



University of
Stavanger

Faculty of Science and Technology

MASTER'S THESIS

Study program/ Specialization:

Environmental Technology /
Water Science and
Technology

Spring semester, 2016

Restricted access

Writer:

Lars Martin Rossi

.....*Lars Martin Rossi*.....
(Writer's signature)

Faculty supervisor: Prof. Torleiv Bilstad

External supervisor: Sindre Åse Lunde

Thesis title:

Thermal treatment of drill cuttings

Credits (ECTS): 30

Key words: Drill cuttings, drilling
waste, OSPAR, dielectric heating,
microwave heating, susceptors,
thermal desorption, nitrogen stripping,
offshore, oil and gas industry

Pages: 109

+enclosure: 0

Stavanger, June 30, 2016

Submitted in partial fulfillment of the requirements for the degree of
Master *of* Science

Thermal treatment of drill cuttings

Lars Martin Rossi
Department of mathematics and natural science
University *of* Stavanger

June, 2016

Abstract

Increased environmental stringency, and focus on cost efficiency, drives the oil & gas industry towards new and better solutions. Members of OSPAR have to follow strict discharge requirements for oil contaminated drill cuttings, based on the BAT, and BEP principles. The most successful technologies rely on thermal desorption. Only the TCC have received acceptance to treat and discharge OBM cuttings on the NCS, at a requirement of 0.05 % oil by weight.

Norwegian-Group AS is currently developing an integrated treatment solution for drilling fluids, waste water, and cuttings. In this thesis, thermal treatment of cuttings is investigated. The treatment concept rely on dielectric heating with microwaves, in combination with environmentally friendly, polar organic compounds. The initial study shows that glycols can be distilled without significant degradation, especially MEG. In addition to the benefits of increased process temperature, a significant reduction in energy requirement is possible. The energy required to vaporize MEG is in the order of magnitudes lower, than what is required to vaporize water.

Due to a higher process temperature , the vapor pressure contribution from the oil was significantly increased. Drill cuttings was successfully treated to well below the OSPAR limit of 1 % oil by weight, by the use of susceptors. The presence of susceptors significantly increased the oil separation from cuttings, especially when the cuttings did not contain water.

It is believed that the use of susceptors in combination with microwaves can challenge the TCC technology as BAT.

Acknowledgements

I would like to express my deepest gratitude to Sindre Åse Lunde at Norwegian-Group, for the opportunity, and guidance needed to perform this work. I would also like to thank Prof. Torleiv Bilstad, and Evgenia Protasova for their efforts, and help, towards the completion of this thesis.

Last but not least, I would like to thank my girlfriend, Janne. Without your support, and encouragement, I could not have completed this work

Contents

| | |
|--|-------------|
| Abstract | i |
| Acknowledgements | ii |
| Contents | iii |
| List of Figures | vi |
| List of Tables | viii |
| List of Equations | ix |
| Nomenclature | x |
| Glossary | xi |
| 1 Introduction | 1 |
| 1.1 Background | 1 |
| 1.2 Problem description | 2 |
| 1.3 Thesis objective | 3 |
| 2 Drilling waste | 4 |
| 2.1 The byproducts of drilling | 4 |
| 2.2 Handling, statistics, and cost | 6 |
| 2.2.1 Statistics | 6 |
| 2.2.2 Cost | 9 |
| 2.3 Legislation | 9 |
| 2.3.1 The OSPAR area | 9 |
| 2.3.2 Other regions | 10 |
| 3 Waste handling methods | 11 |
| 3.1 Onshore | 12 |

Contents

| | | |
|----------|--|-----------|
| 3.1.1 | Skip and ship | 12 |
| 3.2 | Offshore | 12 |
| 3.2.1 | Cuttings re-injection | 12 |
| 3.2.2 | Discharge | 13 |
| | Cuttings dryer | 13 |
| | Thermo-mechanical cuttings cleaner | 14 |
| 4 | A brief introduction to dielectric heating | 17 |
| 4.1 | Electromagnetic theory | 17 |
| 4.2 | The components of dielectric heating | 20 |
| 4.2.1 | The RF heating circuit | 20 |
| 4.2.2 | The microwave | 21 |
| 4.3 | A literature review on microwave treatment of drill cuttings | 23 |
| 5 | Distillation and chemical bonding | 31 |
| 5.1 | Distillation theory | 31 |
| 5.1.1 | Miscible liquids | 31 |
| 5.1.2 | Immiscible liquids | 32 |
| 5.2 | Steam distillation | 33 |
| 5.3 | Chemical bonding and temperature | 35 |
| 5.3.1 | Ionic bonds | 35 |
| 5.3.2 | Covalent bonds | 36 |
| | Polar molecules | 36 |
| | Hydrogen bonds | 37 |
| | Dipole-dipole interactions | 37 |
| | Van der Waals dispersion forces | 38 |
| 6 | Susceptor technology | 39 |
| 6.1 | What are susceptors ? | 39 |
| 6.2 | Alcohols and ethers | 40 |
| 6.3 | Acids, esters, amides, and amines | 44 |
| | Organic acids | 44 |
| | Esters | 45 |
| | Amides | 45 |
| | Amines | 47 |
| 6.4 | Ketones and aldehydes | 50 |
| 6.5 | Solid susceptors | 51 |
| 6.6 | Potential susceptors | 51 |
| 6.7 | Susceptor recovery | 52 |
| 7 | Distilling susceptors and base oils | 54 |
| 7.1 | Experimental setup and method | 54 |
| 7.2 | Results | 56 |
| 7.2.1 | Distilling monoethylene glycol | 56 |

Contents

| | | |
|-----------|--|------------|
| 7.2.2 | Distilling diethylene glycol | 61 |
| 7.2.3 | Distilling triethylene glycol | 63 |
| 7.3 | Discussion | 66 |
| 7.4 | Conclusion | 67 |
| 8 | Characteristics of cuttings | 68 |
| 8.1 | Materials and method | 68 |
| 8.1.1 | Sample preparation | 69 |
| 8.1.2 | Retort | 69 |
| 8.1.3 | Soxhlet extraction | 70 |
| 8.1.4 | Automated solvent extraction | 71 |
| 8.1.5 | A simple bench-top experiment | 73 |
| 8.2 | Results & discussion | 73 |
| 8.3 | Conclusion | 77 |
| 9 | Treating cuttings with susceptors and microwaves | 78 |
| 9.1 | Materials | 79 |
| 9.2 | Experimental setup | 79 |
| 9.3 | Methodology | 81 |
| 9.3.1 | Wet cuttings experiment matrix | 82 |
| 9.3.2 | Dry cuttings experiment matrix | 84 |
| 9.4 | Results | 84 |
| 9.4.1 | Effects of susceptor on centrifuged cuttings oil removal | 84 |
| 9.4.2 | Effects of susceptor on dry cuttings oil removal | 87 |
| 9.5 | Discussion | 92 |
| 9.6 | Conclusion | 95 |
| 10 | Technology applications | 96 |
| 10.1 | Not only for dielectric heating | 96 |
| 10.2 | Geography unlimited | 96 |
| 11 | Conclusions | 98 |
| 11.1 | Evaluation of dielectric heat sources | 98 |
| 11.2 | Evaluating the use of susceptors | 98 |
| 11.3 | Conveyor configurations | 99 |
| 11.4 | BAT and BEP potential | 100 |
| 12 | Further work | 101 |
| | Bibliography | 102 |

List of Figures

| | | |
|----|--|----|
| 1 | Mud circulation system | 6 |
| 2 | Alternatives of solid waste handling offshore | 7 |
| 3 | WBM cuttings released on NCS between 2005-2014 | 7 |
| 4 | OBM cuttings injected or shipped to shore between 2004-2014 | 8 |
| 5 | Number of wells drilled between 2005-2015 | 8 |
| 6 | Waste management hierarchy | 11 |
| 7 | CRI process | 13 |
| 8 | Secondary treatment including cuttings dryer | 14 |
| 9 | TCC process diagram | 16 |
| 10 | The propagation of electromagnetic fields | 18 |
| 11 | Electromagnetic spectrum | 18 |
| 12 | RF heating circuit | 21 |
| 13 | Magnetron microwave tube | 22 |
| 14 | Traveling wave tube | 22 |
| 15 | Simplified klystron circuit | 23 |
| 16 | Experimental seup in Shang <i>et al.</i> (2005b) | 24 |
| 17 | Stirred bed batch system | 25 |
| 18 | Results obtained in Robinson <i>et al.</i> (2012) | 26 |
| 19 | Continuous MW system | 27 |
| 20 | Comparison of N_2 drying, and N_2 in combination with MW | 28 |
| 21 | MW pilot scale rig | 29 |
| 22 | Illustration of Raoult's law in combination with Dalton's law. | 32 |
| 23 | The behavior of immiscible liquids in combination with Dalton's law. | 33 |
| 24 | Lewis structure of sodium chloride | 36 |
| 25 | Lewis structure of water | 36 |
| 26 | Relative strengths of functional groups | 37 |
| 27 | Functional group of alcohols and ethers | 41 |

List of Figures

| | | |
|----|---|----|
| 28 | Carboxyl functional group | 45 |
| 29 | Ester functional group | 45 |
| 30 | Amide functional group | 46 |
| 31 | Amine functional group | 47 |
| 32 | Functional group of aldehydes and ketones | 51 |
| 33 | Initial experimental setup | 55 |
| 34 | Experiment 1. MEG and sipdrill distilled in an aerated atmosphere | 56 |
| 35 | Experiment 2. MEG and sipdrill distilled in an inert atmosphere | 57 |
| 36 | Experiment 3. MEG and clarisol distilled in an aerated atmosphere | 58 |
| 37 | Experiment 4. MEG and clarisol distilled in an inert atmosphere | 59 |
| 38 | GC-FID overlay of sipdrill and sipdrill distilled with MEG | 60 |
| 39 | Experiment 5. DEG and clarisol distilled in an aerated atmosphere | 61 |
| 40 | Experiment 6. DEG and clarisol distilled in an inert atmosphere | 62 |
| 41 | Experiment 7. TEG and sipdrill distilled in an aerated atmosphere | 63 |
| 42 | Experiment 8. TEG and sipdrill distilled in an inert atmosphere | 64 |
| 43 | Experiment 9. TEG and clarisol distilled in an aerated atmosphere | 65 |
| 44 | Experiment 10. TEG and clarisol distilled in an inert atmosphere | 66 |
| 45 | Decreasing sample mass | 76 |
| 46 | Measured OOC for Samples 1-6. | 77 |
| 47 | Initial experimental setup | 80 |
| 48 | Final experimental setup | 81 |
| 49 | Cuttings treatment flow diagram | 82 |
| 50 | Retort analysis of experiments 11-23. | 85 |
| 51 | Volume of susceptor remaining after treatment. | 86 |
| 52 | OOC of water treated cuttings contaminated with dodecane. | 87 |
| 53 | OOC of MEG treated cuttings contaminated with dodecane. | 88 |
| 54 | %-removal of dodecane | 89 |
| 55 | OOC of water treated cuttings contaminated with hexadecane. | 90 |
| 56 | OOC of MEG treated cuttings contaminated with hexadecane. | 91 |
| 57 | %-removal of hexadecane | 92 |

List of Tables

| | | |
|----|---|----|
| 1 | Cost of cuttings handling | 9 |
| 2 | OSPAR decisions | 10 |
| 3 | Theoretical distillation with select compounds mixed with water | 34 |
| 4 | Energy required for distillation | 35 |
| 5 | Characteristics of ionic and covalent compounds | 36 |
| 6 | Properties of select alcohols & ethers | 42 |
| 7 | Distillation of dodecane with various alcohols & ethers | 43 |
| 8 | Distillation of hexadecane with various alcohols & ethers | 44 |
| 9 | Properties of select carboxylic acids & derivatives | 48 |
| 10 | Distillation of dodecane with various acids & derivatives | 49 |
| 11 | Distillation of hexadecane with various acids & derivatives | 50 |
| 12 | Dielectric properties of compounds | 52 |
| 13 | Microwave and distillation equipment | 54 |
| 14 | Retort and soxhlet equipment | 69 |
| 15 | Soxtec sample sizes | 72 |
| 16 | Soxtec sample matrix | 72 |
| 17 | Retort: OOC determination of centrifuged cuttings | 73 |
| 18 | Soxhlet: OOC determination of centrifuged cuttings | 74 |
| 19 | Microwave and distillation equipment | 79 |
| 20 | Centrifuged cuttings experiment matrix | 83 |
| 21 | Dry cuttings experiment matrix | 84 |

List of Equations

| | | |
|----|---------------------------------------|----|
| 1 | Maxwell's equations | 17 |
| 2 | Complex permittivity | 19 |
| 3 | Dielectric loss tangent | 19 |
| 4 | Dielectric heating equation | 19 |
| 5 | Penetration depth | 20 |
| 6 | Dalton's law | 31 |
| 7 | Raoult's law | 31 |
| 8 | Antoine's equation | 31 |
| 9 | Ideal gas law | 34 |
| 10 | Mole fractions | 34 |
| 11 | Dipole moment | 37 |
| 12 | Oil on dry cuttings | 70 |
| 13 | Oil on wet cuttings | 70 |

Nomenclature

| | | | |
|---------------|------------------------|--------------|---------------------------|
| ϵ'' | Dielectric loss factor | M_{H_2O} | Weight of collected water |
| ϵ' | Dielectric constant | M_{oil} | Weight of collected oil |
| λ | Wavelength | M_w | Molecular weight |
| \mathcal{E} | Electric field | mp | Melting point |
| \mathcal{H} | Magnetic field | OOC_{dry} | Oil on dry cuttings |
| $\vec{\mu}$ | Dipole moment | OOC_{wet} | Oil on wet cuttings |
| ρ | Density | P_n^0, p_n | Vapor pressure |
| $\tan \delta$ | Loss tangent | P_d | Power dissipation density |
| A, B, C | Antoine coefficients | T | Temperature (°C) |
| bp | Boiling point | x_n | Molar fraction |
| c | Velocity of light | %wt | Percent by weight |
| D_p | Penetration depth | μm | Micrometer |
| M_d | Weight of dry cuttings | | |

Glossary

A

ABM Aqueous based mud

B

bp boiling point

C

CW continuous wave

D

DEG diethylene glycol

DPG dipropylene glycol

E

EM electromagnetic

EPA United States Environmental Protection Agency

H

HOCNF Harmonized Offshore Notification Format

HTHP High Pressure High Temperature

I

IR infrared

ISM Industrial, Scientific, and Medical

M

MEG monoethylene glycol

MPG monopropylene Glycol

MSDS Material Safety Data Sheet

MW microwave

N

NABM Non-aqueous based mud

NCS Norwegian continental shelf

NOGA Norwegian Oil and Gas Association

NPD Norwegian Petroleum Directorate

NS North sea

O

OBM Oil based mud

OIW oil in water

OOC oil-on-cuttings

OPF Organic Phase Fluids

OSPAR Convention for the Protection of the Marine Environment of the North-East Atlantic

P

PLONOR Pose Little Or No Risk

PSD Particle size distribution

R

Glossary

RF radio frequency

RPM rounds per minute

S

SBM Synthetic based mud

T

TEG triethylene glycol

TGBE triethylene glycol butyl ether

TGME triethylene glycol methyl ether

TWT Traveling Wave Tube

W

WBM Water based mud

WIO water in oil

wt% Percent by weight

Chapter 1

Introduction

In this chapter the background, and the main objectives of this master's thesis is introduced.

1.1 Background

From the beginning of the 20th century, rotary drilling has emerged as the primary technology in the oil and gas industry (Teodoriu & Cheuffa, 2011). The definition of rotary drilling, as described by (Bourgoyne *et al.* , 1986) is : “The hole is drilled by rotating a bit to which a downward force is applied. Generally, the bit is turned by rotating the entire drill string, using a rotary table at the surface, and the downward force is applied to the bit by using sections of heavy thick-walled pipe, called drill collars, in the drill string above the bit.” As the drill bit moves further into the earth, fragments of sediment and rocks are produced. These fragments of sediment and rock are commonly referred to as cuttings.

The rotary drilling process relies heavily on the use of drilling fluids, or so-called drilling “mud”. The drilling fluid has a number of important roles during the drilling process. including, but not limited to (1) transport of cuttings from the well bore, (2) stabilize formation pressure, (3) provide lubrication and cooling, (4) provide buoyancy of drill pipe and casing, (5) clean the face of the hole, (6) suspension of formation soils upon loss of circulation, (7) reduce fluid loss, and (8) corrosion control (El-sayed & El-Naga, 2001). The choice of drilling fluid is crucial for the success of the drilling operation and depends on the type of formation, temperature, pressure, strength, permeability, available water quality, and ecological and environmental considerations (Bourgoyne *et al.* , 1986).

Drilling fluids are commonly divided into three subgroups: Water based mud (WBM), Oil based mud (OBM) and Synthetic based mud (SBM). WBM may also be termed as Aqueous based mud (ABM) while OBM and SBM fall under the category of Non-aqueous based mud (NABM). Substantial amounts of cuttings contaminated with OBM were released on the Norwegian continental shelf (NCS) up to 1993. Cuttings contaminated

with OBM was the main source of hydrocarbons entering the marine environment from the oil and gas industry in the North sea (NS). Furthermore, the average discharge of oil-on-cuttings (OOC) between the years of 1981 and 1986 was 1940 t per year. At the peak of cuttings discharge, disturbances was found more than 5 km away from the source of release (Reiersen *et al.* , 1989; Bakke *et al.* , 2013). Increased environmental focus and stringency caused a required OOC level of less than 1 Percent by weight (wt%) in the year of 1996 (OSPAR, 2000). Cuttings contaminated with WBM are discharged to sea as long as the chemicals are environmentally friendly (Svensen & Taugbøl, 2011). Upon reaching the surface, a primary treatment of the cuttings are normally performed on site by the use of solids handling equipment such as shale shakers, hydrocyclones and centrifuges as well as gravity settling in order to recover as much as possible of the fluid. The primary treated cuttings contain more than 1 % oil from drilling fluid and/or reservoir oil which means that practically no discharge of OBM cuttings is allowed. The Martin Linge field development received acceptance to discharge treated cuttings to the sea with the use of the thermo-mechanical cuttings cleaner (TCC) hammer-mill technology (see Chapter 3). The OOC limit set by the Norwegian government for the TCC at Martin Linge was 0.05 wt% (NEA, 2014) which is lower than the 1 wt% limit set by the Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR). The requirement was set based on the TCC performance on the UK continental shelf (UKCS). If the discharge limit is not met, the cuttings has to be shipped to shore for further processing. The TCC technology did not successfully reach the requirements for discharge on Martin Linge. In many ways this gives an indication of where the bar will be set with regards to the discharge of oil contaminated cuttings in the future. However, since the TCC did not consistently reach the 0.05 wt% goal, there might be grounds for a less stringent requirement in the future.

1.2 Problem description

Norwegian-Group AS is currently developing an integrated treatment solution for drilling fluids, waste water, and cuttings. The use of dielectric heating and especially microwaves have been proposed as a promising technology in thermal treatment of cuttings. The main focus of this thesis is the identification and use of polar organic susceptors¹ in the microwave treatment of OBM contaminated drill cuttings. The goal is, through theory and experimental work, to gain proof of concept that the principle of steam distillation in combination with susceptors will allow cuttings to be treated within the legislative requirements set by OSPAR. To shed light on the potential benefits of this technology and, how it can compete with the current and other upcoming technologies.

¹Susceptors are lossy materials, which can be heated by EM fields

1.3 Thesis objective

The objectives of this thesis is to further develop the cuttings treatment concept of Norwegian Group. The concept consists of utilizing dielectric heating in combination with steam distillation and susceptors. The following objectives are identified:

- Evaluate dielectric heat sources and possible combinations
- Identify potential susceptors and important characteristics
- Evaluate the use of susceptors in MW treatment of drill cuttings
- Review susceptor recovery methods
- Evaluate different conveyor configurations
- Analyze the BAT-potential of the treatment concept

In order to complete the objectives of this thesis it is crucial to have an understanding of the nature of drilling waste and its characteristics, the relevant legislation applicable to the NCS, other regions, and the current and upcoming treatment technologies. Additionally, understanding the concept of Norwegian Groups treatment plant, steam distillation, and the theory behind susceptors and dielectric heating is vital. These subjects are covered in the thesis.

Chapter 2

Drilling waste

2.1 The byproducts of drilling

The drilling process generate a substantial amount of waste and comprises of spent drilling fluids (mud), formation fragments known as cuttings, and slop. The drilling mud carries the cuttings from the well bore to the surface. Drilling fluids will always adhere to the surface of cuttings. Slop is a common denotation applied to oil-containing water and emulsions (Karlsen, 2013).

The main composition of WBM are solids, liquids, and chemicals where water is the continuous phase. The water contains several dissolved substances such as alkalies, salts, surfactants, organic polymers and insoluble constituents such as barite, clay, and cuttings (Caenn *et al.* , 2011). The solids may be divided into active and inactive solids. The main component of active solids are hydratable clays (Bourgoyne *et al.* , 1986). The properties of the hydratable clays are mainly controlled by the addition of chemicals. The inactive solids do not interact with water and other chemicals to a significant degree. Any oil content of a WBM will be present as a oil in water (OIW) emulsion. Despite WBMs being more environmentally friendly, they do not match the superior properties of OBMs and SBMs for all drilling applications (Caenn *et al.* , 2011).

OBMs have a similar composition as WBM. However, in OBMs the continuous phase is oil. Diesel and various mineral oils have commonly been used. It should be noted that diesel is not used on the NCS today. Any water content of an OBM is present as an water in oil (WIO) emulsion. The solids content of an OBM is considered to be comprised only of inactive solids due to no interaction with the oil (Bourgoyne *et al.* , 1986). As previously mentioned, OBMs are not as environmentally friendly as WBM and is subject to more stringent requirements for discharge than WBM. The historical and current legislation on discharge is presented in Chapter 2.

SBMs is another type of NABM where the base fluid is typically esters, polyolefins, acetal, ether, and linear alkyl benzenes (Caenn & Chillingar, 1996). The development of SBMs is a product of the increased environmental focus on the impact of drilling fluids on the environment.

Chapter 2 Drilling waste

Hydrocarbons, water, and other chemical constituents adsorb on the surface of cuttings. The volume of these components adhering to the surface is strongly dependent on the type of formation and the cuttings Particle size distribution (PSD) (EPA, 1993). Also, density, shape, and concentrations are factors that will ultimately affect every piece of equipment utilized to separate cuttings from the drilling fluid. In the ideal well, cuttings created at the drill bit is transported unaltered to the surface. In reality, cuttings are altered by physiochemical interactions with other solids, the drill string, and the well bore. When cuttings reach the surface, they are generally smaller and more round-shaped than at the moment of creation. For instance if we consider a particle of 20 μm in diameter being broken up into 5 μm particles. This represents an increase in surface area of 20 times the original particle and an increase of adsorbed mud by a factor of 20 (Growcock & Harvey, 2005). As the drilling process progresses, additional cuttings are continuously added to the drilling mud. Although a certain degree may be tolerated, or even beneficial, the added cuttings contribute to a significant degree in low-shear-rate and high-share-rate viscosity. This significantly reduce drilling rates and have other negative consequences (Growcock & Harvey, 2005). Upon reaching the surface, a primary treatment of the cuttings are normally performed. This is done on-site by the use of solids handling equipment such as shale shakers, hydrocyclones and centrifuges as well as gravity settling in order to recover as much as possible of the fluid. Figure 1 depicts a graphical illustration of the rotary drilling process and the mud circulation system.

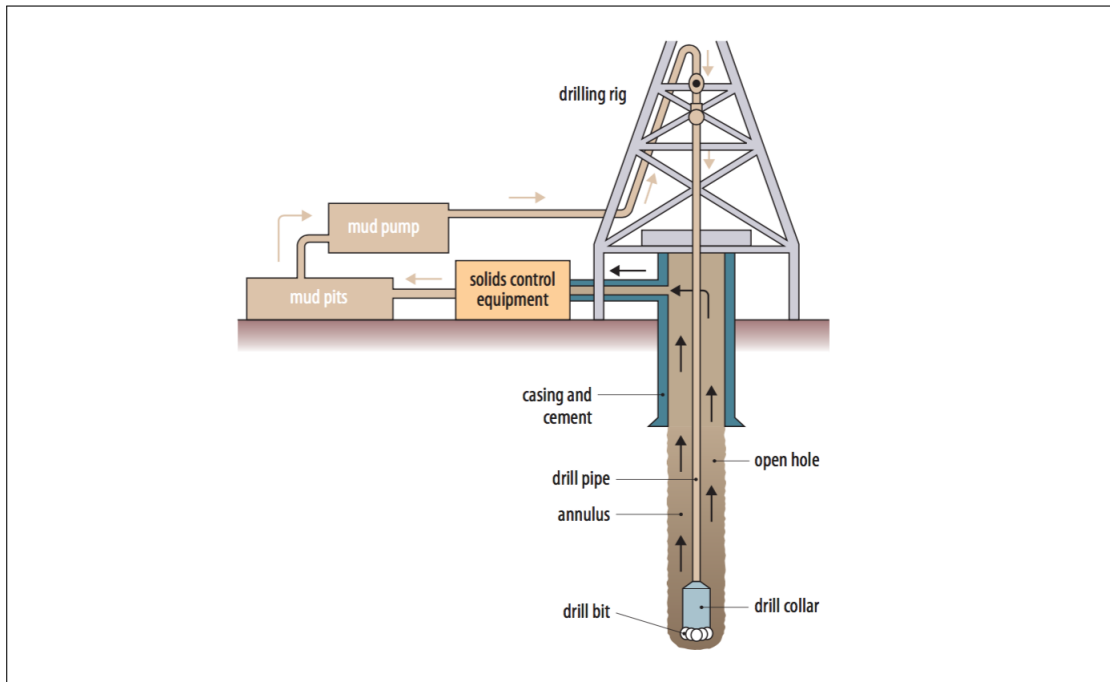


Figure 1: Mud circulation system (IPIECA, 2009)

2.2 Handling, statistics, and cost

The primary separation of circulated drilling fluid is mainly to recover the fluid and separate the *drilled* solids. The resulting residual of cuttings, slop, and oil needs to be handled appropriately as typical NS cuttings are produced with 15 wt% OOC (Shang *et al.* , 2005a). Generally, there is a limited number of choices related to the ways of handling drilling waste such as cuttings, the typical alternatives are illustrated in Figure 2. These alternatives is further addressed in Chapter 3.

For years, operators such as Statoil have applied a holistic approach to drilling- fluids and waste with an aim to plan towards a more cost, and resource efficient operation coupled with a minimization of the environmental impact (Svensen & Taugbøl, 2011). Furthermore, Svensen & Taugbøl (2011) describes the trend of the increasing complexity of drilling operations where long sections, high inclinations and High Pressure High Temperature (HTHP) conditions are a reality. The requirements of such conditions simply cannot be met by WBM.

2.2.1 Statistics

The Norwegian Oil and Gas Association (NOGA) releases an annual environmental report summarizing the “state” of the NCS regarding the oil and gas industry (NOGA, 2015). From the report a decline in the discharge of cuttings contaminated with WBM

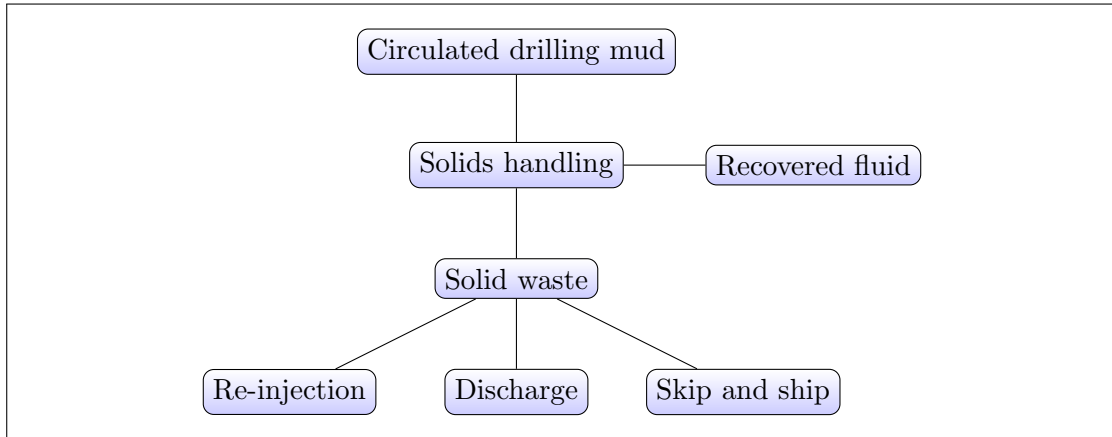


Figure 2: Alternatives of solid waste handling offshore (Bernier *et al.* , 2003)

between 2005 and 2014 can clearly be inferred (see Figure 3). An insignificant amount of WBM contaminated cuttings are either shipped to shore or re-injected. Figure 4 depicts the relationship between OBM contaminated cuttings that was either re-injected into formation or sent ashore for further treatment. Both re-injection and ship to shore are secondary treatment methods discussed in Chapter 3.

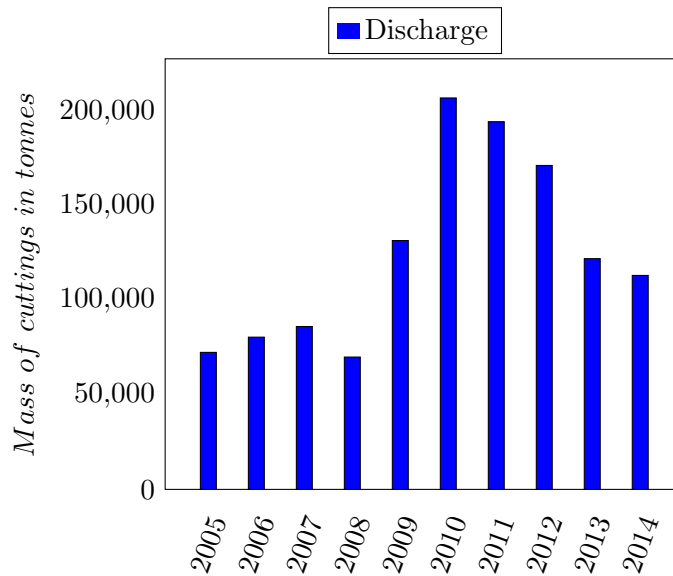


Figure 3: WBM cuttings released on NCS between 2005-2014 (NOGA, 2015).

According to the Norwegian Petroleum Directorate (NPD), the number of development wells drilled in the last years have increased while the number of wells drilled for

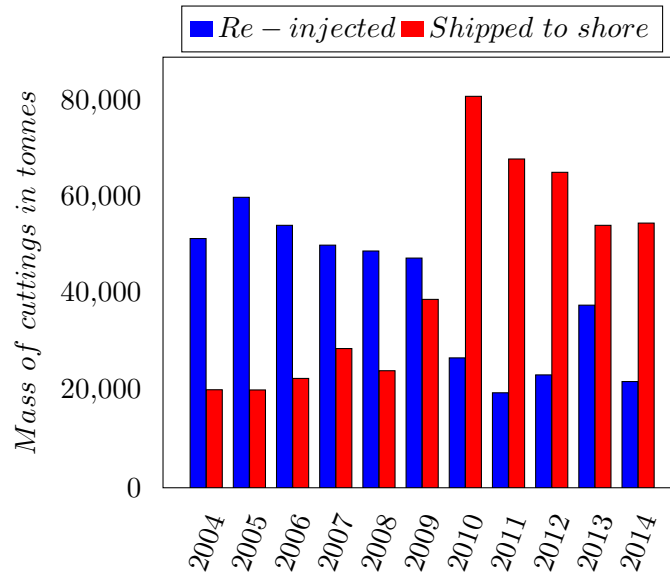


Figure 4: OBM cuttings CRI or shipped to shore between 2004-2014 (NOGA, 2015).

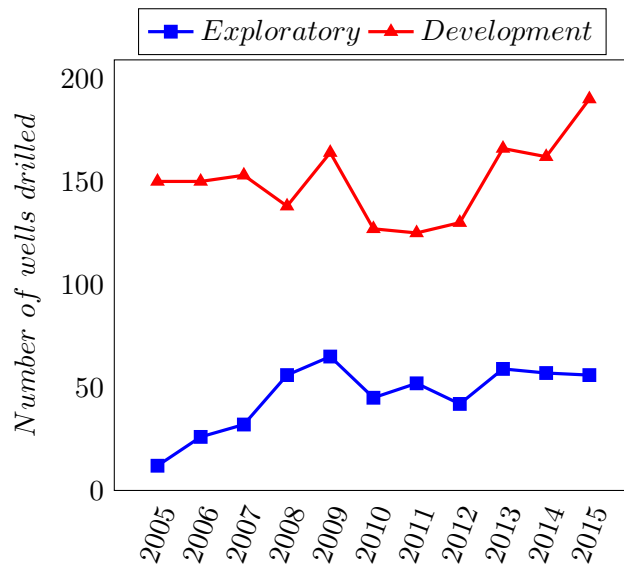


Figure 5: Number of wells drilled between 2005-2015 (NPD, 2016).

exploratory purposes are relatively stable (see Figure 5). This is somewhat contradictory to the trends visible in Figure 3, and 4, where a decline in the amount of cuttings either discharged, re-injected, or sent to shore is apparent. The explanation may be found in the fact that a significant amount of the OBM cuttings are slurrified with water to ease the transfer from rig to ship. This causes the cuttings to be reported as another category

of waste (NPD, 2016).

2.2.2 Cost

In the report by [Karlsen \(2013\)](#) a comparison of the cost associated with onshore treatment, offshore treatment and re-injection was performed. The cost of onshore treatment is field specific and vary with (a) distance to shore, (b) transport to treatment facility, (c) price variation, (d) amount of waste, and (e) the required capacity. On the other hand the costs for re-injection depends on (i) the lifetime of the injection well, (ii) amount of cuttings to be injected and (iii) the receiving capacity of the well. Lastly, the cost to treat cuttings offshore is dependent on (I) equipment cost, (II) equipment operation, and (III) personnel cost. A general estimate is provided by [Karlsen \(2013\)](#) (see Table 1), and it is evident that offshore treatment represents a significant lower cost than any other option. At the time of writing this thesis, only one technology have received acceptance for use on the NCS today ([NEA, 2014](#)).

Table 1: Cost of cuttings handling ([Karlsen, 2013](#))

| Alternative | Cost (<i>per ton cuttings</i>) |
|--------------------|----------------------------------|
| Onshore treatment | 9000 <i>NOK</i> |
| Re-injection | 9600 <i>NOK</i> |
| Offshore treatment | 6500 <i>NOK</i> |

2.3 Legislation

2.3.1 The OSPAR area

The Oslo and Paris Commissions met in Paris in September 1992. The attendees included the ministers responsible for the marine environment for the signatory states of the conventions and other representatives. The most important outcome of this meeting was the adoption of the new OSPAR. The convention also established the OSPAR Commission as a successor to the Oslo and Paris Commissions to administer, and to develop policies and international agreements. It is essential that the resources, biodiversity, and environmental aspects of the North-East Atlantic is preserved. The OSPAR Commission’s task is to make sure that the 16 contracting parties work together in the North-East Atlantic and honor their respective commitments ([OSPAR, 2016](#)). The most important OSPAR decisions for the purpose of this thesis are summarized in Table 2.

The OSPAR convention requires its contracting parties to apply the principles of best available technique (BAT) and best environmental practice (BEP). According to [OSPAR \(2016\)](#) BAT is the latest and best suited technology for limiting waste, discharge, and emissions. BEP is “the application of the most appropriate combination of environmental control measures and strategies.” From this statement it is clear that for a technology to achieve success in the OSPAR area, that particular technology must be considered BAT.

Chapter 2 Drilling waste

In Norway the activities regulation (PSA, 2015) describes the regulations that governs petroleum activities on the NCS.

§60 The water discharged to sea shall contain no more than 30 mg L^{-1} of oil and otherwise be as low as possible.

§68 Cuttings and other solids are not to be discharged to sea if the adherence of oil exceeds 1 % by weight on a dry basis.

Table 2: OSPAR decisions

| Decision | Summary |
|-----------------------|---|
| Decision 2000/2 | Authorities shall ensure and actively promote the continued shift towards the use of less hazardous substances. Introduces the Harmonized Offshore Notification Format (HOCNF). |
| Decision 2000/3 | Discharge of Organic Phase Fluids (OPF) is prohibited. The maximum OOC is 1 wt%. |
| Recommendation 2005/2 | The discharge of chemicals listed on OSPAR's 2004 list of priority chemicals should have been phased out by January 1 2010. |
| Recommendation 2006/3 | By January 1 2017, contracting parties should have phased out the discharge of chemicals that are, or contain, candidates that are identified for substitution. |

2.3.2 Other regions

Outside the OSPAR area there are various degrees of strictness in terms of cuttings discharge. In the gulf of Mexico a 6.9 % wet weight limit exists for internal olefin base fluids (SBM) while 9.4 % is allowed when the fluid is ester based (SBM). The discharge of OBM cuttings is prohibited. In Australia a 1 % discharge limit for OBM is in effect, however, in cases where SBM are used, the limit is 10 % on a dry basis (Whitford, 2009). In Malaysia there is no limitation for discharge of either WBM, SBM, or OBM (Bernier *et al.* , 2003).

Chapter 3

Waste handling methods

Pollution can in many ways be regarded as a wasted resource incurring additional disposal and treatment costs, as well as increased environmental load. The concept of waste management, and minimization (see Figure 6), includes the identification of all sources of waste. It also includes the evaluation of the potential for waste reduction at the source, to re-use waste, or to recycle the waste (Ahnell & O’Leary, 2008). The amount of waste generated is largely dependent on the depth, and diameter of the well that is being drilled (Johnston & Rubin, 2000). The implementation of slim-hole, and extended reach drilling in combination with advanced fluid systems have proven to significantly reduce the amount of generated waste (Zaki & Barabadi, 2014; Ahnell & O’Leary, 2008). However, it is not possible to eliminate the need for treatment and disposal. As previously mentioned in Chapter 2, the main options for treatment and disposal after primary treatment of cuttings is ship to shore, cuttings re-injection (CRI), and discharge.

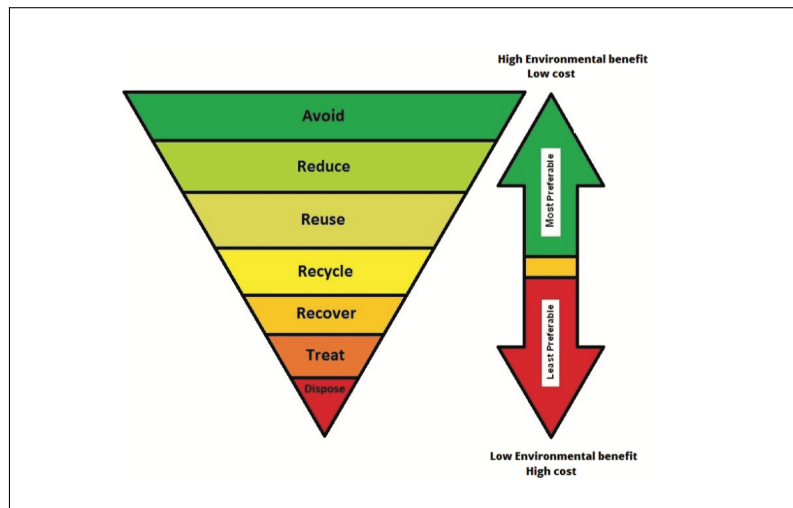


Figure 6: Waste management hierarchy (Zaki & Barabadi, 2014)

3.1 Onshore

3.1.1 Skip and ship

The introduction of OSPARs 1 wt% limit have practically stopped the discharge of oil contaminated cuttings on the NCS. In skip and ship operations, contaminated cuttings, and the fluids that was not recovered in primary treatment are collected in skips. These are sent ashore for further processing. The associated costs and operational challenges are accompanied by Health, Safety, and Environment (HSE) risks related to the number of crane lifts, use of deck space, and the use of high pressure pumping equipment (Morris & Seaton, 2006). Furthermore, Morris & Seaton (2006) estimates that the number of lifts per well may be as high as 1200, including onshore lifting operations.

It is possible to avoid crane lifts by slurrification of the cuttings. This can be beneficial if the cuttings would be injected downhole. A major disadvantage of this methodology is that the volume of waste increase considerably due to the addition of water. In general, transportation to shore is sensitive to weather conditions. This may temporarily halt the entire drilling operation. The treatment of cuttings that are taken to shore can be accomplished through various means, including biological treatment (Chaîneau *et al.* , 2002), incineration, and thermal desorption (Bernier *et al.* , 2003). Thermal desorption is also applicable for offshore discharge. Not restricted by the space and weight requirements that apply offshore, many of these technologies can successfully treat cuttings and recover base oil. The fate of the treated cuttings vary depending on the options that are available, and are generally suited for land farming, or as an additive in construction materials. The treatment and handling options restricted to onshore use are not discussed further in this thesis.

3.2 Offshore

According to Stephenson *et al.* (2004), the footprint and weight of equipment is critical in offshore operations. In many cases the equipment has to comply with the constraints that is set by an existing rig, or installation. This may be a limiting factor when considering the implementation of cuttings handling technology in locations offshore.

3.2.1 Cuttings re-injection

The re-injection of cuttings require slurrification in order to pump the cuttings downhole. Typically the cuttings are disposed into a suitable formation or dedicated wells. Injection has been performed on the NCS since the beginning of the 1990s, where most of the cuttings have been injected into the Utsira formation. A number of incidents where slurry has leached to the seabed has caused a decline in this practice (Karlsen, 2013). Some of the advantages of this method of disposal includes the use of less expensive drilling fluids, the need for transportation to shore is eliminated, and that the technology is proven (Bernier *et al.* , 2003). However, it is costly to re-inject cuttings and this

requires a suitable formation and extensive environmental monitoring (Karlsen, 2013). A schematic representation of the CRI process is depicted in Figure 7.

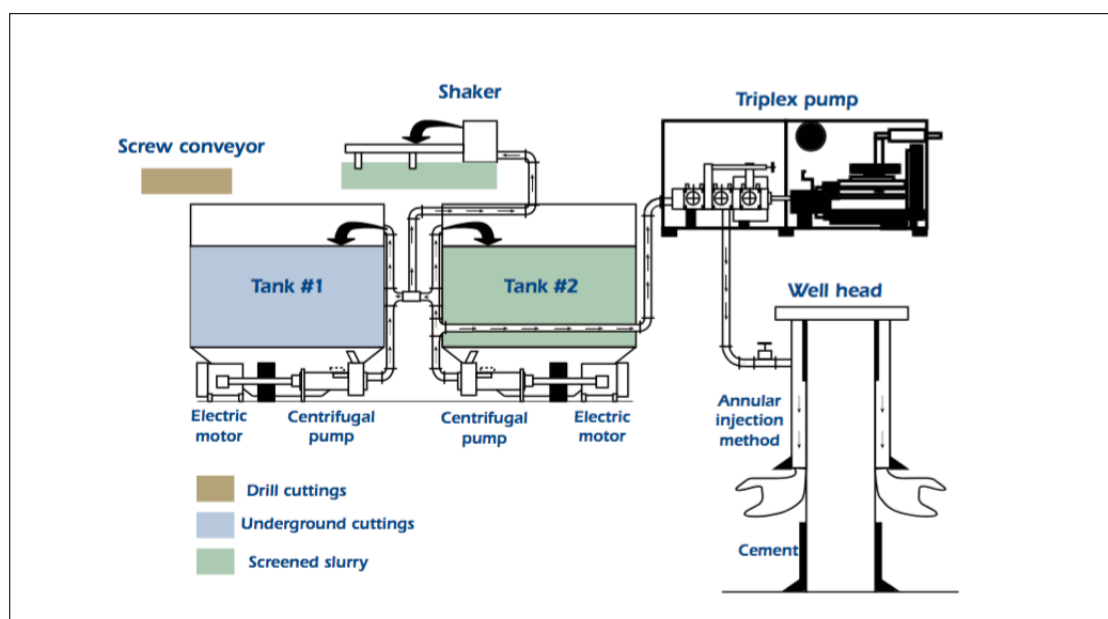


Figure 7: CRI process (Bernier *et al.* , 2003)

3.2.2 Discharge

Cuttings dryer

The cuttings dryer is a secondary treatment method that was adapted from the mining industry. The centrifuge is either vertical or horizontally oriented. The cuttings dryer is commonly employed in regions such as the gulf of Mexico where the discharge requirement for SBMs is 6.9% (Whitford, 2009). Cannon & Martin (2001) collected data on 23 wells where the retained SBM was recorded after primary treatment, following secondary treatment by the use of a vertical basket centrifuge. An average value of 11.47% after primary treatment was recorded. The average value after undergoing treatment in the centrifuge was 3.99%. When operating in the OSPAR area, the cuttings dryer does not fulfill the environmental discharge limit. A cuttings dryer configuration is depicted in Figure 8.

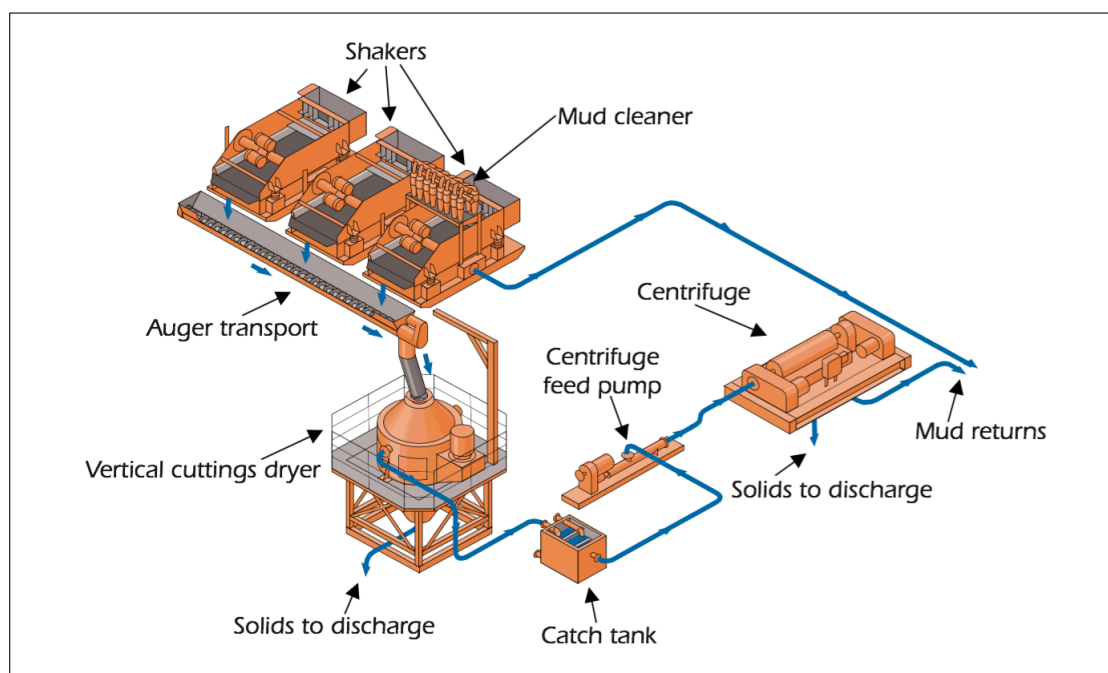


Figure 8: Secondary treatment including cuttings dryer (Bernier *et al.* , 2003)

Thermo-mechanical cuttings cleaner

The TCC is a thermal desorption technology in which the cuttings are subjected to friction heat generated by the hammer mill. The technology has been available on the market for some years and started its qualification on the UKCS during the 1990s (Ormeloh, 2014). A diesel or electrical drive unit rotates the hammer mill. Solid particles are forced towards the wall of the process chamber where friction heat is generated. The operation is continuous and automated by a Programmable logic controller (PLC) system. The liquids are evaporated inside the process chamber and withdrawn to auxiliary processes comprising of a cyclone to remove fines, and a condenser train to separate the water and oil. An additional oil-water separator is included as some lighter oil components will condense with the water (Kleppe, 2009; Ormeloh, 2014). The recovered liquids are reusable as the process temperature is low enough to avoid cracking of the oil. The recovered water is within the 30 mg L^{-1} discharge limit (Svensen & Taugbøl, 2011). According to the TWMA website (TWMA, 2016), based on the trials performed in the United Kingdom, the TCC was accepted as BAT and BEP by OSPAR.

As previously mentioned, the Martin Linge field development received acceptance to discharge TCC treated cuttings provided the requirement of no more than 0.05% retained oil on cuttings was met. Should the limit be exceeded the cuttings had to be shipped to shore. The 0.05 wt% requirement is extremely difficult to achieve consistently and was set on the basis of empirical data from the use of the TCC on the UKCS.

An audit was performed at Martin Linge, where the operator is Total, in the period between 26. - 30. of October. The audit uncovered a breach on the agreed limitations with respect to the OOC levels on discharged drill cuttings as well as a breach on §60 of the activity regulations (NEA, 2015). According to the report by the Norwegian Environment Agency the cuttings discharged in May, August, and September of 2015 was measured to 0.35, 0.58, and 0.17 wt%, respectively. In October the discharged water was recorded to contain as much as 754 mg L^{-1} oil. The use of the TCC was stopped on the basis of the aforementioned audit. It is unclear if the situation has been resolved. It is likely that the TCC uses a polishing step to remove the last traces of oil. In the polishing step the remaining oil is oxidized (Monsen & Michelsen, 2015).

According to Svensen & Taugbøl (2011) the TCC represents 80 000 of the 110 000 tonne annular treatment capacity onshore in Norway.

The theoretical energy consumption was calculated by Murray *et al.* (2008) to be 215 kWh t^{-1} . Kleppe (2009) reports the energy requirement to be 200 kWh t^{-1} . In both cases the composition of oil, water, and solids was 15/15/70 wt%. The actual energy consumption was proven to be lower. The offshore treatment capacity of the TCC was found to be between 5.2 to 7.1 t h^{-1} with a 945 kW drive. Thus, the energy requirement was between 133 kWh t^{-1} and 181 kWh t^{-1} .

The TCC treated cuttings are crushed inside the hammer mill. The process temperature is between 240°C and 260°C , and the recovered oil may be reused (Kirkness & Garrick, 2008). The discharged cuttings is a dry powder. According to Blytt *et al.* (2014) a high content of particulates in the water column can have a negative impact on fish and benthic organisms. Furthermore, Blytt *et al.* (2014) investigated the PSD of TCC treated cuttings. The findings was that the powder could contain a high amount of clay particles. Discharged clay particles could remain in the water column for prolonged periods of time, which can negatively impact the marine ecosystem.

As the TCC is considered to be BAT and BEP, it is likely that any emerging technologies have to perform better than the TCC in order to achieve success. A schematic representation of the TCC process can be seen in Figure 9 (Halliburton, 2014).

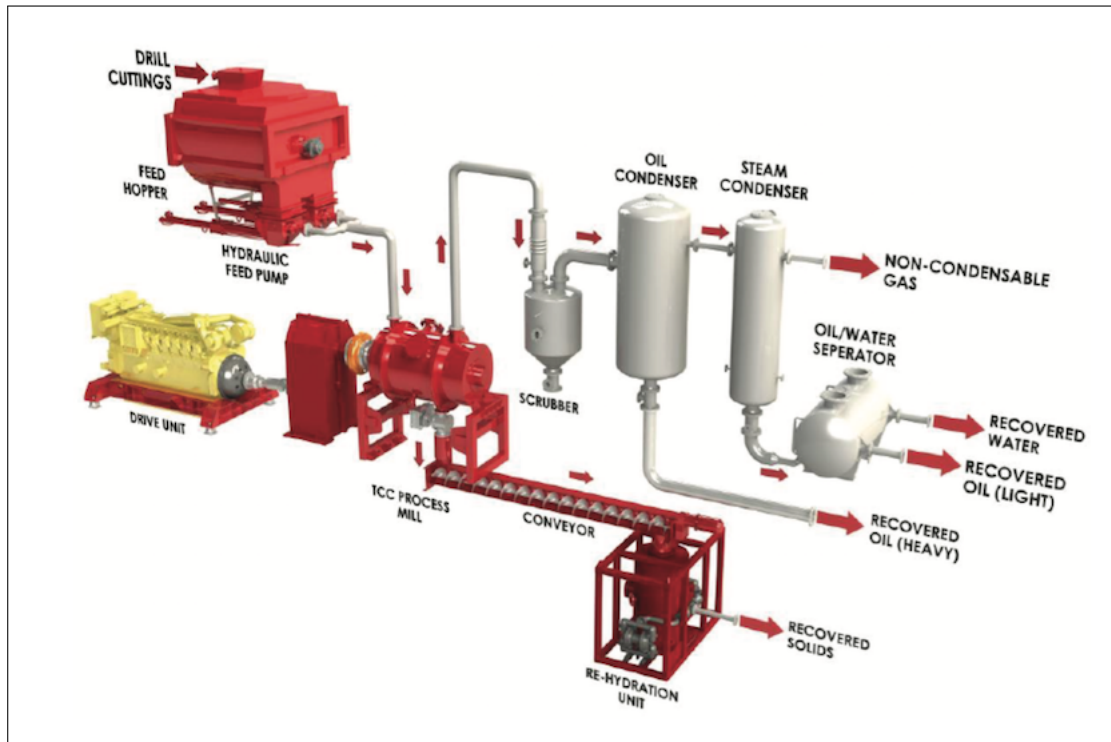


Figure 9: TCC process diagram (Halliburton, 2014)

Chapter 4

A brief introduction to dielectric heating

4.1 Electromagnetic theory

In conventional heating, the required thermal energy must pass through the surface of the compound being heated, and the rate of heating is limited by temperature and thermal diffusivity. Direct heating of materials is possible when the material in question is neither a perfect insulator or a perfect conductor (Meredith, 1998). The theory of electromagnetic (EM) radiation was first published by James Clerk Maxwell in 1865 and resulted in the famous *Maxwell equations* (Equation 1) which represents the physical laws that govern time dependent electromagnetic fields (Thostenson & Chou, 1999). EM radiation is a form of energy traveling at the speed of light, comprising of waves of electric, and magnetic fields that oscillate perpendicular to each other in the direction of propagation (Gupta & Wai Leong, 2011). The propagation of EM fields is depicted in Figure 10.

$$\begin{aligned}\nabla \times \vec{\mathcal{E}} &= \frac{\partial \vec{\mathcal{B}}}{\partial t}, & \nabla \cdot \vec{\mathcal{B}} &= 0 \\ \nabla \times \vec{\mathcal{H}} &= \frac{\partial \vec{\mathcal{D}}}{\partial t} + \vec{I}, & \nabla \cdot \vec{\mathcal{D}} &= \rho\end{aligned}\tag{1}$$

Where $\vec{\mathcal{E}}$ is the electric field vector, $\vec{\mathcal{H}}$, the magnetic field vector, $\vec{\mathcal{D}}$, the electric flux vector, $\vec{\mathcal{B}}$, the magnetic flux vector, \vec{I} , the current density vector, and, ρ is the charge density. It is particularly the electric field that contributes in radio frequency (RF), and microwave (MW) heating (Meredith, 1998).

The main difference between RF and MW heating is the operating frequency and the equipment used to generate the electromagnetic energy. RF heating operates in the 1 to 300 MHz range, and MW heating frequencies lie between 300 MHz and 30 GHz (Sumper & Baggini, 2012). The electromagnetic spectrum and the designated use of Industrial, Scientific, and Medical (ISM) frequency bands is depicted in Figure 11. Lunde (2015) investigated the possible thermal heat sources for Norwegian-Groups treatment concept, and identified RF heating and especially MW heating as promising technologies. Other

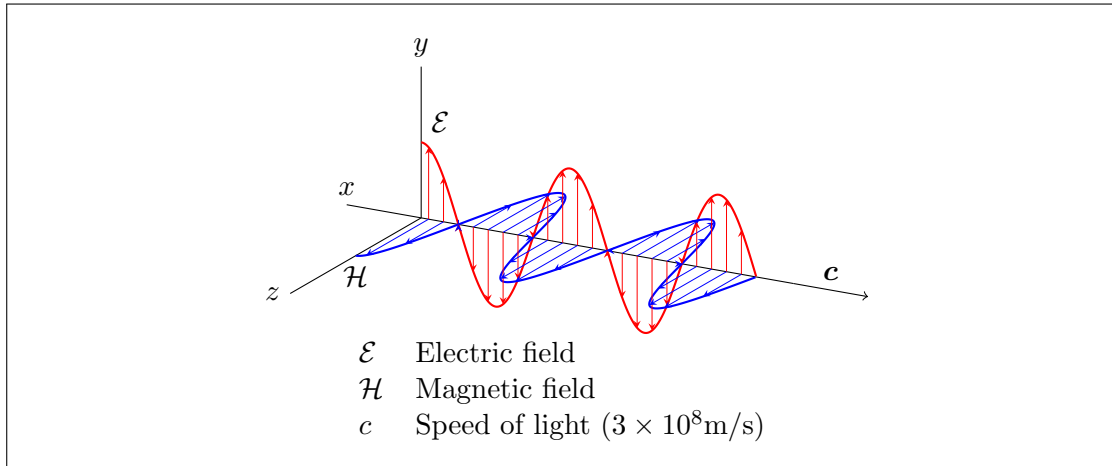


Figure 10: The propagation of electromagnetic fields

heat sources discussed in the report include resistance heating, induction heating, and infrared (IR) heating. The electromagnetic energy utilized in heating applications is the same as used in radar and satellite, television, and radio communications. Meredith (1998) emphasize that care must be taken that no interference between electro-heating and communication systems are allowed.

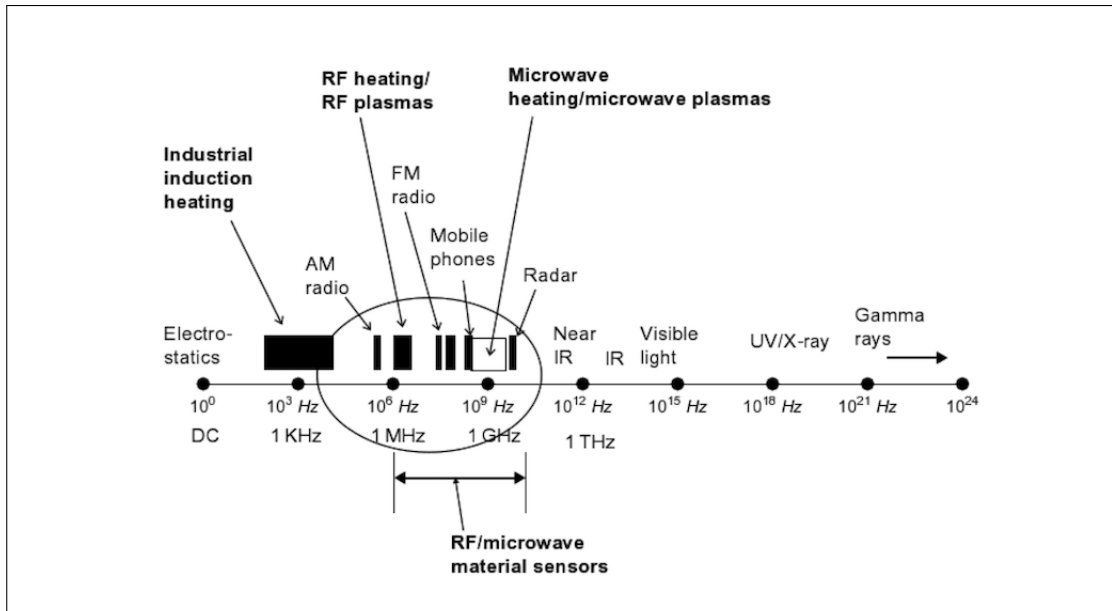


Figure 11: Electromagnetic spectrum (Mehdizadeh, 2009)

When a molecule is subjected to an electric field \vec{E} , the dipole moment $\vec{\mu}$ (see Chapter 5.3.2) experience a torque, $\vec{\tau}$. It is this torque that causes the dipole moment to reorient the material against the oscillating electric field (Stuerga, 2013). In other words, as described by Thostenson & Chou (1999), “The interaction of microwaves with molecular dipoles results in rotation of the dipoles, and energy is dissipated as heat from internal resistance to the rotation.” Dielectric loss results from the fact that molecules are rarely able to reorient in equilibrium with the alternating electric field resulting in a phase lag. The extent of this behavior is dependent on frequency, and the rate of dissipation of energy increase as the frequency is raised (Meredith, 1998), as evident from Equation 4.

There are several mechanisms in which polarization can occur. These include Electronic polarization, atomic polarization, orientation polarization, and Maxwell-Wagner polarization (Metaxas & Meredith, 1983). At microwave frequencies, orientation polarization (dipole polarization) are thought to be the governing mechanism for energy transfer (Chen *et al.*, 1993; Mehdizadeh, 2009).

The capacitive capabilities of dielectrics is described by the dielectric constant, ϵ' , and the conductive capabilities are given by the dielectric loss factor, ϵ'' , both dimensionless and dependent on temperature, and frequency. The relationship between the dielectric constant and loss is given by the complex permittivity ϵ^* (Equation 2). The loss tangent, $\tan \delta$ (Equation 3), is another term commonly used to quantify and compare the dielectric loss of materials. Materials are considered good microwave absorbers if $\tan \delta \geq 0.01$ and poor microwave absorbers if $\tan \delta \leq 0.001$ (Bykov *et al.*, 2001).

$$\epsilon^* = \epsilon' - j\epsilon'' \quad (2)$$

$$\tan \delta = \frac{\epsilon''}{\epsilon'} \quad (3)$$

The power density within the material may be determined by the dielectric heating equation (Equation 4).

$$P_d = 2\pi f \epsilon_0 \epsilon'' E_i^2 \quad (4)$$

Where P_d is the power dissipation density in W m^{-3} , f is the frequency in Hz, ϵ_0 is the permittivity of free space ($8.8 \times 10^{-12} \text{ F m}^{-1}$ (Meredith, 1998)), and E_i represents the internal voltage stress in the dielectric (V m^{-1}).

The penetration depth for low loss dielectrics, D_p (Equation 5), is a measure of the depth of microwave penetration into the material. The penetration depth is the depth at which the magnitude of the EM field is reduced to $1/e$ of its surface value (Gupta & Wai Leong, 2011).

$$D_p = \frac{\lambda\sqrt{\epsilon'}}{2\pi\epsilon''} \quad (5)$$

It is evident that an increase in the dielectric loss factor will cause a decrease in the penetration depth. Penetration depth is also dependent on wavelength, λ , and as the wavelength increase the penetration depth increase due to higher attenuation into the dielectric material. It is clear that the penetration depth is an important parameter in EM heating. Low penetration depths may cause issues with non-uniformity of heating and there is a possibility that the environmental discharge requirement of 1 % OOC by weight cannot be met.

4.2 The components of dielectric heating

4.2.1 The RF heating circuit

In radio frequency heating the electric field component is generated by two electrodes subjected to an alternating voltage and the material to be heated is positioned between the two electrodes as shown in Figure 12. Various RF heating configurations are available depending on the material being heated. *Stray field* electrodes are used when the depth, or thickness, of the material is relatively thin (10 mm or less). *Staggered through* electrodes are useful when a homogenous field is required. *Plate electrodes* are commonly utilized when the material is thick and complex in shape (Sumper & Baggini, 2012).

RF heating enjoys the general benefits of dielectric heating, including high efficiency in the range of 50 to 70 %, high power densities, and heat transfer independent of ambient conditions (Sumper & Baggini, 2012). The high efficiency is related to the electric field coupling with water. As seen in Table 12, the penetration depth of RF energy at a frequency of 30 MHz in distilled water is in the order of 35 m. According to Equation 4, the electric field strength in RF heating has to be increased 10 times in order to match the power dissipation of a microwave heating system. This may cause arcing inside the applicator if the dielectric breakdown threshold of air (30 kV cm^{-1}) is exceeded (Dev et al. , 2012). Berger (2015) lists the dielectric breakdown of air as 0.97, normalized against nitrogen gas. Due to similar dielectric breakdown thresholds, there is a risk of RF arcing also in nitrogen atmospheres.

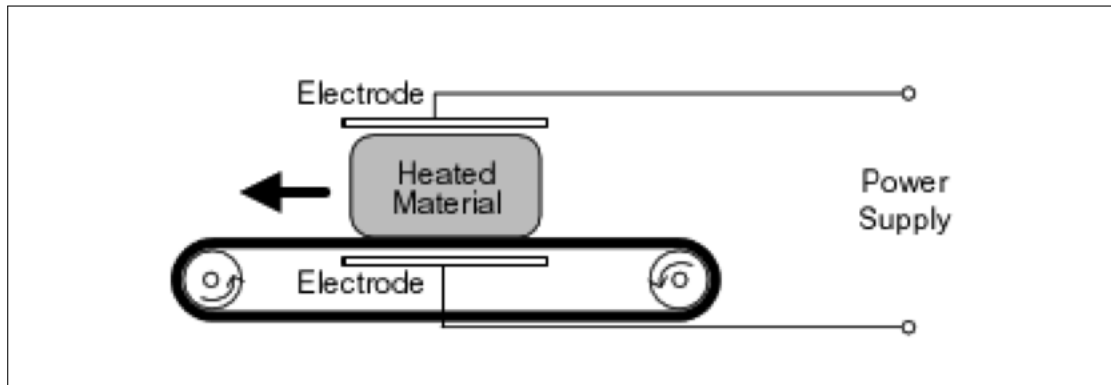


Figure 12: RF heating circuit (Sumper & Baggini, 2012)

4.2.2 The microwave

The microwave generally consist of the following components : (a) a microwave generator, (b) a power supply, (c) a waveguide, and (d) an applicator.

Microwave generators are vacuum tubes capable of generating high power at high frequencies. Vacuum tubes that have been utilized to generate microwave power include *magnetrons*, *traveling wave tubes*, and *klystrons* (Love, 1995; Roach, 1995).

Magnetrons (Figure 13) commonly found in domestic microwave ovens are mass produced, cheap, and readily available on the market (Bogdal, 2006). Magnetrons use resonant cavities to generate the EM field and are thus only capable of operating at *fixed* frequencies. In vacuum tubes such as the magnetron, the difference in potential between the anode and the cathode produces the electric field component. By heating the cathode, the loosely bound valence electrons are removed. By the use of a magnet, the electrons are directed towards the anode, causes a electron cloud to form. As electrons pass the resonant cavities the electron cloud oscillates and the frequency of this oscillation depends upon the physical geometry of the cavities (Thostenson & Chou, 1999). There are two types of magnetrons. Pulsed magnetrons are capable of outputting very high amounts of power up to several megawatts for a short duration. Continuous wave (CW) magnetrons are capable of continuous operation from a few watts up to 100 kW at 915 MHz (Love, 1995; Osepchuk, 2002).

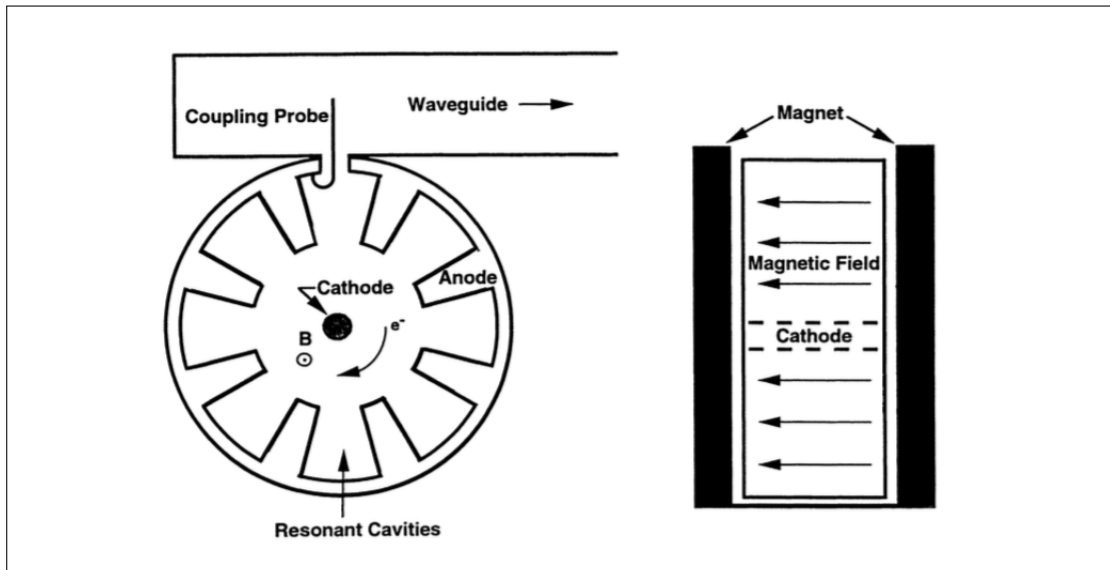


Figure 13: Magnetron microwave tube (Thostenson & Chou, 1999)

Traveling Wave Tubes (TWTs) (see Figure 14) is one type of source that is commonly employed in microwave applications that require a *variable* frequency of operation. In this case the the TWT acts only as an amplifier and the microwave signal has to be generated by a separate oscillator. Typically the frequency of the oscillator is voltage controlled, and allows for rapid alterations in the output frequency of the vacuum tube. Traveling wave tubes are comprised of two main components, the electron gun and the helical transmission line (Thostenson & Chou, 1999).

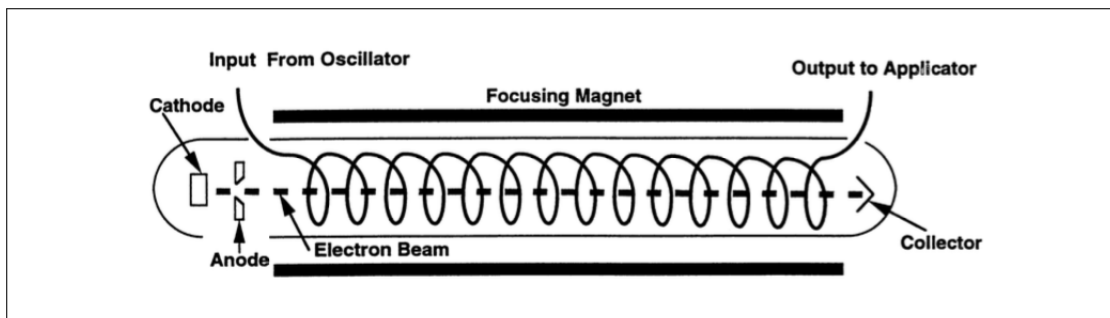


Figure 14: Traveling wave tube (Thostenson & Chou, 1999)

According to Roach (1995) klystrons are narrow-band linear beam tubes, available as both amplifiers, and oscillators and capable of either pulsed or CW mode. Typical operating frequencies lie between 300 MHz and 40 GHz with a peak power output of up to 150 MW. Applications can be found within UHF-television, industrial heating, and

radar among others (Gupta & Wai Leong, 2011).

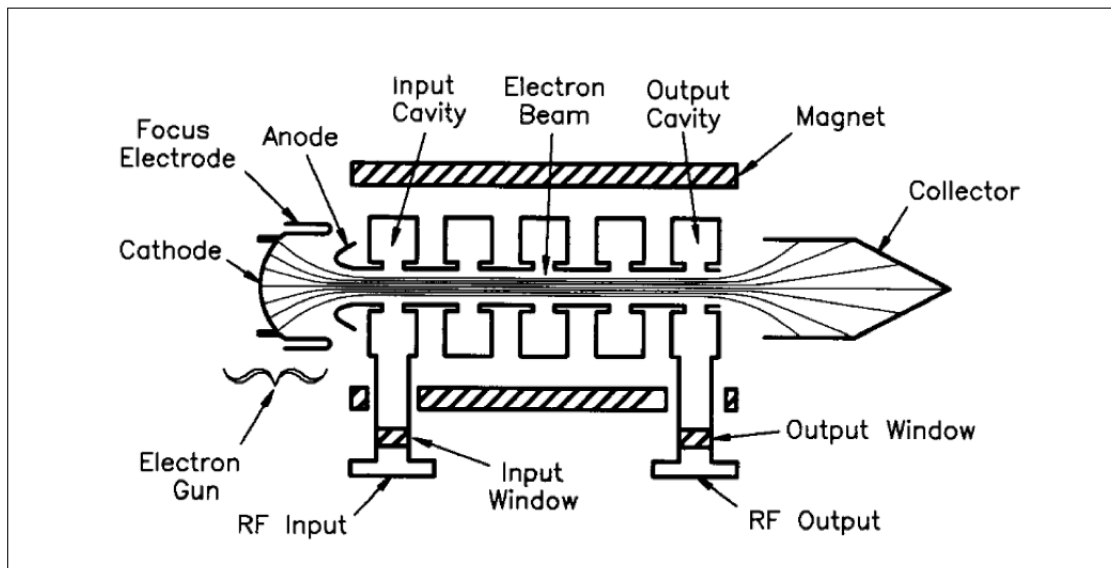


Figure 15: Simplified klystron circuit (Roach, 1995)

Waveguides are often the preferred choice when conveying high power at high frequencies due to the losses in for example coaxial cables. Waveguides are hollow rectangular, or cylindrical, tubes in which the EM energy propagates forward. Two modes of propagation is possible: Transverse electric (TE) or transverse magnetic (TM) where the electric and magnetic intensity is zero in the direction of propagation, respectively (Thostenson & Chou, 1999; Pereira, 2012).

Applicators, or cavities, are the means of which EM energy are transferred to the material. The temperature distribution within the material matrix are highly dependent on the geometry of the cavity. Applicators that are common include multimode and single mode cavities with high field strengths. Single mode cavities typically have a focused field strength, or, a “hot spot”. Multimode cavities support a variety of resonant modes, which results in multiple hot spots. The uniformity of heating may be improved by increasing the cavity size. However, for typical MW frequencies, the cavity would become very large (Thostenson & Chou, 1999).

4.3 A literature review on microwave treatment of drill cuttings

Shang *et al.* (2005a) investigated the microwave treatment of oil contaminated drill cuttings in a multimode cavity where a significant decrease in the residual oil concentration was achieved. The study concluded that a reduction of OOC can be achieved with

an increase in the cavity power, residence time, and moisture content. Shang and co-workers also discovered that the concentration of water in the samples was the limiting factor for oil removal. The addition of extra water allowed for more oil to be separated. This caused the OOC to be reduced to less than the environmental discharge limit of 1% by weight. It was recognized that the multimode cavity was limiting the achievable power density. Nitrogen sweep gas was found to be beneficial by providing even heating throughout the sample. A modified Reynolds number, Re_m , was used to evaluate the effects of laminar and turbulent gas flows. Supplying ambient temperature N_2 gas caused re-condensation of oil, and water vapors, lowering the treatment efficiency.

Shang *et al.* (2005b) continued the work by the utilization of a high power single mode cavity (Figure 16). In these experiments there was evidence of plasma formation when the treatment and power levels was high. A 0 - 15 kW magnetron operating at 2.45 GHz was used. Shang *et al.* identified two mechanisms for oil removal. The first mechanism is the conventional heat transfer from water to oil. The second mechanism is oil steam entrainment, where the oil is carried away by escaping steam. Again, the amount of water in the sample seemed to be the limiting factor. Increasing the amount of water in the sample reduced the OOC to below the environmental discharge limit. The addition of activated carbon also caused a significant reduction of the OOC. The use of a single mode cavity allowed shorter treatment times compared to a multimode cavity.

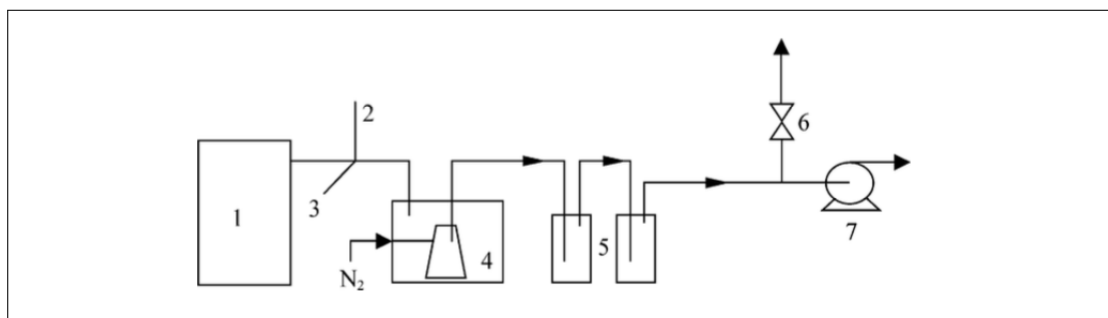


Figure 16: Experimental setup in Shang *et al.* (2005b). (1) Generator, (2&3) E-H tuner, (4) TE_{10n} single mode cavity, (5) condensate collection, (6) pressure relief valve, (7) vacuum pump

Shang *et al.* (2012) investigated the influence of dielectric materials on oil removal from waste. Samples that contained up to 1 mol L^{-1} NaCl was shown to increase the oil removal capacity, compared to water alone. The addition of 5% activated carbon, allowed the samples to be treated within OSPAR limits in less than 60s. Carbon does not evaporate, and thus absorbs energy during the entire treatment period.

Robinson *et al.* (2012) studied and compared a single mode, a fixed bed, and a stirred bed microwave system (see Figure 17). The three different systems were all shown to remove a varying degree of organic contaminants in two different samples. Sample 1

contained 16.42% water, and a total organic content of 1.08%. Sample 2 contained 14.05% water, and a total organic content of 2.06%. The study revealed that a high degree of separation, in combination with high energy efficiency, was achieved in the stirred bed system. Mixing of the sample overcame issues of low penetration depth in the stirred bed system, which caused an increase in organic removal. Figure 18 compares the treatment efficiency of the three systems. It is clear that stirring of the sample bed increased the oil removal significantly. The increase in energy efficiency between the the single mode system and the other two systems was attributed to sample size. Larger samples contain more water, which led to a more efficient dielectric coupling. [Junior et al. \(2015\)](#) assessed three different types of stirrer blades. No significant difference was observed. A 17% increase in n-paraffin removal was achieved with the mixed system, compared to a non-mixed system.

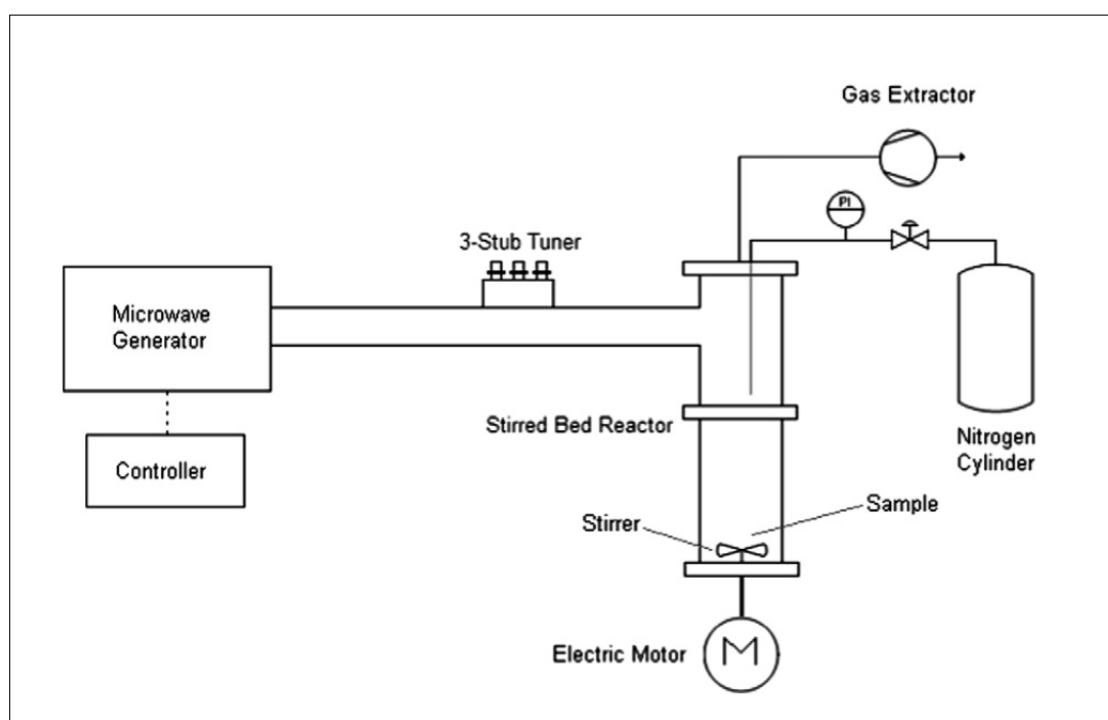


Figure 17: Stirred bed batch system ([Robinson et al. , 2012](#))

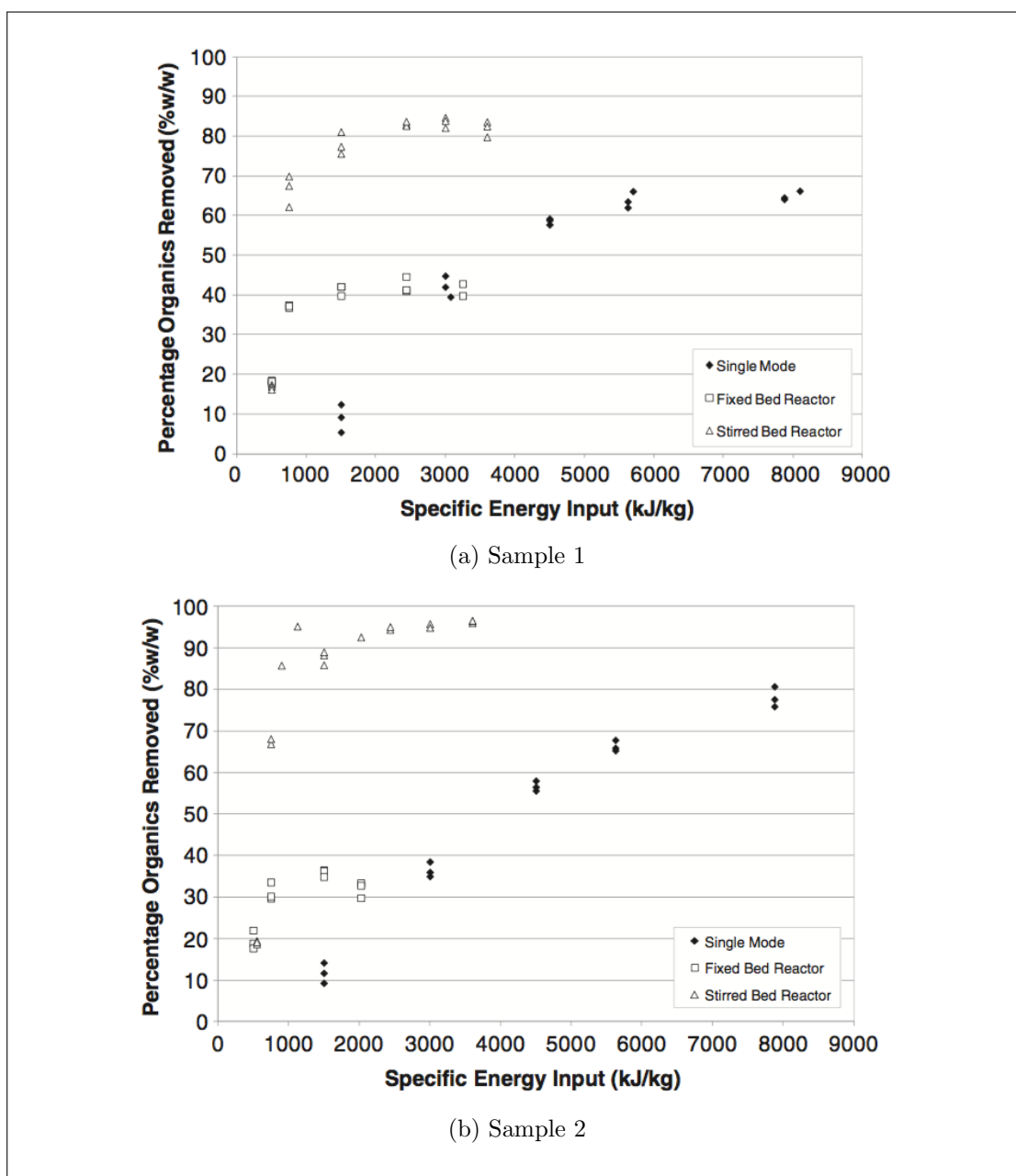


Figure 18: Results obtained in [Robinson et al. \(2012\)](#)

[Robinson et al. \(2010\)](#) demonstrated that the design of a single mode applicator is highly dependent on the bulk dielectric properties of the treated material. In the study a conveyor belt of Nomex fibers was used. Through electromagnetic simulations, relatively small variations in bed depths was shown to significantly impact the uniformity

of heating.

A transverse E-field applicator was compared to a single, and a multimode cavity in the study by [Robinson *et al.* \(2009\)](#). Oil contaminated drill cuttings was treated in a 15 kW MW system at 2.45 GHz. The required energy input was significantly lower in the continuous E-field processing mode. The continuous system treated the cuttings to 0.1 wt% with a energy requirement of approximately 140 kW h t^{-1} . The multimode batch system was able to reduce the OOC to 2% requiring 450 kW h t^{-1} . The single mode batch system was able to treat the cuttings down to 1% when the energy input was around 110 kW h t^{-1} . Thus, it was shown that a continuous process was more beneficial than a batch process. A schematic of the continuous process is depicted in Figure 19

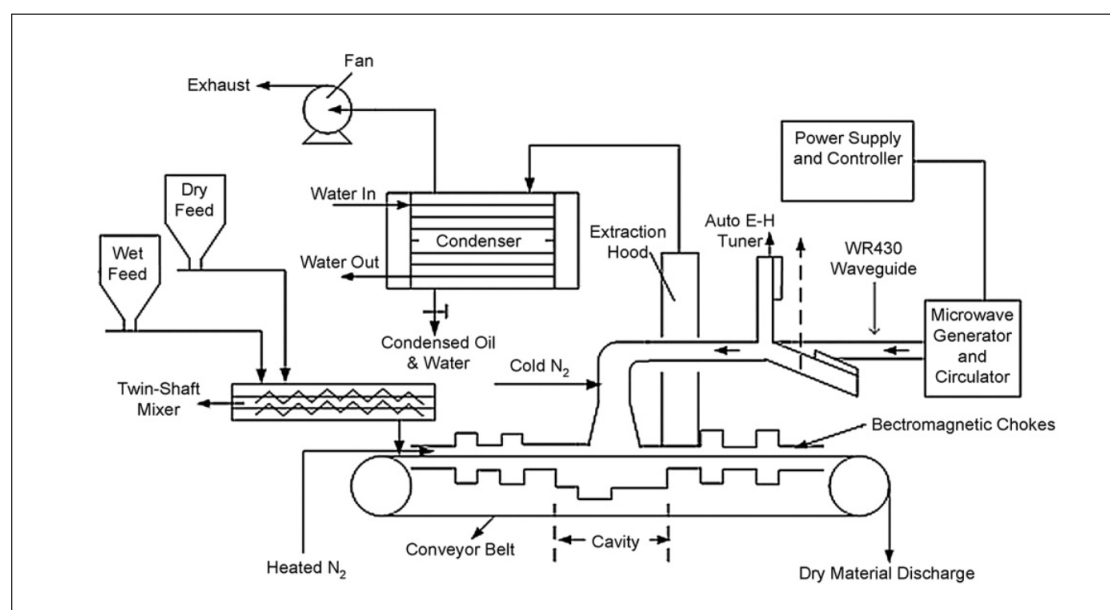


Figure 19: Continuous MW system ([Robinson *et al.* , 2009](#))

[Pereira \(2012\)](#) found that nitrogen drying (20 L min^{-1} @ 16°C) alone was insignificant as an oil separation mechanism, see Figure 20. Furthermore, [Pereira \(2012\)](#) found that the main mechanism of oil and water removal from cuttings is vaporization and entrainment. The effects of nitrogen flow rate on the MW processing of cuttings was found to be significant. Not as a direct desorption method, but due to improved uniformity of heating, improved mass transfer, and less potential re-condensation. The increase in N_2 flow rate from 2 to 7 L min^{-1} caused a 70% increase in liquid desorption by weight. A modified Reynolds number of ≥ 203 was suggested in combination with a N_2 supply temperature of 80°C or more. For the sweep gas to achieve a maximum effect it was supplied below the sample. This enables the gas to flow through the sample and assist in liquid desorption from the cuttings. A comparison of nitrogen drying and nitrogen drying in combination with microwaves was made by [Pereira \(2012\)](#). The results of which

are depicted in Figure 20. It is seen that an OOC of 2% was achieved. The sample was treated at 720 W in combination with a N_2 flowrate of 15 L min^{-1} .

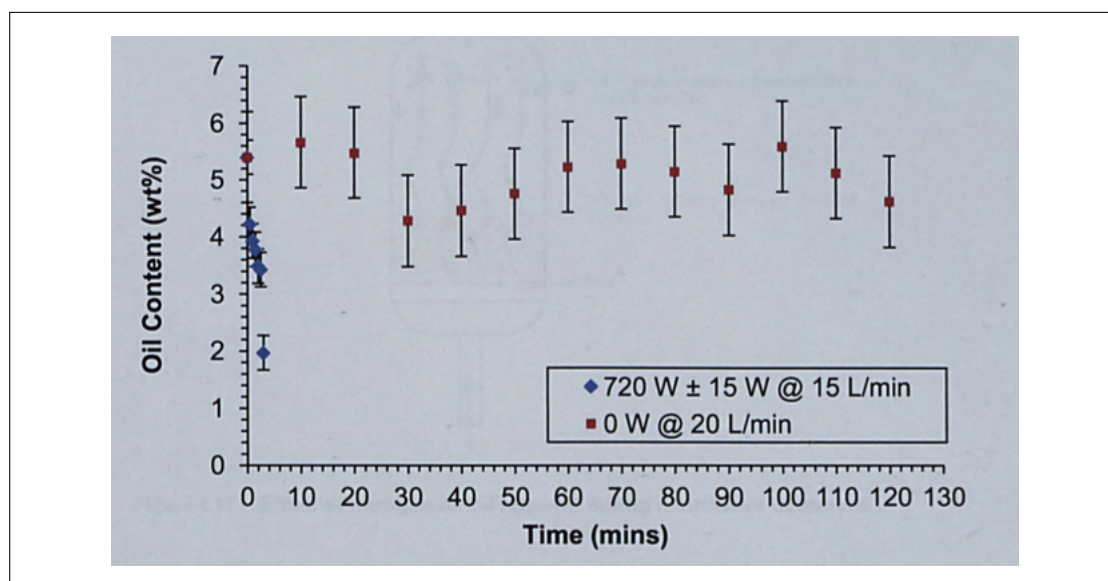


Figure 20: Comparison of N_2 drying, and N_2 in combination with MW (Pereira, 2012)

Samples with high oil content, and surface liquid, experienced a higher percentage of separation through entrainment. Higher power density and energy input also caused a higher percentage of separation to occur by entrainment. Due to higher heating rate, high velocity and pressure steam was generated. This in turn led to more physical carryover of oil. It was shown that most of the oil separation originated from particles between 0.15 and 1 mm. Oil removal from larger particles was insignificant.

A pilot scale rig was used in combination with a 2.45 GHz magnetron source (see Figure 21). At 2.45 GHz, continuous processing of cuttings with 3% oil, and 12% water, required an energy input of 150 kW h t^{-1} to reach an OOC of 1%. As a comparison, 250 kW h t^{-1} was required when the process was a batch type.

Pereira (2012) also investigated continuous processing at 896 MHz. This was shown to significantly improve oil separation compared to processing at 2.45 GHz. $80\text{-}90 \text{ kW h t}^{-1}$ was required to treat cuttings at 300 kg h^{-1} down to 1% OOC by weight. A mass flow rate of 800 kg h^{-1} was treated to 1.5%, requiring only $50\text{-}60 \text{ kW h t}^{-1}$. The initial oil content was 7.8 wt%. The decrease in energy requirement between 2.45 GHz, and 896 MHz was attributed to a shift in polarization mechanisms, increased penetration depth, and an increase in mass transfer due to larger surface area of the waveguide and applicator.

Key attributes was determined to be particle size, nitrogen Re_m numbers, initial oil and water content, and energy requirements (Pereira, 2012).

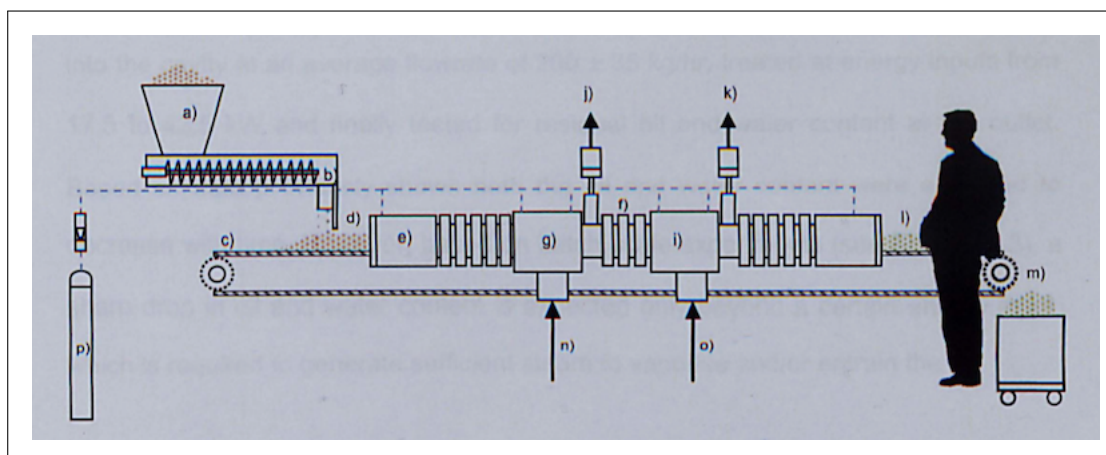


Figure 21: MW pilot scale rig (Pereira, 2012). (a) Hopper, (b) screw conveyor, (c) conveyor belt, (d) cuttings, (e + f) chokes, (g+i) applicators, (j+k) fume extractor, (l) treated cuttings, (m) cuttings collection, (n+o) microwave inlet, (p) nitrogen bottle

Another technology utilizing electromagnetic heating is the “Cutcube” (Vasshus & Malmin, 2013). Cutcube is an invention by Cubility AS. There is relatively little information to be found on this technology, apart from what is described in the patent application. A video is also available which shows the technology in use (Fabel-Media, 2014). The technology seems to be a thermal desorption process where vacuum is combined with a EM heating source. The patent specify the frequency of operation to be in the MW range. However, there is no evidence of either waveguides or something that resembles a vacuum tube in the video. It is possible that RF heating is utilized, as the EM equipment in the video resembles electrodes. In the video it also looked like there was several heating sources in series. Note that this is only speculation, and should not be considered as facts. A screw conveyor was also seen in the video. Both the conveyor and the EM equipment looks to be placed inside the “applicator”. The reported OOC is claimed to be below 1%.

There is still a gap between the capacity of the TCC and the microwave treatment of cuttings. However, the energy requirement is lower when microwaves are utilized.

Conveying. All of the works cited in this literature review, used a flat bed conveyor belt, with exception of the cutcube. Mixing is not achieved inside the process chamber with the use of a flat bed. The cutcube is using a screw conveyor to propel the cuttings through the applicator. In this way, mixing is also achieved within the process chamber. Mixing have the potential to increase oil separation significantly. In order to avoid arcing and inefficient applicator modes, the screw conveyor should preferably be of a transparent material. The material has to withstand the wear and tear that the cuttings will impose. In the case of the screw conveyor, it is likely that the shell of the screw,

Chapter 4 A brief introduction to dielectric heating

also will function as the applicator. Depending on the material of the rotating screw, it may affect the uniformity of heating. If for example the screw is metal, it may act as a mode stirrer. Mode stirrers are devices that are meant to improve the uniformity of heating. Microwave treatment of cuttings would also allow the cuttings to remain in its original shape.

All of the technologies discussed in Chapter 4.3 use thermal desorption. Steam distillation is an important principle in thermal desorption and are discussed in Chapter 5.

Chapter 5

Distillation and chemical bonding

5.1 Distillation theory

Dalton's law of partial pressures (Equation 6) 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 each individual gas.

$$P_{total} = p_1 + p_2 \dots + p_{n-1} + p_n \quad (6)$$

where $p_1 + p_2 \dots + p_{n-1} + p_n$ represents the partial pressure of each gas.

5.1.1 Miscible liquids

The behavior of ideal miscible liquids is described by Raoult's law (Equation 7) where p_a and p_b are the partial vapor pressures of components a and b . x_a and x_b is the molar fraction of each component.

$$\begin{aligned} p_a &= x_a \times P_a^0 \\ p_b &= x_b \times P_b^0 \end{aligned} \quad (7)$$

P_a^0 and P_b^0 represents the vapor pressure of the pure components and may be found by Antoine's equation (Equation 8).

$$\log_{10} P_n^0 = A - \frac{B}{C + T} \quad (8)$$

where

- P_n^0 – vapor pressure [mmHg]
- $A, B,$ and C – Component specific constants [unitless]
- T – Temperature [$^{\circ}\text{C}$]

In Figure 22 an illustration of Raoult's law combined with Dalton's law gives a clear picture of how the total pressure exerted by the gases is governed by the relative amounts of compound (a), and compound (b), present in the mixture.

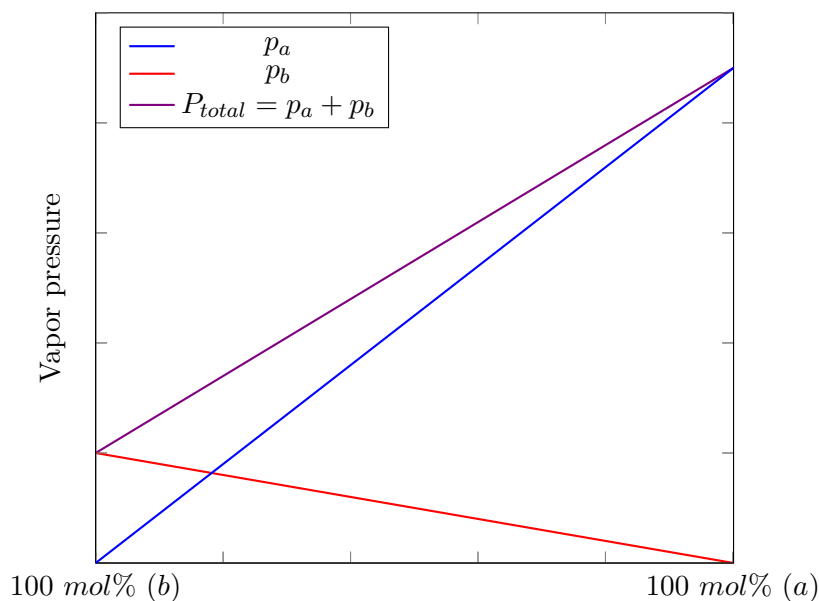


Figure 22: Illustration of Raoult's law in combination with Dalton's law.

5.1.2 Immiscible liquids

Raoult's law holds true for ideal miscible liquids described in Chapter 5.1.1. However, the behavior of the mixture changes substantially when the system consists of immiscible liquids due to no interaction at the molecular level. As a result, the landscape of Figure 22 will change dramatically as each individual compound will establish its own vapor pressure, independent of the molar ratios in the mixture. This behavior is illustrated in Figure 23. In the case where the objective is to isolate each component in the mixture, this technique is not optimal due to the fact that the vapor composition above the boiling liquid will be the same as in the liquid. However, this observation is valuable when attempting a steam distillation.

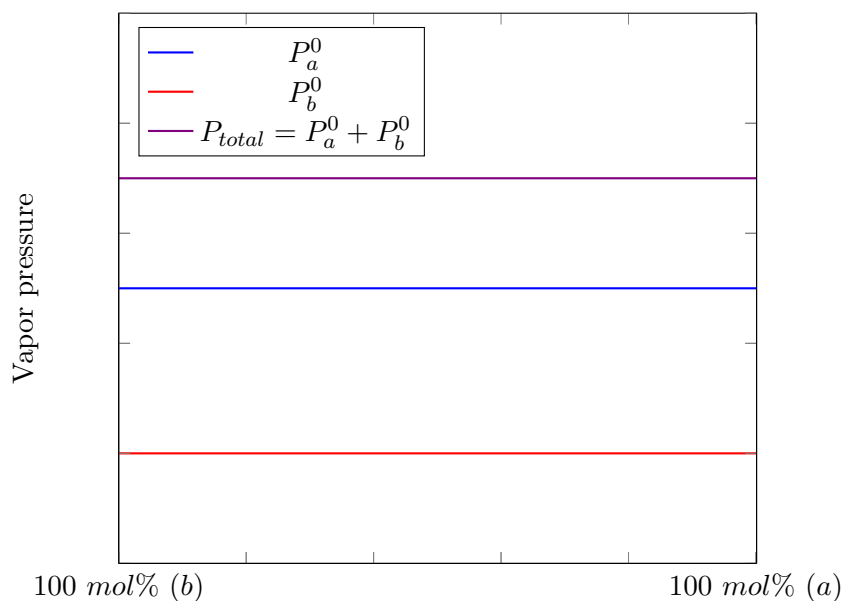


Figure 23: The behavior of immiscible liquids in combination with Dalton's law.

5.2 Steam distillation

Liquids boil once the vapor pressure of the liquid is equal to the surrounding ambient pressure. At sea level the atmospheric pressure is 101.325 kPa or approximately 760 mmHg. If the total vapor pressure exerted by immiscible liquids at a given temperature exceeds, or equal, the ambient pressure, the liquid is boiling. Another important observation is the fact that immiscible mixtures will inevitably boil at a temperature lower than the boiling point (bp) of either of the pure liquids.

Normal distillation of such liquids in their pure form would require a much higher temperature for the liquid to boil. If we consider the immiscible mixture of toluene, an organic compound with the formula C_7H_8 , and water with the formula H_2O the principle of steam distillation is easily explained. At 84.5 °C Toluene has a vapor pressure of approximately 339 mmHg, and water has a vapor pressure of 425 mmHg resulting in a total pressure of 764 mmHg (Yaws & Satyro, 2015). Meaning, at this temperature the mixture is boiling at atmospheric pressure. The bp of toluene is reported to be 111 °C whereas water has an bp of 100 °C (ChemSpider, 2016).

Combining Dalton's law, Antoine's equation, and the principle of steam distillation with the ideal gas law (Equation 9), allows for an estimation of the mole fractions in the distillate.

$$\frac{P_{polar} \times V_{polar}}{P_{oil} \times V_{oil}} = \frac{n_{polar} \times R \times T_{polar}}{n_{oil} \times R \times T_{oil}} \quad (9)$$

where (a) P is the pressure of the gas, (b) V is the gas volume, (c) n is the number of moles, (d) R is the ideal gas constant, and (e) T is the temperature of the gas. Equation 9 reduces to Equation 10 due to the gases occupying the same space, distilling at the same temperature, and that the universal gas constant apply to all gases.

$$\frac{P_{polar}}{P_{oil}} = \frac{n_{polar}}{n_{oil}} \quad (10)$$

where the indexes *polar* and *oil* represents any polar, and any non-polar compound, respectively.

Returning to the example with toluene and water. The theoretical estimations are depicted in Table 3. The amount of toluene in the condensate is expected to be 4.7 mL toluene / mL water. For comparison, examples where dodecane ($C_{12}H_{26}$) and hexadecane ($C_{16}H_{34}$) are distilled with water are also depicted in Table 3. Another important comparison, shown in Table 4, is the energy required to evaporate the organic constituent in the mixture.

Table 3: Theoretical distillation with select compounds mixed with water

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

It is evident that a large amount of energy is required due to the thermal properties of water. This includes specific heat, but especially the heat of vaporization. Significant energy savings can be achieved if the distillation ratio is moved in favor of the organic compound, meaning that the vapor pressure of the organic compound is larger than the vapor pressure of the second component in the boiling mixture. This principle, which is highly dependent on chemical bonding, is further investigated in Chapter 6 and 7.

Steam distillation was proven to separate oil from cuttings by [Pereira \(2012\)](#), where approximately 60% oil by weight were removed during 120 minutes of processing time. More than 50% was separated between the first 40 to 50 minutes.

Table 4: Energy required for distillation

| <i>Organic compound</i> | <i>Polar compound</i> | <i>Enthalpy of vaporization, [kJ kg⁻¹]</i> | <i>Energy consumption per kg oil evaporated, [kJ kg⁻¹]</i> |
|-------------------------|-----------------------|---|---|
| Toluene | Water | 2257 | 480 |
| Dodecane | —” — | 2257 | 8680 |
| Hexadecane | —” — | 2257 | 282 125 |

5.3 Chemical bonding and temperature

The operating temperature of the steam distillation will be crucial in the success of the treatment process. In order to recover the value that the oil from the OBM contaminated cuttings represent, it is important that any treatment method employed does not cause the oil to crack. The distillation temperature will increase with an increase in the bp of the susceptor, however the temperature will not exceed that of the oils bp as long as the oil is present. The susceptor could also be in powdered form, as in the case with activated carbon or graphite. Preheating the susceptor is also a possibility. The method of applying the chemical is also something to be considered, if the susceptor is a powder it might be easier to achieve a homogenous distribution within the cuttings matrix than a liquid compound, depending on the viscosity of the liquid.

Chemistry can in many ways be described by the attraction between opposite charges and repulsion between equal charges. This is relevant because it determines the forces that act within and between molecules (Ashenurst, 2016b). Properties such as boiling points and melting points are a direct consequence of such forces and are measurements of how strong the attractive forces are. Generally there are two extremes when it comes to the interactions that can take place between individual atoms or molecules.

5.3.1 Ionic bonds

Ionic bonds are the strongest bonds and the attractive forces are governed by *Coulomb's law*. Ionic bonds are formed when electrons are *transferred*, one element loses its electrons while the other element gain the electrons, and are held together in a crystal structure due to the attractive forces (Shipman *et al.* , 2013). The attractive forces increase with an increase in charge, and decrease as the atoms or molecules are spaced further apart. A typical example of an ionic bond is sodium chloride, NaCl (Figure 24). The melting point of NaCl is reported to be approximately 800 °C and the boiling point to be 1413 °C (ChemSpider, 2016). Due to the very high melting and boiling points of ionic compounds they are not likely to perform well as a susceptor for Norwegian-Groups treatment concept. More information on susceptors are found in Chapter 6.

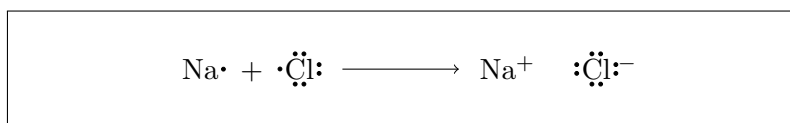


Figure 24: Lewis structure of sodium chloride

5.3.2 Covalent bonds

Covalent bonds is the result when electrons are *shared* between compounds. Due to the nature of the bonds, the properties of covalent compounds differ significantly from those subject to ionic bonds. Many covalent compounds are liquids or gases at room temperature. A well known example of a covalent compound is water, H_2O (Figure 25). Although covalent bonds are strong within the molecule only weak attractions takes place between each molecule of the compound, a substantial lower melting point, and boiling point may be seen compared to that of ionic compounds (Shipman *et al.*, 2013). A comparison of ionic compounds and covalent compounds is represented in Table 5. Ionic compounds exhibits very high boiling points and melting points compared to covalent compounds. It is likely that a suitable susceptor is found within a covalent compound. Another feature that is beneficial is the low conductance attributed to covalent compounds. The three different types of covalent bonds are hydrogen bonds, London dispersion forces, and dipole-dipole interactions.

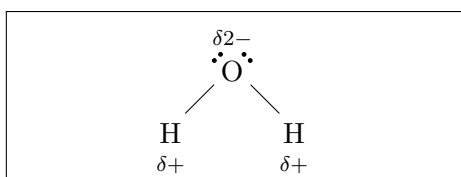


Figure 25: Lewis structure of water

Table 5: Characteristics of ionic and covalent compounds (Shipman *et al.*, 2013)

| Ionic compounds | Covalent compounds |
|----------------------------|---------------------------|
| Crystal solids | Gases, liquids, or solids |
| High bp and melting points | Low bp and melting points |
| Conduct electricity | Poor conductance |

Polar molecules

Polar molecules are molecules whose electrons are more attracted to one end than the other end of the molecule, and results in a slight positive end and a slight negative end.

Such a molecule is a *dipole*, and it has a *dipole moment*, represented by $\vec{\mu}$ (Equation 11).

$$\vec{\mu} = q \times \vec{r} \quad (11)$$

Where q represents the magnitude of the charge in coloumb and r is the distance between the charges in meters. The unit of $\vec{\mu}$ is the debye.

Even if a molecule has polar bonds it is not given that the entire molecule is polar, it depends upon the structure of the chemical. Linear molecules such as beryllium hydride, BeH_2 , has two dipoles oriented in the opposite direction, causing the molecule to be non-polar (Shipman *et al.* , 2013). Ultimately, to predict the polarity of a molecule, both the polarity of the intramolecular bonds and the structure of the molecule has to be known. From Figure 25 it is seen that water is a covalent, polar compound. Generally, the polarity of molecules is determined by its functional groups. The relative strength of some of the functional groups are represented in Figure 26. To sum up:

- If a molecule has no polar bonds, the overall polarity will be zero.
- A molecule with one polar bond is always polar.
- A molecule with multiple polar bonds will be polar depending on the structure of the molecule. The bonds may cancel, causing no overall polarity.

Amides > Acids > Alcohols > Ketones > Aldehydes > Amines > Esters > Ethers > Alkanes

Figure 26: Relative strengths of functional groups (Ophardt, 2003)

Hydrogen bonds

Hydrogen bonds are a special kind of dipole-dipole interactions. Hydrogen bonds occur whenever a compound contains hydrogen atoms that are covalently bound to small atoms with a high electronegativity. Oxygen, Nitrogen, and Fluorine are the only elements fulfilling the criteria to engage in hydrogen bonding. The strength of hydrogen bonds are in the order of 5-10 % to that of covalent bonds. The bp is increased substantially when hydrogen bonds are present. (Shipman *et al.* , 2013; Ashenurst, 2016b).

Dipole-dipole interactions

Dipole-dipole interactions is another type of polar covalent bonding with electronegative atoms. It is similar to hydrogen bonding. The molecules orient themselves so that the

opposite charges attract. The nature of the bond is weaker than that of hydrogen bonds (Ophardt, 2003).

Van der Waals dispersion forces

Van der Waals dispersion forces, or, London dispersion forces are interaction caused by a momentary change in the electron cloud density of the molecule. These forces are the attractive forces present in non-polar compounds such as oil. The strength of these forces is primarily governed by surface area and polarizability. Dispersion forces increase as the molecular weight of the molecule increases, giving rise to larger surface area. Polarizability is a term that describes the compound's ability to form instantaneous dipoles. The symmetry of the molecule also plays an important role where branching decreases the boiling point, and more exposed functional groups will increase the boiling point. (Ashenurst, 2016a; King, 2014).

Chapter 6

Susceptor technology

6.1 What are susceptors ?

According to [Mehdizadeh \(2009\)](#), susceptors are lossy materials that are heated by the EM fields and, transfers the thermal energy to the material which are to be processed. The use of solid susceptors such as activated carbon and silicon carbide have a number of reasons, and are described in the literature ([Besson & Kappe, 2013](#); [Gupta & Wai Leong, 2011](#)).

While vaporization of lighter hydrocarbon fractions with lower boiling points require less energy, an increase in both energy and temperature is expected in order to vaporize the heavier fractions of oil that is typically found in oil based drilling fluids. [Pereira \(2012\)](#) identifies that high processing temperatures may be an issue and difficult to achieve when the main MW absorbing phase of the cuttings material matrix is water. Replacing water with environmentally friendly organic polar compounds with a relatively high bp enables the steam distillation to run at a higher temperature. By doing this, the oil present in the mixture act as the “steam” component during the steam distillation process due to the principles of Daltons law (see Chapter 5). The oil component will have a higher vapor pressure. This will increase the amount of oil recovery from the OBM cuttings. Another significant advantage with this technique is the fact that the heat of vaporization offered by some compounds is magnitudes lower than the energy required to vaporize water. As mentioned in Chapter 4.3, [Pereira \(2012\)](#) successfully treated cuttings at 350 kg h^{-1} to less than 1.0 % OOC, requiring an energy input of $90\text{-}100 \text{ kW h t}^{-1}$ at 896 MHz. In the same study, [Pereira \(2012\)](#) stated that a flow rate of 800 kg h^{-1} could be treated to 1 % with an energy requirement of $50\text{-}60 \text{ kW h t}^{-1}$. If we consider the previous statement that the main absorbing phase of the cuttings is water, the energy requirement can be significantly less when utilizing the susceptor technology. For example, ΔH_{vap} of monoethylene glycol (MEG) is approximately 2.5 times less than water, causing a decline in energy requirement from 100 kW h t^{-1} to 40 kW h t^{-1} at 350 kg h^{-1} . Likewise a decline from 60 kW h t^{-1} to 24 kW h t^{-1} at 800 kg h^{-1} . As mentioned in Chapter 3, the energy requirement for the TCC is $133 - 181 \text{ kW h t}^{-1}$ ([Ormeloh, 2014](#)). This means

that it may be possible to treat cuttings at a mere fraction of the energy required by the TCC. This reduction in energy requirement may be optimistic. Water does not make up the only energy requirement for treatment. However, this can represent a best case scenario.

In order to screen chemicals that may be suitable for this application it is important to define a set of favorable characteristics, and attributes that is required in such a compound. The compound utilized as a susceptor also represents value, thus, the potential for resource recovery is also to be evaluated. Depending on the nature of the susceptor, the chemical may or may not be eligible for discharge to sea. If the chemical is not allowed for discharge, a system for susceptor recovery has to be implemented in the design. There are many aspects that affect the suitability of a specific compound's ability to function as an efficient substitute for water as a microwave susceptor. Key attributes such as the materials dielectric properties, bp, melting point, decomposition temperature, environmental toxicity, and price are all important factors that has to be taken into account when evaluating potential susceptors. By the use of specific compounds representing each functional group, potential susceptors are evaluated in this chapter. Decomposition of compounds may result in either the compound returning to its original building blocks or the decomposition process may form intermediate radicals that are highly reactive and participate in the formation of other products. The decomposition of the susceptor is an important topic because the formation of explosive, toxic, and environmentally harmful compounds may be the result. Thermolysis of organic compounds is not only dependent on temperature but also on other factors, including the composition of the fluid mixture and the ambient atmosphere, and the material specification of the equipment. Organic compounds range in the thousands and individual assessments of suitable susceptors are virtually impossible. The approach to evaluate functional groups have made this task more manageable although still comprehensive. Even though functional groups inhabit properties and behaviors that are general for each specific group, there are still exceptions to the general behavior of each group, which further complicates the process of eliminating groups such as ethers as potential susceptors.

6.2 Alcohols and ethers

Alcohols and ethers can be considered as derivatives of water. One or both of the hydrogen atoms are replaced with an organic group, see Figure 27. Alcohols are capable of forming hydrogen bonds due to the substantial dipole moment provided by the O-H bond. Alcohols have significantly higher bp's than alkenes or alkanes of similar molecular weight. Alcohols are classified as primary, secondary, or tertiary depending on what type of carbon the O-H group is bonded to. Particularly diols and triols are investigated in this thesis. Glycols such as MEG, Diethylene glycol (DEG), Triethylene glycol (TEG), Monopropylene Glycol (MPG), Dipropylene glycol (DPG), and glycerol are familiar chemicals that are employed in various applications such as anti-freeze, hydrate inhibition, and food additives. MEG is currently on OSPAR's Pose Little Or No Risk

(PLONOR) list which is a very attractive feat in a susceptor.

Rossiter *et al.* (1985) found that the main degradation product of MEG was glycolic acid with oxalic and, formic acid as minor products. Higher levels of glycolic acid was observed when the oxidation took place in the presence of copper, and in the presence of aluminum the degradation was less dependent on temperature. Furthermore, Rossiter *et al.* found that in contrast, the main degradation product from the thermal oxidation of MPG was found to be lactic acid with oxalic, formic, and acetic acids as minor products. Likewise, in the case of propylene glycol, copper had a catalytic effect on the degradation, causing primarily lactic acid byproducts. In the presence of aluminum the degradation of propylene glycol was the same as for ethylene glycol. Observations from the study concluded that glycolic acid and lactic acid precipitated with copper to form copper(II) complexes. Another important observation from this study was that glycol degradation was inhibited when an oxygen deprived atmosphere were introduced. Typical signs of glycol degradation is discoloration, sweet and pungent odor, as well as a pH level below 7.0. Dow chemical company reports that with proper installation and maintenance, hot glycol fluid systems may last on average 5 to 10 years (Dow, 2016b). In general, the higher the temperature the more degradation products is observed. The kinetics of thermal degradation of glycols are generally slow under 100 °C and the resistance against thermal degradation is in the order of MEG > MPG > DEG (Dow, 2016a).

Glycerol can theoretically yield eleven oxidation products, including Glyceraldehyde, glyceric acid and dihydroxy acetone (SDA, 1963). In aqueous solutions glycerol is decomposed by alkali at high temperature and pressure. At 288 °C, and a period of 7 minutes, 4% degradation of glycerol for each percent NaOH in the solution was observed. In the investigations by Mattikow & Cohen (1943) no significant degradation was evident in temperatures below 260 °C. Furthermore, Mattikow & Cohen found that substituting air with nitrogen (N_2) gas reduced the degradation of glycerol. It is likely that an inert atmosphere reduces the degradation of other glycols as well. Due to glycols being employed in numerous applications world wide the the availability of these compounds are high. The cost of common glycols are retrieved from Sigma-Aldrich and depicted along with other properties such as boiling points for alcohols and ethers in Table 6.

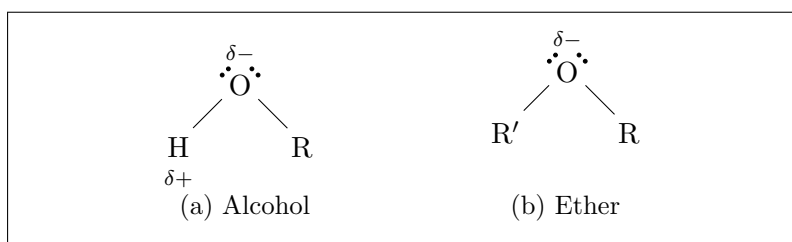


Figure 27: Functional group of alcohols and ethers

Ethers are on the other hand not capable of hydrogen bonding and thus experience

boiling points of intermediate nature compared to alkenes and alkanes. Ethers generally have low reactivity compared to alcohols (Averill & Eldredge, 2011). Inhalation of ether vapors cause unconsciousness by depressing the activity of the central nervous system (Ball *et al.*, 2011). As a general rule, ethers absorb oxygen from the air resulting in the formation of unstable peroxides that may *detonate* when distilled in the presence of other compounds or disturbed in other ways by thermal radiation, friction, or, shock. Exceptions to the peroxide forming ethers include methyl-tert-alkyl ethers such as methyl tert-butyl ether (MTBE) and tert-amyl methyl ether (TAME), however, these compounds have a boiling point of 55 °C and 86 °C, respectively (Karas & Piel, 1994). These temperatures are too low for steam distillation of oil. Aryl ethers such as anisole (C_7H_8O) and anethole ($C_{10}H_{12}O$) are utilized as heat transfer fluids due to their thermal stability, according to Karas & Piel (1994). Due to the potential formation of peroxides, ethers are generally evaluated to be unsuited as potential susceptors, with the exception of aryl ethers and glycol ethers. Glycol ethers such as triethylene glycol butyl ether (TGBE) ($C_{10}H_{22}O_4$) and triethylene glycol methyl ether (TGME) ($C_8H_{20}O_5$) have relatively high boiling points and low melting points as seen in Table 6.

Table 6: Properties of select alcohols & ethers

| <i>Polar compound</i> | M_w g mol ⁻¹ | <i>bp</i> , °C (@760 mmHg) | <i>mp</i> , °C | ρ , g cm ⁻³ | <i>Cost</i> , ^d NOK |
|-----------------------|------------------------------|----------------------------------|--------------------|--------------------------------|-----------------------------------|
| Alcohols | | | | | |
| MEG | 62.07 | 198 ^c | -13 ^c | 1.11 ^c | 197 ⁱ |
| DEG | 106.12 | 245 ^c | -10.5 ^c | 1.12 ^c | 970 ⁱ |
| TEG | 150.17 | 288 ^c | -7 ^c | 1.12 ^c | 370 ⁱ |
| MPG | 76.1 | 184 ^c | -57 ^c | 1.03 ^c | 400 ⁱ |
| DPG | 134 | 232 ^c | -39 ^c | 1.02 ^c | 550 ⁱ |
| Glycerol | 92.1 | 290 ^c | 18 ^c | 1.26 ^c | 1200 ⁱ |
| Ethers | | | | | |
| Anisole | 108.14 | 154 ^c | -37 ^c | 0.99 ^c | 120 ^h |
| Anethole | 148.20 | 234 ^c | 21 ^c | 1.00 ^c | 280 ^h |
| TGBE | 206 | 283 ^{e,g} | -39 ^e | 0.99 ^e | 561 ⁱ |
| TGME | 164 | 250 ^e | -44 ^e | 1.05 ^e | 690 ⁱ |

^a Retrieved from NIST (2016)

^b Retrieved from Chickos & Acree Jr. (2003) ^c Retrieved from

ChemSpider (2016) ^d Retrieved from Sigma-Aldrich

^e Retrieved from UNEP (2016a)

^f Dow chemical company Material Safety Data Sheet (MSDS)

^g Decomposes ^h Cost per kg ⁱ Cost per L

Chapter 6 Susceptor technology

As previously mentioned in Chapter 5.2, Sipdrill and Clarisol are common base fluids in OBM. The exact composition of these oils are not known but the boiling point range is known. Sipdrill boils between 210 and 260 °C while Clarisol boils between 230 and 335 °C according to their respective MSDS provided by Baker Hughes. As the composition is unknown a substitute alkane is chosen based on the boiling point range. Dodecane ($C_{12}H_{26}$) can act as a substitute for Sipdrill as it has a boiling point range of 214 to 218 °C and hexadecane ($C_{16}H_{34}$) as a substitute for Clarisol as the boiling point is approximately 287 °C. It is clear from Table 7 that the theoretical advantages in terms of potential energy savings are significant. Distilling dodecane with water requires an energy input of 8680 kJ kg⁻¹ oil evaporated as seen in Table 4, whereas the same distillation with glycerol requires only 50 kJ kg⁻¹ oil evaporated! This truly depicts the potential energy savings of replacing water with environmentally friendly, polar organic compounds. The required energy is a function of the distillation ratio and the heat of vaporization, ΔH_{vap} .

Table 7: Distillation of dodecane with various alcohols & ethers

| <i>Polar compound</i> | <i>Combined bp</i> ^a , °C | P_{oil}^0/P_{polar}^0 ^a , mmHg/mmHg | <i>Distillation ratio</i> , | ΔH_{vap} , kJ kg ⁻¹ | <i>Required energy per kg oil evaporated</i> , kJ kg ⁻¹ |
|-----------------------|--------------------------------------|--|-----------------------------|--|--|
| Alcohols | | | | | |
| MEG | 182 | 0.7 | 2.9 | 858 ^c | 296 |
| DEG | 202 | 2.5 | 5.9 | 546 ^c | 93 |
| TEG | 210 | 6.0 | 10.3 | 416 ^b | 40 |
| MPG | 174 | 0.5 | 1.5 | 880 ^b | 587 |
| DPG | 199 | 1.9 | 3.3 | 455 ^c | 138 |
| Glycerol | 213 | 12.7 | 39.5 | 996 ^b | 25 |
| Ethers | | | | | |
| Anisole | 148 | 0.2 | 0.3 | 388 ^b | 1290 |
| Anethole | 197 | 1.6 | 3.2 | 466 ^b | 145 |
| TGBE ^e | - | - | - | 231 ^d | - |
| TGME ^e | - | - | - | 301 ^d | - |

^a Determined with Antoine's equation ^b Retrieved from NIST (2016) ^c Retrieved from Chickos & Acree Jr. (2003) ^d Dow chemical company MSDS ^e Antoine data not available

Table 8: Distillation of hexadecane with various alcohols & ethers

| <i>Polar compound</i> | <i>Combined bp,^a</i> °C | P_{oil}^0/P_{polar}^0 , ^a mmHg/mmHg | <i>Distillation ratio,</i> | ΔH_{vap} , kJ kg ⁻¹ | <i>Required energy per kg oil evaporated,</i> kJ kg ⁻¹ |
|-----------------------|---------------------------------------|---|----------------------------|---|--|
| Alcohols | | | | | |
| MEG | 195 | 0.09 | 0.2 | 858 ^c | 4290 |
| DEG | 234 | 0.4 | 0.8 | 546 ^c | 680 |
| TEG | 250 | 0.7 | 1.8 | 416 ^b | 231 |
| MPG | 185 | 0.06 | 0.2 | 880 ^b | 4400 |
| DPG | 225 | 0.26 | 0.5 | 455 ^c | 910 |
| Glycerol | 262 | 1.25 | 5 | 996 ^b | 200 |
| Ethers | | | | | |
| Anisole | 153 | 0.02 | 0.04 | 388 ^b | 9700 |
| Anethole | 226 | 0.26 | 0.66 | 466 ^b | 706 |
| TGBE ^e | - | - | - | 231 ^d | - |
| TGME ^e | - | - | - | 301 ^d | - |

^a Determined with Antoine's equation ^b Retrieved from NIST (2016) ^c Retrieved from Chickos & Acree Jr. (2003) ^d Dow chemical company MSDS ^e Antoine data not available

6.3 Acids, esters, amides, and amines

Acids are highly polar compounds, and from this perspective a potential susceptor candidate. Strong acids are usually available commercially as concentrated acids in solution. This means that when using a strong acid as a susceptor, one would also add water. This is counterproductive due to the high heat capacity and heat of vaporization of water. The toxicity and corrosive nature of especially mineral acids makes them unsuitable as susceptors. The fact that strong acids are very corrosive cause a more stringent requirement to material specification in any equipment in contact with the acid.

Organic acids are commonly known as weak acids, typically inhabiting the carboxyl functional group as seen in Figure 28. The boiling points of carboxylic acids are generally higher than alcohols due to the fact that most carboxylic acids form dimers in liquid and vapor phase (Averill & Eldredge, 2011). Carboxylic acids with up to 4 carbons are completely miscible in water. As the number of carbons increase the properties become more "alkane like", thus the solubility decreases with increasing carbon chain length. Concentrated organic acids, although weak, increases corrosion rates due to the corrosive properties of acids in general. Citric acid melts at 153 °C and upon further heating results in the formation of methyl maleic anhydride. An oxygen rich atmosphere caused the decomposition rate to increase (Barbooti & Al-Sammerrai, 1986). In a study by Wyrzykowski *et al.* (2011) the intermediate dehydration products of citric acid, *trans*-aconitic acid, and its isomer *cis*-aconitic acid were investigated in an Argon atmosphere. The use of IR and MS gave evidence that the compounds are dehydrated and decarboxylated leading to the formation of citraconic anhydride or itaconic anhy-

dride, or a mixture of these. In the experiments performed by Wyrzykowski *et al.*, the onset temperatures and the end temperatures of thermal degradation of the three acids were investigated. The general trend is that the temperature of which the onset of degradation occurs is increasing with the increase in heating rate. For citric acid at a heating rate of 5 K min^{-1} the onset temperature is reported as 475.8 K while the onset temperature at a rate of 15 K min^{-1} is reported to be 495.3 K. Similar trends are observed for *trans*-aconitic acid and *cis*-aconitic acid. Although not discussed, it would be most interesting to see if similar trends were achieved with a higher rate of heating, and if this applies to other functional groups. The cost of organic acids are considered to be low, however, reviewing the MSDSs of various organic acids including the ones listed in Table 9 it is clear that the corrosive and toxic nature of these compounds make them unsuitable as susceptors in Norwegian-Groups treatment concept.

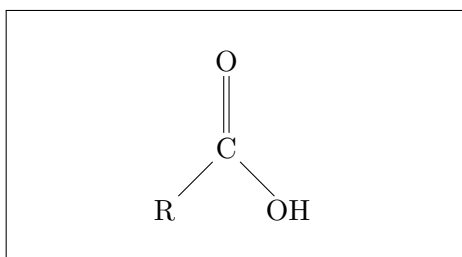


Figure 28: Carboxyl functional group

Esters have polar covalent bonds but are not capable of hydrogen bonding as seen in Figure 29. Esters have a considerable lower boiling point than their isomeric carboxylic acid counterparts, and their solubility borders around 3-5 carbons (Ball *et al.*, 2011). In order to reach a desired susceptor boiling point with esters a relatively large molecule would have to be utilized. As an example pentyl acetate ($C_7H_{14}O_2$) have a bp of approximately 145°C (ChemSpider, 2016). According to Tau *et al.* (1994) dry esters of low molecular weight are relatively stable, and can be distilled without decomposition.

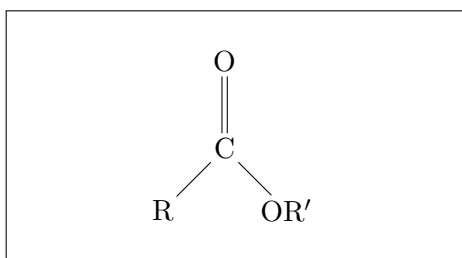


Figure 29: Ester functional group

Amides have a nitrogen attached to the carbonyl functional group. In simple amides the nitrogen is bonded to two hydrogen atoms while in secondary and tertiary amides one

or two hydrogen atoms are replaced with alkyl groups as seen in Figure 30. Amides have the ability to form hydrogen bonds which gives them relatively high melting and boiling points. Formamide is a liquid at room temperature, while other amides are generally solids (Clark, 2004). Loidreau & Besson (2011) reports that the thermal degradation products from MW heating of formamide are carbon monoxide (CO) and ammonia (NH_3).

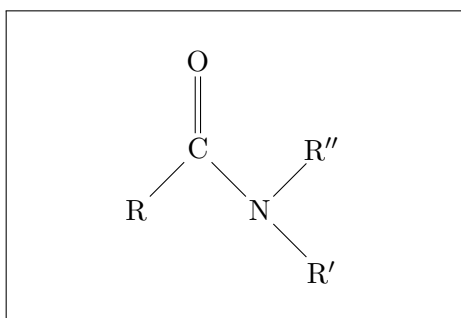


Figure 30: Amide functional group

Amines are derivatives of ammonia with either one, two, or three of the hydrogen atoms replaced by alkyl groups as shown in Figure 31. Amines with alkyl groups of five carbons or less are known as lower aliphatic amines, otherwise they are known as fatty amines. According to [Turcotte & Johnson \(1992\)](#), monobutylamines have a high solubility towards water and hydrocarbons and can be steam distilled, however, all four isomers of butylamine have relatively low boiling points which makes them unsuitable as susceptors. Alkylamines are corrosive to copper, aluminum, zinc, and galvanized surfaces ([Turcotte & Johnson, 1992](#)). Amines have C-N bonds that are much less polar than C-O bonds which indicate that the boiling point of amines are lower than for example alcohols of similar molecular weight ([Averill & Eldredge, 2011](#)).

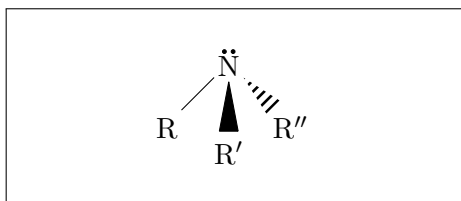


Figure 31: Amine functional group

Chapter 6 Susceptor technology

Table 9: Properties of select carboxylic acids & derivatives

| <i>Polar compound</i> | M_w , g mol ⁻¹ | bp , °C (@760 mmHg) | mp , °C | ρ , g cm ⁻³ | $Cost$, ^f NOK |
|-----------------------|--------------------------------|-----------------------------|------------------|--------------------------------|------------------------------|
| Acids | | | | | |
| Butanoic acid | 88.11 | 163.5 | -7.9 | 0.96 | 68 ^d |
| Hexanoic acid | 116.16 | 205.8 | -3.4 | 0.93 | 120 ^d |
| Nonanoic acid | 158.24 | 255.6 | 12.5 | 0.90 | 160 ^d |
| Esters | | | | | |
| Pentyl acetate | 130.18 | 149.3 | -70 | 0.88 ^c | 310 ^d |
| Dimethyl maleate | 144.13 | 204 | -41 | 1.15 ^c | 1150 ^d |
| Diethyl maleate | 172.18 | 225 ^c | -10 ^c | 1.06 ^c | 227 ^d |
| Dibutyl maleate | 228.28 | 281 ^a | -85 ^f | 0.99 ^f | 550 ^e |
| Amides | | | | | |
| Formamide | 45 | 210 ^c | 2 ^c | 1.13 | 370 ^e |
| Dimethyl formamide | 73 | 153 ^c | -61 ^c | 0.94 | 930 ^e |
| Amines | | | | | |
| Di-n-butylamine | 129.24 | 159.6 | -61.9 | 0.76 | 330 ^e |
| Tri-n-butylamine | 185.35 | 214 | <-70 | 0.78 | 542 ^e |
| Triisobutylamine | 185.35 | 191.5 | -22 | 0.77 | 8840 ^e |

General note: Data retrieved from Kirk-Othmer Encyclopedia of Chemical Technology unless otherwise indicated. ^a Retrieved from NIST (2016) ^b Retrieved from Chickos & Acree Jr. (2003) ^c Retrieved from ChemSpider (2016) ^d Cost per kg ^e Cost per L ^f Retrieved from Sigma-Aldrich

In Table 10 the theoretical advantages in terms of energy efficiency are depicted when distilling dodecane with various carboxylic acids and derivatives. All of the listed compounds have an energy requirement which is significantly lower than water (2257 kJ kg⁻¹), with exception of pentyl acetate, whose energy requirement are similar to water.

Chapter 6 Susceptor technology

Table 10: Distillation of dodecane with various acids & derivatives

| <i>Polar compound</i> | <i>Combined bp,^a °C</i> | P_{oil}^0/P_{polar}^0 , ^a mmHg/mmHg | <i>Distillation ratio,</i> | ΔH_{vap} , kJ kg ⁻¹ (@bp) | <i>Required energy per kg oil evaporated,</i> kJ kg ⁻¹ |
|-----------------------|--|---|----------------------------|--|--|
| Acids | | | | | |
| Butanoic acid | 157 | 0.23 | 0.57 | 540 ^c | 950 |
| Hexanoic acid | 185 | 0.82 | 1.50 | 567 ^c | 378 |
| Nonanoic acid | 205 | 3.4 | 4.40 | 487 ^b | 110 |
| Esters | | | | | |
| Pentyl acetate | 144 | 0.14 | 0.21 | 388 ^b | 1850 |
| Dimethyl maleate | 184 | 1.00 | 1.80 | 375 ^b | 208 |
| Diethyl maleate | 194 | 1.31 | 1.80 | 320 ^b | 178 |
| Dibutyl maleate | 209 | 5.50 | 5.40 | 180 ^b | 33 |
| Amides | | | | | |
| Formamide | 192 | 1.17 | 6.70 | 1420 ^b | 212 |
| Dimethyl formamide | 148 | 0.16 | 0.47 | 671 ^c | 1430 |
| Amines | | | | | |
| Di-n-butylamine | 153 | 0.20 | 0.27 | 379 ^b | 1400 |
| Tri-n-butylamine | 188 | 0.95 | 0.90 | 260 ^c | 290 |
| Triisobutylamine | 174 | 0.94 | 0.46 | 291 ^c | 630 |

^a Determined with Antoine's equation (2003)

^b Retrieved from NIST (2016)

^c Retrieved from Chickos & Acree Jr.

Table 11: Distillation of hexadecane with various acids & derivatives

| <i>Polar compound</i> | <i>Combined bp,^a °C</i> | P_{oil}^0/P_{polar}^0 , ^a mmHg/mmHg | <i>Distillation ratio,</i> | ΔH_{vap} , kJ kg ⁻¹ (@bp) | <i>Required energy per kg oil evaporated,</i> kJ kg ⁻¹ |
|-----------------------|--|---|----------------------------|--|--|
| Acids | | | | | |
| Butanoic acid | 162 | 0.02 | 0.08 | 540 ^c | 6750 |
| Hexanoic acid | 202 | 0.11 | 0.26 | 567 ^c | 2180 |
| Nonanoic acid | 247 | 0.48 | 0.81 | 487 ^b | 600 |
| Esters | | | | | |
| Pentyl acetate | 148 | 0.01 | 0.03 | 388 ^b | 12930 |
| Dimethyl maleate | 201 | 0.10 | 0.27 | 375 ^b | 1390 |
| Diethyl maleate | 218 | 0.20 | 0.36 | 320 ^b | 890 |
| Dibutyl maleate | 255 | 0.86 | 1.10 | 180 ^b | 164 |
| Amides | | | | | |
| Formamide | 214 | 0.17 | 0.54 | 1420 ^b | 2630 |
| Dimethyl formamide | 152 | 0.02 | 0.06 | 671 ^c | 11180 |
| Amines | | | | | |
| Di-n-butylamine | 158 | 0.02 | 0.04 | 379 ^b | 9475 |
| Tri-n-butylamine | 209 | 0.14 | 0.18 | 260 ^c | 1445 |
| Triisobutylamine | 189 | 0.07 | 0.08 | 291 ^c | 3638 |

^a Determined with Antoine's equation (2003)

^b Retrieved from NIST (2016)

^c Retrieved from Chickos & Acree Jr.

6.4 Ketones and aldehydes

Ketones and aldehydes both contain the carbonyl functional group. They possess a significant dipole moment due to the polar C=O bond, evident from Figure 32. As the molecular weight of the compound increases the functional group become less and less important in defining the properties of the compound. Aldehydes are a group of very reactive compounds. Generally, aldehydes have boiling points between those of the corresponding alkane and alcohol and the C_3 to C_{11} aldehydes are liquids (Miller, 1991). Ketones typically consist of the most toxic compounds found in essential oils and according to Cheremisinoff (2003) may cause epileptic seizures, convulsions and mental confusion among others. Not all ketones are toxic, however, no advantages over other susceptors have been identified. Aldehydes nor ketones are considered as a potential susceptor and are not discussed further in this thesis.

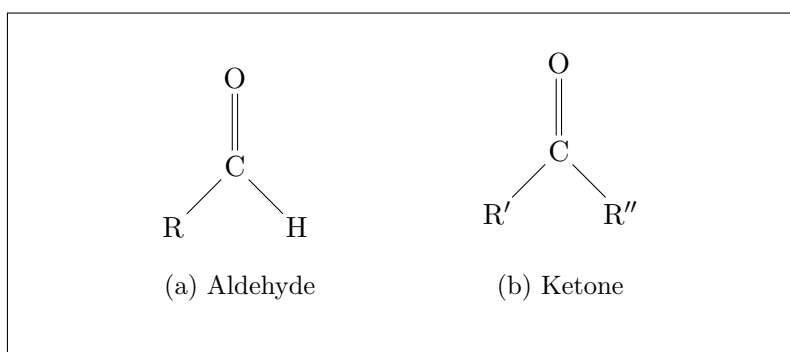


Figure 32: Functional group of aldehydes and ketones

6.5 Solid susceptors

Graphite and amorphous carbon couple very strongly with microwaves. At 2.45 GHz temperatures in excess of 1000 °C within 1 min is possible, additionally graphite may also exhibit catalytic behavior. In some occasions, process optimizations have resulted in rapid and strong heating by the use of 10 wt% graphite (Besson & Kappe, 2013). Another high MW absorbing material is found in sintered silicon carbide (SiC). Besson & Kappe (2013) describes various ways that SiC may be employed, including small reaction vessels made of SiC, and powdered and granular SiC. The mechanism of heating is not orientation polarization as described in Chapter 4.1 but rather through ohmic heating mechanisms. Sumper & Baggini (2012) provides an overview over such mechanisms.

Shang *et al.* (2012) investigated the influence of dielectric properties of materials on oil removal from solid waste and found that water, although high in dielectric properties was not efficiently removing heavy oils. Furthermore, Shang *et al.* (2012) found that a NaCl concentration of up to 1.0 M improved the removal efficiency and that residual OOC of 0.1 % was obtainable with the addition of 5 % activated carbon.

The use of solid susceptors instead of liquid compounds is not considered to be attractive for the application of drill cuttings treatment, due to loss of benefits from the steam distillation process. However, adding a small amount of graphite or SiC can potentially increase the effect of the treatment process when low amounts of liquid phase MW absorbers are present. Another application of solid susceptors, or, susceptor aids, can be in the pretreatment step where dielectrically heated graphite or another carbon species are used to supply the sensible heat. Graphite is currently on OSPAR's PLONOR list. Solid susceptors can possibly be applied in a polishing step where the temperature is increased drastically to burn of any remaining oil before discharge.

6.6 Potential susceptors

Based on Chapter 6.2 throughout 6.4 it is evident that a susceptor is most likely found within the alcohol, ether, or ester functional group. The following potential susceptors

Chapter 6 Susceptor technology

have been identified: (1) MEG, (2) DEG, (3) TEG, (4) MPG, (5) DPG, (6) glycerol, (7) anethole, (8) dibutyl maleate, and (9) diethyl maleate. The compounds listed above are potential susceptors evaluated on a theoretical basis, and in order to evaluate the compounds further the chemicals have been tested using a laboratory setup described in Chapter 7. Note that only MEG, DEG, TEG, MPG, DPG, and glycerol was available during the experimental work of this thesis. As discussed in Chapter 4, it is crucial to have knowledge about the dielectric properties of materials subject to electromagnetic heating. Dielectric data of typical susceptors at microwave and radio frequency is not readily available in the literature, however, an attempt to summarize properties of identified potential susceptors is provided in Table 12. Along with other compounds. The frequencies are approximate and the reader is referred to the original author for the exact experimental conditions, in some cases the dielectric properties are determined with linear interpolation between adjacent frequencies.

Table 12: Dielectric properties of compounds

| <i>Polar compound</i> | <i>Temperature, °C</i> | ϵ''/ϵ' (D_p [cm]) | | | <i>Ref.</i> |
|-----------------------|------------------------|--------------------------------------|-----------------|-----------------|--------------|
| | | 30 MHz | 915 MHz | 2.45 GHz | |
| MEG | 25 | 3.5/41 (291) | 8/20 (2.7) | 12/12 (0.6) | ^b |
| DEG | 25 | - | 10.5/23.7 (2.2) | 12.3/10.6 (0.5) | ^c |
| MPG | 25 | - | 11/10 (1.4) | 6.0/5.0 (0.7) | ^d |
| Glycerol | - | 8.30/42.1 (124) | 6.4/8.4 (2.2) | 3.4/6.3 (1.4) | ^a |
| Activated carbon | - | - | - | 2/7 (2.6) | ^e |
| SiC | 20 | - | - | 11/30 (1.0) | ^b |
| Water, distilled | 25 | 0.4/78 (3515) | 5.2/77 (8.0) | 13/77 (1.3) | ^b |
| Water, distilled | 85 | 0.3/58 (4040) | 1/56 (35.7) | 3/56 (4.9) | ^b |
| Water, 1.0 M NaCl | 25 | 480/76 (3.0) | 30/76 (1.4) | 20/76 (0.8) | ^b |
| Fuel oil | 25 | - | - | 0.002/2 (1378) | ^f |

^a Gabriel *et al.* (1998) ^b Meredith (1998) ^c Sengwa & Kaur (1999) ^d Sengwa *et al.* (2002)

^e Vos *et al.* (2003) ^f Robinson *et al.* (2008)

6.7 Susceptor recovery

The potential susceptors listed in Chapter 6.6 are all liquids. During the thermal treatment the susceptors will be vaporized and withdrawn together with oil, and water vapor. A condenser operated at a suitable temperature will allow the susceptor to be recovered in the same way as the oil, and water. Depending on the boiling point of the susceptor, the oil will typically be condensed first, followed by the susceptor. Lastly the water phase will be condensed. A similar arrangement (see Figure 9) is provided by Halliburton (2014) on page 16 for the TCC unit. In this case the process mill and the drive unit would be replaced by the MW heating equipment. One additional condenser would be needed to recover the susceptor.

Chapter 6 Susceptor technology

It is likely that some susceptor will remain on the cuttings after treatment. This was shown to be the case during microwave treatment of drill cuttings in Chapter 9. Liquid and solids may for example be separated by the use of a centrifuge, or a solid-liquid cyclone. Cyclones require a pressure drop in order to function. Taking this into account, a mechanical separation method such as a decanter centrifuge or a disc stack centrifuge may be more suitable, depending on the particle size ([Alfa-Laval, 2016](#)). If the susceptor is not eligible for discharge this step has to be implemented. If the susceptor is eligible for discharge, as in the case of MEG, the benefits has to be weighed up against the disadvantages. This includes, cost, energy requirements, operation, and maintenance.

Chapter 7

Distilling susceptors and base oils

To the author's knowledge, steam distillation in combination with microwaves, liquid organic susceptors, and OBM base oils are performed here for the first time. Note that pictures are best viewed in the electronic version of the report. The experiment goal was to determine if the steam distillation process will cause the oil, or the susceptor, to decompose.

7.1 Experimental setup and method

The materials utilized in these experiments are depicted in Table 13.

Table 13: Microwave and distillation equipment

| Equipment | Model | Manufacturer |
|---------------------------------|--------------|---------------|
| Domestic microwave | MW-2706 | Tristar |
| Pressurized N_2 gas | Yara Praxair | - |
| Standard distillation glassware | | |
| Sipdrill | - | Baker-Hughes |
| Clarisol | - | Baker-Hughes |
| MEG | | VWR Chemicals |
| DEG | | Sigma-Aldrich |
| TEG | | Sigma-Aldrich |

A domestic microwave oven was modified to allow the sample flask to be placed inside the microwave applicator while connected to the rest of the distillation glassware which were situated outside of the applicator. This allowed the vapors to escape the cavity, condense, and be collected in a receiving cylinder, see Figure 33. The susceptor was added to the boiling flask along with the oil. The respective volumes of each liquid was not recorded since the goal of the experiment was to unveil any degradation of the distilled liquids. The distillation equipment was assembled and the boiling flask placed inside the modified domestic microwave oven cavity. As mentioned in Chapter

6.2, an inert atmosphere reduced the degradation of glycerol. To confirm this behavior the experiments were performed in both aerated and inert conditions, where the inert atmosphere was provided by pressurized N_2 gas. The gas was introduced to the boiling flask through a vertical glass pipe from the top of the glassware as seen in Figure 33b. Power was applied in the form of microwaves until the volume of the condensed liquids was sufficient for analysis. The selected susceptors were distilled with both sipdrill and clarisol which are common base oils found in OBM. The susceptor and the oil was separated by the use of a separation funnel. The distilled liquids physical appearance was used as an indication for degradation. Additionally, one sample of sipdrill base oil and one sample of the same oil distilled with MEG as susceptor was analyzed by GC-FID. Intertek Westlab in Stavanger performed the analysis. The exact runtime for each experiment was not recorded, however, most of the distillations required between 20 and 40 min.

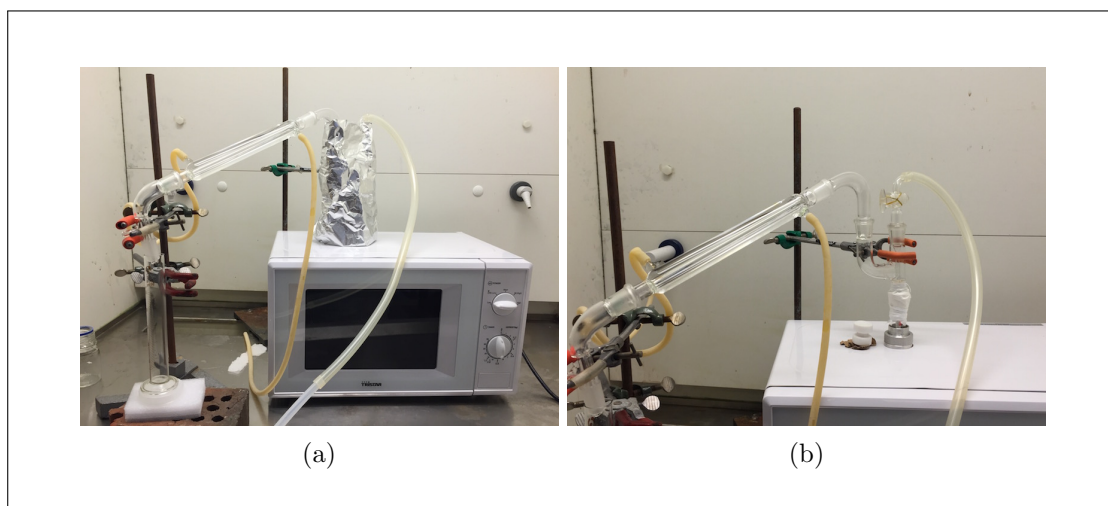


Figure 33: Initial experimental setup

7.2 Results

7.2.1 Distilling monoethylene glycol

Experiment 1. The distillation of MEG (Figure 34a), and sipdrill (Figure 34b) in an aerated atmosphere did not show any visual signs of degradation. The observed distillation ratio was 0.58 compared to a theoretical ratio of 2.9 mL oil per mL MEG.

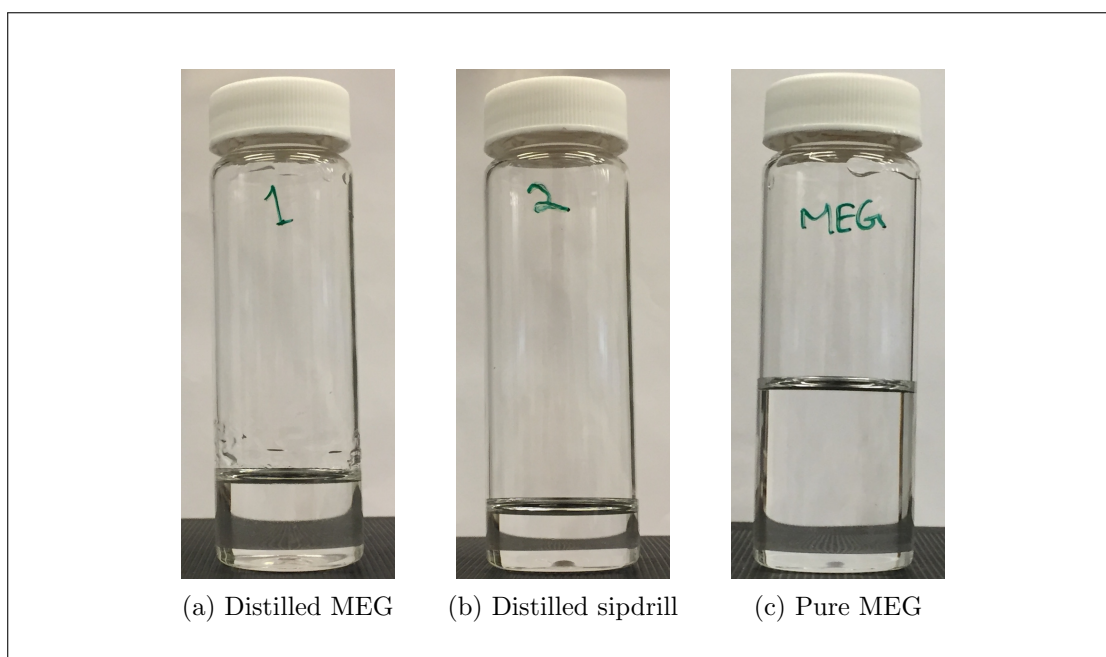


Figure 34: Experiment 1. MEG and sipdrill distilled in an aerated atmosphere

Experiment 2. When distilling MEG (Figure 35a), and sipdrill (Figure 35b) in an inert N_2 atmosphere the initial observations revealed no discoloration or sweet pungent smell. The theoretical distillation ratio of 2.9 (Table 7) is substantially lower than the observed ratio of 4.5 mL oil per mL MEG.

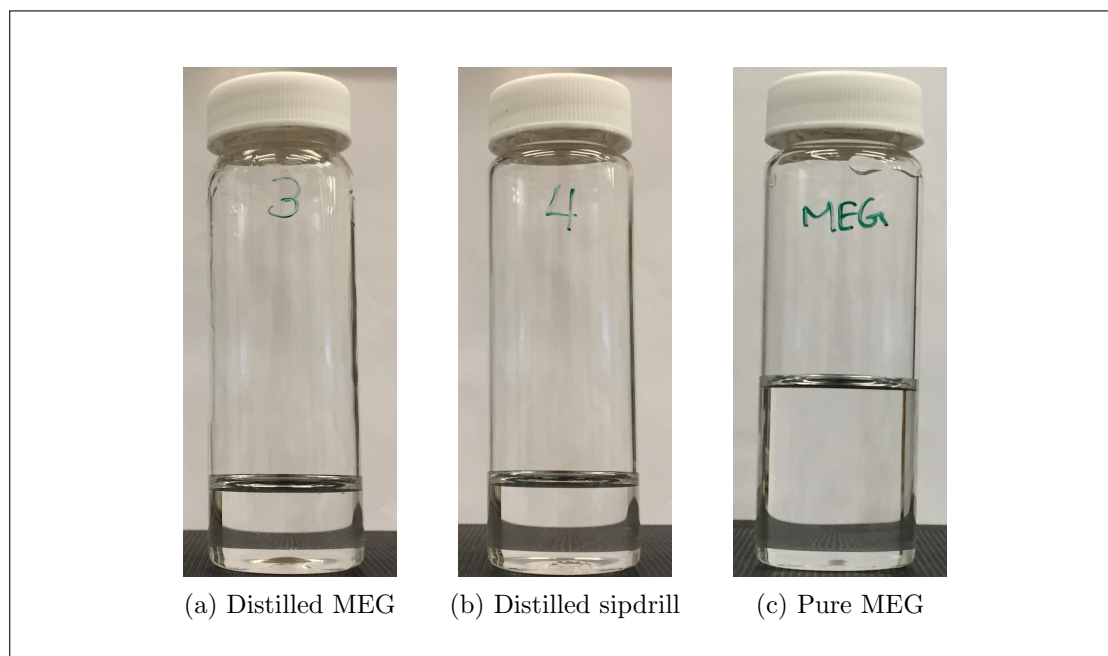


Figure 35: Experiment 2. MEG and sipdrill distilled in an inert atmosphere

Experiment 3. Low discrepancy was evident when distilling MEG (Figure 36a) with clarisol (Figure 36b) where the observed ratio of oil to MEG was 0.36, and the theoretical is 0.2 mL oil per mL MEG. Samples were also collected from the boiling flask (Figure 36c and 36d). A slight discoloration is visible, indicating that some degradation of the susceptor took place.

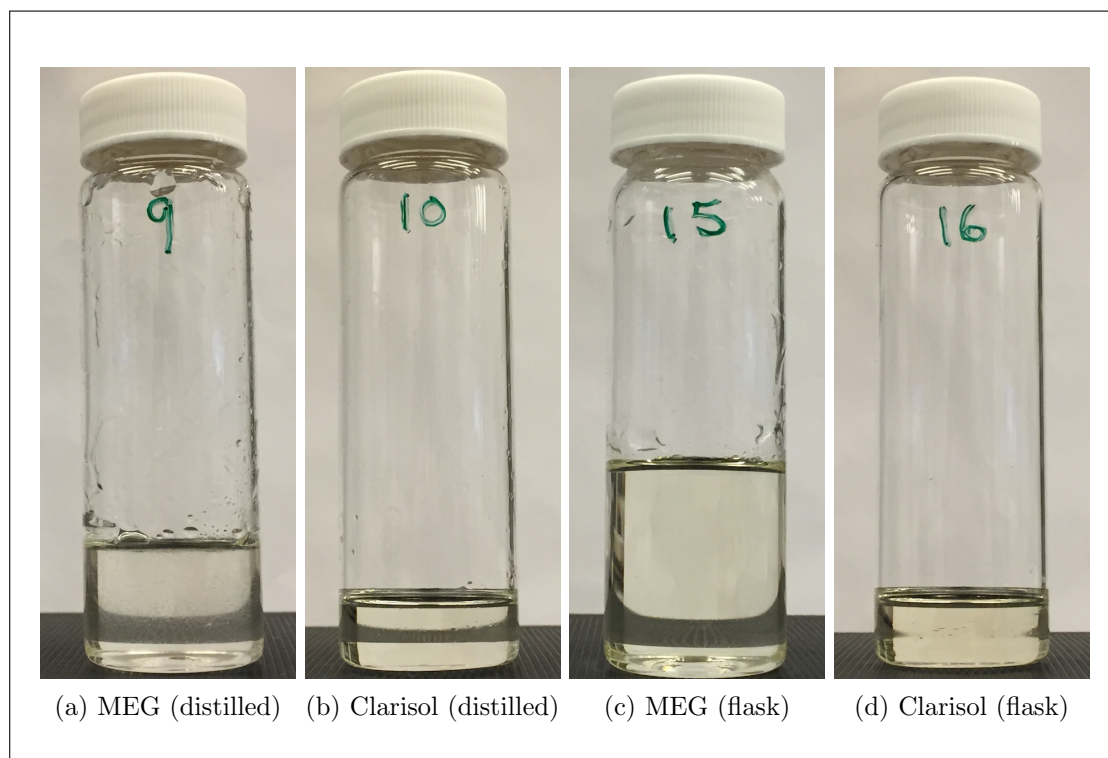


Figure 36: Experiment 3. MEG and clarisol distilled in an aerated atmosphere

Experiment 4. Distillation of MEG (Figure 37a), and clarisol (Figure 37b), in combination with N_2 gas yielded a distillation ratio of 0.84 which is higher than the expected ratio of 0.2 mL oil per mL MEG. Figures 37c and 37d show MEG and clarisol from the boiling flask, respectively. The EM power was applied for a duration of 40 minutes.

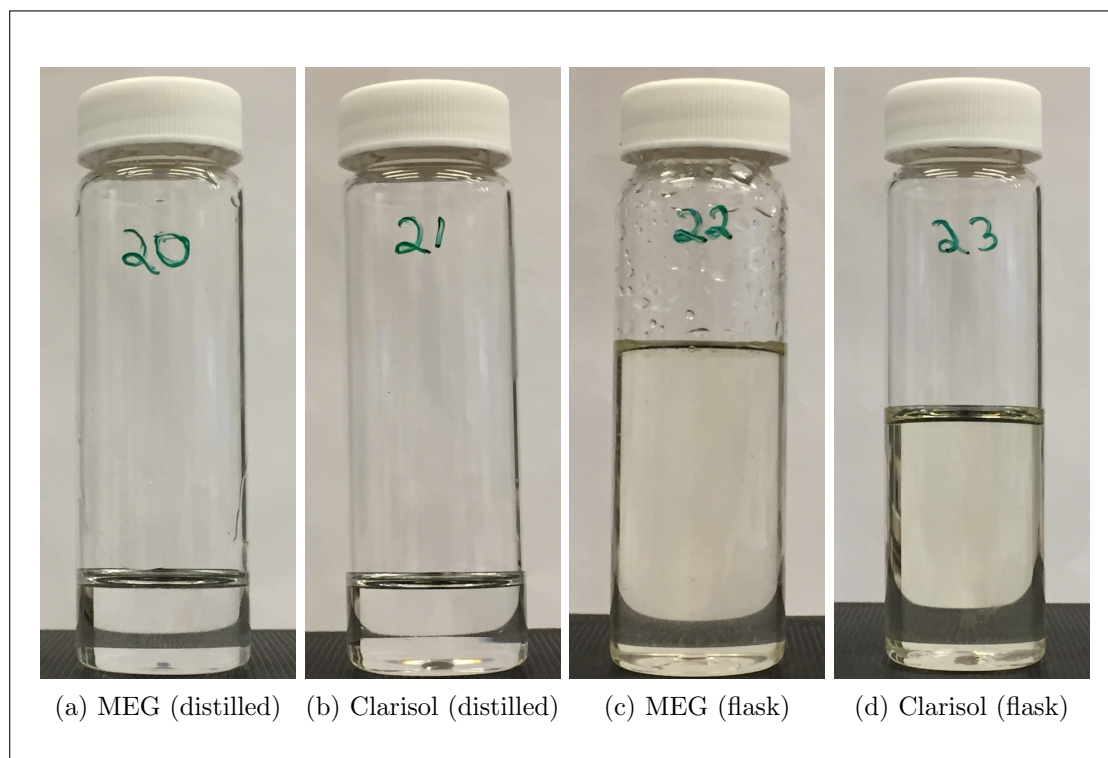


Figure 37: Experiment 4. MEG and clarisol distilled in an inert atmosphere

Chapter 7 Distilling susceptors and base oils

Intertek Westlab was not able to detect the composition of the oil, which made it difficult to verify if the oil decomposed or not. Traces of C_6 was found in the distilled oil. This most likely comes from n-Hexane which was used to wash the condenser and receiving cylinder. Overall, based on the visual analysis and GC-FID (Figure 38), the sipdrill base oil did not seem to decompose.

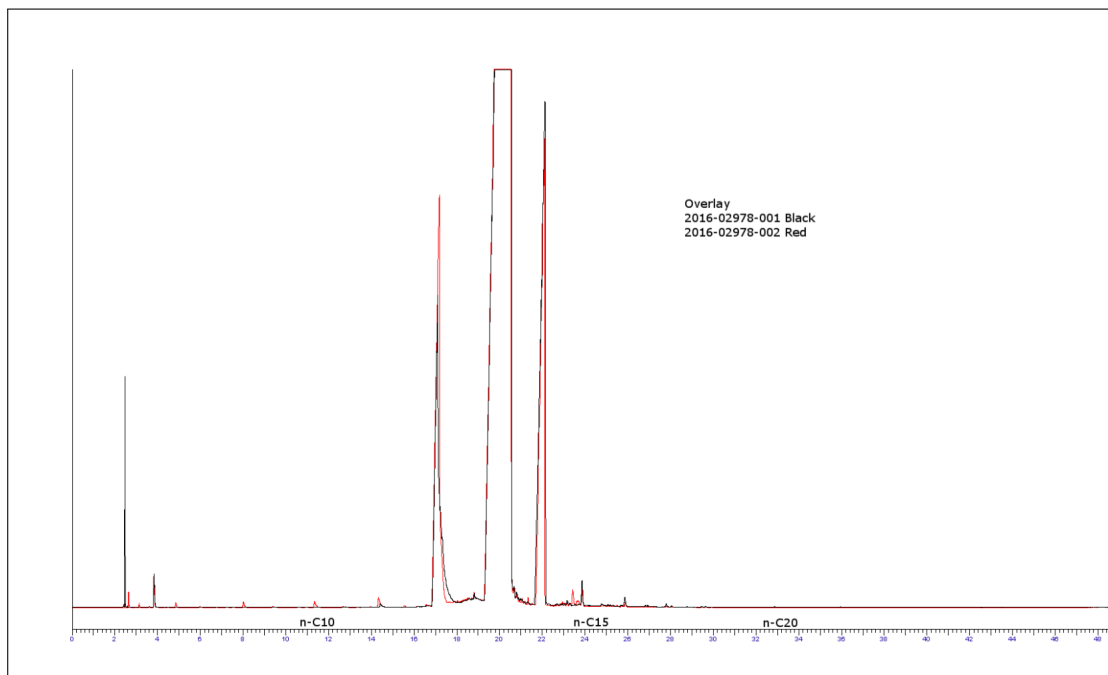


Figure 38: GC-FID overlay of sipdrill and sipdrill distilled with MEG

7.2.2 Distilling diethylene glycol

Experiment 5. No visual impairment of the distilled liquids was evident (Figure 39). Microwave power was applied intermittently for a duration of approximately 40 minutes. The distillation ratio was not recorded. Figure 39a and 39b shows the distilled DEG and clarisol, respectively. Figure 39c and 39d is DEG, and clarisol collected from the boiling flask. The liquids collected from the boiling flask show a slight discoloration.

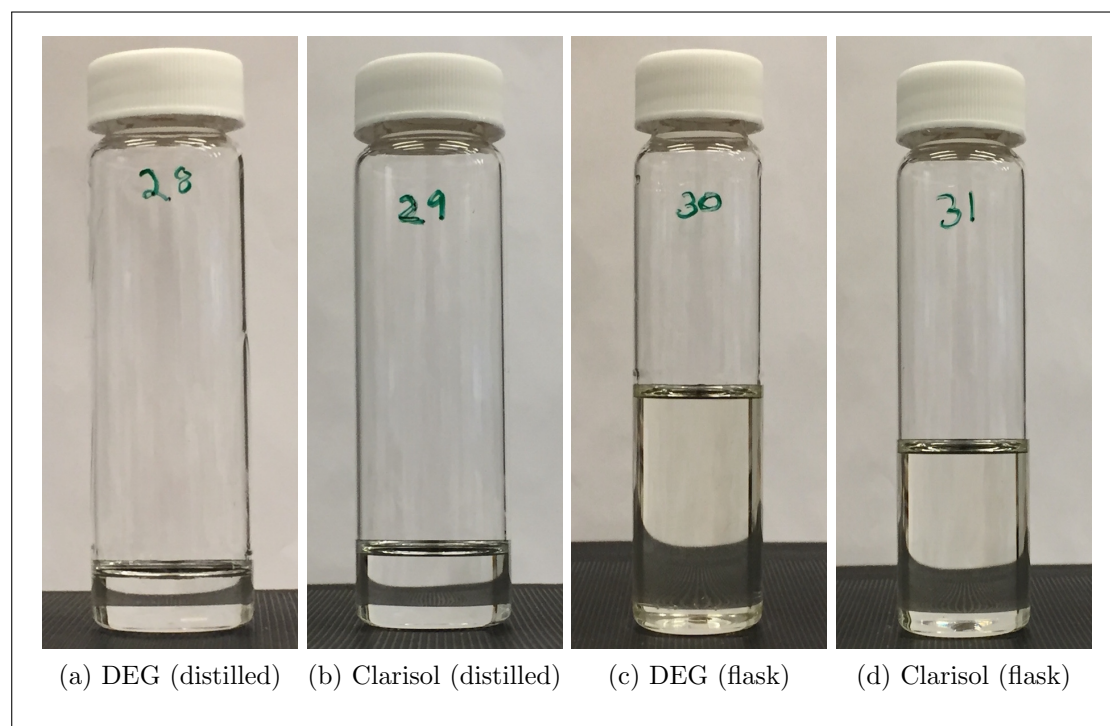


Figure 39: Experiment 5. DEG and clarisol distilled in an aerated atmosphere

Experiment 6. The volumetric distillation ratio of DEG (Figure 40a) and clarisol (Figure 40b) in an inert atmosphere was recorded to be 2.0 mL oil per mL DEG which is higher than the theoretical ratio of 0.8 as seen in Table 8. No visual discoloration of the distilled liquids was evident during 30 minutes of microwave heating. Some discoloration is still evident in the liquids collected from the boiling flask as seen in Figure 40c and 40d.

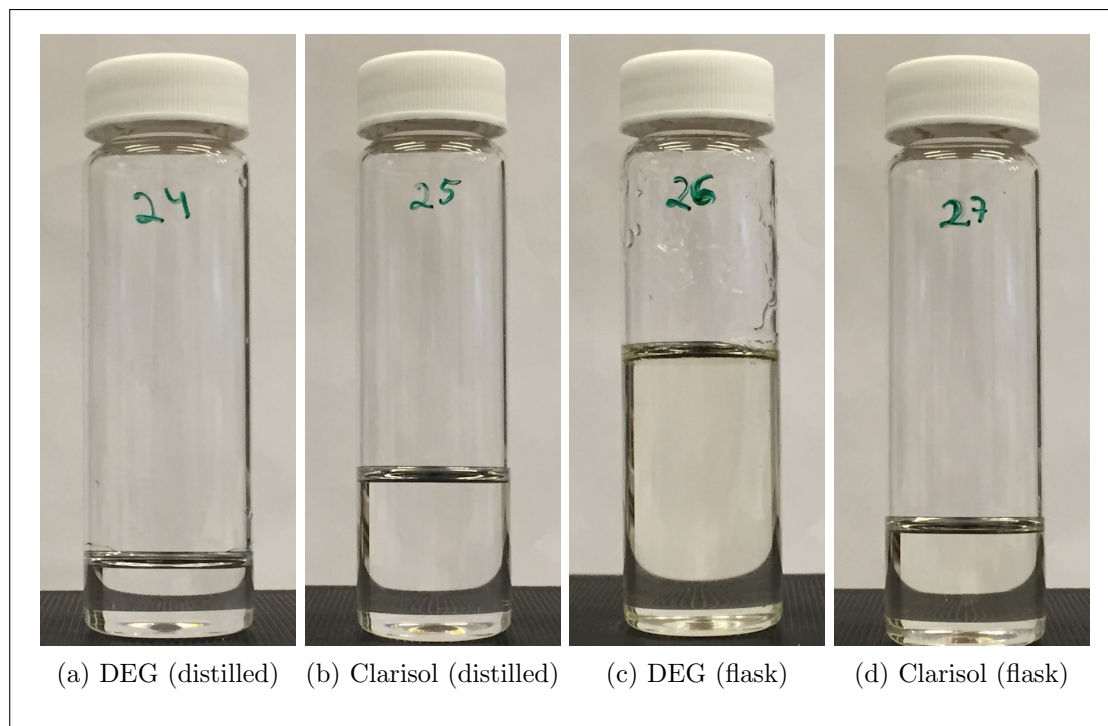


Figure 40: Experiment 6. DEG and clarisol distilled in an inert atmosphere

7.2.3 Distilling triethylene glycol

Experiment 7. TEG (Figure 41a) was distilled with sipdrill. Without N_2 gas the distillation ratio was 6.67 mL oil per mL TEG which is lower than the theoretical ratio of 10.3. The distilled oil was cloudy but clarified after some time (Figure 41b) or when centrifuged (Figure 41c). No apparent degradation was observed.

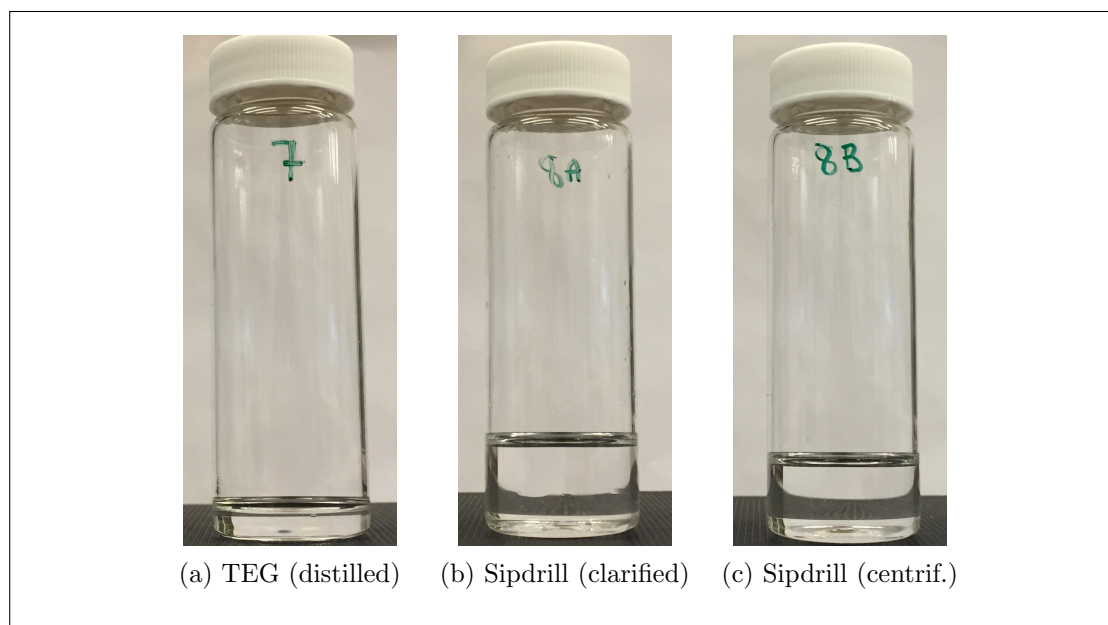


Figure 41: Experiment 7. TEG and sipdrill distilled in an aerated atmosphere

Experiment 8. TEG (Figure 42a) distilled with sipdrill (Figure 42b) in combination with N_2 yielded a distillation ratio of 1.47 which is significantly lower than the theoretical ratio. This is the opposite of that observed for MEG in combination with N_2 gas. No visual impairment was visible.

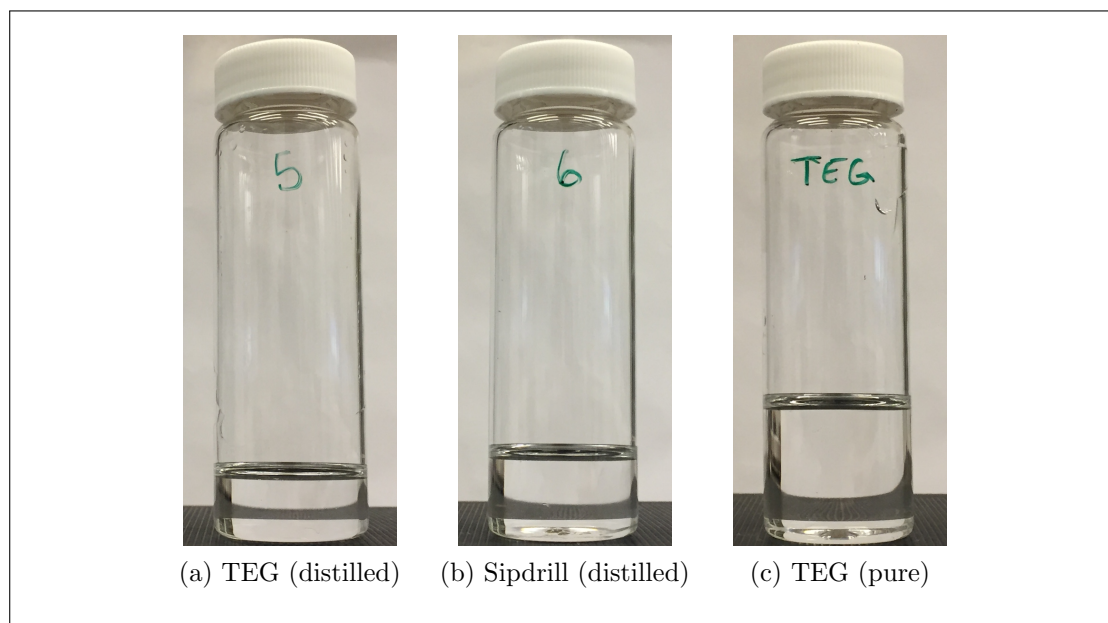


Figure 42: Experiment 8. TEG and sipdrill distilled in an inert atmosphere

Experiment 9. Distilling TEG (Figure 43a) with clarisol (Figure 43b) in an aerated atmosphere resulted in a distillation ratio of 1.36 mL oil per mL TEG which is in line with the theoretical ratio of 1.80. Some discoloration of TEG was evident, suggesting that degradation of the compound did take place. Heavily discoloration of the TEG, and clarisol collected from the boiling flask was observed (Figure 43c and 43d, respectively).

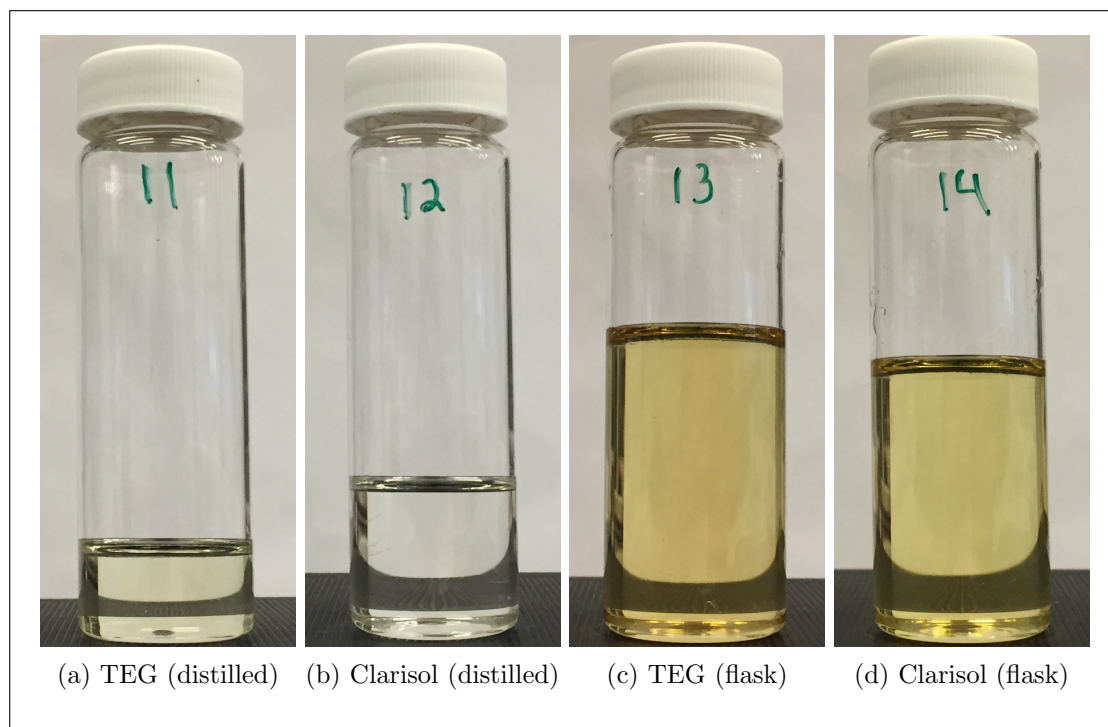


Figure 43: Experiment 9. TEG and clarisol distilled in an aerated atmosphere

Experiment 10. When distilling clarisol (Figure 44b) with TEG (Figure 44a) in an inert atmosphere the distillation ratio appeared to be 5.67 mL oil per mL TEG, which is higher than the theoretical distillation ratio of 1.80. The distillate revealed little evidence of degradation. Discoloration of the susceptor recovered from the boiling flask is also evident in this case (Figure 44c). The volume of oil remaining in the boiling flask was less than that required for analysis.

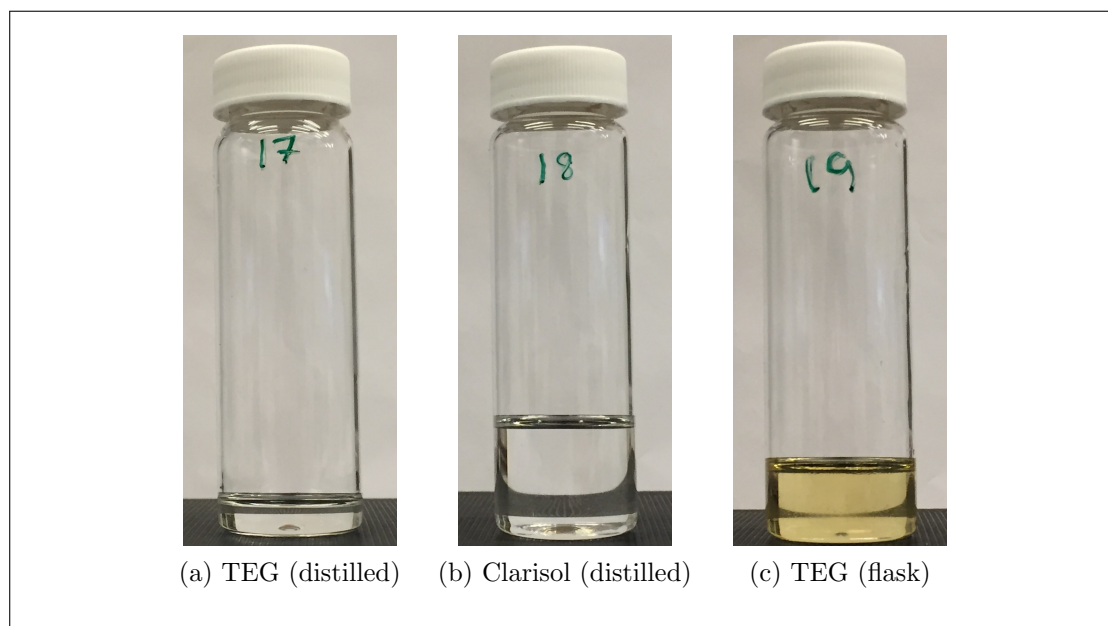


Figure 44: Experiment 10. TEG and clarisol distilled in an inert atmosphere

7.3 Discussion

A general note, especially for cases where clarisol was distilled, is that vapors were continuously condensing on the N_2 supply line and the glassware around the N_2 tube before reaching the actual condenser. Due to this behavior the susceptor and oil are likely to be condensed and re-vaporized a number of times before being collected for analysis, which may impact the results. Premature condensing was also an issue during treatment of cuttings, see Chapter 9. After a sufficient amount of power was applied, the vapors successfully reached the condenser, and condensed into the receiving cylinder. Premature condensing can compare to the recycling of susceptors in an actual treatment process, however, the susceptor is likely to spend less time absorbing EM power in an actual treatment process. This is most likely beneficial when considering degradation due to less power being absorbed. Another observation that was made is that higher flows of N_2 gas is more beneficial to avoid re-condensation, as it provides a sweeping effect. In the study by [Pereira \(2012\)](#), where drill cuttings was treated with microwaves and N_2 sweep

gas, benefits of increased nitrogen flow rate was also observed up to a certain point. The behavior was also evident in experiments without N_2 gas. It should be noted that the distillation ratios in the preceding experiments were only recorded once and are meant as an indication, due to the fact that not all of the vapors were successfully condensed, this is most likely due to an undersized condenser. The theoretical distillation ratios were calculated using dodecane and hexadecane. In reality the actual bp of sipdrill and clarisol is likely to differ from dodecane and hexadecane. This cause a difference in the distillation ratios. Another error may be that the ambient temperature N_2 gas was causing a lot of premature condensation. The main disadvantage of using a domestic microwave oven of this type is the pulsating duty mode cycle utilized to control the amount of power applied, i.e. the magnetron is switched off and on at a fixed powerlevel (Bogdal, 2006). This was evident during the experiments, resulting in very vigorous boiling. At certain points the mixture was boiling almost at the inlet of the condenser, this could also affect the distillation ratio. It is believed that the discoloration in the samples arise from the decomposition of the organic compound at high temperatures. However, it may be possible that the oil degrades and cause the discoloration at high temperatures as well.

7.4 Conclusion

Experiments 1-10 have shown that it is possible to distill common OBM base oils by the use of polar organic liquids with microwaves as the heat source. Based on the GC-FID and the visual observations, it seems that sipdrill does not decompose in the MW distillation process. Likewise, based on the visual analysis, clarisol shows little evidence of discoloration. Ambient temperature N_2 gas was found to negatively affect the process. The gas caused premature condensation causing the susceptor to absorb more energy than what was needed for vaporization. MEG did not seem to decompose significantly based on the visual analysis.

Chapter 8

Characteristics of cuttings

In order to evaluate the effects of susceptors and dielectric heating, it is important to know the initial oil, and water content in the cuttings. Three methods have been identified for OOC determination; Retort, traditional soxhlet extraction, and automated solvent extraction. The oil contaminated cuttings used in the following experiments were of North Sea origin with high clay content. Note that the characteristics presented below are only applicable for the cuttings used in the experiments of this thesis. The goal of this experiment is to determine the OOC and water levels of cuttings that have been centrifuged, and to verify that retort and soxhlet extraction are suitable principal methods for OOC determination. The OBM base oil was proven to evaporate relatively fast, and in an attempt to quantify this behavior a simple bench-top experiment was conducted.

8.1 Materials and method

In addition to the specific equipment described in Table 14, the following chemicals and equipment were also used in the experiments:

- Analytical scale (0.1 g)
- Analytical scale (0.0001 g)
- n-Hexane
- Dichloromethane
- Acetone
- Petroleum Ether
- Various glassware
- Protective clothing

- Plastic container with lid
- Centrifuge (Hettich rototfix 46)
- Rotary evaporator
- Anhydrous Calcium sulfate (Drierite)
- Defatted cotton pads
- 10-100 μ L pipette
- 1-10 μ L pipette

Table 14: Retort and soxhlet equipment

| Equipment | Model | Manufacturer | Method |
|-----------------------------|--------------------|--------------|---------|
| 50 mL electronic retort kit | 165-14-3 | OFITE | Retort |
| Soxhlet extractor | 250 mL | – | Soxhlet |
| Graham condenser | – | – | Soxhlet |
| Heating mantle | PILZ LG2/ER/500 mL | Isopad | Soxhlet |
| Extraction thimble | 33 x 80 mm | Whatman | Soxhlet |
| Glass wool | – | – | Soxhlet |
| Soxtec system | HT 1043 | Foss-Tecator | Soxtec |

8.1.1 Sample preparation

In order to determine the initial OOC approximately 2 L of cuttings were collected. Any free liquid was disposed of as waste. The cuttings was centrifuged at 2000 rounds per minute (RPM) for 2 minutes to remove free liquid and the resulting supernatant was disposed of as waste. The cuttings was transferred to a suitable container and mixed until homogenous and the sample was kept in a cool room to keep biological activity to a minimum. When needed, the container was retrieved to collect samples and placed back in the cooling room.

8.1.2 Retort

A retort test is a relatively fast and uncomplicated method to measure water and oil content in cuttings. In this report, a gravimetric approach to the retort analysis was applied, as it is more accurate than a volumetric approach. A known mass of OBM containing cuttings is heated in a retort instrument. Upon vaporization the gases are collected and condensed. The condensed liquids are employed to determine the OOC concentrations gravimetrically. The methodology applied is based on the equipment instructions supplied with the OFITE 50 mL retort kit and API RP 13B-2 - Recommended practice for field-testing Oil-Based Drilling Fluids. The procedure below was employed

to determine the OOC levels in eight separate samples of cuttings originating from the same drilling waste.

The retort chamber was cleaned and care was taken to make sure that the condenser pipe was not plugged by using the T-handle drill bit and pipe cleaner included in the retort kit. The tare weight of the retort assembly including the wool was noted. The homogeneously mixed sample was added to the retort cup sample holder and the weight of the assembly including the wool and the wet sample weight was noted. Care was taken to make sure that no air remained in the sample cup by compressing the sample with the spatula, and that the threads were lubricated sufficiently. The wet sample weight, M_w , was determined by weighing. The liquid receiver weight was noted. The retort assembly was placed inside the heating chamber, the condenser attached and the graduated receiver placed underneath. The heating chamber was turned on and allowed to run for approximately one hour until no more liquid was condensing. Afterwards, the liquid receiver and the equipment were allowed to cool.

The total water volume was determined by reading the water level, V_{H_2O} (M_{H_2O}), in the liquid receiver. It is an assumption that the water has a density of 1 g L^{-1} , that the water contains no oil-in-water emulsion and as a result the total water volume may be directly translated as mass, where $1 \text{ mL} = 1 \text{ g}$. The weight of the liquids (M_{liquid}) was determined by subtracting the weight of the liquid receiver from the weight of the receiver, including the liquid. The mass of the retort assembly including the dry cuttings was determined. Finally, the weight of the dried retort cuttings, M_d , was determined by subtracting the tare weight of the retort assembly from the measured dry weight. The mass of the oil, M_{oil} , was determined from the total liquid weight and subtraction of the water weight. Finally, the oil on dry cuttings (OOC) was determined by Equation 12 and the oil on wet cuttings by Equation 13. Additional information regarding the experimental methodology of the retort test may be found in API RP 13B-2 (API, 2014). The experimental results from 8 separate retort analyses are shown in Table 17.

$$OOC_{dry} = \frac{M_{oil}}{M_{oil} + M_d} \times 100\% \quad (12)$$

$$OOC_{wet} = \frac{M_{oil}}{M_w} \times 100\% \quad (13)$$

8.1.3 Soxhlet extraction

By using the soxhlet extraction technique, and a solvent such as n-Hexane, the OOC may be determined gravimetrically. The soxhlet extraction is a reflux method in the sense that the solvent that is used for extraction is passed through the sample multiple times until the solvent has extracted all of the non-polar compounds, in this case, oil.

The hexane solvent has a bp of 67 °C which is lower than the bp of the oil. The solvent may be evaporated after the extraction in order to determine the OOC of the sample. The methodology employed in this report is a procedure for extraction of non-volatile and semi-volatile compounds.

Two samples of approximately the same weight were collected from previously centrifuged drill cuttings. One of the samples were used to determine the dry cuttings weight by drying the sample at 105 degrees overnight in a crucible with a known weight. The dry cuttings weight was noted as M_d .

The other sample was used for extraction with n-Hexane. Approximately 30 g of sample was added to an extraction thimble. Glass wool was also added on top of the sample inside the extraction thimble to reduce the amount of solids carried into the solvent. Attaching the extractor column onto the boiling flask and adding hexane to the column until the level reached the siphoning tube and the solvent was withdrawn into the flask determined the required amount of hexane. The thimble was then placed inside the extractor and a small amount of additional hexane was added to wet the sample and the glass wool. Upon attaching the condenser and starting the coolant flow the heating jacket was switched on and the extraction was run for a sufficient amount of time. EPA 3540C refers to an extraction time of 16-24 h with 4-6 cycles per hour.

When the extraction completed the extract was allowed to cool down to room temperature and transferred to another boiling flask suitable for use on the rotary evaporator. A small amount of hexane were used to wash the extract boiling flask and also transferred to the rotavapor boiling flask. Care was taken to ensure as little transfer of solids as possible.

By the use of a rotary evaporator the solvent was evaporated from the sample at 40 °C and a vacuum of approximately 200 mbar. The vacuum was in some cases lowered to shorten the time for evaporation. When no more solvent was present in the sample, the weight of the oil were determined as M_{oil} . The dry and wet OOC was then calculated by Equation 12 and 13. Additional information on soxhlet extraction may be found in EPA 3540 C (EPA, 1996). One successful soxhlet analysis was conducted. The results are depicted in Table 18.

8.1.4 Automated solvent extraction

By utilizing the Randall modification, the Soxtec method requires only 20 - 25 % of the time required for traditional soxhlet extraction. The sample is submersed in boiling solvent and the fact that oil is more soluble in hot solvent forms the principle for this method (Anderson, 2004).

The handling and preparation of samples in the soxtec method is very important, especially as the sample sizes are typically smaller than traditional soxhlet extraction. Anderson (2004) provides a guideline on sample sizes (15), however, it is recommended that the size of the sample is as large as possible in order to mitigate errors. According to the literature, water can affect the outcome of the analysis by decreasing the efficiency of the solvent extraction. Samples containing moisture are typically dried or mixed with

Chapter 8 Characteristics of cuttings

a drying agent such as anhydrous calcium sulfate (C_aSO_4), commercially available as Drierite, which is suitable for most organic compounds ([Armarego & Chai, 2013](#)).

Table 15: Soxtec sample sizes

| <i>Oil content (%)</i> | <i>Sample weight (g)</i> |
|------------------------|--------------------------|
| 0-10 | 2-3 |
| 10-25 | 1-2 |
| >25 | 0.5-1 |

Six samples of centrifuged cuttings was prepared according to Table 16 and weighed directly into extraction thimbles appropriate for the Soxtec system. In order to keep the samples in place a defatted cotton pad was placed on top of the sample. Samples 3, 4, and 6 were mixed with Drierite in order to determine if the moisture content of the samples affected the outcome of the analysis. The thimbles were then placed in the Soxtec machine.

Table 16: Soxtec sample matrix

| <i>Sample</i> | <i>M_{cuttings},</i> g | <i>M_{C_aSO₄},</i> g | <i>M_{tot},</i> g |
|---------------|-----------------------------------|--|------------------------------|
| 1 | 3.0225 | (-) | 3.0225 |
| 2 | 3.0894 | (-) | 3.0894 |
| 3 | 1.496 | 1.5046 | 3.0006 |
| 4 | 1.5179 | 1.4500 | 2.9679 |
| 5 | 3.0843 | (-) | 3.0843 |
| 6 | 1.5116 | 1.5629 | 3.0745 |

Six extraction cups containing boiling chips were dried at 105 °C for 1 h and placed in a desiccator until the weight of the cups (M_{cup}) stabilized. The Soxtec system was turned on and an appropriate solvent boiling temperature was set, for a light petroleum ether (bp range of 30-40) this is in the range of 100 - 110 °C. Approximately 50 mL of light petroleum ether were added to each of the cups and placed in the machine. It is paramount that the cups are secure in place to prevent any leakage of solvent, which will most likely ruin the sample and also pose HSE risk. If any of the cups were not secure the cups was reseated again until secure. The thimbles was lowered into the solvent and boiled for 1 h, followed by 1 h of rinsing. Afterwards the condenser valves were closed and solvent was recovered for 2 min. Care was taken that there was solvent left in the extraction cups after the solvent recovery step as a significant amount of the oil being analyzed have proven to evaporate if all of the solvent is attempted to be recovered. After the extraction completed, the cups were placed inside a fume hood and the weight of the cups were recorded every 10 min over a period of 120 min. The weight of the cups

were plotted against time, and the mass of the oil, M_{oil} , was determined at the time when all of the solvent was evaporated from the sample. This was seen from the slope of the weight curves.

8.1.5 A simple bench-top experiment

Knowing that the OBM base oil evaporates in ambient conditions, two small bench-top experiments was conducted. Assuming that the extraction of 10 g of treated cuttings yielded 0.088 g (0.1 mL) of oil. Two samples was prepared in separate beakers. Sample 1 contained 3 mL light petroleum ether and 0.088 g of C_{12} oil (dodecane). This simulates an OOC of 0.88 %. Sample 2 contained only 0.0752 g of C_{12} oil, which simulates an OOC of 0.752 %. The weight of the samples was then recorded over a period of 1 h in order to determine the oil evaporation at ambient conditions.

8.2 Results & discussion

Retort. The results depicted in Table 17, show that the oil and water within the cuttings are homogenously distributed when the wet sample mass is relatively large (95 g). In order to determine if the oil and water content of the cuttings varied significantly over time, a new batch of centrifuged cuttings was prepared 6 months after tests 1-5. The results of retort number 6, 7, and 8 show that the cuttings does not vary significantly over time with respects to the oil and water content. The retort analysis showed that the centrifuged cuttings comprised of approximately 10 % oil, 18 % water, and 72 % solids on a dry weight basis. The soxhlet result in Table 18 show similar results to that of the retort. The retort analysis is a fast and reliable method for OOC determination. However, when the OOC concentration is towards the lower end the method becomes increasingly inaccurate, and the use of soxhlet extraction principle is necesseary. Erroneous reading of the liquid receiver may cause inaccurate results. A 50 mL glass cylinder of ± 1 mL accuracy was used to collect the liquid and due to the capillary forces it is easy to over estimate the collected water volume. Another source of error in the retort occurs when there is air trapped within the retort sample chamber, so care must be taken to avoid air entrainment.

Table 17: Retort: OOC determination of centrifuged cuttings

| <i>Test #</i> | 1 | 2 | 3 | 4 [†] | 5 [†] | 6 [‡] | 7 [‡] | 8 [‡] | <i>mean</i> | <i>Unit</i> | <i>S.E.</i> | <i>95% CI</i> |
|---------------|------|------|------|----------------|----------------|----------------|----------------|----------------|-------------|-------------|-------------|---------------|
| M_w | 97.0 | 95.2 | 94.9 | 89.9 | 96.7 | 97 | 95.5 | 96.4 | 95.33 | g | 0.29 | ± 1.1 |
| M_d | 72.1 | 70.4 | 70.3 | 66.6 | 71.5 | 72.5 | 71.1 | 71.9 | 70.80 | g | 0.30 | ± 1.2 |
| M_{H_2O} | 16.0 | 15.5 | 15.5 | 14.8 | 15.9 | 15.1 | 15.2 | 15.3 | 15.41 | g | 0.05 | ± 0.2 |
| M_{oil} | 7.6 | 7.6 | 7.7 | 7.1 | 7.8 | 7.7 | 7.8 | 8.0 | 7.66 | g | 0.03 | ± 0.1 |
| H_2O_{dry} | 18.2 | 18.0 | 18.0 | 18.2 | 18.2 | 17.2 | 17.6 | 17.5 | 17.9 | % | 0.05 | ± 0.2 |
| H_2O_{wet} | 16.5 | 16.3 | 16.3 | 16.5 | 16.4 | 15.6 | 15.9 | 15.8 | 16.2 | % | 0.04 | ± 0.2 |
| OOC_{wet} | 7.84 | 7.98 | 8.11 | 7.90 | 8.07 | 7.9 | 8.17 | 8.25 | 8.03 | % | 0.02 | ± 0.1 |
| OOC_{dry} | 9.54 | 9.74 | 9.87 | 9.63 | 9.84 | 9.6 | 9.89 | 9.96 | 9.76 | % | 0.02 | ± 0.1 |

[†] Not performed by the author of this report.

[‡] Performed approximately 6 months after tests 1-5.

Soxhlet. In the initial runs of the soxhlet extraction process, it was easy to observe that the solvent contained a significant amount of solids when the extraction was complete. This is most likely related to the fact that glass wool was used to stop solids from traveling from the sample and into the solvent boiling flask. The glass wool was then replaced with proper extraction thimbles, which still produced undesirable results with solids in the solvent. It is likely that the solids was transferred into the solvent when the solvent was poured into the soxhlet before the start of the experiment. The results from the three initial soxhlet analyses are not represented as they contain little value towards the OOC determination. It should be noted however, that this information is valuable towards the final set-up of the experiment. In the final experiment the solvent was transferred prior to the introduction of the sample in the soxhlet extractor. Also, glass wool was used as additional insulation on the top of the thimble. The solvent showed significantly less amount of solids. The use of n-Hexane instead of a 1:1 (v/v) hexane/acetone solvent system is considered a possible error source. Water was present in the sample, which may have caused inaccurate results as well. In literature, it is recommended to dry the sample at 105 °C or to add a drying agent. The base oil of the drilling fluid is likely to evaporate to some extent upon drying, and drying agents was unavailable at the time of the soxhlet experiments.

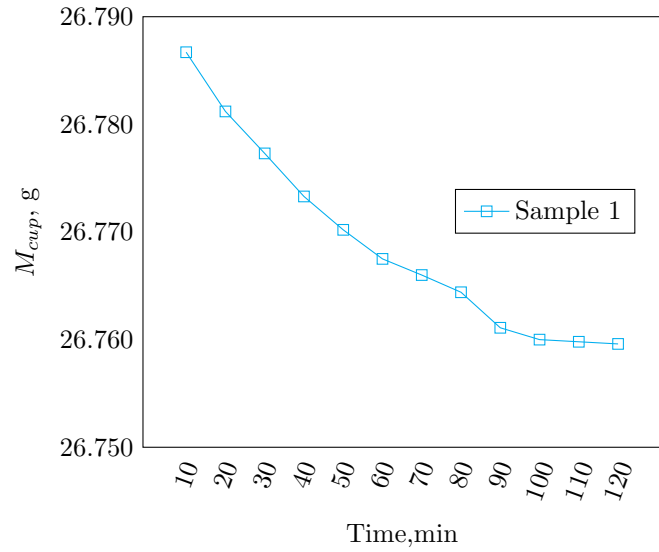
Table 18: Soxhlet: OOC determination of centrifuged cuttings

| <i>Test #</i> | 1 | Unit |
|--------------------------|-------|------|
| <i>Runtime</i> | 9.5 h | |
| <i>M_d</i> | 23.40 | g |
| <i>M_{oil}</i> | 2.60 | g |
| <i>OOC_{dry}</i> | 10 | % |

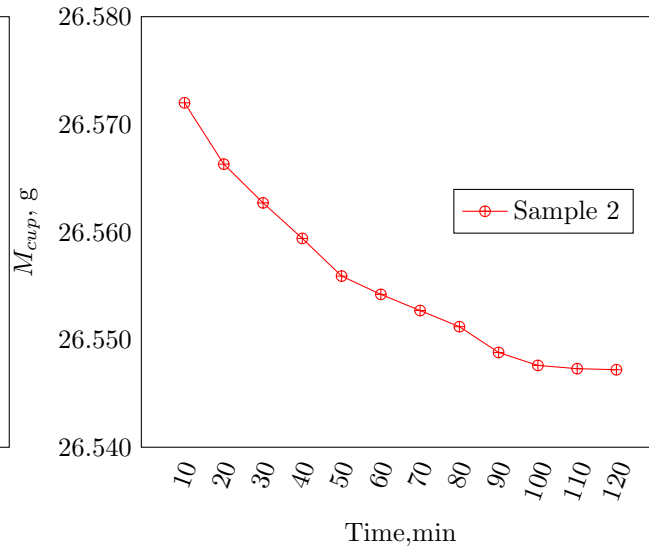
A simple benchtop experiment. In the course of 1 h Sample 1 lost 0.008 g which means the OOC decreased from 0.88 to 0.80 %. Sample 2 lost 0.0072 g in the course of 1 h which means that the OOC decreased from 0.752 to 0.68 %. The oil was dodecane, and for higher bp oils the evaporation is likely to be less than what is presented here.

Soxtec. A large effort was directed towards this method due to the short time required for analysis compared to the traditional soxhlet. A significant amount of base oil evaporates from the samples when attempting to recover all of the solvent in the Soxtec system, depending on the bp of the oil. To ensure solvent free samples the suggested steps in the Soxtec manual include drying of the samples post extraction. This was proven to evaporate a substantial amount of the base oil, causing any analysis to be void. In the initial runs of the Soxtec system, the samples was most likely affected during solvent recovery. To mitigate this effect the samples were not dried post extraction but rather heated just above the solvents bp and swirled on a hot plate inside a fume hood to evaporate the last traces of solvent, however, this method was also proven to

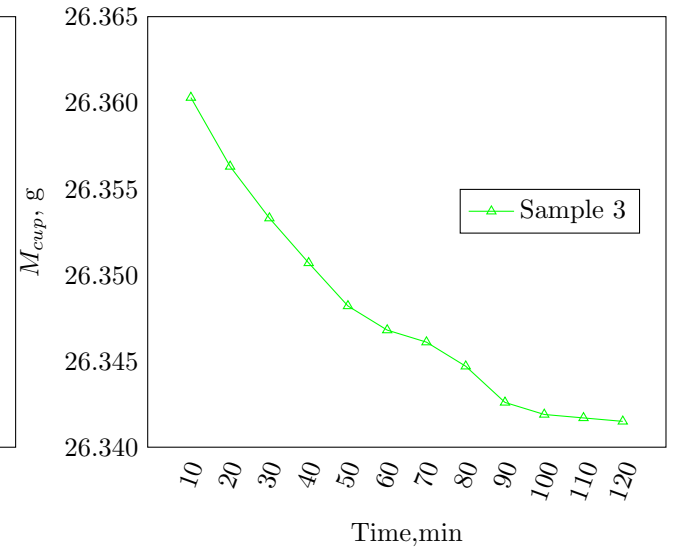
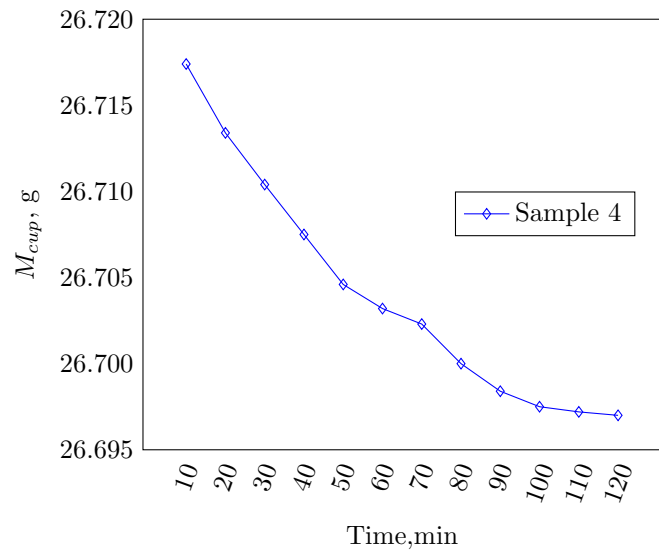
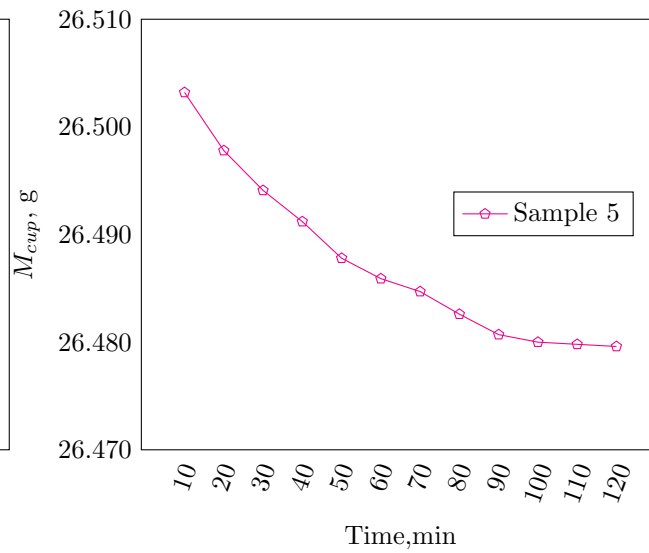
cause a significant amount of oil to evaporate. The final method that was employed was to avoid solvent recovery entirely. When the rinsing period was over the soxtec system was turned off and the extraction cups were allowed to cool to room temperature (~ 10 min) and placed under a fume hood. When the amount of solvent in the cups became low (approximately 5-10 mL) the weight of the cups was recorded every 2 min to determine the exact time when the extract became solvent-free. Since the the vapor pressure of the solvent is much higher than the vapor pressure of the oil it is expected that the slope of the curve is much higher when the sample is containing solvent compared to the slope of the curve when only oil is present. The resulting plots of the 6 samples is depicted in Figure 45 and suggests that all of the solvent had evaporated at 50 min. The resulting wet weight OOC at 50 min is seen in Figure 46. Note that the results depicted in Figure 45 and 46 followed a 10 min weighing schedule, which is most likely to long and that solvent recovery was performed for 2 min which may have caused some premature oil evaporation due to the cups being almost solvent free at the start of the weighing schedule. There is a discrepancy between the soxtec and retort results, the reasons for this discrepancy can be that the retort sample size is much larger than the soxtec sample size (meaning that larger variations in oil content is seen in smaller samples), inaccurate reading of the retort liquid receiver, and due to the evaporation of oil along with solvent during analysis in the soxtec method, which have been discussed previously. Taking into account these error sources, including the fact that some oil evaporates during weighing it is likely that the soxtec produce accurate results and is a suitable method for OOC analysis.



(a) Centrifuged cuttings



(b) Centrifuged cuttings

(c) Centrifuged cuttings + $CaSO_4$ (d) Centrifuged cuttings + $CaSO_4$ 

(e) Centrifuged cuttings

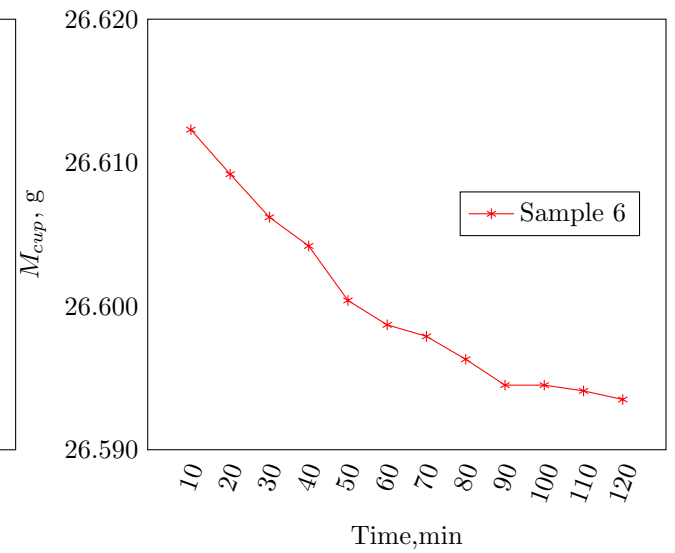
(f) Centrifuged cuttings + $CaSO_4$

Figure 45: Decreasing sample mass

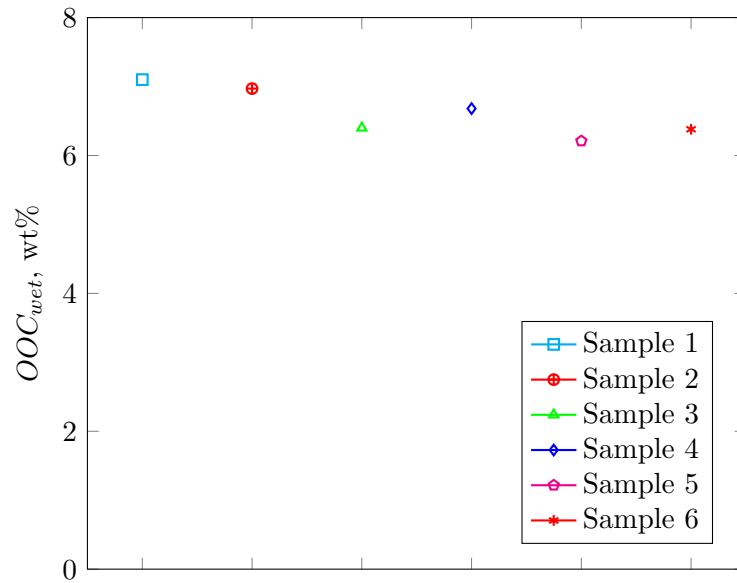


Figure 46: Measured OOC for Samples 1-6.

8.3 Conclusion

When relatively large samples were analyzed in the retort, a homogenous distribution of the oil within the material matrix was evident. It was found that the heterogeneity of the samples increased with a decrease in sample size, to a certain extent. The soxtec method is considered to be the most suitable method when a low oil content is expected in the sample. The centrifuged cuttings used in the experimental work of this thesis contain between 7 and 8% oil, 16-17% water, and 76% solids on a dry weight basis.

Chapter 9

Treating cuttings with susceptors and microwaves

The experiments described in Chapter 7 have confirmed that it is possible to distill mineral oils which are commonly used as base fluids in OBM with the use of susceptors and microwave power. In actual drilling fluids there are more chemical components than just the base oil, hence, there is a need to evaluate the effects when actual OBM cuttings are processed. As discussed in Chapter 4.3, treating cuttings utilizing microwaves as the heat source have been confirmed by many workers, but never combined with the use of organic liquids as susceptors. Two types of cuttings have been treated. Centrifuged cuttings containing both water and oil in combination with susceptors, as well as cuttings that contained oil in combination with susceptors *or* water. The second type of cuttings was prepared by retorting cuttings and then adding the preferred amount of oil, and susceptor or water. In order to demonstrate the true effects of the susceptor, a comparison was made. First, cuttings where pure water acted as the susceptor was treated and analyzed. Secondly, cuttings where a polar organic liquid acted as susceptor was treated and analyzed. In these experiments a known amount of oil is added to a known amount of retorted cuttings, along with a known amount of water *or* susceptor. The oils used to simulate base oil was dodecane ($C_{12}H_{26}$) with a bp of 216 °C and hexadecane ($C_{16}H_{34}$) with a bp of 287 °C ([ChemSpider, 2016](#)).

9.1 Materials

The equipment employed in the following experiments are depicted in Table 19.

Table 19: Microwave and distillation equipment

| Equipment | Model | Manufacturer |
|---------------------------------|--------------|---|
| Microwave chemical reactor | WBFY-205 | Zenhzhou Keda Machinery & Inst. Equip. Co., Ltd |
| Hot air gun | KX2200K-QS | Black & Decker |
| Hot air gun | - | Meecc tools |
| Pressurized N_2 gas | Yara Praxair | - |
| Standard distillation glassware | | |
| 2 x large casseroles | 20 L | - |
| North Sea cuttings | | |
| Dodecane | - | Sigma-Aldrich |
| Hexadecane | - | Sigma-Aldrich |
| MEG | | VWR Chemicals |
| DEG | | Sigma-Aldrich |
| TEG | | Sigma-Aldrich |
| MPG | | Sigma-Aldrich |
| DPG | | Sigma-Aldrich |
| Glycerol | | Sigma-Aldrich |

9.2 Experimental setup

The microwave reactor supplied a maximum of 750 W in a multimode applicator and the magnetron input power is adjustable up to 1100 W. The microwave was also equipped with an onboard magnetic stirrer and the applicator floor was lined with a material that directs EM energy towards the material being heated.

Initial operating and start up issues. In the start of the experimental work, the microwave reactor would instantly cease to function when power was applied. Inspection of the magnetron revealed that metal fragments from the manufacturing of the reactor was attached to the magnetron causing the equipment to malfunction. When the fragments were removed the MW reactor functioned more satisfactory. The microwave reactor had some operational issues, the fuse would sometimes burn out when the amount of EM absorbing material became too low. When the amount of EM absorbing material is low, it is more difficult to achieve MW coupling. It is believed that as a result of poor MW coupling the electronics in the microwave absorbed more power and caused the fuse to burn out. Another likely cause is the previously mentioned metal fragments. The microwave functioned satisfactory at 900 W input power, which means that the power available to heat the cuttings is approximately 700 W due to the power efficiency of the microwave. Figure 47 depicts the initial setup of the microwave with the distillation equipment in place.

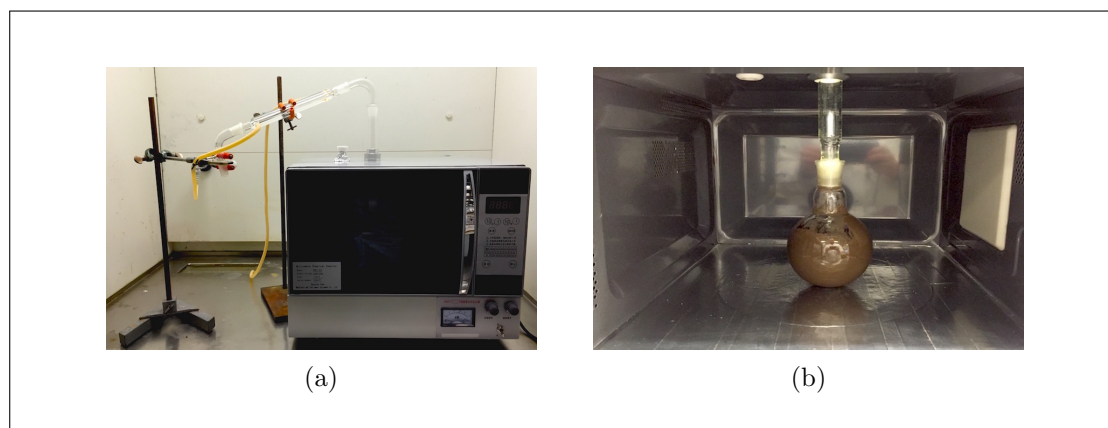


Figure 47: Initial experimental setup

Mixing. Mixing of the cuttings during treatment is a parameter which has been shown to improve the treatment process and mitigate the effects of low penetration depth (Junior *et al.* , 2015; Robinson *et al.* , 2012), see Chapter 4.3. It became evident during the initial trials that the onboard magnetic stirrer was unable to sufficiently stir the cuttings as the cuttings become quite hard when water and oil leave the sample, this applies to samples containing centrifuged cuttings. If the sample is dry cuttings from the retort it may be possible to achieve mixing with a suitable magnet. An attempt to equip an external mixing device was made by the use of an electric drill and a stirring rod soldered onto to a metal extension piece. After several attempts, stirring of cuttings during treatment was abandoned as the stirring rod would repeatedly brake at the point of soldering as the cuttings solidified. A more rigorous stirring rod could be used. Otherwise, modification of the microwave reactor is most likely necessary to incorporate mechanical mixing of the cuttings during treatment.

The problem of re-condensation. During the first runs it became clear that vapors were condensing prematurely. This means that instead of condensing in the designated condensers, a substantial amount of gas were condensing on the glassware immediately outside of the microwave reactor, causing the condensed liquids to fall back into the boiling flask. Condensed liquids that returned to the boiling flask affected the analysis of the dried cuttings, which produced inaccurate results. To counter this problem, a hot air gun was used to heat the glassware upstream of the condensers. In order to reduce the heat loss a large casserole with a lid was utilized to cover the glassware, and holes was drilled to accommodate the hot air gun and the glassware.

Sweep gas and inerting. When distilling compounds such as hydrocarbons of various volatility it is important to ensure an inert atmosphere to lower the risk of explosions. In these experiments pressurized nitrogen gas was utilized to provide the inert atmosphere

required. Previous works have also proved that nitrogen is useful as it can provide a sweeping effect in addition to the inert capabilities of the gas. Injection of ambient temperature nitrogen gas had a negative effect on the premature condensing mentioned in the previous paragraph. In order to mitigate this effect, a large casserole with a lid was equipped with a copper coil including an inlet and an outlet for the nitrogen gas. A hot air gun was utilized to heat the copper coil and in effect, the nitrogen gas. The gas was routed into the microwave reactor, and into the boiling flask through modified glass tubes, as seen in Figure 48b. As the goal of the experiment is not to determine the effects of nitrogens sweeping effect, the flow rate of the injected nitrogen gas was not measured, however, the supply pressure of the gas was adjusted to the same level for each experiment. The final setup of the experiment is shown in Figure 48.

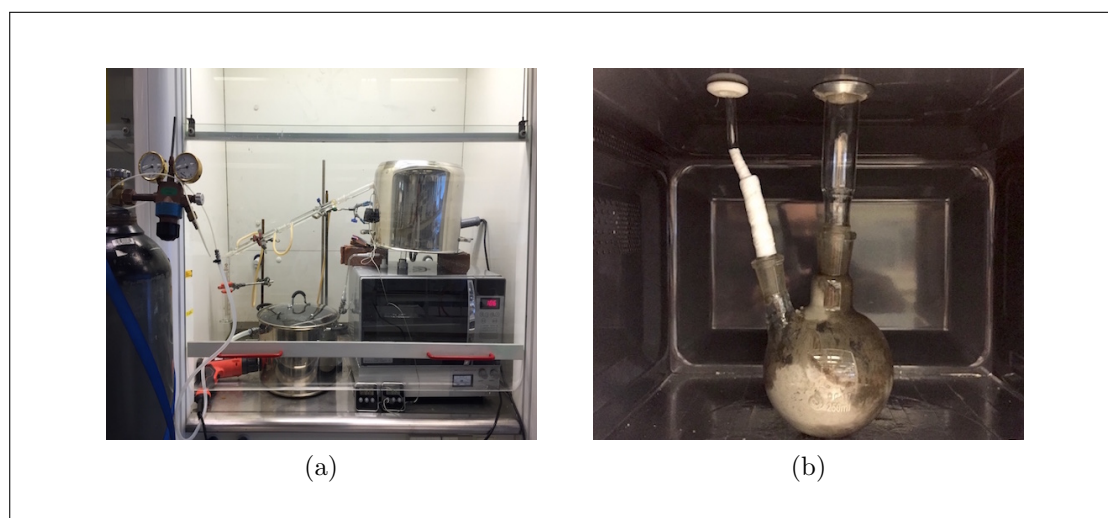


Figure 48: Final experimental setup

9.3 Methodology

A flowchart of the method developed for MW cuttings treatment is depicted in Figure 49. The experimental methodology to analyze collected samples are provided in Chapter 8. Typical sample sizes was 50 - 200 g. The experiment allowed for a variation of microwave power, treatment time, sample sizes, and the added volume of susceptors. In some cases the effect of re-mixing with additional susceptor was investigated by first running the experiment for a designated time, T_1 , and thereafter adding additional susceptor which was mixed into the sample. Afterwards, the experiment ran for a designated time, T_2 , causing the total runtime for each experiment to be $T_1 + T_2$. The experiments in Chapter 9.4.1 were analyzed in the retort while the experiments described in Chapter 9.4.2 were analyzed by automated solvent extraction. The volume of remaining susceptor was

recorded during the retort analysis, as this can be used as an indication of the amount of susceptor that will remain on the cuttings.

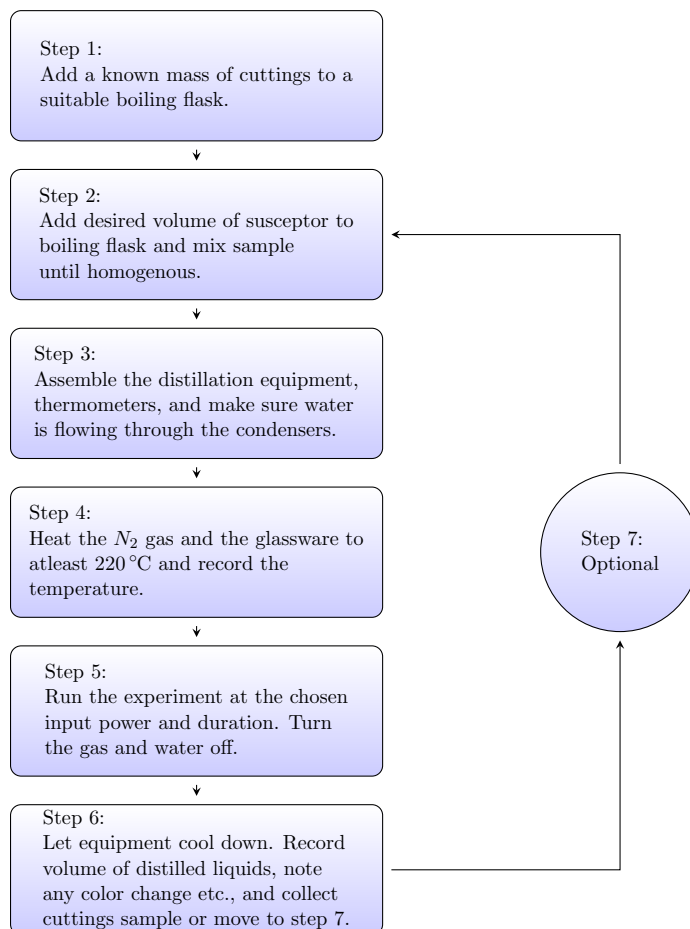


Figure 49: Cuttings treatment flow diagram

9.3.1 Wet cuttings experiment matrix

Table 20 depicts the experimental parameters used in the experiments involving centrifuged cuttings containing both oil and water. In these experiments the susceptor, amount of susceptor, and treatment time was variable.

Table 20: Centrifuged cuttings experiment matrix

| <i>Experiment #</i> | Parameters | | | | | | Distillate volume | | |
|---------------------|--|--|-------------------------|--------------------|--|---|---|---|--|
| | <i>Power input</i> ^c , W | <i>Time</i> ^a , min T_1 (T_2) | <i>Sample weight</i> ,g | <i>Susceptor</i> , | <i>Volume added</i> ,mL @ T_1 (T_2) | N_2 <i>temp.</i> , °C @ T_1 (T_2) | V_{liquid} , mL @ T_1 (T_2) | V_{polar} ^b , mL @ T_1 (T_2) | V_{oil} , mL @ T_1 (T_2) |
| 11 | 900 | 5 (5) | 200.0 | MEG | 40 (40) | 216 (216) | 51 (81) | 41 (75) | 10 (11) |
| 12 | 900 | 5 (-) | 200.0 | MEG | 40 (-) | 226 (-) | 51 (-) | 41 (-) | 10 (-) |
| 13 | 900 | 5 (5) | 200.1 | MEG | - (40) | 230 (230) | 28 (60) | 21 (50) | 7.5 (10) |
| 14 | 900 | 5 (-) | 200.0 | MEG | 20 (-) | 240 (-) | 45 (-) | 34 (-) | 11 (-) |
| 15 | 900 | 5 (-) | 201.6 | MEG | 10 (-) | 245 (-) | 39 (-) | 28 (-) | 11 (-) |
| 16 | 900 | 5 (-) | 200.7 | MEG | 5 (-) | 240 (-) | 34 (-) | 25 (-) | 9 (-) |
| 17 | 900 | 5 (5) | 200.0 | MPG | 40 (40) | 233 (230) | 54 (91) | 44 (79) | 10 (11) |
| 18 | 900 | 5 (-) | 200.6 | MPG | 20 (-) | 240 (-) | 45 (-) | 34 (-) | 11 (-) |
| 19 | 900 | 5 (-) | 201.1 | MPG | 10 (-) | 240 (-) | 36 (-) | 28 (-) | 8 (-) |
| 20 | 900 | 5 (5) | 200.1 | DEG | 40 (40) | 230 (230) | 47 (87) | 36 (70) | 11 (11.5) |
| 21 | 900 | 5 (5) | 202.3 | DEG | - (40) | 240 (240) | 29 (60) | 22 (49) | 7 (11) |
| 22 | 900 | 5 (5) | 200.6 | DPG | 40 (40) | 240 (243) | 44 (85) | 34 (74) | 9.5 (11) |
| 23 | 900 | 5 (-) | 200.0 | - | - (-) | 230 (-) | 31 (-) | 24 (-) | 7 (-) |

^a Total treatment time for each sample = $T_1 + T_2$. ^b V_{polar} represents all polar compounds.

^c Refers to magnetron input power.

9.3.2 Dry cuttings experiment matrix

Table 21 depicts the experimental conditions for tests that was performed using dry cuttings¹. In these experiments the type and amount of susceptor, and oil was the variable parameters.

Table 21: Dry cuttings experiment matrix

| <i>Experiment #</i> | Parameters | | | | | | |
|---------------------|-----------------------|------------------|-------------------------|------------|-----------------------|-------------------|-------------------------------|
| | <i>Power input, W</i> | <i>Time, min</i> | <i>Sample weight, g</i> | <i>Oil</i> | <i>OOC Initial, %</i> | <i>Susceptor,</i> | <i>Amount added, wt% (mL)</i> |
| 24 | 900 | 5 | 50.5 | Dodecane | 15.0 | MEG | 22 (10) |
| 25 | 900 | 5 | 51.1 | Dodecane | 15.1 | MEG | 33 (15) |
| 26 | 900 | 5 | 51.2 | Dodecane | 14.8 | MEG | 43 (20) |
| 27 | 900 | 5 | 104.3 | Dodecane | 14.8 | MEG | 27 (25) |
| 28 | 900 | 5 | 104.4 | Dodecane | 14.4 | MEG | 21 (20) |
| 29 | 900 | 5 | 101.3 | Dodecane | 15.4 | MEG | 33 (30) |
| 30 | 900 | 5 | 101.6 | Dodecane | 15.9 | Water | 25 (25) |
| 31 | 900 | 5 | 100.9 | Dodecane | 15.0 | Water | 30 (30) |
| 32 | 900 | 5 | 107.3 | Dodecane | 15.6 | Water | 33 (35) |
| 33 | 900 | 5 | 100.4 | Dodecane | 14.9 | Water | 40 (40) |
| 34 | 900 | 5 | 105.8 | Dodecane | 15.1 | Water | 43 (45) |
| 35 | 900 | 5 | 101.9 | Dodecane | 15.3 | Water | 20 (20) |
| 36 | 900 | 5 | 99.7 | Hexadecane | 15.3 | MEG | 22 (20) |
| 37 | 900 | 5 | 107.1 | Hexadecane | 14.4 | MEG | 26 (25) |
| 38 | 900 | 5 | 100.1 | Hexadecane | 15.1 | MEG | 33 (30) |
| 39 | 900 | 5 | 100.6 | Hexadecane | 15.2 | MEG | 39 (35) |
| 40 | 900 | 5 | 101.2 | Hexadecane | 15.1 | MEG | 44 (40) |
| 41 | 900 | 5 | 100.2 | Hexadecane | 15.3 | MEG | 50 (45) |
| 42 | 900 | 5 | 101.1 | Hexadecane | 15.0 | Water | 20 (20) |
| 43 | 900 | 5 | 102.0 | Hexadecane | 14.7 | Water | 25 (25) |
| 44 | 900 | 5 | 101.6 | Hexadecane | 15.1 | Water | 30 (30) |
| 45 | 900 | 5 | 101.7 | Hexadecane | 15.1 | Water | 34 (35) |
| 46 | 900 | 5 | 100.2 | Hexadecane | 15.3 | Water | 40 (40) |
| 47 | 900 | 5 | 100.2 | Hexadecane | 15.2 | Water | 45 (45) |

9.4 Results

9.4.1 Effects of susceptor on centrifuged cuttings oil removal

For experiment parameters the reader is referred to Table 20. From Figure 50 it is clear that the addition of susceptors has a significant impact on the initial recovery of oil when treated in the microwave setup described Chapter in 9.2. Treating 200 g of centrifuged cuttings for 5 minutes at 900 W without any addition of susceptor in experiment 23 removes approximately 50 % of the oil, causing the remaining OOC to be 3.8 % on a wet weight basis and 4 % on a dry weight basis.

The addition of 5 mL MEG in experiment 16 caused a decrease in the remaining OOC to 2.6 %, which represents a 5 % decline in oil content. Increasing the susceptor volume

¹Cuttings containing no water.

up to 10 mL MEG caused a further increase in oil removal causing the remaining oil content to be 1.6% on a dry basis in experiment 15, while the addition of 20 mL MEG caused the OOC to drop to 1.2% in experiment 14. When the sample was treated with 40 mL MEG in experiment 12 the remaining OOC was recorded to 1 wt%. In experiment 13, centrifuged cuttings were first treated for 5 min, remixed with 40 mL susceptor, and treated for additional 5 min which resulted in an OOC of 0.5%. By treating cuttings with 40 mL MEG for 5 min, and remixing the cuttings with another 40 mL of MEG the resulting OOC was recorded to 0.7%.

In experiment 17 the sample was treated twice with 40 mL MPG for 5 minutes which resulted in an OOC of 0.5%. In experiments 18, and 19, centrifuged cuttings were treated for 5 minutes with 20 mL and 10 mL MPG, respectively. The resulting oil on cuttings was 2.4% in both experiments.

Two experiments utilizing DEG as the susceptor were conducted. Treating 200 g of cuttings twice with 40 mL for 5 minutes gave a remaining oil content of 0.4% in experiment 20. An OOC of 0.6% was recorded when treating the centrifuged cuttings for 5 minutes following remixing with 40 mL DEG in experiment 21.

Treating cuttings twice with 40 mL DPG reduced the OOC to 0.9% in experiment 22.

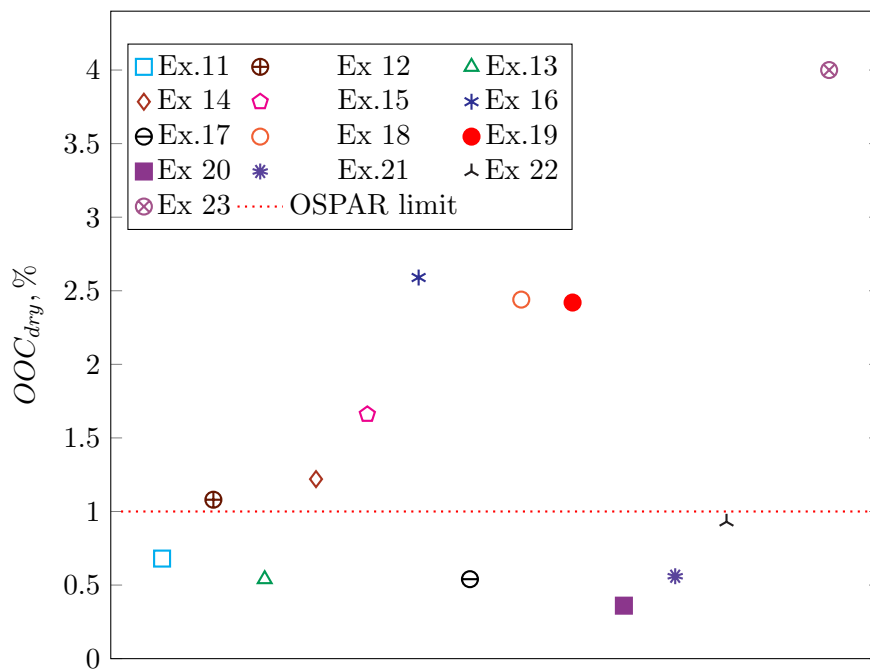


Figure 50: Retort analysis of experiments 11-23.

MEG and MPG does not suffer from any notable discoloration, DEG and DPG experience a moderate discoloration, whereas TEG was repeatedly subject to a high amount of discoloration. Treating cuttings with glycerol in a microwave caused the glycerol to immediately decompose. This behavior is in line with the theory presented in Chapter 6. After treatment the sample cuttings become very hard and resembles a type of *light expanded clay aggregate*, a material commonly utilized in construction. The aggregate seems to loose some of its hardness when it is broken up. Small variations in N_2 gas supply temperature does not seem to have a significant impact on the level of oil recovered.

Figure 51 gives an indication on the volume of susceptor that is still remaining on the cuttings after treatment, except for experiments 17 and 22. The volumes of susceptor remaining on the cuttings are varying from 4.4 mL in experiment 12 to 1 mL in experiment 11. It is difficult to identify a trend and it seems that the volume of susceptor remaining on the cuttings are relatively stable regardless of the type and added volume prior to the treatment.

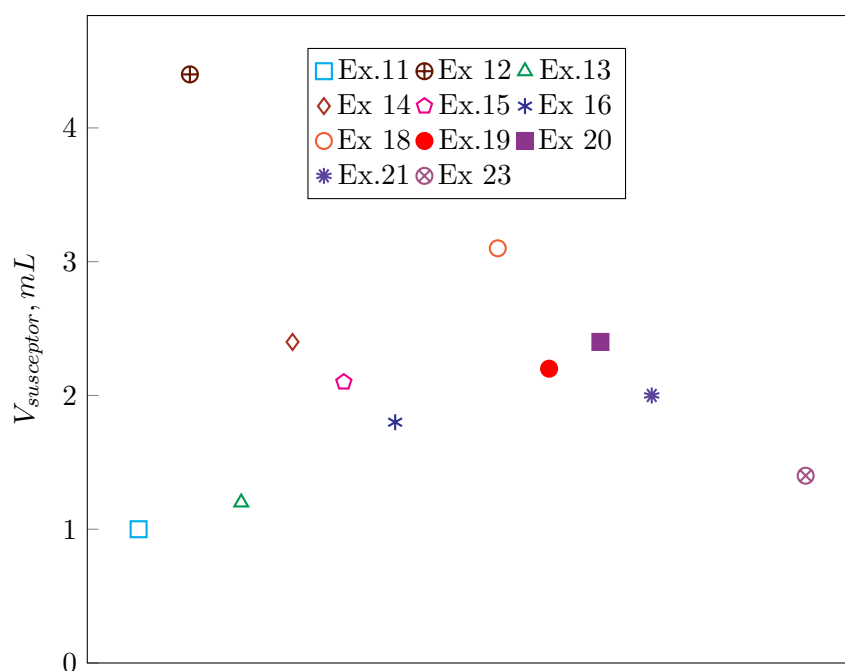


Figure 51: Volume of susceptor remaining after treatment.

9.4.2 Effects of susceptor on dry cuttings oil removal

Compared to the centrifuged cuttings which became very hard and resembled a light expanded clay aggregate, the dry cuttings prepared in the retort and treated in the microwave became less hard and remained more powder like. This can indicate that the retort affects the attraction forces that act between the cuttings particles.

Dodecane and water. Dry cuttings containing approximately 15 wt% dodecane oil, was treated with various amounts of water as microwave susceptor. The results are depicted in Figure 52. Exact experiment parameters is provided in Table 21. In experiment 35 20 wt% water was added to the sample and treated for 5 min in the microwave. The remaining OOC was recorded to 2.25 wt%. The OOC decreased to 1.72 % when 25 wt% water was added in experiment 30. A further decrease was observed in experiment 31 where 30 wt% water decreased the OOC to 0.65 %. The remaining oil on cuttings in experiment 32 was 0.99 % when 33 wt% water was added to the sample. In experiments 33, and 34, where 40 and 43 % water was added, the OOC was recorded to 0.78 % and 0.86 %, respectively. The results are depicted graphically in Figure 52.

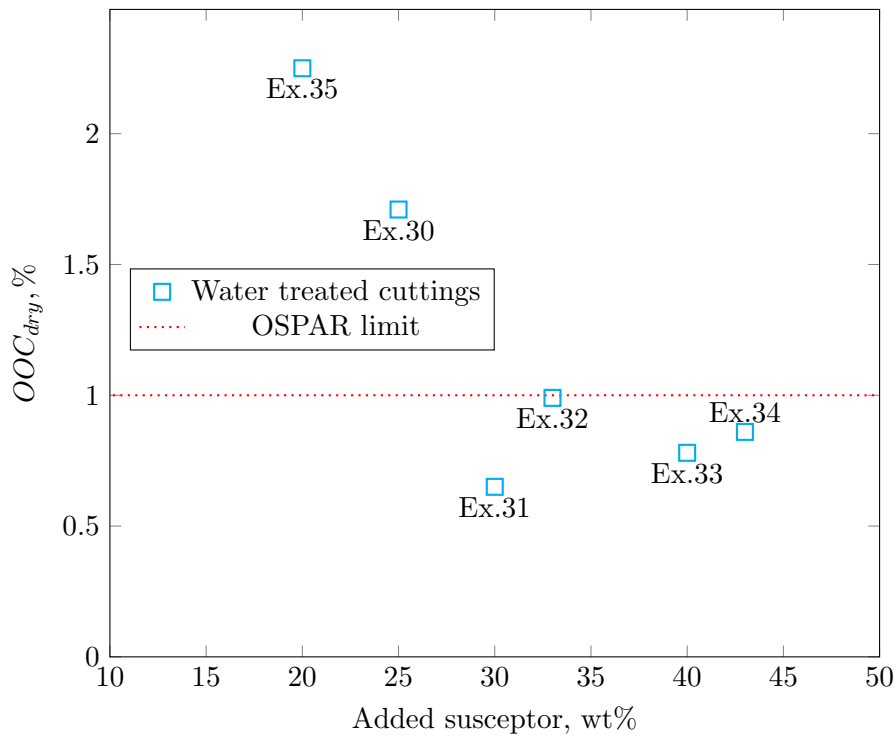


Figure 52: OOC of water treated cuttings contaminated with dodecane.

Dodecane and MEG. The oil on cuttings analysis of experiments 24-29 are depicted in Figure 53. In experiment 24, 22 wt% MEG was added to the sample and the sample was subjected to MW power for 5 min. The OOC was recorded to 0.05 %. In experiment 25, a sample containing 33 wt% MEG, was treated to an oil content of 0.02 wt%. When cuttings containing 43 % MEG (Experiment 26) was treated, the remaining oil on cuttings was recorded to 0.05 %. In experiment 27, the sample contained 27 wt% MEG, and the OOC was recorded to 0.028 %. In experiment 28 and 29, which contained 20 and 30 % MEG, the OOC was recorded to 0.026 and 0.027 wt%, respectively. Note that in experiments 24-26 the sample mass was approximately 50 g and in experiments 28-29 the sample mass was approximately 100 g. A comparison of the percentage oil removal is shown in Figure 54. MEG increased the oil separation compared to water.

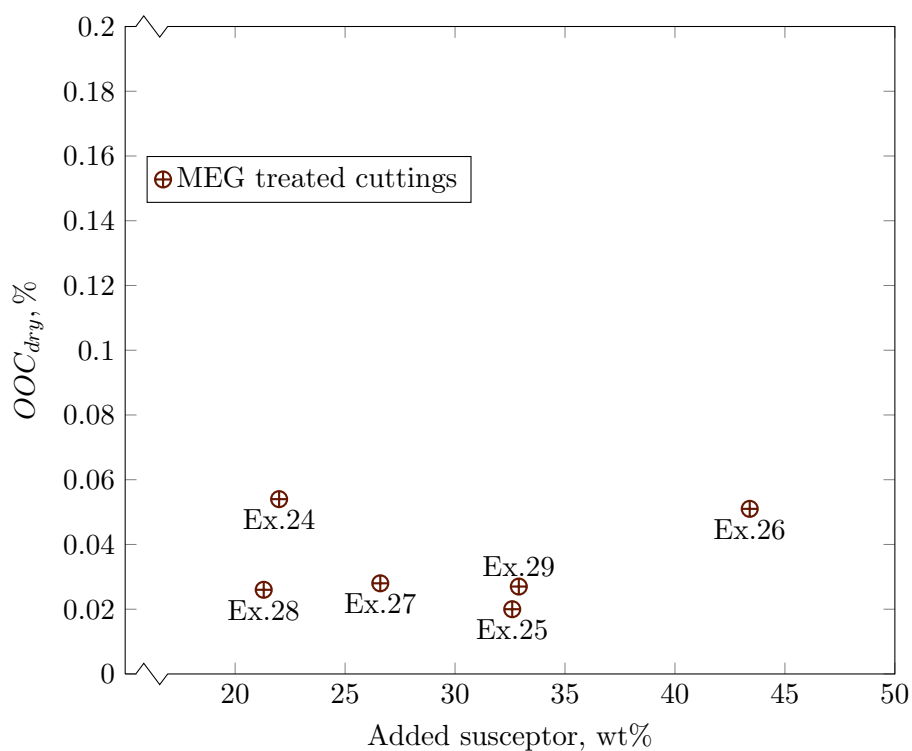


Figure 53: OOC of MEG treated cuttings contaminated with dodecane.

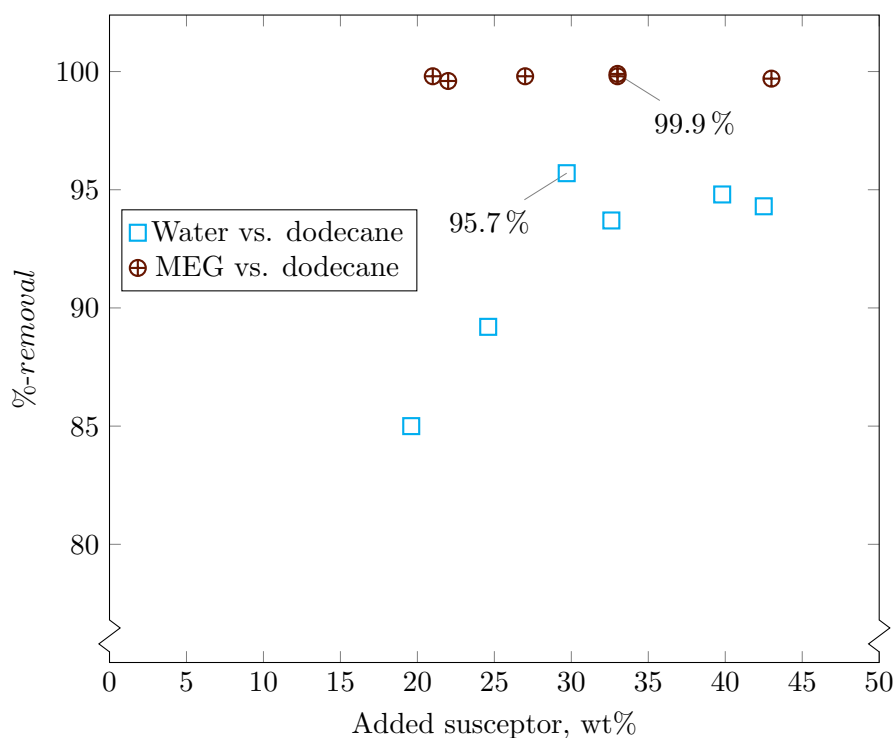


Figure 54: %-removal of dodecane

Hexadecane and water. Figure 55 depicts the results of the oil on cuttings analysis for experiments 42-47 (Table 21). All of the samples initially contained 15 wt% hexadecane. In experiment 42, a sample containing 20 wt% water was treated to an OOC of 8.6 wt%. When the sample contained 25 wt% water in experiment 43 the observed OOC was 9%. Similarly, the remaining oil on cuttings was 9 wt%, when the water content was 30% by weight in experiment 44. The observed OOC decreased to 7.7 wt% in experiment 45 when the sample contained 34% water. In experiments 46 and 47, which contained 40 and 45% water, the OOC was recorded to 8.5 and 8.6 wt%, respectively. The highest removal of hexadecane with water was 48.9%.

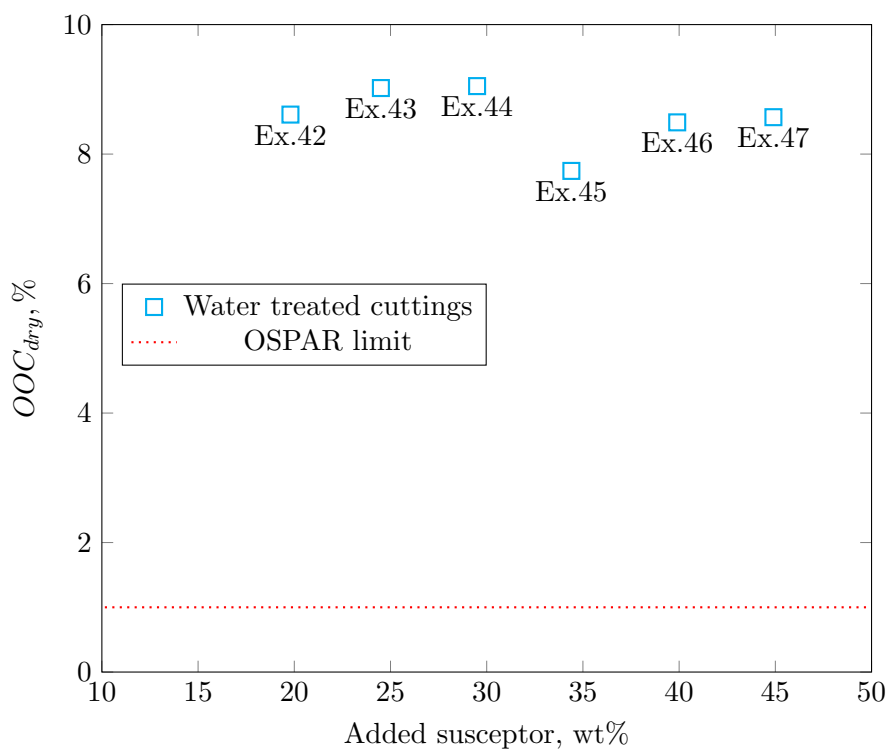


Figure 55: OOC of water treated cuttings contaminated with hexadecane.

Hexadecane and MEG. The effects of adding MEG to hexadecane contaminated cuttings is shown in Figure 56. For initial oil content refer to Table 21. A sample containing 22 wt% MEG was treated to 1.8% OOC in experiment 36. Increasing the amount of MEG to 26 wt% in experiment 37 caused a decrease in the OOC to 0.8 wt%. The addition of 33 wt% MEG in experiment 38 caused the observed oil on cuttings to be 0.5%. A sample containing 39 wt% MEG was treated to 0.45% in experiment 39. In experiment 40, a sample containing 44% MEG resulted in an OOC of 0.17%. A further increase in oil removal was achieved in experiment 41 when the amount of MEG was 50 wt%. The recorded oil on cuttings was 0.15%. The percent removals of hexadecane is depicted in Figure 57. The highest removal of hexadecane with MEG was 99.0%.

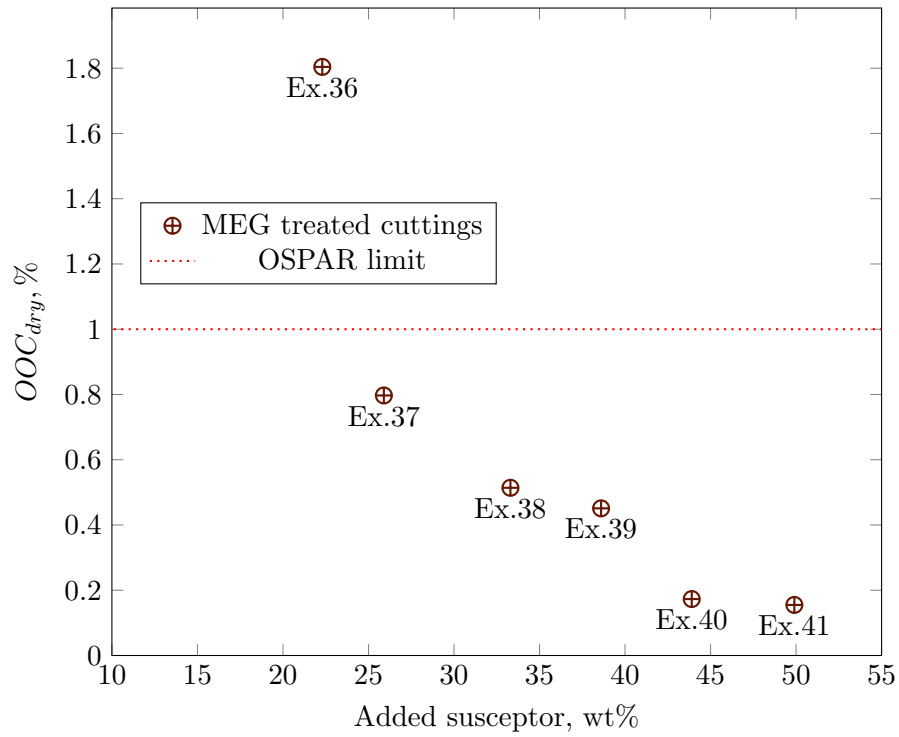


Figure 56: OOC of MEG treated cuttings contaminated with hexadecane.

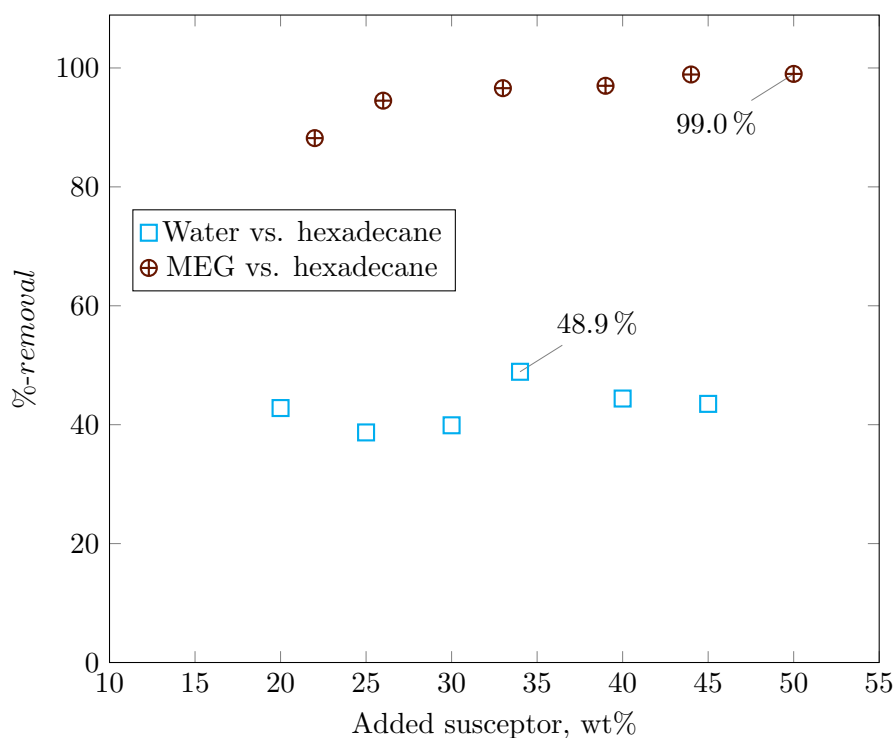


Figure 57: %-removal of hexadecane

9.5 Discussion

The treatment of centrifuged cuttings in Chapter 9.4.1 have shown that it is possible to achieve an OOC lower than the 1 wt% set by OSPAR by the use of polar organic liquids. The samples in these experiments were analyzed using the retort method. In the retort, inaccurate readings of the liquid receiving cylinder (as a result of high capillary forces), causes erroneous results. In experiments where a susceptor was employed there was no water left in the treated cuttings, thus there was no water in the retort receiving cylinder. The amount of oil was typically very low which caused an exact determination of M_{oil} to be difficult. Due to this, the results from the retort are weighted less. In retrospect it might have been better to analyze these samples using the soxtec method.

As discussed in Chapter 5.2, with water present in the cuttings the steam distillation process remain at a lower temperature (bp of water). As the water is vaporized, it is also likely that a significant amount of the susceptor was vaporized. Less susceptor is therefore available for dielectric heating and steam distillation of oil, as the sample become water free. Lower process temperature equals lower vapor pressure contribution from the oil. Ultimately, this leads to a lower oil recovery from the cuttings. If the sample was water free from the beginning or had less water content than 16% it could have improved the oil removal efficiency. After the samples had been treated in the microwave,

a cool down period followed before the sample could be safely handled. During this period, some of the oil could have evaporated. However, this error is difficult to mitigate and it is assumed to be insignificant compared to the oil remaining on the cuttings. The amount of susceptor remaining on the cuttings was relatively stable and not affected by the added amount prior to treatment. This suggests that it can be possible to recover most of the susceptor by distillation as long as the process of condensing is maintained properly.

It was possible to achieve an OOC of less than 1 % when dry cuttings contaminated with dodecane oil was treated with water. In experiments 31-34 the remaining oil on cuttings was fluctuating between 0.65 and 0.86 wt% which suggests that the limitation of the experimental setup had been reached for these parameters. Increasing the applied power, or the utilization of stirring may further help the oil desorption process (Pereira, 2012; Shang *et al.*, 2005a; Robinson *et al.*, 2012). The experiments were performed with the addition of 20 mL water and up to 45 mL, which, for a sample size of 100 g conforms to a water content from 20 to 45 % by weight. Considering that the TCC was restricted to an OOC of 0.05 % or less on the Martin Linge field, the amount of water that would have to be added to reach this goal is likely to be very high. Another solution could be to incorporate a polishing step to separate the last traces of oil from the cuttings. The TCC is most likely depending on a polishing step as well (Monsen & Michelsen, 2015), see Chapter 3.2.2.

By utilizing MEG as susceptor to treat dry cuttings contaminated with dodecane the remaining oil on cuttings was demonstrated to be very low. Even the addition of 22 wt% MEG to cuttings containing 15 wt% dodecane was successfully treated to 0.05 % on a dry weight basis. The boiling point of dodecane is in the lower range of what can be expected in a OBM base oil, so the oil content reported for these experiments is likely to be lower than the OOC for higher bp base oils with the particular equipment that was employed. Dodecane oil was observed to evaporate at some extent when left in a fume hood, it may be possible that this caused the reported OOC to be lower. However, a small amount of solvent is likely to remain in the oil which somewhat mitigates the effect of the evaporation of dodecane oil.

When using water to distill samples containing 15 % hexadecane on dry cuttings in experiments 42-45, the various amounts of added water had very little effect on the OOC of the treated sample. This is likely due to the low oil vapor pressure at the bp of water. All of the treated samples seemed to have a remaining OOC between 7.7 (Ex.45), and 9.0 % (Ex.43). The addition of 34 wt% water caused an OOC of 7.7 wt% in Experiment 45. However, the OOC increased when more water was added. This indicates that an OOC of 7.7 % is unlikely. A decrease from 15 to approximately 9 % oil for all samples is more likely. Samples containing a high hexadecane content was not successfully treated with water as susceptor. This illustrates that it can be unlikely to achieve the required OOC with the only MW absorber being water or that an extremely large amount of water, and energy have to be supplied in order to achieve the desired OOC. A better setup, and optimization of sweep gas may also improve the oil separation when water is the susceptor.

As previously discussed in Chapter 4.3 (Pereira, 2012; Shang *et al.*, 2005a,b), N_2 sweep gas was flowing through the sample. This is believed to be more beneficial than the “surface drying” effect that most likely was the case in the work of this thesis. Figure 20 shows that a decrease from 5 to 2% was achievable. The sample was treated at 720 W with a N_2 flow rate of 15 L min^{-1} . The power levels are comparable to the ones expected in the work of this thesis. A direct comparison of the results may therefore be possible. The oil related to the sample treated in Figure 20, included C_{11} - C_{17} components. The bulk composition was C_{12} - C_{14} chains (Pereira, 2012). In this thesis, C_{12} oil was used, so this can provide a good comparison. In experiments 24-29, cuttings contaminated with 15% dodecane were treated. The lowest recorded OOC was 0.02%, and the highest was 0.05%. Another important observation is the fact that in this work, N_2 sweep gas was not supplied from below the sample like it was in Pereira (2012). Allowing the sweep gas to percolate through the sample improves heating, and may cause additional liquid separation. These benefits was not present in this work. Further improvements on the OOC is therefore likely through sweep gas optimization.

The addition of MEG to dry cuttings contaminated with 15 wt% hexadecane caused an incremental decrease in the recorded OOC, as expected. This truly depicts the potential of the technology. An OOC of less than 1% was achieved when 26 wt% MEG was added to the sample. A stepwise decrease was observed when more susceptor was added. Treating samples containing 50 wt% MEG resulted in an OOC of 0.15 wt% which is significantly lower than the OSPAR limit. The 0.05% TCC requirement was not met, however, it is likely that it is possible to reach this goal by optimizing the process in terms of the amount of susceptor added, residence time, power density, and applicator design as well as mixing and sweep gas. Many of the other works cited, were able to reduce the OOC below 1% as well. It should be noted that for example in the work by Pereira (2012), the cuttings contained a maximum of 10.3% oil. Ultimately, the percentage of oil reduction, was higher in this work.

Mixing was not present in the experiments of this thesis. As discussed in Chapter 4.3, Robinson *et al.* (2012) and Junior *et al.* (2015) investigated the effects of mixing. In these studies it was demonstrated that mixing of the sample could overcome the limitations of non-uniformity of heating, and penetration depth. A significant increase in oil removal was also evident. In addition to a proper sweep gas set-up, mixing have the possibility to further increase the separation efficiency. In combination with susceptors, it is possible that this technology will be very attractive in the near future.

The attraction forces between retorted cuttings, oil, and water/susceptor are most likely not as strong as the attraction forces in centrifuged cuttings, which may cause the oil content where dry cuttings was used to be lower than the result would be if cuttings which was not subjected to the high temperature in the retort. As the dry cuttings was treated immediately after the addition of oil and susceptor there might not be a sufficient amount of time for the cuttings to establish a strong equilibrium condition in terms of attraction forces, which may cause the oil desorption to require less energy and volume of susceptor than if a strong equilibrium condition was established. However, based on the results it is highly recommended that Norwegian-Group pursue this concept further.

9.6 Conclusion

The general conclusion is that it is possible to successfully treat cuttings well below the OSPAR limit with susceptors. An incremental reduction of the OOC was possible by increasing the amount of susceptor added. A higher water content negatively affected the oil removal, due to lowering of the process temperature. Efficient pre-treatment is therefore important. Based on the visual analysis of the distilled liquids, MEG is believed to be the most suited susceptor.

The volume of susceptor remaining on the cuttings after treatment seemed to be consistent, and unaltered by the initial amount.

The treatment of centrifuged cuttings left the sample resembling a light expanded clay aggregate. The aggregate was very hard and difficult to crush into smaller pieces of rock. This is most likely beneficial when considering the discharge of treated cuttings. If mixing is applied, the aggregate will most likely be broken into smaller fragments.

When the EM absorbing phase was water, cuttings contaminated with a low bp oil, could be treated within OSPAR limits. When the oil contaminant was a high bp oil, it was not possible to reduce the OOC further than 7% with the tested amounts of water. In general, water alone is not considered to provide sufficient oil removal.

The addition of MEG significantly enhanced the oil separation efficiency. When the contaminant was a low bp oil, the oil retention was below 0.05% in several cases. Cuttings contaminated with a high bp oil, was successfully treated to 0.15%. By implementation of mixing, and optimized sweep gas, a further OOC reduction is considered possible. A continuous cuttings treatment plant, of very high efficiency, is likely to be achievable with susceptors and microwaves.

Chapter 10

Technology applications

10.1 Not only for dielectric heating

The advantages that susceptors offer can not only be utilized in dielectric heating. Thermal processes employed by technologies such as the TCC, may also take advantage through the replacement of water with other compounds. In this type of treatment, the benefit would only arise from lower energy requirements for vaporization. As claimed by [Kleppe \(2009\)](#), water represents 60 % of the energy requirement in a cuttings treatment process. If water was replaced with a compound where the energy requirements was less, a lowering of the energy requirement would likely occur. However, the full potential of energy decrease that dielectric heating represents would not be present in such a case.

10.2 Geography unlimited

The main focus of this thesis have been the NCS and OSPAR area. However, the oil and gas industry is *international* in nature. [Ormeloh \(2014\)](#) states that 55 TCC units are scattered over the globe. Both in countries where discharge is subject to strict regulation (e.g. Norway), and countries with less strict requirements apply (e.g. Congo). Due to the potential energy savings of the combined microwave, and susceptor technology, there should be no reason that the marked of such a technology is limited.

The literature investigated in this thesis, gave little evidence of the footprint, and weight that can be expected from a MW cuttings plant. The TWMA Rotomill (TCC) is 12.8 m long, 3.5 m wide, and 4.35 m high. The equipment is divided in three containerized modules. The operational weight is specified to 63.5 t. Where the mill module weighs 19 t, the process module weighs 17 t, and the engine module weighs 27.5 t ([Ormeloh, 2014](#)).

In comparison, a 100 kW microwave generator weighs approximately 2.7 t. The size of the generator is only 1.2 m wide, 1.8 m long, and 2 m high ([Thermex-Thermatron, 2016](#)). The waveguide are not included in the previous remark. The size of a waveguide

is very much dependent on the frequency of operation. One of the configurations that was used by [Pereira \(2012\)](#), consisted of two applicators in series. The report states that the length of this setup was approximately 3 m. Based on these observations, it may be possible, that a full scale MW treatment can have less footprint, and weight, than the TCC. More research is required to accurately predict the full scale size of a MW cuttings treatment plant.

The size and weight of the equipment is likely to increase with capacity. A high treatment capacity is needed for offshore implementation. Microwave equipment has a small footprint, and weight. In combination with the high energy efficiency, there may be an opportunity for the construction of a small, mobile unit. Such a unit may easily be implemented in hard to reach places for *in-situ* remediation. One example of where this could be implemented is Nigeria. The United Nations Environment Programme (UNEP) is, upon request from The Federal Republic of Nigeria, assessing the environmental, and health impacts of oil contamination in Ogoniland of the Niger Delta. The assessment will also include options for remediation ([UNEP, 2016b](#)).

Chapter 1

Conclusions

The goal of this thesis was, through theory and experimental work, to gain proof of concept that the principle of steam distillation in combination with susceptors will allow cuttings to be treated within the legislative requirements set by the OSPAR. To shed light on the potential benefits of this technology, and how it can compete with the current and other upcoming technologies.

11.1 Evaluation of dielectric heat sources

Many workers have successfully treated cuttings within environmental requirements by the use of microwave heating. To the authors' knowledge, no applications of RF heating have been found for this purpose. The high power density that a microwave heating system offers is highly attractive and is the recommended thermal heating source.

11.2 Evaluating the use of susceptors

Through the theoretical analysis in Chapters 5 and 6, and the experiments performed in Chapters 7 and 9, the following conclusions can be drawn.

Steam distillation of oil by the use of water, requires a high amount of energy. A higher process temperature, will cause a higher vapor pressure contribution from the oil. In order to achieve a higher process temperature, water can be replaced with environmentally friendly polar organic compounds. Depending on the compound, the energy requirement will be significantly reduced.

Of the investigated organic compounds, glycols are the most suitable. Especially MEG, as it did not seem to decompose significantly during MW treatment. The fact that MEG is currently on OSPAR's PLONOR list contributes to its value as the recommended choice of susceptor.

Based on the reviewed literature, water was the only MW absorbing phase, and the limiting factor for oil removal. In this work, when distilling with susceptors, it was

found that water had a negative effect on the treatment efficiency, due to lowering of the process temperature.

The treatment of centrifuged cuttings left the sample resembling a light expanded clay aggregate. This is most likely beneficial when considering the discharge of treated cuttings. The treatment of retorted cuttings did not result in the same hardy aggregate. More research is required in order to determine if water is the reason for this behavior, or if the attractive forces was destroyed in the retort.

Susceptors was added to centrifuged cuttings containing 7-8 wt% oil, and 16 - 17 % water. In several cases, the OOC was reduced to 0.5 % or less, which is below the environmental discharge limit. In samples where no susceptor was added, the OOC was recorded to 4 % on a dry basis. This clearly shows that the use of susceptors can increase oil separation from cuttings.

The OOC of susceptor treated dry cuttings was recorded to well below the OSPAR limit of 1 %. When a low bp oil was the base, OOC levels below 0.05 % was possible. When the base oil had a high bp the OOC was reduced to 0.15 %. The same level of treatment with water did not match the results obtained with MEG. A very low OOC was obtainable when there was no water content in the cuttings. It is therefore highly recommended to eliminate, or lower, the amount of water present in the cuttings. This applies when susceptors are to be used.

The recovery of the vaporized susceptor is possible through condensing. Current technology also uses this principle. The use of susceptors most likely require one additional condenser, compared to existing thermal desorption methods. Some of the susceptor was shown to remain on the cuttings post treatment. Recovering susceptor from treated cuttings may be accomplished through centrifugal separation. More research with respects to the amount of susceptor that will remain on the cuttings and the method of recovery is needed.

11.3 Conveyor configurations

Norwegian-Groups treatment concept is still in the early stages of development. The methods of conveying in other works have been a flat bed conveyor. With the exception of Cutcube, which utilize a screw conveyor. It is difficult to give a recommendation at this stage. However, screw conveying have the added benefit of stirring the cuttings during treatment. Stirring can increase the oil separation from cuttings. The presence of a screw conveyor is likely to complicate the design of a suitable applicator. One of the benefits of the flat bed conveyor is that it allows for the investigation of bed height adjustments. Another benefit offered by the bed conveyor is that the cuttings, which may become hardy agglomerates, are not broken up into smaller fractions. In order for Norwegian-Group to explore the concept further, a continuous MW processing rig of pilot size is very useful, if not needed. In this respect, a flat bed conveyor is a good choice. The use of such a conveyor is found many places in the literature, and experience may be drawn from that.

11.4 BAT and BEP potential

It is believed that the use of susceptors in combination with microwaves can challenge the TCC technology as BAT. A decrease in energy requirement to treat cuttings is evident with the use of microwaves compared to the TCC. Additional reduction in energy requirements is possible with the use of susceptors. The TCC energy requirement was 133 kWh t^{-1} to treat 5 t cuttings. The use of microwaves and susceptors can reduce the requirement to 24 kWh t^{-1} in a best case scenario. In order to determine the actual energy requirements to treat cutting with the use of susceptors and microwaves, the use of a continuous processing rig is necessary. Energy requirements have shown to be significantly less in continuous processing than batch processing.

Chapter 12

Further work

In this thesis, an overall indication of the benefits of microwave treatment in combination with susceptors have been presented. More research is required in most aspects of the treatment concept. Including susceptors, pretreatment, sweep gas optimization, mixing, and conveying. Suggested research are itemized below.

- The amount of susceptors added are important as they represent value. Therefore it is recommended that more research is directed towards finding the optimal ratio of added susceptor to the initial oil content.
- It was shown that water lowered the treatment efficiency of susceptors. Although it may be difficult to achieve a cuttings feed that are completely water-free, a lower water content is beneficial. It is suggested that future endeavors focus on a pretreatment step that effectively lowers the liquid content of the cuttings. This will enable a more efficient treatment process. The author recognizes that an ongoing research on this matter is performed by Norwegian-Group, parallel to the work performed in this thesis.
- An optimization of the sweep gas set up can increase oil separation. It is therefore recommended that this is a priority in future research. Determination of the drying effects that heated nitrogen gas is also of interest.
- Mixing of the sample during treatment is believed to enhance oil separation significantly. Upgrading the microwave set up to include mixing is included in the recommended further work.
- Research the possibilities to replace nitrogen sweep gas with steam.
- Estimate the footprint of a MW treatment cuttings plant in order to assess the suitability for implementation offshore.
- Research the possibilities of an onboard nitrogen generator. Membrane separation is one possibility.

Bibliography

- Ahnell, A., & O'Leary, H. 2008. General Introduction. *Chap. 1 of:* Orszulik, Stefan T. (ed), *Environmental Technology in the Oil Industry*. Springer Science + Business Media B. V.
- Alfa-Laval. 2016. *Alfa Laval - disc stack separation technology*. http://www.alfalaval.com/globalassets/documents/industries/pulp-and-paper/pchs00022en_lowres.pdf. [Accessed 23.06.2016].
- Anderson, Shirley. 2004. Soxtec: Its Principles and Applications. *Chap. 2 of:* Luthria, D. L. (ed), *Oil Extraction and Analysis: Critical Issued and Competitive Studies*. The American Oil Chemists Society.
- API. 2014. *13B-2 - Recommended practice for Field Testing Oil-Based Drilling Fluids*.
- Armarego, W. L. F., & Chai, Christina Li Lin. 2013. *Purification of laboratory chemicals*. Butterworth-Heinemann.
- Ashenhurst, James. 2016a (February). *3 Trends That Affect Boiling Points*. <http://www.masterorganicchemistry.com/2010/10/25/3-trends-that-affect-boiling-points/>. [Accessed 23.06.2016].
- Ashenhurst, James. 2016b (February). *The Four Intermolecular Forces and How They Affect Boiling Points*. <http://www.masterorganicchemistry.com/2010/10/01/how-intermolecular-forces-affect-boiling-points/>. [Accessed 23.06.2016].
- Averill, Bruce A., & Eldredge, Patricia. 2011. *General Chemistry: Principles, Patterns, and Applications*. Flatworld Knowledge Book.
- Bakke, Torgeir, Klungsøyr, Jarle, & Sanni, Steinar. 2013. Environmental impacts of produced water and drilling waste discharges from the Norgwegian offshore petroleum industry. *Marine Environmental Research*, 1564–169.
- Ball, David W., Hill, John W., & Scott, Ronda J. 2011. *The Basics of General, Organic, and Biological Chemistry*. Flatworld Knowledge Book.
- Barbooti, Mahmood M., & Al-Sammerrai, Dhoaid A. 1986. Thermal Decomposition of Citric Acid. *Thermochinica Acta*, **98**, 119–126.

Bibliography

- Berger, L. I. 2015. Dielectric strength of insulating materials. *In*: Haynes, William M. (ed), *CRC Handbook of Chemistry and Physics*, vol. 96. CRC Press.
- Bernier, Rene, Garland, Emmanuel, Glickman, Andy, Jones, Fred, Mairs, Heide, Melton, Rodger, Ray, Jim, Smith, Joseph, Thomas, Dominic, & Campbell, John. 2003. *Environmental aspects of the use and disposal of non aqueous drilling fluids associated with offshore oil & gas operations*. Report 342. International Association of Oil & Gas Producers.
- Besson, Thierry, & Kappe, C. Oliver. 2013. Microwave Susceptors. *Chap. 7 of: de la Hoz, Antonio, & Loupy, André (eds), Microwaves in Organic Synthesis*. Wiley-VCH.
- Blytt, Line Diana, Vik, Eilen Arctander, Stang, Pascale, Hennings, Liv B., & Kjønne, Ocelie. 2014. *Characterising Thermal Treated OBM Drill Cuttings*. Tech. rept. Aquateam COWI AS.
- Bogdal, D. 2006. *Tetrahedron Organic Chemistry Series, Volume 25 : Microwave-assisted Organic Synthesis : One Hundred Reaction Procedures*. Elsevier Science & Technology.
- Bourgoyne, Adam T., Millheim, Keith K., Chenevert, Martin E., & Jr., F.S. Young. 1986. *Applied Drilling Engineering*.
- Bykov, Yu. V., Rybakov, K. I., & Semenov, V. E. 2001. High-temperature microwave processing of materials. *Journal of Physics D: Applied Physics*.
- Caenn, Ryen, & Chillingar, George V. 1996. Drilling fluids: State of the art. *Petroleum Science and Engineering*, **14**, 221–230.
- Caenn, Ryenn, Darley, H. C. H., & Gray, George R. 2011. *Composition and Properties of Drilling and Completion Fluids*. Elsevier.
- Cannon, R. W., & Martin, Dale. 2001. Reduction of Synthetic Based Fluid Discharges Offshore by the Use of Vertical Basket Centrifuges. *Society of petroleum engineers*.
- Chaîneau, Claude-Henri, Setier, Jean-Claude, & Morillon, Anne. 2002. Is Bioremediation A solution for the Treatment of Oily Waste ? *Society of petroleum engineers*.
- ChemSpider. 2016. *Search and share chemistry*. <http://www.chemspider.com/>. [Accessed 23.06.2016].
- Chen, M. and Siochi, E. J., Ward, T. C., & Mcgrath, J. E. 1993. Basic Ideas of Microwave Processing of Polymers. *Polymer engineering and science*.
- Cheremisinoff, Nicholas P. 2003. *Industrial solvents handbbok*. Marcel Dekker, Inc.
- Chickos, James S., & Acree Jr., William E. 2003. Enthalpies of Vaporization of Organic and Organometallic Compounds, 1880-2002. *Journal of Physical and Chemical Reference Data*, **32**(2), 519–878.

Bibliography

- Clark, Jim. 2004. *Introducing Amides*. <http://www.chemguide.co.uk/organicprops/amides/background.html#top>. [Accessed 23.06.2016].
- Dev, S. R. S., Birla, S. L., Raghavan, G. S. V., & Subbiah, J. 2012. Microbial decontamination of food by microwave (MW) and radio frequency (RF). In: Demirci, Ali, & O Ngadi, Michael (eds), *Microbial Decontamination in the Food Industry: Novel Methods and Applications*. Woodhead Publishing.
- Dow. 2016a. *LTTF - DOWCAL, DOWTHERM SR-1, DOWTHERM 4000, DOWFROST - Thermal Degradation*. http://dowac.custhelp.com/app/answers/detail/a_id/11979. [Accessed 23.06.2016].
- Dow. 2016b. *LTTF - Signs of Glycol Fluid Degradation*. http://dowac.custhelp.com/app/answers/detail/a_id/9425. [Accessed 23.06.2016].
- Doyle, A.B., Pappworth, S.S.R., & Caudle. 2008. Drilling and Production Discharges in the Marine Environment. *Chap. 6 of: Orszulik, Stefan T. (ed), Environmental Technology in the Oil Industry*. Springer Science + Business Media B. V.
- El-sayed, Abdullah, & El-Naga, Kamal H. Abu. 2001. Treatment of drill cuttings. *Society of petroleum engineers*.
- EPA. 1993. *Development Document For Effluent Limitations Guidelines and New Source Performance Standards for the Offshore Subcategory of The Oil And Gas Extraction Point Source Category*. U.S. Environmental Protection Agency.
- EPA. 1996. *3540C - SOXHLET EXTRACTION*.
- Fabel-Media. 2014. *Produktfilm - Cubility Cutcube*. <https://vimeo.com/96201148>. [Accessed 23.06.2016].
- Gabriel, Camelia, Gabriel, Sami, Grant, Edward H., Halstead, Ben S. J., & Mingos, D. Michael P. 1998. Dielectric parameters relevant to microwave dielectric heating. *Chemical Society Reviews*, **27**, 213–223.
- Growcock, Fred, & Harvey, Tim. 2005. *Drilling Fluids Processing Handbook*. Gulf professional publishing. Chap. 2.
- Gupta, Manoj, & Wai Leong, Eugene Wong. 2011. *Microwaves and Metals*. Singapore: Singapore: John Wiley & Sons (Asia) Pte Ltd. this chapter contains sections titled: development of microwave heating characteristics of microwave heating types of microwave heating future developments summary references.
- Halliburton. 2014. *Thermomechanical Cuttings Cleaner - Data sheet*. http://www.halliburton.com/public/bar/contents/Data_Sheets/web/Sales_Data_Sheets/H010843.pdf. [Accessed 23.06.2016].

Bibliography

- IPIECA. 2009. *Drilling fluids and health risk management - A guide for drilling personnel, managers and health professionals in the oil and gas industry*. Tech. rept. OGP.
- Johnston, Carey A., & Rubin, Marvin. 2000. *Development Document for Final Effluent Limitations Guidelines and Standards for Synthetic-Based Drilling Fluids and other Non-Aqueous Drilling Fluids in the Oil and Gas Extraction Point Source Category*. Tech. rept. United States Environmental Protection Agency.
- Junior, Irineu Petri, Pereira, Marina S., dos Santos, Jessika M., Duarte, Claudio R., Ataide, Carlos H., & de A. Panisset, Curt M. 2015. Microwave remediation of oil well drill cuttings. *Journal of Petroleum Science and Engineering*, 23–29.
- Karas, Lawrence, & Piel, W. J. 1994. Ethers. In: Howe-Grant, Mary (ed), *Kirk-Othmer Encyclopedia of Chemical Technology*, vol. 9. John Wiley & Sons.
- Karlsen, Kjersti Reppen. 2013. *Vurdering av oljeholdig avfall fra petroleumsvirksomheten til havs*. Report. DNV.
- King, S. 2014. *Introduction to Organic Molecules and Functional Groups*. http://ocw.uci.edu/upload/files/51a_chapter_3_2014.pdf. [Accessed 23.06.2016].
- Kirkness, Alister, & Garrick, David. 2008. Treatment of Nonaqueous-Fluid-Contaminated Drill Cuttings—Raising Environmental and Safety Standards. *Society of petroleum engineers*.
- Kleppe, Stein. 2009. Reusing Recovered Base Oil from OBM Cuttings. *Society of petroleum engineers*.
- Loidreau, Yvonnick, & Besson, Thierry. 2011. Microwave-assisted thermal decomposition of formamide: a tool for coupling a pyrimidine ring with an aromatic partner. *Tetrahedron*, **67**(26), 4852–4857.
- Love, Wayne. 1995. Magnetrons. In: Koryu Ishii, T. (ed), *Handbook of Microwave Technology*. Academic Press.
- Lunde, Sindre Åse. 2015. *ENERGY EFFICIENT DRILL CUTTINGS TREATMENT PLANT DESIGNED BY NORWEGIAN-GROUP AS: A FEASIBILITY STUDY*. Thesis, University of Stavanger.
- Mattikow, M., & Cohen, B. 1943. Behavior of Glycerin in the Presence of Alkali at High Temperatures. *Journal of Oil & Soap*, **20**, 135–136.
- Maxwell, J. C. 1865. A Dynamical Theory of the Electromagnetic Field. *Philosophical Transactions of the Royal Society of London*, **155**(January), 459–512.
- Mehdizadeh, Mehrdad. 2009. *Microwave/RF Applicators and Probes for Material Heating, Sensing, and Plasma Generation : A Design Guide*. Elsevier Science & Technology.

Bibliography

- Meredith, Roger. 1998. *Engineers Handbook of Industrial Microwave Heating*. The Institution of electrical engineers.
- Metaxas, A. C., & Meredith, R. J. 1983. *Industrial microwave heating*. Peter Peregrinus Ltd.
- Miller, David J. 1991. Aldehydes. In: Howe-Grant, Mary (ed), *Kirk-Othmer Encyclopedia of Chemical Technology*, vol. 1. John Wiley & Sons.
- Monsen, Stein Kyrre, & Michelsen, Eirik. 2015. *A method for reducing the amount of oil in an oil containing mixture*. WO Patent App. PCT/NO2014/050,207.
- Morris, Ron, & Seaton, Simon. 2006. Design and Testing of Bulk Storage Tanks for Drill Cuttings Offers Operators Safer Solution in Zero Discharge Operations. *AADE*.
- Murray, A. J. and Kapila, M., Ferrari, G., Degouy, D., Espagne, B. J., & Handgraaf, P. 2008. SPE 116169 Friction-Based Thermal Desorption Technology: Kashagan Development Project Meets Environmental Compliance in Drill-Cuttings Treatment and Disposal. *Society of petroleum engineers*.
- NEA. 2014. *Boring av Produksjonsbrønner - Martin Linge PL 043*. http://www.miljodirektoratet.no/Documents/Nyhetsdokumenter/martinlinge_3609-2013-tillatelse040814.pdf. [Accessed 23.06.2016].
- NEA. 2015 (November). *Revisjonsrapport: Revisjon ved Martin Linge*. <http://www.miljodirektoratet.no/Documents/Nyhetsdokumenter/martinlinge-revisjon-total201115.pdf>. [Accessed 23.06.2016].
- NIST. 2016. *NIST Chemistry WebBook*. <http://webbook.nist.gov/chemistry/>. [Accessed 23.06.2016].
- NOGA. 2015. *Environmental report 2015*. Tech. rept. Norwegian Oil & Gas Association.
- NPD. 2016 (January). *Factpages - wellbore statistics*. <http://factpages.npd.no/factpages/>. [Accessed 21.01.2016].
- Ophardt, Charles E. 2003. *Virtual Chembook - Elmhurst College*. <http://chemistry.elmhurst.edu/vchembook/213organicfcgp.html>. [Accessed 23.06.2016].
- Ormeloh, Jan. 2014. *Thermomechanical Cuttings Cleaner - Qualification for Offshore Treatment of Oil Contaminated Cuttings on the Norwegian Continental Shelf and Martin Linge Case Study*. Thesis.
- Osepchuk, John M. 2002. Microwave Power Applications. *IEEE Transactions on microwave theory and techniques*, **50**(3), 975–985.
- OSPAR. 2000. *Decision 2000/3 - On the use of Organic Phase drilling fluids (OPF) and the Discharge of OPF-contaminated Cuttings*. <http://www.ospar.org/work-areas/oic>. [Accessed 23.06.2016].

Bibliography

- OSPAR. 2016. <http://www.ospar.org>. [Accessed 23.06.2016].
- Pereira, Igor S. M. 2012. *Microwave Processing of Oil Contaminated Drill Cuttings*. Ph.D. thesis, University of Nottingham.
- PSA. 2015. *The activities regulation*. http://www.psa.no/activities/category399.html#_Toc407534829. [Accessed 23.06.2016].
- Reiersen, L.O., Gray, J.S., & Palmork, K.H. 1989. Monitoring in the vicinity of oil and gas platforms; results from the Norwegian sector of the North Sea and recommended methods for forthcoming surveillance. *Pages 91–117 of: Engelhardt, F. R., & Ray, J. P (eds), Drilling wastes : proceedings of the 1988 International Conference on Drilling Wastes Calgary, Alberta, Canada, 5-8 April*. Elsevier.
- Roach, Brian. 1995. Klystrons. *In: Handbook of Microwave Technology*. Academic Press.
- Robinson, J. P., Kingman, S.W., & Onobrakpeya, O. 2008. Microwave-assisted stripping of oil contaminated drill cuttings. *Journal of Environmental Management*, **88**, 211–218.
- Robinson, J. P., Kingman, S.W., Snape, C.E., Barranco, R., Shang, H., Bradley, M.S.A., & Bradshaw, S.M. 2009. Remediation of oil-contaminated drill cuttings using continuous Remediation of oil-contaminated drill cuttings using continuous microwave heating. *Chemical Engineering Journal*, 458–463.
- Robinson, J. P., Kingman, S.W., Lester, E. H., & Yi, C. 2012. Microwave remediation of hydrocarbon-contaminated soils – Scale-up using batch reactors. *Separation and Purification Technology*, **96**, 12–19.
- Robinson, J.P., Kingman, S.W., Snape, C.E., Bradshaw, S.M., Bradley, M.S.A., Shang, H., & Barranco, R. 2010. Scale-up and design of a continuous microwave treatment system for the processing of oil-contaminated drill cuttings. *Chemical Engineering Research and design*.
- Rossiter, Walter J., Godette, McClure, Brown, Paul W., & Galuk, Kevin G. 1985. An Investigation of the Degradation of Aqueous Ethylene Glycol and Propylene Glycol Solutions using Ion Chromatography. *Solar Energy Materials*, **11**, 455–467.
- SDA. 1963. *Chemical Properties and Derivatives of Glycerol*. <http://www.cleaninginstitute.org/science/glycerine.aspx>. [Accessed 23.06.2016].
- Sengwa, R. J., & Kaur, Kulvinder. 1999. Microwave absorption in oligomers of ethylene glycol. *Indian Journal of Biochemistry and Biophysics*, **36**, 325–329.
- Sengwa, R. J., Chaudhary, R., & Mehrotra, S.C. 2002. The study of dielectric relaxation in propylene glycol-poly(propylene glycol) mixtures. *Polymer*, **43**, 1467–1471.

Bibliography

- Shang, H., Snape, C.E., Kingman, S.W., & Robinson, J.P. 2005a. Microwave treatment of oil contaminated North Sea drill cuttings in a high power multimode cavity. *Separation and purification technology*, **44**, 84–90.
- Shang, Hiu, Guo, Yonggang, Yang, Xiaoqing, & Zhang, Wenhui. 2012. Influence of materials dielectric properties on the petroleum oil removal from waste under microwave irradiation. *The Canadian Journal of Chemical Engineering*, **90**.
- Shang, Hui, Snape, Colin E., Kingman, Sam W., & Robinson, John P. 2005b. Treatment of Oil-Contaminated Drill Cuttings by Microwave Heating in a High-Power Single-Mode Cavity. *Ind. Eng. Chem. Res.*, **44**, 6837–6844.
- Shipman, James, Wilson, Jerry D., & Higgins, Charles A. 2013. *An Introduction to Physical Science*. Cengage Learning.
- Stephenson, Ralph L., Seaton, Simon, McCharen, Robert, Hernandez, Edgardo, & Pair, R. Benson. 2004. Thermal Desorption of Oil from Oil-Based Drilling Fluids Cuttings: Processes and Technologies. *Society of petroleum engineers*.
- Stuerga, Didier. 2013. Microwave-Materials Interactions and Dielectric Properties: from Molecules and Macromolecules to Solids and Colloidal Suspensions. *Chap. 1 of: de la Hoz, Antonio, & Loupy, André (eds), Microwaves in Organic Synthesis*. Wiley-VCH.
- Sumper, Andreas, & Baggini, Angelo. 2012. *Electrical energy efficiency*. Wiley.
- Svensen, Torgrim, & Taugbøl, Knut. 2011. Drilling Waste Handling in Challenging Offshore Operations. *SPE*.
- Tau, Kwoliang D., Elango, Varadaraj, & McDonough, Joseph A. 1994. Esters, Organic. *In: Howe-Grant, Mary (ed), Kirk-Othmer Encyclopedia of Chemical Technology*, vol. 9. John Wiley & Sons.
- Teodoriu, C, & Cheuffa, C. 2011. A comprehensive review of past and present drilling methods with application to deep geothermal environment.
- Thermex-Thermatron. 2016. *INDUSTRIAL MICROWAVE POWER GENERATOR*. https://www.thermex-thermatron.com/wp-content/uploads/2015/05/56833_Industrial-Microwave-Generator.pdf. [Accessed 23.06.2016].
- Thostenson, E.T., & Chou, T.-W. 1999. Microwave processing: fundamentals and applications. *Composites: Part A*, **30**, 1055–1071.
- Turcotte, Michael G., & Johnson, Thomas A. 1992. Amines. *In: Howe-Grant, Mary (ed), Kirk-Othmer Encyclopedia of Chemical Technology*, vol. 2. John Wiley & Sons.
- TWMA. 2016. *TWMA*. <http://www.twma.co.uk/offshore-processing>. [Accessed 23.06.2016].

Bibliography

- UNEP. 2016a. *OECD SIDS Assessments*. <http://webnet.oecd.org/hpv/ui/Search.aspx>. [Accessed 23.06.2016].
- UNEP. 2016b. *UNEP mission in Nigeria*. <http://www.unep.org/disastersandconflicts/CountryOperations/Nigeria/UNEPMissioninNigeria/tabid/54131/Default.aspx>. [Accessed 23.06.2016].
- Vasshus, J.K., & Malmin, A. 2013. *Cleaning device*. US Patent App. 13/878,528.
- Vos, B., Mosman, J., Zhang, Y., Poels, E., & Blik, A. 2003. Impregnated carbon as a susceptor material for low loss oxides in dielectric heating. *Journal of Materials Science*, **38**(1), 173–182.
- Whitford, Jaques. 2009 (July). *Cuttings Treatment Technology Evaluation*. Tech. rept. 166. Environmental Studies Research Funds.
- Wyrzykowski, D., Hebanowska, E., Nowak-Wiczek, G., Makowski, M., & Chmurzynski, L. 2011. Thermal behaviour of citric acid and isomeric aconitic acids. *Journal of Thermal Analysis and Calorimetry*, **104**, 731–735.
- Yaws, Carl L., & Satyro, Marco A. 2015. *The Yaws Handbook of Vapor Pressure: Antoine Coefficients*. Second edn. Gulf professional publishing.
- Zaki, R., & Barabadi, A. 2014. Drilling Waste Minimization in the Barents Sea. *Proceedings of the 2014 IEEE IEEM*.