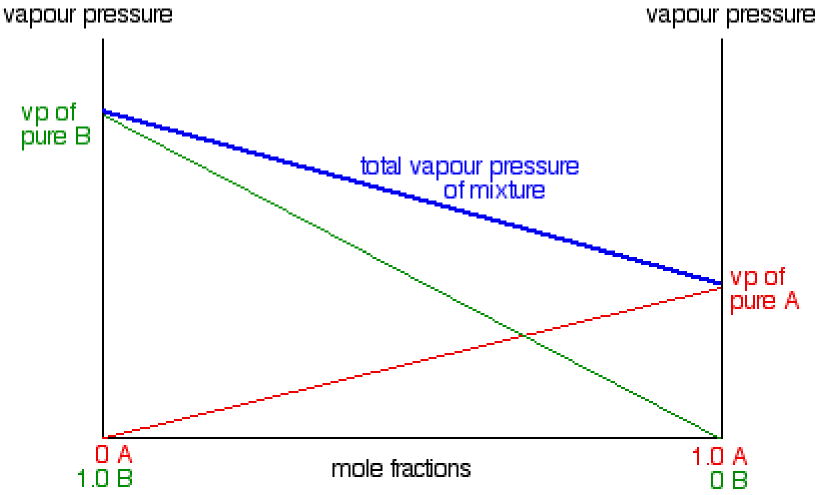

Figure 20: A combination of Raoult’s and Dalton’s laws

5.1.1.2 ***Immiscible-liquids***

Non-ideal mixtures will deviate from Raoult’s law to give a curve instead of a straight line. This is due to higher or lower actual vapour pressures than expected from Raoult’s law. In this case, the intermolecular forces between ‘A’ and ‘B’ are less than they are in their pure liquid forms, resulting in a positive deviation (see Figure 21). In the same way, vapour pressures can be lower than expected leading to a slightly negative deviation (Clark, 2005). Raoult’s law applies only to ideal miscible liquids.

It is important to note that with slight deviations, such as that illustrated in Figure 21, the mixture still behaves like an ideal mixture as far as distillation is concerned.

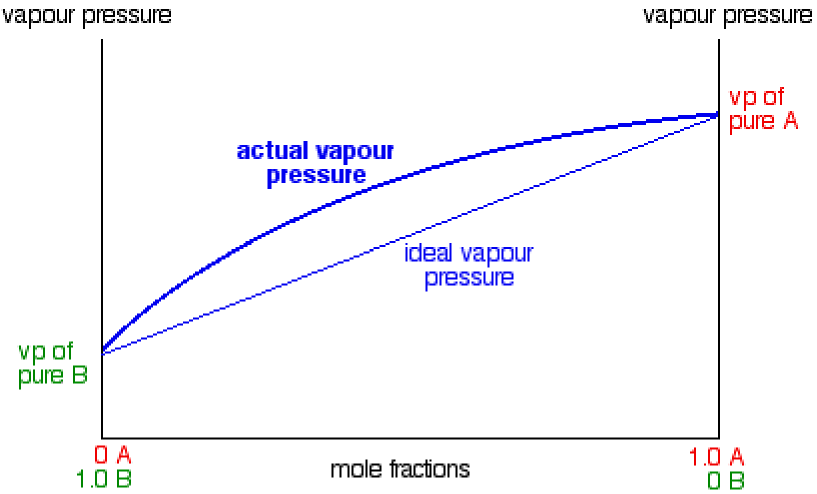

Figure 21: Slightly positive deviation from Raoult’s law

Some liquid mixtures have very large deviations from Raoult’s law with a more distorted curve. In such cases, Raoult’s law is no longer valid, since each component in the mixture will establish its own vapour pressure independent of the molar ratios in the mixture; Dalton’s law of partial pressures come to play as illustrated in Figure 22. It is observed that the vapour pressures do not change as a function of concentration. This means that the ratio of components above the boiling liquid never changes, since they have similar boiling points. There is no interaction at the molecular level. This makes it difficult for them to be separated by traditional distillation. Steam distillation is a way to separate components in such mixtures.

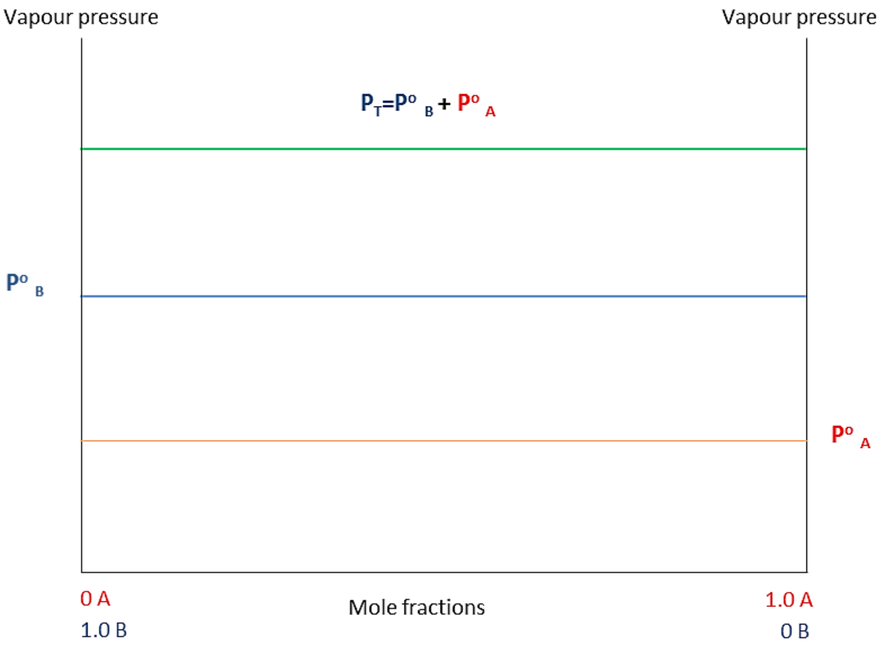

Figure 22: The behaviour of immiscible liquids as described by Dalton's law.

5.2 Steam Distillation Process

This type of distillation is what is being adopted for the treatment of OCDC, since microwaves do not heat materials directly, but rely on heating of water and susceptor. Steam distillation is the mechanism used to separate oil from the cuttings. As described in section 5.1.1, immiscible liquid mixtures obey Dalton's law where various components establish individual vapour pressures, which help in the separation process. Generally, liquids boil when the total vapour pressure equals atmospheric pressure. At sea level atmospheric pressure is 101.325kPa or 760mmHg.

Immiscible liquid mixtures boil at a temperature lower than the boiling point (bp) of either of the pure liquids. This is because their combined vapour pressures reach atmospheric pressure before the vapour pressure of either of the individual components will. A mixture of toluene (C_7H_8) and water (H_2O) is a good example for explaining steam distillation of two immiscible liquids.Toulene has a bp of 111 °C and water has a bp of 100 °C (SIGMA-ALDRICH, 2017). A mixture of the two liquids boil at 84.5 °C. Toluene has a vapour pressure of approximately 339 mmHg and water ,425 mmHg adding up to 764 mmHg at this temperature (Yaws, 2007). Their combined vapour pressures is the reason for boiling at a lower temperature.

A simple steam distillation set-up is shown in Figure 23. The boiling flask is filled with an amount of OCDC (includes a mixture of water, oil and cuttings). When heat is applied (from microwave) to the mixture in the boiling flask, it begins to boil and water, which has a lower boiling point, begins to distill out and condense into the receiving flask. The oil also establishes its own vapor pressure in the space above the flask independent of that of the water. As the water vapour moves out, it entrains some oil with it into the receiving flask. This process continues until almost all the liquids are removed from the boiling flask leaving 'clean cuttings' in the boiling flask.

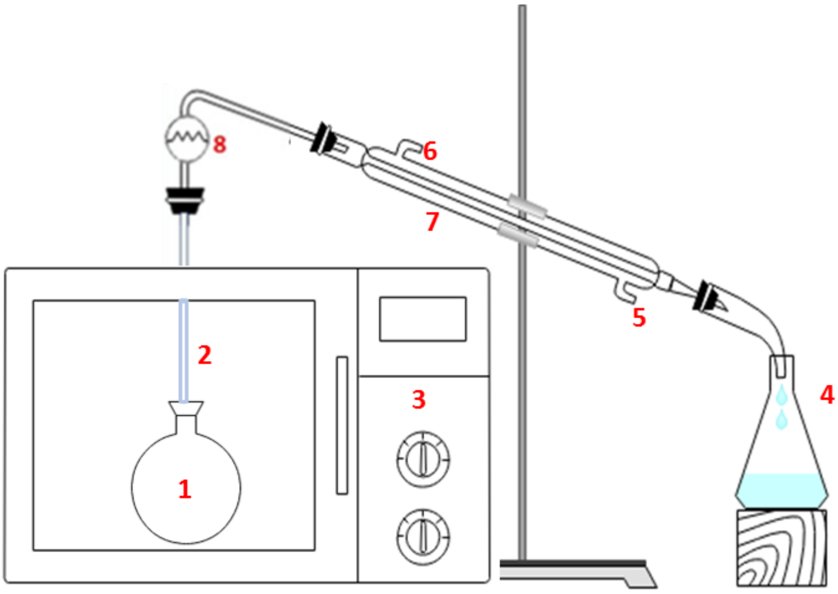

Figure 23: Steam distillation apparatus

1. Boiling flask/reactor	5. Cooling water-in
2. Still head	6. Cooling water-out
3. Microwave	7. Condenser
4. Receiving flask	8. Glassware heater

A combination of Dalton's law, Antoine's equation, and the principle of distillation with the ideal gas law can be used to estimate the mole fractions or distillation ratios of the components in the distillate (refer to equations 17 & 19). This is accomplished using boiling point diagrams, explained in section 5.2.1.

$$\frac{P_{polar} \cdot V_{polar}}{P_{oil} \cdot V_{oil}} = \frac{n_{polar} \cdot R \cdot T_{polar}}{n_{oil} \cdot R \cdot T_{oil}} \tag{17}$$

Where 'P' is the pressure of the gas, 'V' is the gas volume, 'n' is the number of moles, 'R' is the ideal gas constant, and 'T' is the temperature of the gas. The indexes polar and oil represent any polar and any organic compound respectively. Equation 17 is simplified to 18 since the gas constant applies to both components. The gases occupy the same volume and distillation is at the same temperature and can be eliminated.

$$\frac{P_{polar}}{P_{oil}} = \frac{n_{polar}}{n_{oil}} \qquad (18)$$

Referring to the example with toluene and water, Rossi, (2016) made theoretical estimations of amount of toluene expected in the condensate as 4.7 mL/ mL water. This is compared to where dodecane ($C_{12}H_{26}$) and hexadecane ($C_{16}H_{34}$) are distilled with water in Table 5. The energy requires is also presented in Table 6.

Table 5: Theoretical distillation with select compounds mixed with water

Organic compound	Theoretical bp, °C	Vapour pressure ratio, mmHg	Distillation ratio, mL oil/mL polar
Toluene/water	84.5	339/425	4.7
Dodecane/water	99	15/733	0.14
Hexadecane/water	100	0.8/760	0.008

Considering the thermal properties of water, large amount of energy is needed for distillation due to the high enthalpy of vaporization of water. The energy can be offset if the vapour pressure of the organic compound is larger than that of the second component in the boiling mixture (Rossi, 2016), Table 6.

Table 6: Energy required for distillation

Organic compound	Polar compound	Enthalpy of vaporization, (kJ/kg)	Energy consumption per kg oil evaporated, (kJ/kg)
Toluene	Water	2257	480
Dodecane	Water	2257	8680
Hexadecane	Water	2257	282125

5.2.1 Boiling Point Diagrams/Phase Diagrams

Boiling point diagrams are used to estimate the equilibrium compositions of the components in liquid mixture at different temperatures and fixed pressure (in this case 1 atmosphere is used). In other words, the mole fraction of the component in the liquid phase and its corresponding mole fraction in the vapour phase can be known using these diagrams. As mentioned earlier, the technology makes use of the combined vapour pressure contributions of the various liquids. The phase diagrams give information on what temperatures each component is boiling, the temperature at which the components boil together and what temperatures to expert pure components. Consequently, the vapour pressures of the liquids can also be estimated at various temperatures. For this thesis work, the diagrams were produced for a mixture of some organic compounds, which are described further in Chapter 7. Figure 24 shows an example of a boiling point diagram and how it is used.

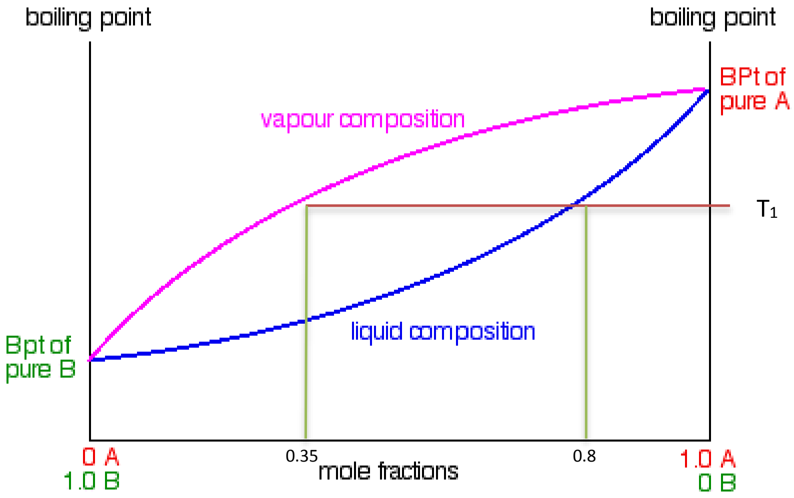

Figure 24: Phase diagram for a mixture of components ‘A’ and ‘B’ , (Clark, 2005)

It is expected that during boiling the component with a lower boiling point escapes and forms vapour easier than the less volatile one. This implies that a higher proportion of the more volatile component would be in the vapour than in the liquid. This phenomenon is explained using Figure 24. If we assume 80 mole percent (mole fraction = 0.8) of component ‘A’ at a temperature T$_1$, the vapour composition, which accounts for the vapour pressure above the liquid, can be determined using the phase diagram. This is done by drawing a vertical line to touch the liquid curve (green line) and a horizontal isotherm (red line) to touch the vapour composition curve. The vapour above the boiling liquid can be read down from this point to about 35% of ‘A’ and 75% of ‘B’. If this vapour is condensed and reheated, the vapour composition will be even richer in the more volatile component ‘B’ than it was in the original mixture. The analogy is used in later chapters to explain the behavior of various mixtures of susceptors.

5.3 Meeting Industry Standards and Collaboration with IRIS for Toxicology Test

OSPAR regulations of < 1 wt% OOC is the recognized limit on the NCS. However, regulatory bodies and companies in Norway set their own standards, which are stricter. There is regular monitoring to ensure that these standards are upheld.

IRIS AS is recognized for providing an integrated research environment in Energy, Environment, and Social Science. They provide services such as but not limited to; marine ecotoxicology, biological effect and ecological functioning studies and environmental risk assessment.

As part of this thesis, samples treated with alternative processes described in chapter 9 were sent there for toxicological testing. The purpose is to investigate if there are any chemicals in the treated sample and how they impact on aquatic life. The outcome of this investigation will crown the impact of this new microwave technology, on the oil and gas industry. The samples sent to IRIS are listed in Appendix B.

6 Susceptor Technology for Microwave Treatment of OCDC

6.1 Liquid Susceptors

Water has been identified as having challenges with the removal of heavy oil from drill cuttings during microwave steam distillation process (Pereira, 2012, Shang et al., 2012), due to its low boiling point temperature. The use of environmentally friendly polar organic compounds with relatively high boiling point, ensures steam distillation, at temperatures that can vaporize oil fractions typically found on OBM (Rossi, 2016). More so, these polar organic compounds have lower heat of vaporization than water. For instance, Mono ethylene glycol (MEG) has heat of vaporization of approximately 2.5 times less that of water (Rossi, 2016). In a study conducted by Pereira, 2012, cuttings were treated at 350 kgh^{-1} to less than the environmental threshold using energy input between 90-100 kWht^{-1} at 896 Mhz using water as the microwave absorbing medium. If the water were to be replaced with MEG, the energy input would be reduced to 40 kWht^{-1}. This is a significant reduction in the amount of consumed energy and this makes the susceptor technology very promising for sustainable microwave treatment of OCDC.

Rossi, 2016 demonstrated the effects of susceptors in combination with microwave treatment of OCDC. The study disclosed that the use of the right quantity, under the right conditions reduced OOC to less than 1 wt% (Rossi, 2016). In the study, the effect of MEG was tested on oil separation in centrifuged cuttings. The results showed that when 200g of centrifuged cuttings was treated without susceptor in a 900W microwave for 5 minutes, the OOC was about 3.8 wt%. Addition of 40 mL susceptor reduced the OOC to 0.5 wt% (Rossi, 2016). Other organic compounds were tested; however, MEG was identified as the best compound to use since it showed little indication of decomposition after the treatment processes. More so MEG is already on the PLONOR (Pose Little or No Risk to the Environment) list of chemicals which adds value to its use, in that getting new chemicals onto the PLONOR list is a lengthy and cumbersome process.

6.2 Solid Susceptors

It is known that mixtures of high explosives with materials that readily absorb microwave ignite speedily when exposed to microwave energy (Perry et al., 2006). A study by Vargas et. al from Texas Technical University demonstrated how carbon additives influence microwave heating of Trinitrotoluene (TNT). They analysed five different carbon additives namely 1) carbon nanotubes, 2) spherical powder, 3) diamond nano particles, 4) graphene nano-flakes and 5) graphite micron-flakes. This was done by adding 1 wt% to TNT and subjecting it to microwave radiation at 1.7 GHz for one minute. A high resolution high speed infrared (IR) camera was used to measure transient temperature.

It was reported that the tubes absorbed more energy. However, experimentally the flakes induced melting of the TNT faster. This was as a result of the role played by inter-particle connectivity in promoting heat transfer upon absorption of microwave (Vargas et al., 2016). The carbon additives acted as solid susceptor in this example. Solid susceptors have been tested and found to enhance microwave heating. They have been used for the sintering of ceramics, polymer processing, ore, metal and alloy processing, glass and semiconductor processing, solid state synthesis and waste treatments (Bhattacharya and Basak, 2016). It has been reported that the use of 5-10 wt% of grafoil strips or char lead to rapid heating of poor microwave absorbing material in sewage sludge between 800 -1000 ^{o} C in a 1000W-2.45 GHz multimode oven. Direct microwave heating could not increase temperatures close to 200 ^{o} C (Domínguez et al., 2006, Menéndez et al., 2010).

Advantages of Liquid Over Solid Susceptors in Microwave Treatment Process

Liquid susceptors distribute heat energy through pours in the entire cuttings matrix due to its wetting capabilities. Solid susceptors on the other hand, distribute the energy through surface heating only. This has limitations such as generating very high temperatures, leading to thermal runoff (refer to section 4.2). Additionally, a large amount of microwave energy is wasted since it is not absorbed into the material matrix. High temperatures will also, crack oil and is not suitable for cuttings treatment, where recycling of oil is of importance. Furthermore, the benefits of steam distillation will be lost when solid susceptors are used.

6.3 Potential Susceptors

Rossi, 2016, identified some polar organic compounds based on the following criteria;

- Cost or value of material
- Illegibility for discharge to sea
- Dielectric properties
- Boiling and melting point temperatures
- Decomposition temperatures
- Environmental toxicity

Glycols such as mono ethylene glycol (MEG), diethylene glycol (DEG), mono propylene glycol (MPG) and dipropylene glycol (DPG) were identified as common potential chemicals. It is important to note that the decomposition of these compounds when exposed to high temperatures can result in products that are explosive or toxic with debilitating environmental impacts (Rossi, 2016). Decomposed susceptors may negatively affect oil separation. This makes the subject of decomposition very relevant as far as the technology is concerned.

Another critical characteristic of susceptors is their dielectric properties as explained in chapter 4. A summary of the dielectric properties of some relevant compounds can be found in the works of (Rossi, 2016).

6.4 Susceptor Recovery

Water in the drill cuttings will contaminate the susceptor after the first cycle of treatment. It is important to recover it for reuse. This is however challenging since both substances are miscible. Fractional distillation appears to be the best method to recover the susceptor. However, it presents some challenges with repetitive heating. Depending on the degree of susceptor purity that is required, the distillation process will have to be repeated severally. This translates to high energy consumption. In addition to that, the process has a high potential to decompose the susceptor, which is undesired. Applications of fractional distillation is demonstrated with phase diagrams presented in Chapter 7.

Considering the challenges presented above, it is critical to reduce the amount of water in the cuttings prior to dousing in susceptors.

7 Effect of Susceptor Contamination by Water during Recycling and Susceptor Optimization

7.1 Theoretical Evaluation of Vapour Pressures

Vapor pressure plays a fundamental role in microwave steam distillation and susceptor technology based on Raoult’s law. A relatively high process temperature is required for optimum oil separation from OCDC. In this section we discuss how water affects process temperatures during the distillation process.

Antoine’s equations and related gas laws were used to calculate vapour pressures at various temperatures. This information was used to contruct boiling point diagrams, which are useful for various distillation calculations.

7.2 Effect of Water on Boiling Point Temperature (BPT) and Decomposition of Susceptors

7.2.1 Effect on BPT For Mixtures of MEG and Water

The BPT of MEG mixed with water was calculated at various proportions of the two substances. Mole ratios of both substance were assumed for the calculations. Temperatures were recorded to correspond to total vapour pressure, approximately equal to atmospheric pressure of 760 mmHg. The calculated values were used to produce a phase diagram, Figure 25. This can be used for various calculations with respect to distillation.

For instance, it provides information on the effects of varying ratios of water on process temperature. Bearing in mind that a high process temperature is required for optimum oil separation, information from the graph can be used to determine to what extent OCDC must be dewatered.

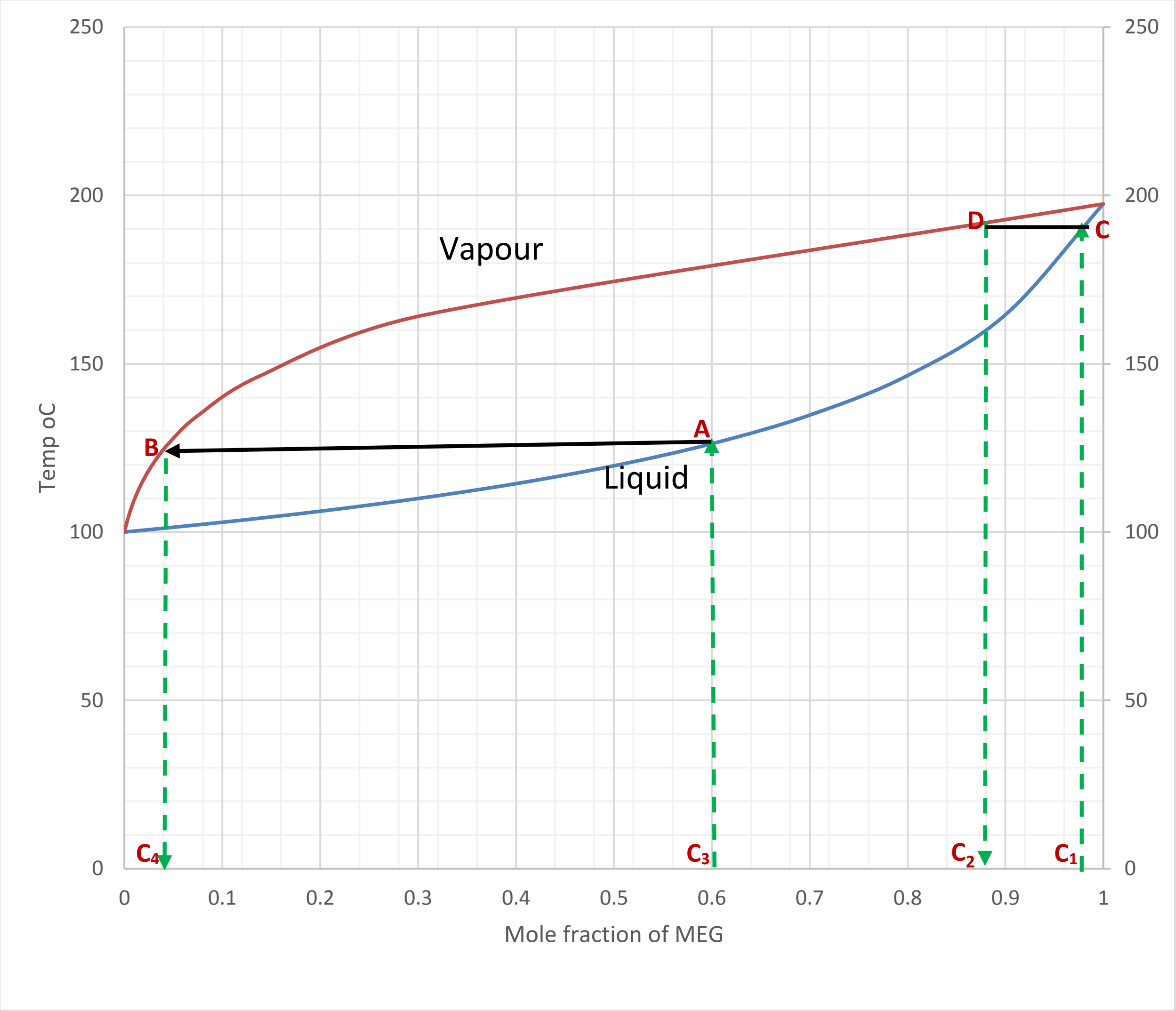

Figure 25: Phase diagram for a mixture of MEG and Water

The phase diagram in Figure 25 demonstrates the behavior of the components in the mixture with temperature during distillation. It shows the vapour phase above the red line and the liquid phase below the blue line. The area bounded by both curves has a combination of vapour and liquid phases.

It is possible to determine at what temperature the mixture will begin to boil. The composition in the vapor phase can also be determined at different temperatures. Subsequently, the composition and volume of the distillate can be estimated. This is necessary for planning purpose during treatment of OCDC since the susceptor will be recovered and recycled.

It is observed that at a temperature of approximately 100 ^{o}C the liquid begins to boil. At this point the composition of the vapour will be purely, the most volatile component, water. At much higher temperatures, various compositions of the components can be determined. For instance, taking a mole fraction of MEG at 0.98 (mole percent of 98), the liquid boils at approximately 190 ^{o}C. The vapour composition can be determined by drawing a vertical line from point C_1 to the liquid composition line at 'C'. A horizontal isotherm drawn from 'C' to 'D' gives us the point C_2, where the composition is 88% MEG and 12 % water. If this vapour is condensed and reheated, the vapour composition will have more of the water. Following these steps severally yields substance that is richer in the more volatile component, water. Again, if we assume the mole fraction of MEG to be 0.6 (mole percent of 60) at C_3, the liquid boils at temperature of about 126 ^{o}C. Following the same procedure, the vapour composition at C_4 will be approximately 4 % of MEG and 96 % water. Repeating this process severally yields a purer substance and is the basis for fractional distillation.

As mentioned earlier, fractional distillation is energy-intensive and can potentially decompose the susceptor. This is a draw back to the recovery process for this technology.

It is also evident from the graph that a high concentration of water reduces boiling point temperature. Consequently, process temperature is reduced, which when is too low, does not favour efficient oil separation.

This presupposes that water should be removed from the drill cuttings before addition of susceptors. Dewatering becomes significant as a pre-treatment measure in microwave susceptor technology. Based on this, the operator can determine how much water to remove from the drill cuttings before treating it with MEG.

In another scenario, the presence of water may also be a way to reduce process temperatures in cases where decomposition is evident. In this case addition of water is a way to optimize the susceptor to make it resilient towards high temperatures. For instance, TEG has a higher boiling point than MEG, meaning it will operate at a higher temperature. To have control over the process temperature and to avoid decomposition, water may be added.

Similar calculations were made with corresponding graphs (Figure 27, 28 and 29) to show the impact of water on other susceptors. The analogy described for the combination of MEG and water apply to these as well.

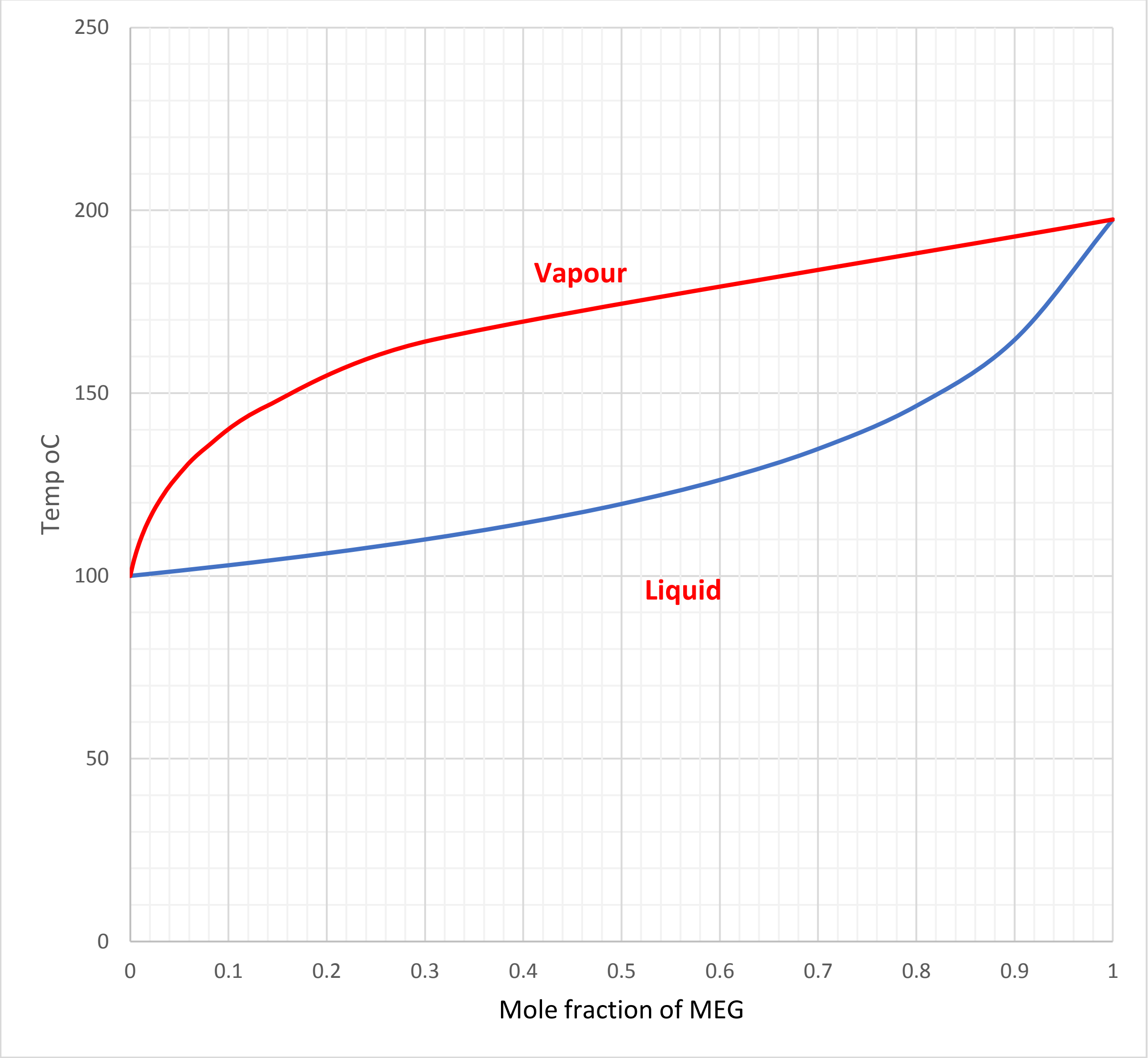

Figure 26: Phase diagram for a mixture of MEG and water

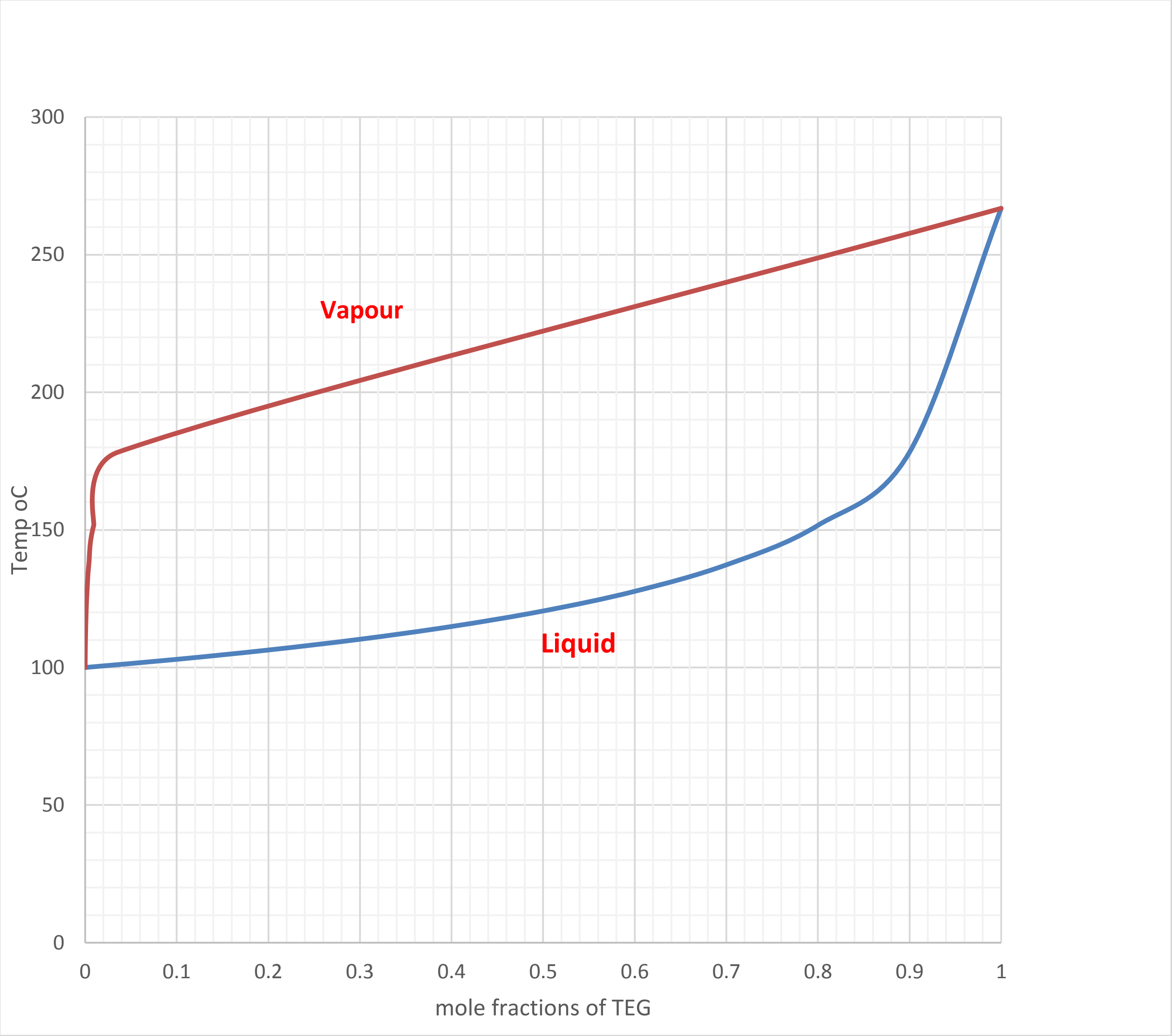

Figure 27: Phase diagram for a mixture of TEG and Water

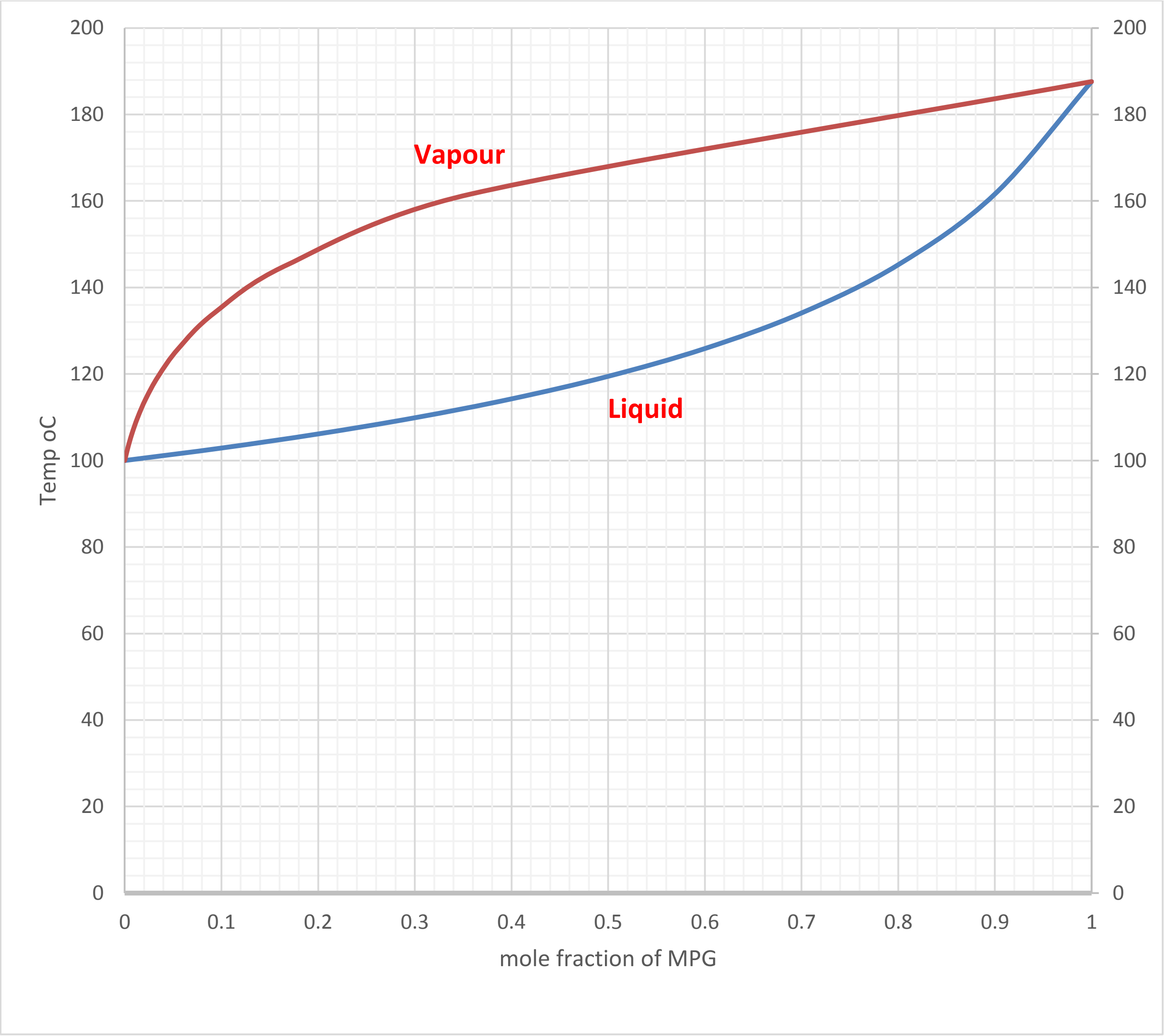

Figure 28: Phase diagram for a mixture of MPG and water

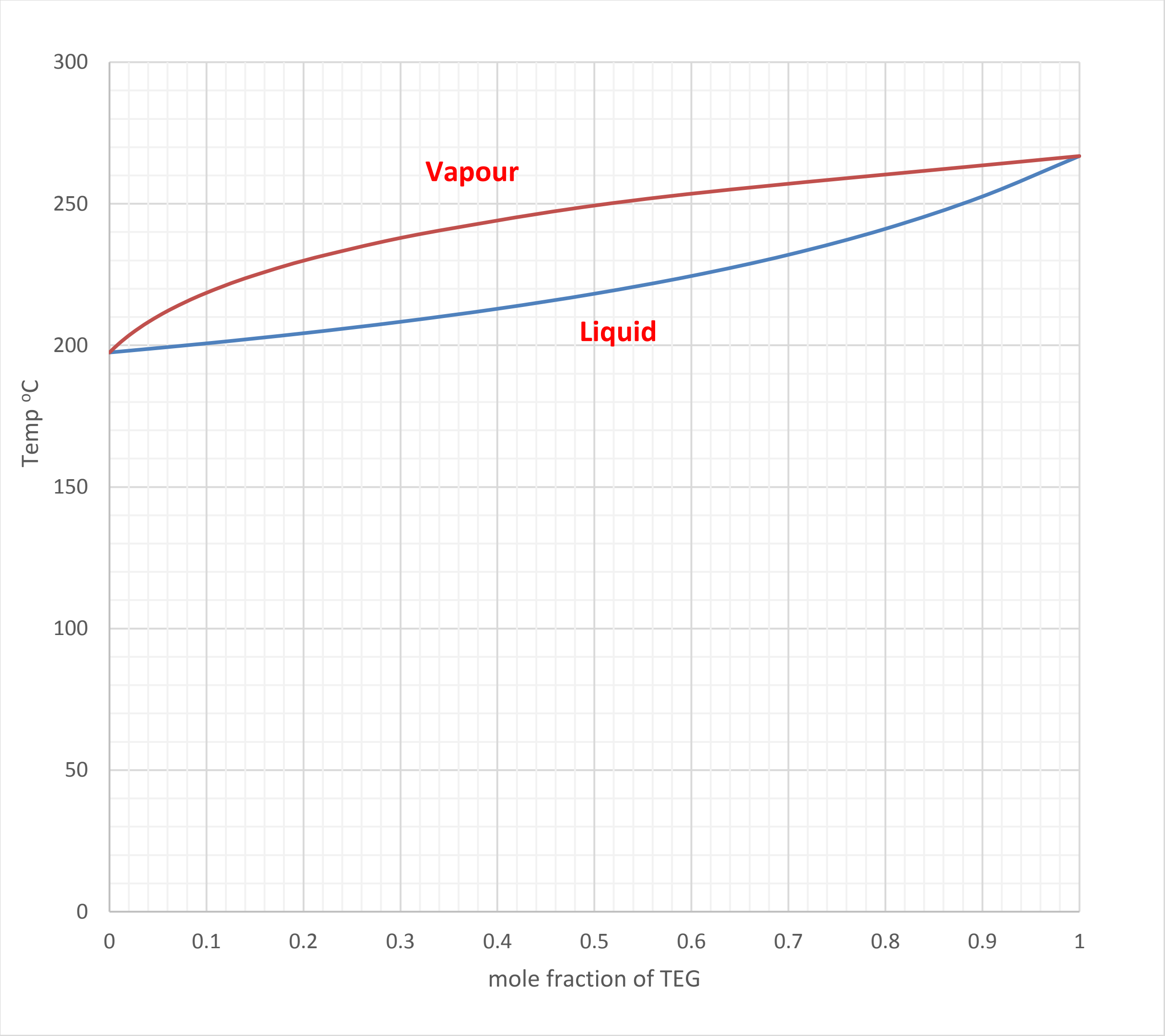

Figure 29: Phase diagram for a mixture of TEG and MEG

PART 3-LABORATORY STUDY

8 Decomposition and Optimization of Susceptors

8.1 Distillation of Susceptors to Evaluate Decomposition

With the theory from Chapter 7, experiments were conducted to investigate these parameters. There is a reason to believe that during microwave processing susceptors can be exposed to temperatures that will cause them to decompose. This is because of the inhomogeneous heating of materials in microwave cavity. Heating occurs in layers during microwave heating. The first layer could be heated up to about 200 °C or more when the susceptor in that section has boiled off. The susceptor that boils in the next layer will be subjected not only to microwave energy but the high temperature in the first layer of cuttings, as shown in Figure 31. This process leads to thermal run off (refer to section 4.2) which can cause decomposition. Another possible reason for decomposition is that microwave heating causes rapid chemical synthesis with short reaction times (Kappe and Dallinger, 2006). These reactions could be the cause of decomposition.

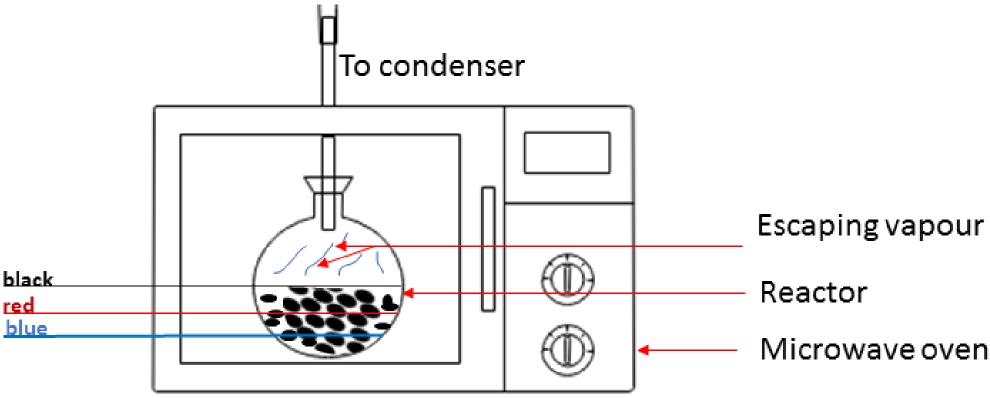

Figure 31: Thermal runoff during processing

The susceptor in the black layer may be heated first and escape, vapour escaping below the red layer is subject to heat of the layer above it. This means the vapour escaping from the bottom layers are not exposed to microwave energy alone but also heat from the layers above them.

Two sets of bench top experiments were carried out to investigate decomposition of susceptors. One by mixing different susceptors only (without cuttings) and the other, by adding the susceptor to cuttings.

Experiment 1

Experimental Setup and Method

Materials

Table 7: Microwave distillation equipment

Equipment	Model	Manufacturer
Microwave reactor	WBFY-205	Zenhzhou Keda Machinery
Pressurized N2 gas	Nitrogen 4.0	Yara Praxair
Distillation glassware	-	-
MEG (99.5%)	-	Sigma-Aldrich
TEG (99%)	-	Sigma-Aldrich
Water	-	-

A modified microwave oven was fitted with a normal distillation apparatus and placed in a hood, to suck out all gases. See Figure 33 for a schematic of the microwave set-up used for the experiments. One of the reasons for modification is to direct nitrogen gas into the sample through a thin glass. The other reason is to enable the vapour from the boiling flask to escape through a glassware into the condenser. Nitrogen gas creates inert environment and sweeps out vapour that is generated. It does not absorb microwaves and will not be heated by it either. Previous studies have reported that pre-condensation of vapour occurred on the walls of glassware before reaching the condenser because of the use of cold N_2 (Robinson et al., 2009b). To prevent this, the gas was heated before reaching the reactor. The glassware that connects the condenser to the reactor was also heated to avoid the condensation of vapour back into the reactor.

8.2 Methodology

A known volume of the susceptor or a mixture of susceptors was placed in the boiling flask (reactor) and heated with the microwave at full power (900 W). When the liquid began to boil, the power was reduced to a minimum power (180 W) to maintain boiling in the flask. A cylinder was placed at the end of the condenser to collect the distillate. The microwave oven was opened intermittently to observe any visible change in the colour of the susceptor in the reactor. When a change in colour was observed, the boiling flask was taken out to measure the temperature. Measuring the temperature is an arduous task since the boiling flask had to be taken out of the oven whilst hot before using the thermometer. This may have caused errors in the readings. To reduce errors, the flask was positioned in the microwave cavity in such a way that taking it out was fast enough to minimise heat lose.

The time for the onset of decomposition and temperature at the time was recorded using a timer and glass thermometer respectively. The colour change of the susceptor was used as an indicator for its degradation. Figure 32 shows the interior of the microwave cavity and the reactor, while Figure 33 shows the overall process set-up.

Figure 32:Interior set up of the microwave oven.

The flask contains the susceptor. Heated Nitrogen gas flows through the tube on the left-hand side and the vapour from the boiling liquid flows through the other opening into the condenser outside

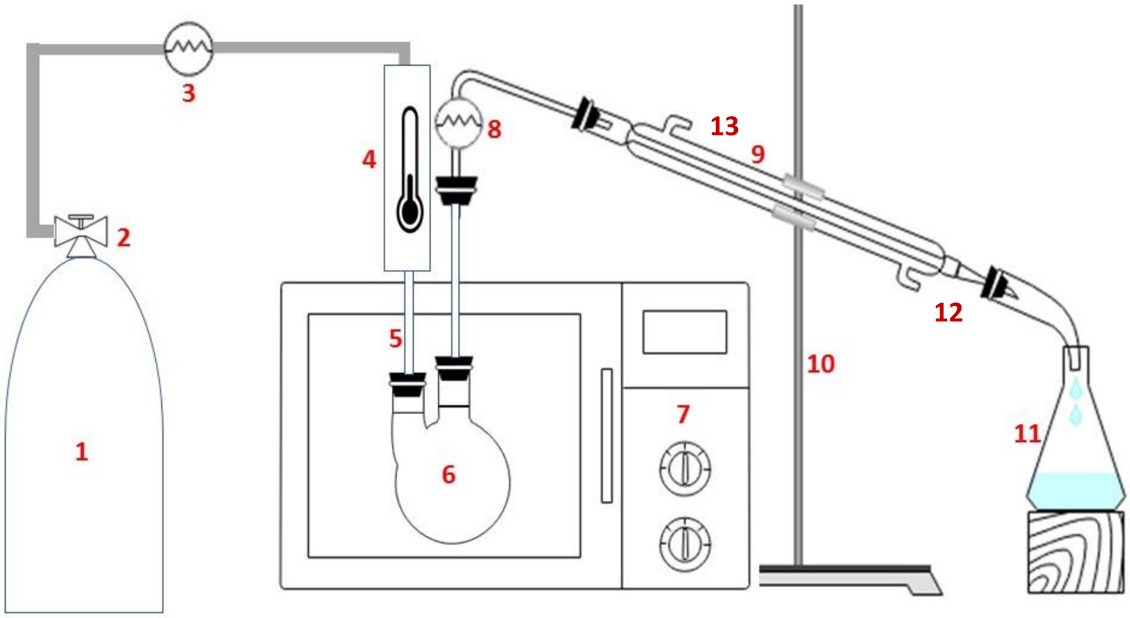

Figure 33: Set-up of microwave treatment process

1. Compressed N_2
2. Flow valve & display
3. N_2 heater
4. N_2 Temp. monitor
5. Inlet of hot N_2
6. Reactor
7. Microwave oven
8. Glassware heater
9. Condenser
10. Retort stand
11. Distillate receiver
12. Cooling water in
13. Cooling water out

8.2.1 Distillation of Susceptors to Test Decomposition

The purpose of these experiments was to evaluate the decomposition and duration before decomposition occurs. This gives an indication of the number of times the susceptor can be recycled during cuttings treatment. The reason for mixing susceptors was to optimize them so that they can be resilient to high temperatures and decomposition.

8.2.1.1 *Distillation of Monoethylene Glycol (MEG)*

Test 1

Pure MEG was distilled and observed for decomposition. Water was then added in various proportions and observed. The parameters are displayed in Table 8. Figure 34 and Figure 35 show the comparison between pure MEG and distilled MEG.

8.2.1.1.1 Results

Table 8:Observations made during distillation of mixture of MEG and H2O

MEG %	Water%	Time/mins	T/ °C	TBT/ °C	Observation	Total Vol/mL
99.5	0	27	-	197	no color change	100
99.5	0	37	157	197	light yellow	100
95	5	36	142	178	light yellow	100
90	10	26	142.5	165	light yellow	100
85	15	12	142	154	no change	100
85	15	24	128	154	light yellow	100

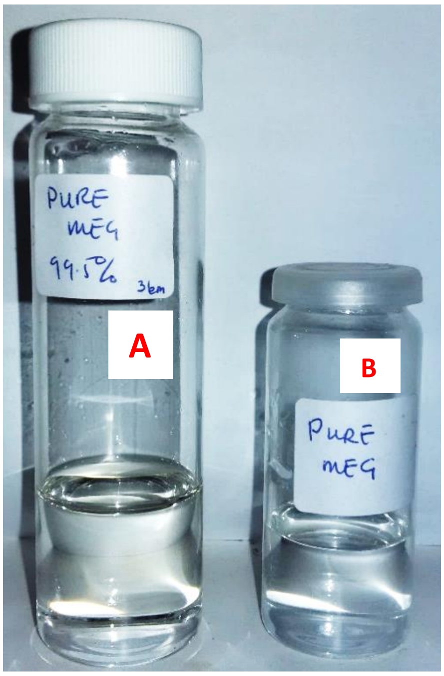

Figure 34: Decomposition test for MEG

Bottle ‘B’ contains pure MEG (99.5%) with no interaction with microwaves, bottle ‘A’ contains pure MEG exposed to microwave radiation for 36 mins. A change in colour is observed after treatment, an indicator for decomposition.

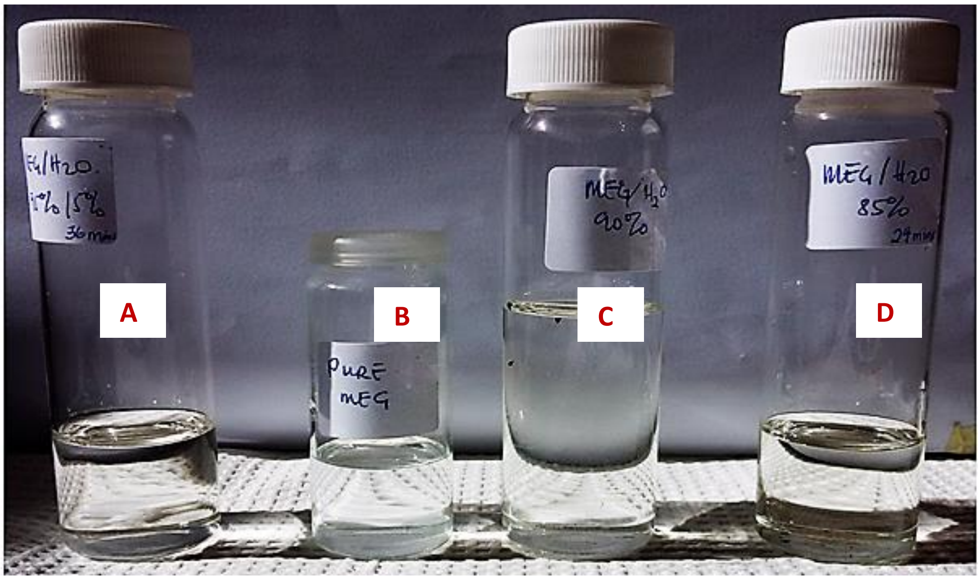

Figure 35: Decomposition test for MEG with different water ratios

Bottles with labels A (95% MEG), C (90% MEG) and D (85% MEG) show slightly yellowish colouration compared to pure MEG in bottle B.

8.2.1.2 *Distillation of Triethylene Glycol (TEG)*

Test 2

Pure TEG was distilled and observed for decomposition. Water was then added in various proportions and observed. The parameters are displayed in Table 9. Figure 36 also shows the change in colour for the mixtures as compared to pure TEG.

8.2.1.2.1 Results

Table 9: Observations made during distillation of mixture of TEG and H_2O

TEG %	Water %	Time/mins	T/ °C	TBT	Observation	vol/ml
99	0	16	202	266	no change	70
99	0	22	172	266	light yellow	70
95	5	11	202	205	no change	70
95	5	17	180	206	light yellow	70
90	10	10	196	178	no change	70
90	10	16	192	178	light yellow	70

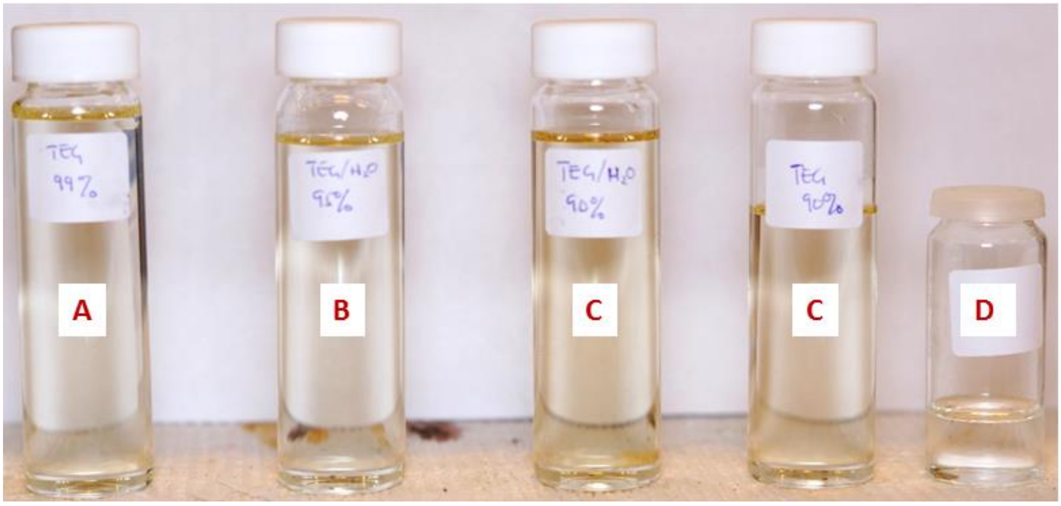

Figure 36: Decomposition of TEG in the various TEG/Water ratios

8.2.1.3 *Distillation of a Mixture of TEG and MEG*

Test 3

From Figure 29 in Chapter 7, it is evident that a combination of these two susceptors give a much higher process temperature (according to Raoult's and Dalton's laws) than any of the other mixtures described so far. This presupposes a more robust susceptor, which might not decompose. The experimental results however demonstrated that, decomposition occurred. The results are shown in Table 10. The decomposition can be observed in Figure 37.

8.2.1.3.1 Results

Table 10:Observations made during distillation of mixture of TEG and MEG

TEG%	MEG%	Time/min	T/ °C	TBT	observation	Vol/mL
95	5	17	180	259	light yellow	70
95	5	24	182	259	light yellow	70
90	10	14	192	253	light yellow	70
50	50	8	176	218	no change	70
50	50	13	206	218	light yellow	70

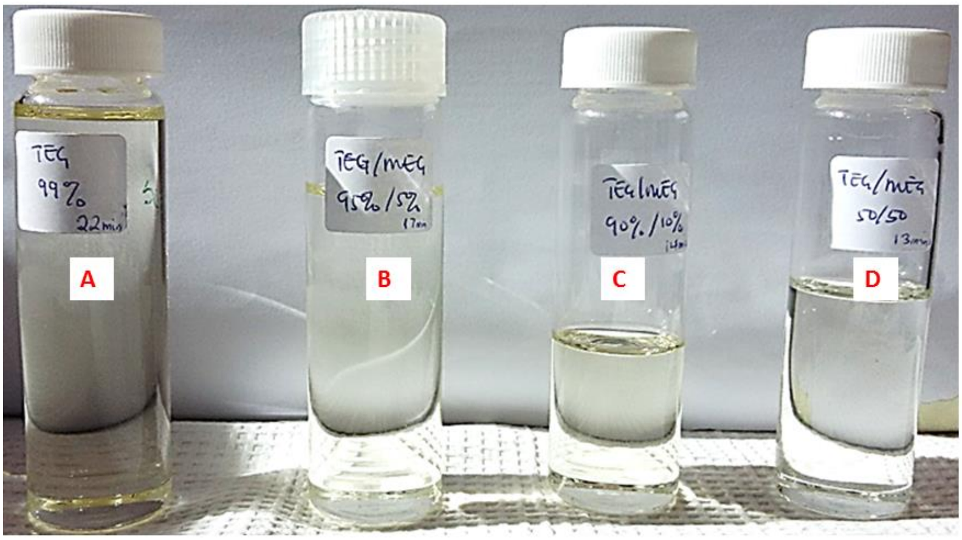

Figure 37: Decomposition of TEG/MEG mixture at different ratios

8.2.1.4 *Distillation of TEG on Drill Cuttings Using Microwave Processing*

Test 4

A simple bench top experiment was conducted to test how TEG reacts with OCDC sample during microwave heating.

The same set-up used in Figure 33 was used during this test. In this case, the reactor contained OCDC mixed with TEG. 200 g of dewatered OCDC was placed in a boiling flask. 60 mL of TEG was added and mixed into the sample before placing it in the microwave for treatment. The microwave operated at full power (900W).

8.2.1.4.1 Results

Table 11: Parameters observed during decomposition test with TEG

Sample weight (g)	**T of N_2 (°C)**	**Initial vol of TEG (ml)**	**Distillate vol (ml)**	**Time (mins)**
200	204	60	48	7:11

Figure 38: Decomposition of TEG on drill cuttings

8.2.1.5 *Distillation of MEG on Drill Cuttings Using Microwave Processing*

Test 5

Using the same microwave setup described in Figure 33, MEG was used as the susceptor in this test. The objective of this test was to recycle the susceptor many times until decomposition was prominent. This will give an indication of MEG's resilience to decomposition.

125 mL of MEG was added to 500g of dewatered cuttings and repeatedly distilled in the microwave. After each cycle of distillation, the distillate was poured back onto the hot cuttings in the microwave and redistilled. The distillate contains oil and water removed from the cuttings, and MEG. With the initial amount of MEG added to the sample, 10 cycles were achieved. For each treatment cycle, the process was stopped at the point when little condensation in the receiving flask was observed. Table 12 shows the parameters for this experiment.

8.2.1.5.1 Results

Table 12: Parameters observed during decomposition test with MEG

No. of cycle	Sample weight (g)	T of N_2 (^{o}C)	Vol of distillate (mL)	t (mins)
1	500	216	130	9:14
2	500	231	123	8:40
3	500	240	119	6:34
4	500	237	115	7:00
5	500	220	92	6:30
6	500	210	73	6:00
7	500	205	66	7:22
8	500	254	49	4:25
9	500	230	43	3:51
10	500	233	34	3:47

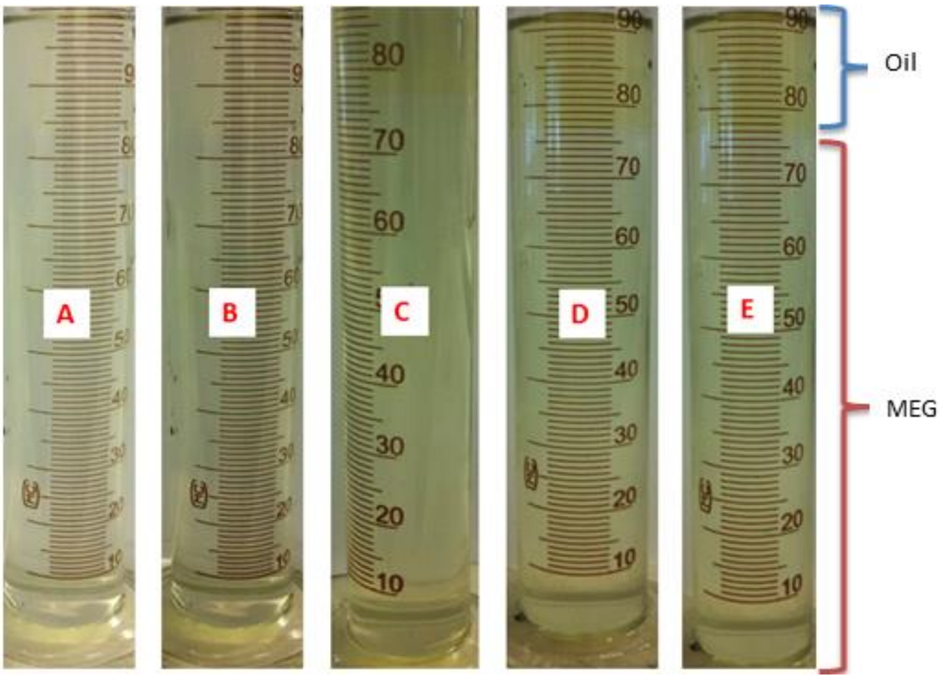

Figure 39: Decomposition test for MEG

Observation of colour change in the first 5 cycles is presented in Figure 39. ABCD represent cycles 1,2,3,4, and 5 respectively. No significant change of colour was observed except for very light yellow colour of floating oil (note that emphasis is laid on colour change and not volume for this experiment).

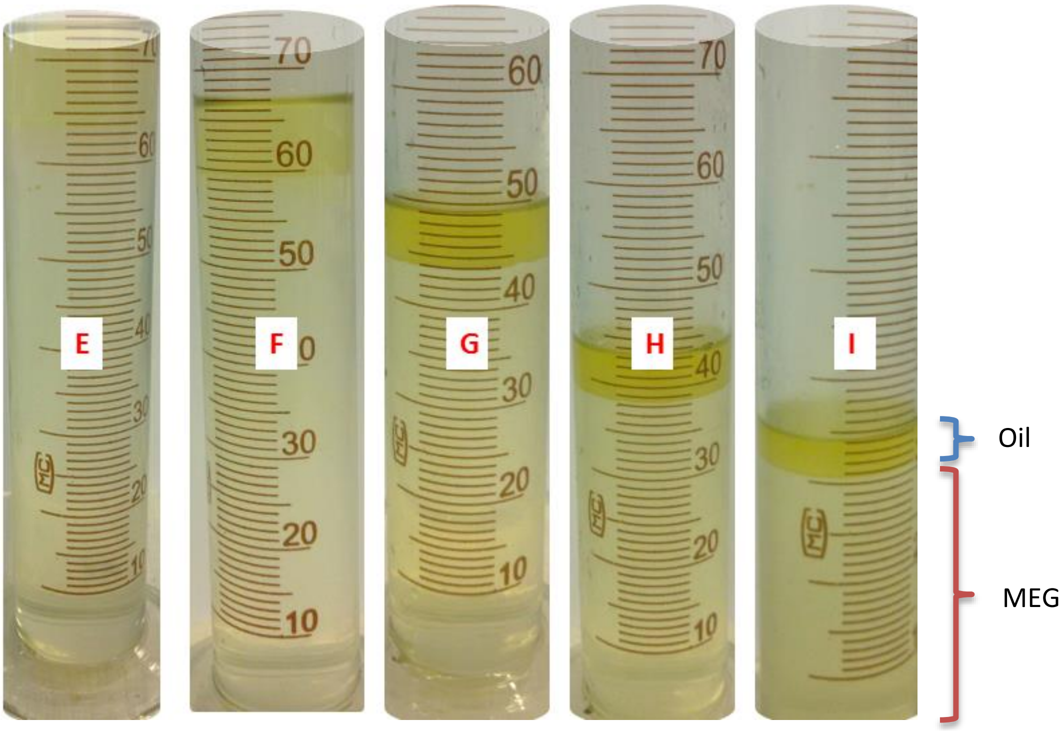

Figure 40: Decomposition test for MEG

Observation of colour change in the last 5 cycles is presented in Figure 40. E, F, G, H, I represent cycles 6,7,8,9, and 10 respectively. Each bottle has oil (yellow colour) floating on top of MEG (almost colourless). (Emphasis is laid on colour change and not volume for this experiment).

8.2.1.6 *Comparison between End Products of MEG and TEG after Decomposition Tests*

Figure 41 shows a comparison of the distillates after decomposition test. MEG showed little signs of decomposition after 10 recycles whilst TEG showed substantial signs of decomposition after one cycle. The darker section floating on top is degraded oil.

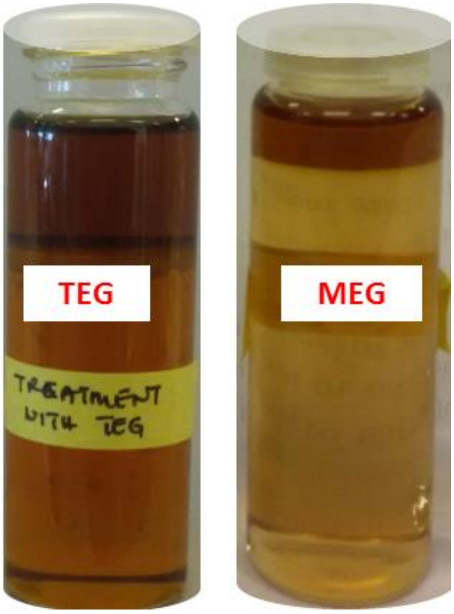

Figure 41: Final decomposition results for TEG and MEG

8.2.2 Discussion

Distillation of MEG without OCDC

Based on Antoine's equations and Raoult's law, it was expected that addition of water to MEG or TEG will make the organic compounds more resilient since the BPT of the mixtures was expected to be lower than the BPT of the individual components.

MEG has a boiling point temperature of 197 °C. However, during the distillation of pure MEG the boiling point temperature was 157 °C instead of the expected theoretical temperature (refer to Table 8). The different proportions of MEG and water mixtures also yielded lower temperatures than expected. This could be due to one of the following reasons or the combination of all;

1. Cold nitrogen gas was used during the experiment to create inert atmosphere
2. Reduction of microwave power at the onset of boiling.

The microwave was stopped intermittently to observe any changes taking place in the reactor. When change was detected, the flask was taken out to read the temperature of the boiling liquid. This is a possible source of cooling since there was continuous flow of cold nitrogen gas when the microwave was stopped. Another possible cause of temperature drop is the fact that the microwave power was turned down when boiling was detected. It was assumed at this point that a higher power was not necessary to maintain boiling. This assumption may not have worked well in this case, where cold nitrogen was continuously introduced into the flask.

The fact that the compound showed signs of degradation at these temperatures could mean that the chemical properties of MEG also changed. General heat loses between the time when the flask was taken out and when the thermometer was inserted could account for marginal temperature drop.

To confirm these accessions, the experiment was repeated for pure MEG with a modified set-up. In this case, the nitrogen gas was heated up to 197-200 ^{o}C. The glassware that connects the boiling flask to the condenser was also heated to avoid pre-condensation into the reactor. The microwave power was also kept at 360 W at the onset of boiling instead of 180 W, used in the previous set-up.

After 7 minutes the temperature of the boiling MEG was recorded to be 194 ^{o}C. After 15mins, the color began to change to yellow and the temperature recorded was 194 ^{o}C. This confirms that the use of cold nitrogen influences the results. Another observation is that the duration for the onset of decomposition was 15 minutes in the latter experiment, compared to 36 minutes in the former. Microwave heating is noted for rapid reactions at high temperatures during a short retention time. Meaning that, there could have been some chemical reactions which caused the susceptor to change its colour.

Distillation of TEG without OCDC

From section 8.2.1.2.1, similar observations were made when TEG was distilled. A previous study indicated that TEG had a high tendency to decay during microwave processing (Rossi, 2016). Experimental results confirmed this. A peculiar observation was made when 90% volume of TEG was added to 10 % volume of water, the BPT value was rather high than what was expected. This might be due to some chemical synthesis occurring during the heating process. Since the goal here was to check for decomposition, no further test was carried out.

Distillation of Mixture of MEG and TEG

Reference to section 8.2.1.3.1, it is observed that no matter the ratios of each component in the mixtures, decomposition was observed. Further tests should be conducted to include water, due to its ability to reduce process temperature.

Distillation of TEG on OCDC

Reference to section 8.2.1.4.1, adding TEG to OCDC before microwave processing caused the distillate to turn yellow at the onset of condensation. The yellow colour got darker over time and turned from dark yellow to brown at the end of the test, as seen in Figure 38.

The distillate contains TEG, oil and water (contained in the cuttings). The darkest section, on the upper part of the sample is most likely decomposed oil, floating on top of TEG and water mixture. This is an indication that very high temperatures were reached during processing in the reactor.

Thermal runoff is one cause of such high temperatures. Inhomogeneous heating of the sample could have exposed the vapourized oil moving from the bottom layers of the sample bed to higher temperatures in the layers above. Another reason for the dark colour is most likely, the decomposition of the oil. A way to reduce inhomogeneous heating and improve penetration depth is to maintain a low bed thickness during processing.

Distillation of MEG on OCDC

From section 8.2.1.5.1, no significant change in colour is observed in the distillate for the first five cycles. Oil that is removed from the cuttings during steam distillation floats on the MEG, as indicated in Figure 39 and Figure 40. It is significant to note that due to the quality of the pictures, it may be difficult for the reader to observe the oil component in Figure 39 in a print out of this document.

Figure 40 shows the last five cycles, where the colour change in the oil is more prominent. The colour change observed in the oil can be said to be resulting from decomposition of oil, as it is repeatedly exposed to high temperatures. The distilled MEG, however, showed little signs of decomposition with visible but very little change in colour, compared to pure un-distilled MEG.

Another observation made during this test is that the initial volume of MEG reduced consistently after each distillation. In this test, about 70% of the initial volume of MEG was lost after the last cycle. This is due to evaporation effect as the susceptor was added to heated cuttings and poor condensation set up. If the set-up for the condenser is optimized, more vapour will be condensed leading to better recovery of the susceptor. This is important information to note in the design and operation of a condenser for a scale up system.

8.2.3 Conclusions

From the theory on phase diagrams presented in Chapter 7, it was expected that susceptor optimization by addition of water will reduce its boiling point temperature and subsequently, prevent decomposition. The experiments confirm reduction of boiling point temperatures. As explained earlier it was not easy to read the temperatures accurately and a better way must be sought to accomplish this task with more accuracy. The results however, show that regardless of the composition of the susceptor, susceptor decomposition occurs. Bearing in mind that decomposition here, refers to colour change since no test was conducted to test the chemical properties of the susceptor after exposing them to microwave heating.

Using the criteria of colour change as an indicator for decomposition and comparing MEG to TEG, it can be concluded that MEG will serve a better purpose than TEG. TEG has a higher boiling point than MEG which would have been favourable for treatment of drill cuttings if it did not decompose. More so MEG is considered environmentally friendly. This means that, technically, if there should be any residual MEG left in the cuttings after treatment, it will be acceptable to discharge to sea under current environmental regulations. On the other hand, TEG is not on PLONOR list and would have restrictions for discharging to sea. This implies every iota (or acceptable limits) of susceptor must be removed from the cuttings before discharge. This raises other issues such as cost and footprint requirements for additional compartment and process to remove residual susceptor.

Furthermore, if we consider the parameters used for these bench top experiments, and assuming full recovery of susceptors, 6 tons of OCDC will require 1500 L of MEG to treat. Consequently, over 60 tons of cuttings could be treated with the same quantity of MEG due to recycling. If TEG were to be used and assuming the same preamble for MEG, only 6 tons of cuttings would be treated since TEG decomposes after one cycle. The cost savings here cannot be overemphasized. MEG is therefore the most preferred polar organic compound for dielectric steam distillation until proven otherwise.

9 Cuttings Treatment

9.1 Alternating Treatment Parameters for Improved Oil Separation

To further understand the dynamics of this new technology, some treatment parameters were further investigated. Drill cuttings sample from the North Sea origin was treated with susceptors, applying different parameters such as dewatering, mixing and applying heated nitrogen gas. Another tested parameter was applying the susceptor on hot pretreated/dewatered cuttings.

9.1.1 Experimental Set-up and Method

Table 13: Equipment and materials

Equipment	Model	Manufacturer
Microwave reactor	WBFY-205	Zenhzhou Keda Machinery
Hot air gun	-	Black & Decker
Pressurized N_2	Nitrogen 4.0	Yara Praxair
Distillation glassware	-	-
MEG (99.5%)	-	Sigma-Aldrich
Centrifuge	Rotomix 46	Hettich
Plastic containers with lid	-	-

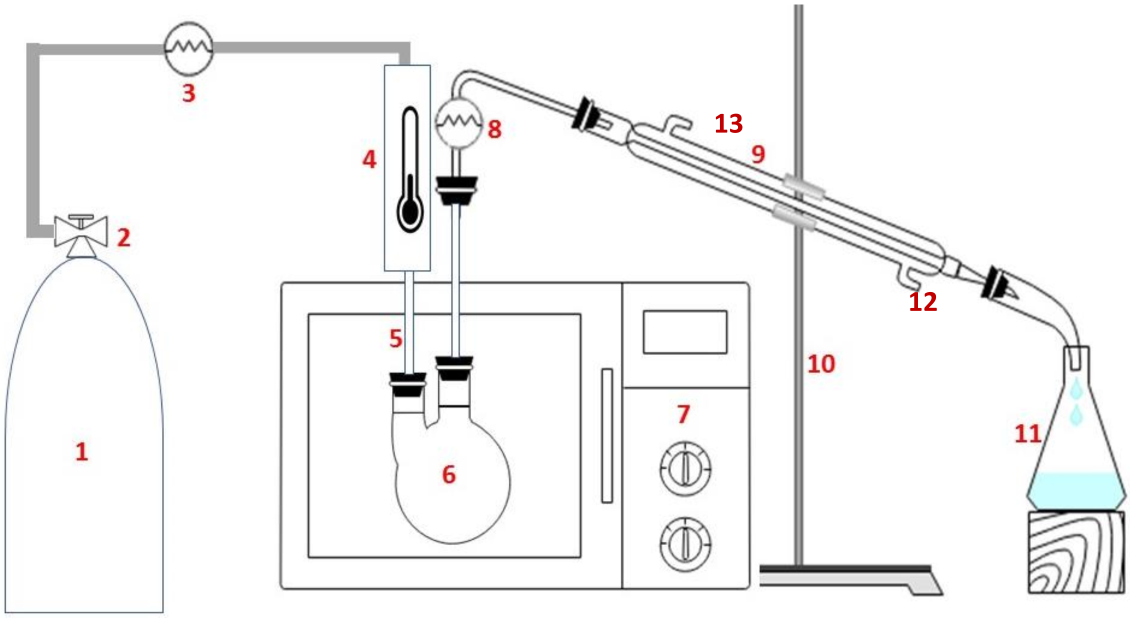

Figure 43: Schematic of microwave setup used for experiment

1. Compressed N_2
2. Flow valve & display
3. N_2 heater
4. N_2 Temp. monitor
5. Inlet of hot N_2
6. Reactor with sample
7. Microwave oven
8. Glassware heater
9. Condenser
10. Retort stand
11. Distillate receiver
12. Cooling water in
13. Cooling water out

9.1.2 Preparation of Samples

Sample of about 5 kg of contaminated drill cuttings was centrifuged for 2.5 minutes and 2500 rounds per minute (RPM). Centrifuges separate substance based on their densities. Consequently, excess water and oil was separated from the cuttings. The separated liquid was discarded and the rest of the cuttings was transferred into a suitable container and stored in a cold room to reduce biological activity.

9.1.3 Dewatering of Samples Using the Microwave

The centrifuged cuttings were mixed well to ensure homogeneity. A known mass of a well-mixed centrifuged cuttings was placed in a flask and placed in a microwave. Heated nitrogen gas flowed into the sample through a thin glass pipe connected from outside the microwave at a rate of 20 L/min. The glassware connecting the reactor to the condenser was heated to prevent pre-condensation of the vapour back into the reactor. A condenser was connected to complete the setup, Figure 43. The microwave supplied 900 W effective power. The samples were dewatered in 500 g batches for an average time of 10 mins. Dewatering here means that the sample was irradiated until the flow rate of the distillate was observably reduced. It forms part of the pre-treatment process for two essential reasons; 1) to maintain a high process temperature for efficient oil separation and 2) the structure of the pre-treated cuttings (lumpy and more porous) makes absorption of susceptor more efficient.

9.1.4 Results

After dewatering, the particles lump up to form a hard, solid, and porous structure. Figure 44 shows crushed sample. It had to be crushed into smaller particle sizes to get it out of the reactor during the experiments. Figure 45 shows an enlarged diagram which clearly shows the pours. In Figure 46, a piece of the sample was doused with MEG, which immediately percolates and wets the interstitial structure as well, Figure 47- the sample doused with MEG was crushed to observe the extent of wetness.

Figure 44: Structure of dewatered cuttings

Figure 45: Dewatered cuttings showing pours

Figure 46: Dry sample on the left and sample doused with MEG on the right

Figure 47: Crushed sample showing its wet interior structure

9.2 Treatment of Dewatered Cuttings with MEG, Mechanical Mixing and N2 Configuration

Previous studies using a stirred bed microwave system proved that up to 95% of organics can be removed from hydrocarbon contaminated soils. Stirring also mitigates the effect of low penetration depth (Robinson et al., 2012). This gives an indication that, mixing will improve microwave distribution throughout the material. Meaning that oil and susceptor removal will also be optimal. A bench top experiment was performed to test this.

The microwave set-up in Figure 43 was modified to include a mixer, which operated at 12 rounds per minute (RPM). About 130 g of dewatered cuttings was mixed with about 30 mL of MEG before positioning it in the microwave cavity. N_2 was heated to 250 ^{o}C and applied from the bottom of the reactor at a rate of 20 L/min. It was expected that the mass transfer out of the reactor will be more efficient than when the gas is applied on top of the sample. The mixer was introduced from the top of the microwave oven through the same glassware that sends vapour to the condenser (Figure 48). Power of 700 W was supplied from the microwave. It was challenging to keep the reactor stable whilst the mixer was in operation. But this was overcome by repositioning the reactor and adjusting the speed of the mixer.

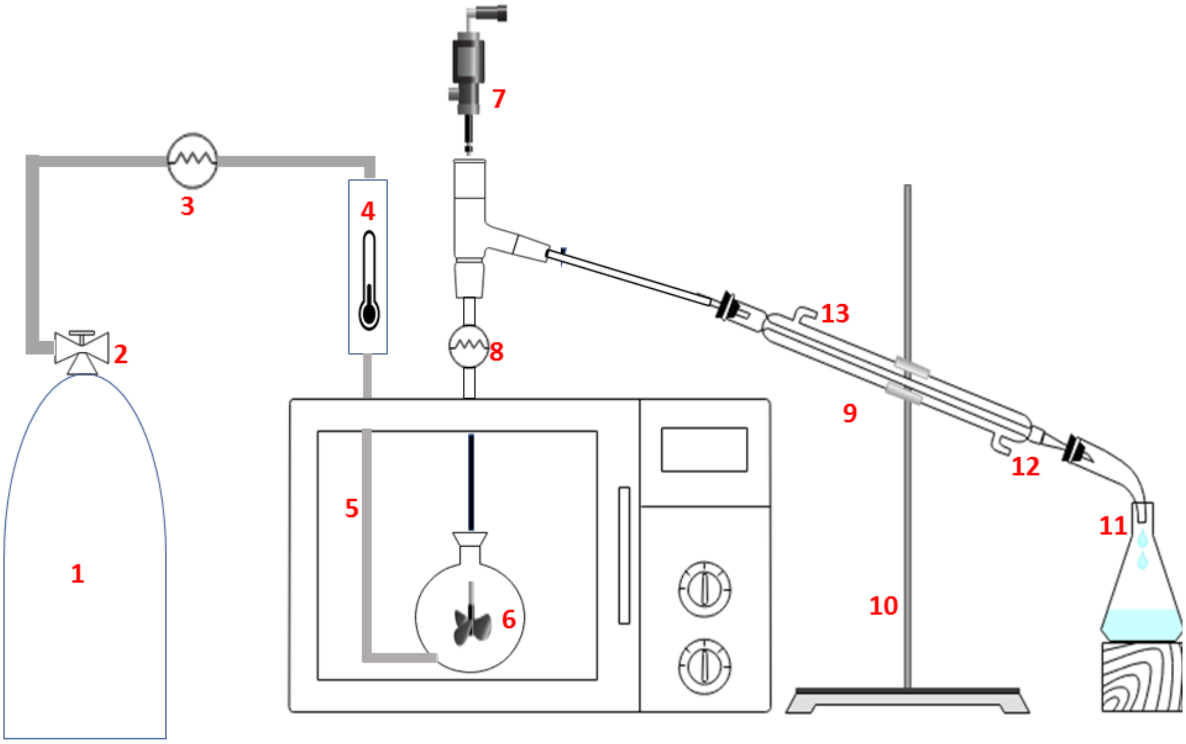

Figure 48: Microwave set-up with a mixer and N_2 applied from the bottom of the sample

1. Compressed N_2
2. Flow valve & display
3. N_2 heater
4. N_2 Temp. monitor
5. Inlet of hot N_2
6. Reactor with sample
7. Mixer
8. Glassware heater
9. Condenser
10. Retort stand
11. Distillate receiver
12. Cooling water in
13. Cooling water out

9.2.1 Results

Stirring was successfully executed. The mass transfer was very high with particles from the sample moving into the condenser as shown in Figure 49.

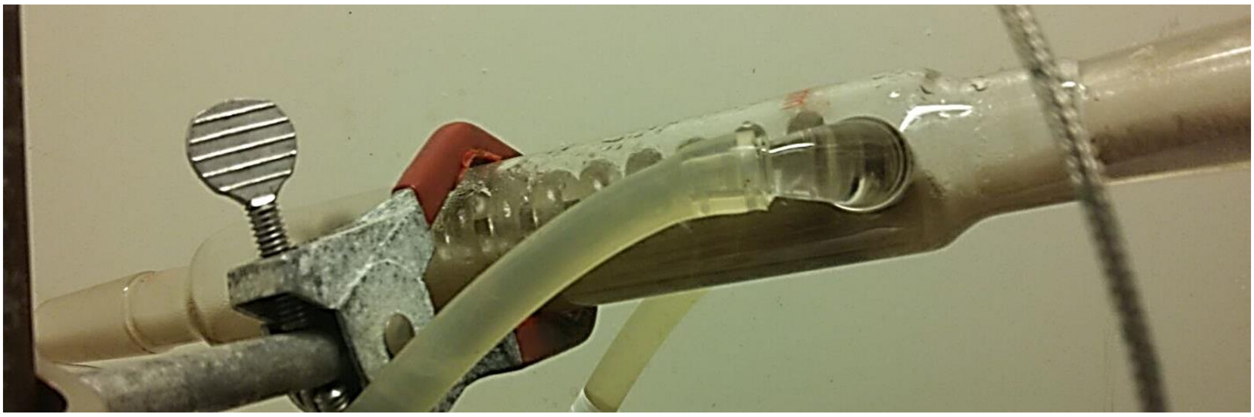

Figure 49: Condenser with solids entrainment

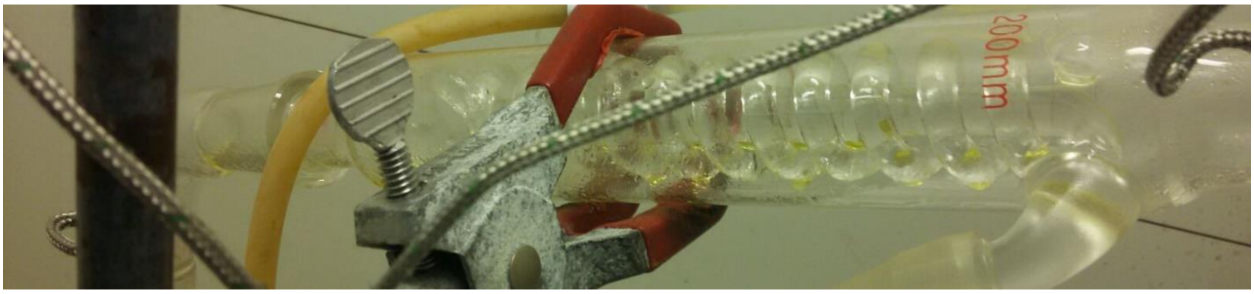

Figure 50: Condenser without solids entrainment

9.3 Treatment with MEG, No Mixing, and N_2 Configuration

For this experiment, the only change made to the set-up was to remove the mixer. The purpose was to compare the impact on oil removal when the sample is stirred during treatment to when treatment is conducted without stirring. Sample size was 200 g, mixed with approximately 50 ml of MEG and 900 W microwave power. The schematic is shown in Figure 51.

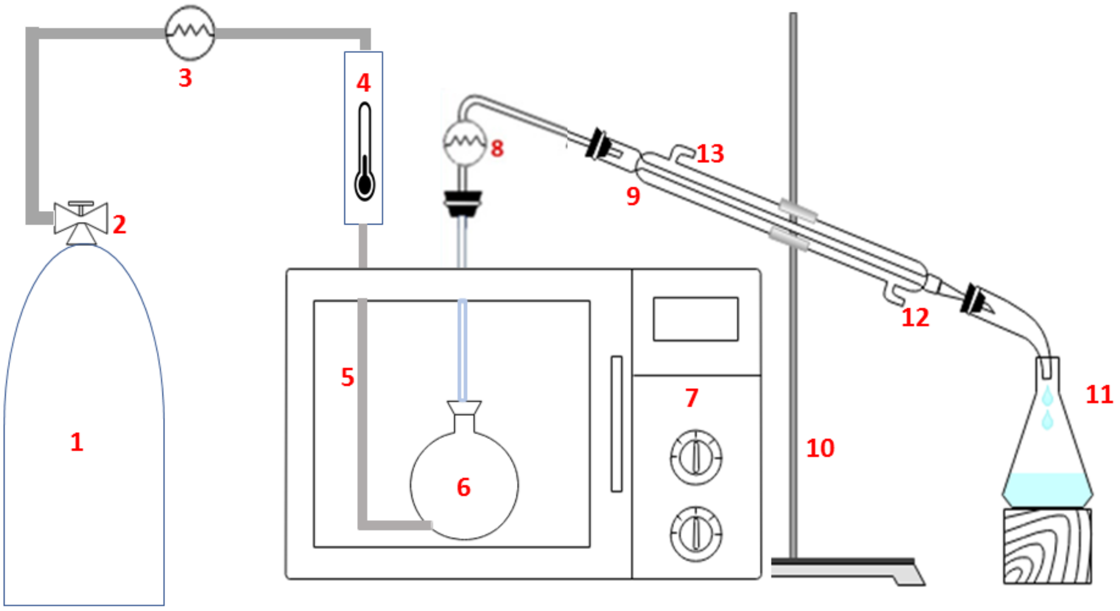

Figure 51: Microwave set-up with N_2 applied from the bottom of the sample

1. Compressed N_2
2. Flow valve & display
3. N_2 heater
4. N_2 Temp. monitor
5. Inlet of hot N_2
6. Reactor with sample
7. Microwave oven
8. Glassware heater
9. Condenser
10. Retort stand
11. Distillate receiver
12. Cooling water in
13. Cooling water out

9.3.1 Results

There was absolutely no solids entrainment in the condenser, during and after the experiments as shown in Figure 50. The treated sample formed a hard clayey-like structure in the reactor.

9.4 Treatment of Hot Dewatered Cuttings with MEG

This test was conducted to study the effect of oil removal when the susceptor is immediately added to hot cuttings.

The set-up used in Figure 43 was used for this experiment. Power supply, N_2 flow rate and other parameters remained unchanged. 200 g of centrifuged cuttings was dewatered for 3.5 minutes and 75 ml of MEG was immediately added to sample, whilst it was still very hot. This run for 4 mins in the microwave.

9.4.1 Results

The OOC was determined immediately using the retort method to be 1.08 wt %. This experiment was repeated but with a second dousing of 75 ml of MEG. N_2 flow through the sample for extra 2 minutes. The retort analysis determined the OOC to be 0.95 wt % after the second cycle. A summary of all the OOC results obtained with alternating parameters is given in Table 14.Table 14 OOC obtained for alternating parameters

9.4.2 Summary of OOC results for alternating parameters

Table 14 OOC obtained for alternating parameters

Test #	Power input (W)	Time/min T1	Sample weight, g	Susceptor	Volume added/mL	N_2 temp. / ºC	OOC_{dry} %	OOC_{wet} %	OOCs %	Total volume of MEG/Water (mL)
S1	900	-	-	-	-	-	13.24	10.24	-	18.0
S2	900	-	-	-	-	-	4.32	4.15	-	1.4
S3	900	5	200	MEG	40 (1)	200	0.72	0.68	0.18	1.6
S4	900	5	200	MEG	50 (2)	200	0.74	0.71	0.23	1.2
S6	900	4	200	MEG	75 (1)	245	1.08	1.02	-	2.0
S7	900	4	200	MEG	75 (2)	253	0.95	0.91	-	1.2
S8	900	5	205	MEG	80 (1)	265	0.64	0.61	0.09	1.6
S9	900	5	200	MEG	80 (2)	265	0.62	0.59	0.08	1.7
N_2 *	900	5	200	MEG	50	250	-	-	1.07	-
N_2**	700	5	130	MEG	30	250	-	-	1.28	-

N_2 * - Nitrogen from bottom without mixing

N_2** - Nitrogen from bottom with mixing

OOC_{dry} and **OOC_{wet}** were obtained using the retort

OOCs was obtained using the soxtec

S1- centrifuged cuttings

S2- dewatered cuttings

S3-susceptor added to cold sample and stirred

S4-2nd treatment of **S3**

S6 & **S7**-Susceptor was added to hot cuttings and treated immediately

S8-Susceptor was added to cold sample and allowed to soak into the pores

S9-2nd treatment of S8

9.5 Discussion

Dewatering of Samples

Reference to section 9.1.4, dewatering forms part of the pre-treatment process. It plays a significant role by creating a more porous material to absorb susceptor into the core structure of the sample. Meaning that when the sample is exposed to microwave energy, the energy is distributed more homogeneously into the entire matrix of the material. This enhances oil removal especially when interstitially bound. The fact that the dewatered sample absorbs the susceptor to its core by simply dousing, is promising for the design of a continuous microwave processing system. This is because a conveyor system, equipped with nozzles can be used to apply the susceptor to the samples instead of mixing the susceptor into the samples before processing. This takes away the requirement of a bulk mixer prior to final treatment, and may also reduce the amount of susceptor used.

Comparing Effect of Mixing Sample and No Mixing of Sample

From section 9.2.1 it was observed that the treated sample was powdery due to mixing, during treatment. The particles accumulated in the condenser and other connecting glassware at the end of the process. The sweeping effect of the N_2 gas also contributed to particle entrainment. On the other hand, when the mixer was removed, no particle entrainment was observed (Figure 50).

This observation is an indicator that a cyclone will have to be included in the design of a scale up. Considering the overarching objective of *Norwegian Technology AS*, to create a compact system, the idea of introducing a cyclone for particle removal is a draw back. More so cyclones are expensive and would need a high temperature resistant pump for successful operation. These will inflate the cost of the system and does not make mixing, during treatment attractive.

Furthermore, Soxtec analysis (refer to Table 14) of the mixed sample gave OOC to be 1.28 wt % and the unmixed sample to be 1.07 wt %. The mixed sample was expected to have a lower OOC than the unmixed sample, since the entire matrix was broken down to powdery particles, with large surface area for better microwave distribution. The results indicated otherwise.

The main reason is that, in a multi-mode cavity oven, the temperature distribution is nonuniform due to inhomogeneous electric field distribution within the cavity (Shang et al., 2006). Another reason is that the susceptor evaporates faster during mixing than without mixing. A possible solution to the latter challenge is to improve the set-up to include a complimentary susceptor dousing point, where additional susceptor can be added to make up for what is lost. This will however complicate the system and treatment process, making it unattractive.

Additionally, it is worth stating that the sample size and amount of susceptor used were different in both tests. This could have caused this unexpected result and is an indication of how sensitive the parameters could be. More so the microwave power during mixing was 700 W compared to 900 W in the other. According to a study conducted in 2002, if power is too low the susceptor may not transfer enough energy into the sample for desorption to occur (Reuß et al., 2002). The test was not repeated mainly due to the solids entrainment, which is most undesirable.

If we consider a scenario where better oil removal is achieved with mixing and accurate susceptor dousing, this must be juxtaposed with the cost and footprints of adding a cyclone to the design. In addition to that, the product after treatment in powdery form, also means that the treated cuttings will have low settling speed when discharged to sea. Meaning that it will float for long and be available to fish. This may cause adverse effects on aquatic life, especially if some harmful substances like heavy metals remain in the discharged material.

Treatment of Hot Dewatered Cuttings

Dousing susceptor onto hot cuttings causes some amount of it to be lost to evaporation. There is high possibility that the susceptor does not wet the entire matrix before treatment. Meaning that desorption will not be efficient throughout the sample. Dousing for the second time did not significantly improve the OOC either.

This is another challenge to this technology which must be remedied with a better set-up to prevent lose to evaporation. However, it will complicate the system and the idea of adding susceptor to hot cuttings should be shelved. Adding it to cooled cuttings will allow for the susceptor to permeate the pores better to improve oil removal during treatment.

Residual Susceptor Removal

Retort analysis (see Appendix A) indicates that there is a residual substance in addition to oil, after treatment. Rossi, 2016 concluded it to be susceptor. Test conducted during this thesis confirms a residual substance, though it is difficult to conclude if it is susceptor since there is a possibility that the substance is a result of moisture absorbed from the atmosphere.

Considering that susceptors are very volatile it is unlikely to remain in the cuttings after intense microwave irradiation. However, assuming there is residual susceptor which must be removed before discharge, a suggestion is to use a suitable solid susceptor (graphite or activated carbon) to burn it off (Rossi, 2016). There is, however, an imminent disadvantage in terms of additional energy supply for burning. Another challenge will be to find a suitable conveyor belt that can withstand such high temperatures produced by solid susceptors. These have additional cost implications which may counteract the purpose of this technology.

However, considering that not all microwaves are absorbed within the matrix of the material during treatment, efforts could be directed at diverting the reflected waves into a separate compartment, where the treated cuttings are mixed with some activated carbon or graphite. The trapped microwave energy in the compartment can then be used to burn off any residual hydrocarbons or liquid susceptors left in the material before discharge to sea.

9.6 Discrepancy in OOC Levels in Soxtec and Retort Methods

It is seen from Table 14, that the oil levels obtained using the soxtec method are much lower than the when the retort method is used, for the same sample. This could be due to larger sample size used during the retort analysis. Most critical source of error during the retort analysis is inaccurate reading of liquid volume in the receiver as a result of capillary forces of attraction in the walls. The soxtec method also has a shortfall of oil evaporating with the solvent.

9.7 Conclusions

Alternating various treatment parameters has been a fact-finding process to build a robust microwave treatment system. It is also a way to find the best method to meet statutory regulator standards and company standards of < 1 wt% OOC. Although mixing samples during treatment was appealing in the beginning, test conducted during this thesis shows some disadvantages to the process. It is also certain that adding susceptor to hot cuttings does not allow it to entirely wet the interior of the cuttings, which has a negative effect on oil separation. The susceptor evaporates faster from the sample than is required. The amount of microwave power applied also seems to have an impact on oil removal. Extending the retention time in the microwave with commensurate amount of susceptor will most likely provide enough energy to the susceptor for better desorption.

10 Conclusions and Recommendations

The main aim of this thesis was to investigate susceptor properties with respect to decomposition and susceptor recovery such as: decomposition as a function of microwave heating, recycling times for MEG in relation to decomposition and the impact of water on the properties of susceptors. It also included alternating parameters such as increased susceptor dosage, mixed system, and nitrogen configuration to increase oil separation.

The decomposition tests conducted with MEG, TEG and water without cuttings showed colour changes after irradiation. On the other hand, when the susceptors were added to OCDC, MEG showed little signs of decomposition after ten recycles whilst TEG decomposed immediately after the first cycle. About 70 % of the initial amount of MEG used during the test was lost to evaporation due to poor condenser configuration. The presence of water also reduced process temperature during the tests. According to some reports, it was challenging to meet regulatory standards using water, when heavy base oil with a high boiling point had to be separated. Water was used to treat cuttings to < 1wt%, when the base oil had low bp. This was confirmed in this thesis when centrifuged cuttings with approximately 21 wt% water and 13 wt% of oil was treated without organic compound. The OOC was reduced to between 4.3-6.1 wt% when the water content was 2.06 wt% and 2.4 wt% respectively. Using MEG, reduced the OOC to between 0.05 – 1.08 wt% depending on the variation of parameters discussed in Chapter 9. It is significant to note that little variations in parameters can significantly change the results. Organic compounds provide high process temperatures to vaporize the oil. This ensures better desorption and reduced energy consumption since the oil contributes higher vapour pressure at high process temperatures.

It was discovered that increasing the susceptor dosage did not cause a significant change in the OOC. This implies that adding the right amount of susceptor to the OCDC under the right conditions, especially, reduced water content, in a single treatment is good enough to reduce OOC to regulatory standards.

The author recommends:

1) Gas Chromatography-Mass Spectroscopy (GC-MS) be conducted on distilled susceptors to find out if their chemical properties change after microwave treatment.

2) Investigating the effect of decomposed susceptor on oil separation should be carried out. Although TEG showed signs of decomposition, it is premature to rule it out of this technology since it has not yet been determined that the colour change is due to chemical synthesis. It is most likely due to decomposition of the base oil as a consequence of thermal runoff.

3) Further test should be conducted using TEG and varying water content in the drill cuttings to explore how much water is needed to reduce process temperature, just enough to vaporize the oil and subsequently, avoid decomposition. The prospects of TEG are promising with regards to desorption and energy savings, due to its high process temperature and vapour pressure contribution from the oil.

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Appendices

Appendix "A"

Methods for Analyzing OOC

SOXTEC and Retort Methods

In order to control cuttings properties to reduce the amount of oil to levels set by regulators, the amount of oil before and after treatment should be known. The Retort offers a method for measuring the percentage of oil, water, and solids contained in a sample of OCDC. Unlike the retort which gives information on both OOC and WOC, the SOXTEC method only gives information on the percentage of oil.

Table 15: Equipment used for Analysis

Equipment	Model	Manufacturer
Soxtec Extraction System	HT 1043	Foss-Tecator
Extraction thimble	33x80mm	Whatman
Glass wool	-	-
50mL electronic retort kit	165-14-3	OFITE

Other materials:

1. Defatted cotton pads
2. Analytical scale (0.1 g)
3. Analytical scale (0.0001 g)
4. Petroleum ether
5. Different glassware
6. Personal Protective Equipment

Procedure for Retort Analysis

A gravimetric approach was applied to the use of this retort. The process involves putting a known mass of OBM into a retort and heating it up until all the liquids are removed. The liquids vaporize upon heating and condenses to get the oil and water/susceptor on cuttings.
The following steps are key to ensuring safe and efficient process:

- The retort chamber was washed well and dried after each test
- The condensing pipe was cleaned with a T-handle drill bit and thick threadlike pipe cleaner after each test
- The retort threads were lubricated to ensure easy opening after heating
- Steel wool of about 3g was placed in the retort to prevent particles from moving into the condensing pipe

The tare weight of the empty retort assembly including the steel wool was taken **M_R**. The sample was then added and weighed. It was ensured that air pockets were removed by breaking the samples into very small particles. Weight of sample was determined as Mw. The weight of cylinder for collecting the condensed liquid was recorded, **Mc**. The retort assembly was then placed in the heating chamber and the condenser attached, whilst the cylinder was positioned directly below the condenser collect the condensed liquid. The heat chamber was turned on and allowed to run for about 45 minutes. After this time, it was turned off and the retort assembly was taken out of the heating chamber and placed on a workbench to cool. The cylinder and liquid was weighed, Mc+ M_{liquid}. The condensate usually comprises two liquids, oil, and water or susceptor. Their volumes were determined, sometimes with the help of a pipette. Capillary forces on the walls of the cylinder made reading the volumes extremely challenging. Basically, the volume recorded could be subjective, which may lead to different final results of OOC. The density of water was also assumed to be 1 gL^{-1} which implied that the volume of water was translated as the mass and 1 mL=1 g. The weight of the liquid, **M_{liquid}**, was determined by subtracting **Mc** from **Mc+ M_{liquid}**. The weight of the cooled retort assembly with cuttings was recorded, **M_3**. The weight of the retorted cuttings, **M_d** was determined by subtracting **M_3** from **M_R**. The mass of the oil, **M_{oil}** was determined and the OOC was calculated based on the formula below.

$$OOCdry = \frac{\mathrm{Moil}}{\mathrm{Moil} + Md} \times 100\% \qquad (19)$$

$$OOC\mathrm{wet} = \frac{\mathrm{Moil}}{\mathrm{Mw}} \times 100\% \qquad (20)$$

Procedure for Soxtec Analysis

The system consists of the following components:

- 1043 Extraction unit HT 6
- 1046 Service unit
- Extraction cups-
- Thimbles and adapter
- Holder for extraction cups.

For this method, the sample is placed in thimbles and submerged in a boiling solvent to extract the oil from the sample. Sample size guide provided by (Anderson, 2004) is shown in **Error! Reference source not found.**Table 16 It is recommended that the sizes are big enough to reduce errors. The method is very sensitive and caution must be taken to minimize errors.

Table 16: Soxtec sample size

Oil content (%)	**Sample weight (g)**
0-10	2-3
10-25	1-2
>25	0.5-1

Depending on the test, samples of different sizes were weighed directly into extraction thimbles. A defatted cotton wool was placed on them to keep them intact during the process. The thimbles were then placed in the extraction machine. The extraction cups were cleaned and weighed (W1) with a stable scale up to four decimal places. About 50 ml of solvent (petroleum ether/dichloromethane) was added to the extraction cups and tarred with boiling stones, to control vigorous boiling effects. The cups were positioned in the machine and secured to prevent leaks during the extraction process. By gently twisting the cups one could tell if they were secured or not. It is critical to avoid leaks since that would spoil the sample. Leakage of the extraction liquid also poses health and safety risks. The service unit was turned on and the thimbles were lowered into the solvent to boil for approximately 40 mins.

Immediately after boiling, rinsing began. The samples were suspended over the boiling solvent for another 40 mins to enable any residual traces of oil to flash out of the sample into the extraction cups. The condenser valves were closed and the soxtec system was turned off. By using the cup holder, the extraction cups were lifted above the heating plate to prevent rapid evaporation. After 2-3 mins, the cups were moved to the fume hood for the remaining solvent to evaporate. The solvent was allowed to evaporate until oil was visible in the extraction cup. Caution should be taken to prevent oil from evaporating prior to weighing. The cup plus oil extract was weighed (W2). OOC is calculated using the formula:

$$\mathrm{OOC}\ (\%) = \left[\frac{\mathrm{W2} - \mathrm{W1}}{\mathrm{T2}}\right].100 \tag{21}$$

W1=weight of extraction cup
W2=weight of extraction cup plus extract
T2 =weight of sample + oil
T1 =weight of sample

It is significant to note that analysis of the same sample using both methods of analysis yield different results. The reasons could be that the retort samples are much larger than the soxtec samples. Most critical source of error during the retort analysis is inaccurate reading of liquid volume in the receiver. The soxtec method has a shortfall of oil evaporating with the solvent.

Appendix “B”

Table 17: Parameters for cuttings delivered to IRIS for Toxicology Test

Test #	**Power input (W)**	**Time/min T1**	**Sample weight, g**	**Susceptor**	**Volume added/mL**	**N_2 temp. / ºC**	**OOC_{dry} %**	**OOC_{wet} %**	**Total volume of MEG/Water (mL)**
S1	900	-	-	-	-	-	13.24	10.24	18.0
S2	900	-	-	-	-	-	4.32	4.15	1.4
S3	900	5	200	MEG	40 (1)	200	0.72	0.68	1.6
S4	900	5	200	MEG	50 (2)	200	0.74	0.71	1.2
S6	900	4	200	MEG	75 (1)	245	1.08	1.02	2.0
S7	900	4	200	MEG	75 (2)	253	0.95	0.91	1.2
S8	900	5	205	MEG	80 (1)	265	0.64	0.61	1.6
S9	900	5	200	MEG	80 (2)	265	0.62	0.59	1.7

All analysis for OOC were carried out using the retort method. In the tenth column, MEG/water is not a ration but an indication that the substance collected in the retort cylinder, in addition to oil could be MEG or water.

S1-Centrifuged cuttings S2-Dewatered cuttings S3-S7 are cuttings treated with MEG for two cycles
(1)-first cycle (2)-second cycle

Table 18: Soxtec results matrix

Test #	**OOC1** %	**OOC2%**	**OOC3** %	**OOC average** %
S3	0.154	0.218	-	0.186
S4	0.325	0.262	0.11	0.232
S8	0.097	0.107	0.067	0.091
S9	0.104	0.102	0.058	0.088
N2*	1.199	0.931	-	1.066
N2**	1.296	1.278	-	1.287

N2*	Nitrogen from bottom and no mixing
N2**	Nitrogen from bottom with mixing