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MASTER'S THESIS

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Writer: Bahareh Kamandi	……………………………………… (Writer's signature)

Faculty supervisor: Dr. Torleiv Bilstad

External supervisor(s): Dr. Saeed Bikass

Title of thesis:

Tracing of PAH Concentrations in Drill Cuttings through the TCC Process.

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Abstract

Strict regulations for polycyclic aromatic hydrocarbons (PAH) concentrations in discharged water prompts the oil and gas industry to improve treatment for produced water and drilling fluids which are the main sources of hazardous components such as heavy metals, additives and PAH. The objective of the research was to analyze PAH concentrations before and after TCC treatment in drilling fluids and in recovered substances such as oil, water and solids.

The intention of the research was to determine the presence of 16 hazardous PAH components in drill cuttings before and after the TCC process and to evaluate PAH distribution. Measurement of PAH concentrations and density and weight percentage for cuttings, recovered oil, water and solids was performed. The main method implemented for analysis was gas chromatography (GC) coupled with preparation procedures such as liquid-liquid extraction, solid-liquid extraction, clean-up and up-concentration. TCC was proven to be efficient at removing PAH from cuttings as well as from water. The total PAH removal observed during the research was approximately 87 %. Some PAH components in the recovered solids such as *Anthracene*, *Fluorene* and *Pyrene*, decreased by more than 95 % after TCC, while *Methylnaphthalene* decreased by 98.38 % and *Anthracene* by 99.46 %. Concentration of PAH in the recovered water was close to zero and satisfied all the requirements for treated water to be discharged. Some PAH which were not found after the TCC process were assumed to have evaporated during the TCC procedure or followed the sludge. The recovered oil contains most of the PAH which were removed from the drill cuttings during the TCC process. This research proved that the efficiency of the TCC method for drilling fluids treatment is significantly high, providing recovered oil and water of high quality and solids with low oil content. This study can contribute to a better understanding of hazardous components distribution in TCC treatment of oil-based drill cuttings.

Key words: *PAH, Thermo-mechanical Cuttings Cleaner, drilling fluids, hazardous components.*

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Abbreviations

BOD:	Biological Oxygen Demand
BTEX:	(Benzene, Toluene, Ethylbenzene and Xylene)
CMC:	Carboxymethyl Cellulose
DC:	Drill Cuttings
DCM:	Dichloromethane
EPA:	Environmental Protection Agency
GC:	Gas Chromatography
IOS:	Internal Olefins
IAOs:	Linear Alpha Olefins
LPs:	Linear Paraffins
LTMBF:	Low Toxicity Mineral oil Based Fluids
NAF:	Non-aqueous based fluid
NCS:	Norwegian Continental Shelf
OBF:	Oil Based Fluid
OSPAR:	Oslo-Paris Commission
PAH:	Poly Aromatic Hydrocarbon
PW:	Produce Water
SBF:	Synthetic Based Fluid
SRD:	Solid Recovery Denmark
TCC:	Thermomechanical Cuttings Cleaner
THC:	Total Hydrocarbon
TOC:	Total Organic Carbon
TPH:	Total Polycyclic Aromatic Hydrocarbons
TVD:	True Vertical Depth
UKCS:	United Kingdom Continental Shelf
WBF:	Water Based Fluid
PAO:	Poly Alpha Olefins

Chapter 1: Introduction

1 Introduction

The first drilling operation in Norway dates backs to 1966 (Bilstad et al., 2014). During Drilling operation, drilling fluid or mud is used in order to improve the drilling operation. The function of a drilling fluid is defined by its composition and additives depend on the operating conditions (e.g. depth, pressure, temperature) and formation of a well. Oil based fluids (OBF) are the most common fluids used in drilling operations due to their efficiency and low cost compared to the another fluid types (e.g. water based fluids). A drilling operation produces a significant amount of drill cuttings which principally are consisting of small rocks and fragments produced during the operation coated or mixed with drilling fluid. An oil based drill cutting can contain polycyclic aromatic hydrocarbons (PAH) from the fluid additives which makes the cutting hazardous for the environment. PAH are of interest because they are persistent; they can stay in the environment for long periods of time. Most of them do not break down easily in the water (Environmental Protection Agency Washington, 2008). Since 1993 in Norway all the cutting from drilling operations using OBM has been considered as hazard waste which should not be disposed to the environment without any treatment. Two aspects of the environmental impact of oily drill cutting piles has been noticed: 1) The cutting amount and properties, 2) The effect of these contaminants on species (Cripps et al., 1998).

Therefore treatment of drill cuttings is very crucial as if not correctly treated and disposed of, they will cause serious harm to the environment. Among various methods of treating drill cuttings, thermal desorption method is a common method. The Thermo-mechanical Cutting Cleaner (TCC) process is an example that is specially designed for processing of oil contaminated drilling waste such as typical drill cuttings, slop-mud and spent drilling fluid. TCC treats drill cuttings and produces recovered oil, recovered water, non-condensable gas and cleaned solid.

This study investigates the effectiveness of treating drill cuttings using the TCC method. The composition of drill cutting samples was determined before (as the process feed) and after (as the process product) the TCC process.

In this thesis the focus is kept mostly on environmentally hazardous chemicals and measurement of PAH concentrations, since, as mentioned, PAH is one of the most harmful components in oil based drilling fluids and consequently in the cuttings. PAH concentrations are traced by comparing the sample analysis before and after the process.

1.1 Problem Description

The US Environmental Protection Agency has made a list of 16 important PAH that are pollutants. These PAH are usually referred to as the EPA 16 PAH (Figure 7) most commonly analyzed. PAHs represent the group of compounds in oil that has received the greatest attention due to their carcinogenic and mutagenic properties, as well as their persistence. More precisely, intermediates formed are far more toxic than the mother compounds during cellular detoxification of the PAH in vivo[1] metabolism (Conney, 1982).

Due to the toxicity of the PAH metabolites the oil industry in some areas of the world (e.g. North Sea, Mediterranean Sea, Australian Northwest Shelf, Gulf of Mexico) are required to monitor their discharges to the aquatic environment in a very strict way (Daniela et al., 2013).

This research analyses to what degree TCC method can help to remove oil and PAH from drill cuttings.

1.2 Objectives

The objective of this study is to investigate PAH concentration in particular drilling cuttings before and after TCC, as well as PAH concentration in separated water after the TCC process.

In this thesis, samples of cuttings are collected before and after TCC treatment. The recognized substances are categorized, selected and traced through the process.

The following 5 steps were included in this master thesis to achieve the object of this study:

- ✓ Coverage of the Environmental effects of PAH in drilling cutting.
- ✓ Selection of a suitable method for PAH analysis.
- ✓ Measurement of the PAH in drilling cutting before TCC, as well as in recovered solids, recovered water by TCC.

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[1] In microbiology in vivo is often used to refer to experimentation done in live isolated cells rather than in a whole organism.

- ✓ Comparison of the quantity of PAH in cutting before and after TCC.
- ✓ Comparison of our result with results from previously published research.

1.3 Thermtech AS Company

This research has been carried out by the collaboration of Thermtech AS with the University of Stavanger (UiS). Thermtech AS is a Norwegian technology and knowledge based company aiming. to set the global standard for the treatment of cuttings from oil-based and synthetic based drilling fluid Thermtech has spent 30 years developing a thermal desorption process, so-called Thermo-mechanical Cutting Cleaner (TCC), in order to treat oil based cuttings. The TCC method enables a safe and economically attractive use of all components in the waste (Thermtech, 2014). The TCC has been utilized by different oil and gas operators such as TWMA, Halliburton, Slumberger/Ml-Swaco and SAR.

The samples required for this study have been supplied by Thermtech. The analysis of the samples has been performed at UiS.

1.4 Thesis Outline

In this thesis Chapter 1 includes Introduction and Objective of the research. Chapter 2 provides theoretical background for drilling fluid and drill cutting composition, drilling waste treatment, TCC technology and process. Chapter 3 covers research methods including extraction of solids and liquids, GC methods, measurement of the density and solids content. Chapter 4 presents about results and discussion, also comparing the results with older research and report documents. Chapter 5 summarizes main conclusions of the research. Chapter 6 is recommended future study.

Chapter2: Theoretical Background

2 Theoretical Background

Oil and gas wells are drilled to depths of estimated at more than 5,000 meters (Zoveidavianpoor et al., 2012). In order to achieve such depths, drilling fluids are required.

2.1 Drilling Fluids

Drilling fluid, which is also called drilling mud is defined as any fluid or mixture of fluids and solids, which is used to drill wellbores into the earth (Schlumberger, 2012). Drilling fluids consist of a base fluid and a mixture of chemical additives to achieve a desired functions during drilling (B. Roddie et al., 1999). Drilling fluid as continuous phase was used for the first time in the middle of 1930's (Simpson et al., 1961).

During the drilling process proper drilling fluid is needed to carry out drilling activity, as well as to enable the required functionality of implemented equipment. Drilling fluid controls subsurface pressure by hydrostatic pressure. Hydrostatic pressure increases with depth and can be controlled by the density of fluid in true vertical depth (TVD) (Amoco, 2010).

Drilling fluids are pumped through the bit nozzles down the well and up the circular space between the drill pipe and hole. The drilling fluid composition depends on the well formation it is used for, maintains pressure control of the well as it is being drilled (Zoveidavianpoor et al., 2012).

Drilling fluid fulfils the following functions in a well drilling:

- ✓ Controls subsurface pressure.
- ✓ Supports and stabilize wellbore.
- ✓ Transports cuttings (Walker et al., 2012).
- ✓ Smoothes and cools the drill bit.
- ✓ Removes cutting from hole up to the surface (Zoveidavianpoor et al., 2012).

Drilling fluids can be categorized in to overall types; aqueous drilling fluids (ADF) and non-aqueous drilling fluids (NADF) (Melton et al., 2004). ADF are water-based fluid (WBF) and NADF include oil-based fluid (OBF) and synthetic-based fluid (SBF). Each type of fluid is used for a specific purpose for example NADF are used more offshore due to borehole stability (Campbell., 1998). Several additives can be used in fluids depending on the drilling needs (schlumberger, 2013).

2.1.1 Aqueous Drilling Fluids (ADF)

As mentioned earlier, ADF are water- based fluid (WBF). Water-based fluids are a combination of Iron (III) oxide, CaCO3, BaSO4, bentonite clay, polymers, lignosulfate deflocculant, viscosifier and various salts (Bilstad et al., 2014).Water mixed with bentonite clay and barium sulphate (barite) in a WBF can control fluids density (Melton et al., 2004).

Water based fluids are formulated either with fresh or sea water or with a brine (e.g. KCI). The salinity ranges from 0 to about 900 kg/m3, depending on the salt type and desired density of the fluid.

Water-based fluids are classified in three kinds (as shown in Figure 1):

I) Inhibitive fluids prevent clay swelling by cations: Potassium (K+), Calcium (Ca2+) or mix of two cations.

П) Non-inhibitive fluids contain clays or bentonites with caustic soda. They may have deflocculants like lignites or phosphates. A fluid can be inhibitive or non-inhibitive depending on the cation used (Amoco, 2010).

Ш) Polymer fluids are macromolecules either with or without clay and they can have thermal stability up to 400°F (Amoco, 2010).

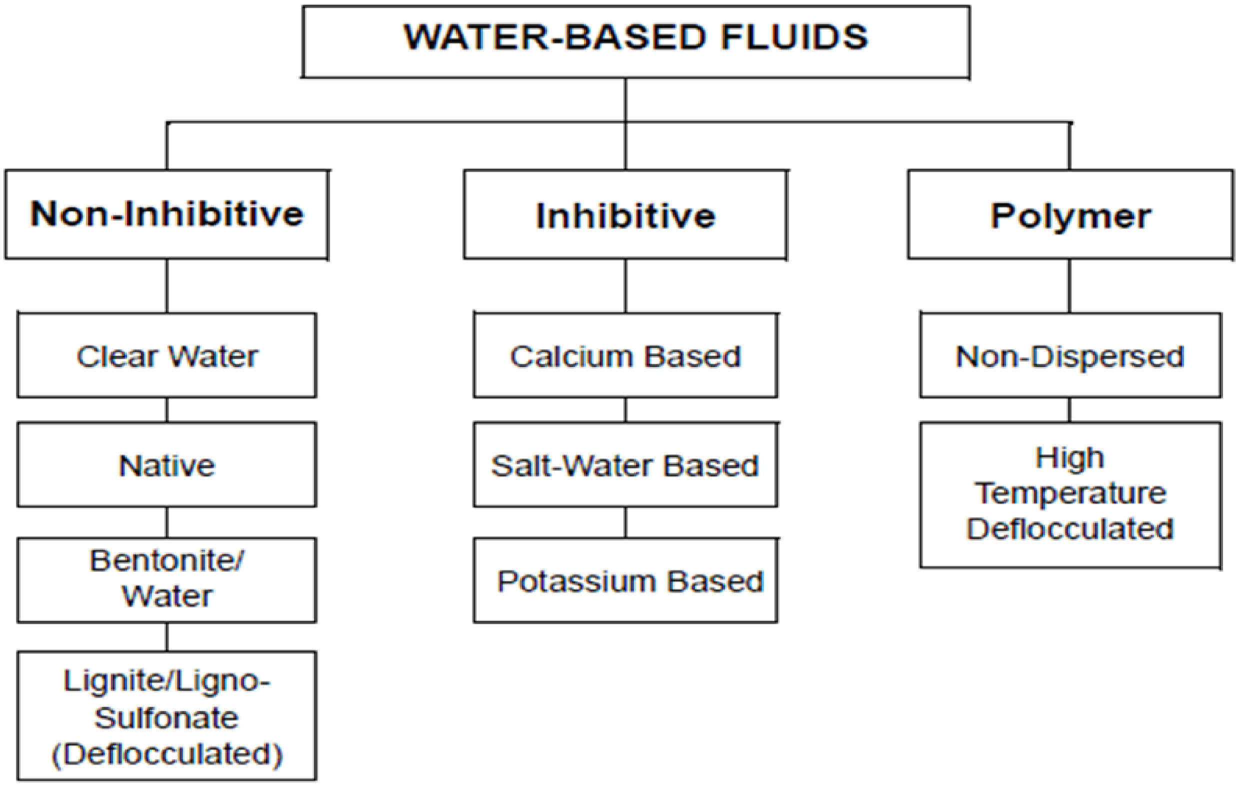

Figure 1. Water based fluids classifications (Melton et al., 2004)

2.1.2 Non-Aqueous Drilling Fluids (NADF)

NADF are emulsions in which the continuous phase is the non-aqueous based fluid contain water and chemicals are the internal phase. As mentioned earlier NADF can be OBF or SBF. In a Similar way to WBF, additives are used to control the properties of NADF. Figure 2 illustrates overall composition of NADF compared to WBF. The details of Non-aqueous fluids composition is shown in Figure 3.

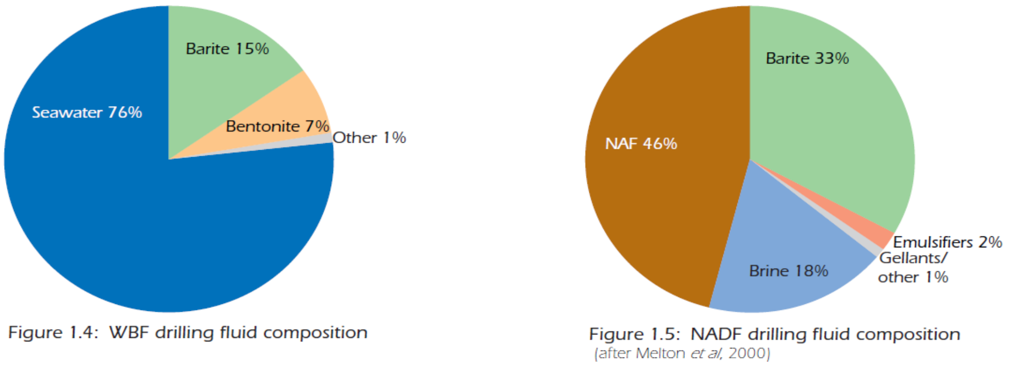

Figure 1.4: WBF drilling fluid composition

Figure 1.5: NADF drilling fluid composition
(after Melton *et al*, 2000)

Figure 2. Composition of WBF and NADF (Melton et al., 2004)

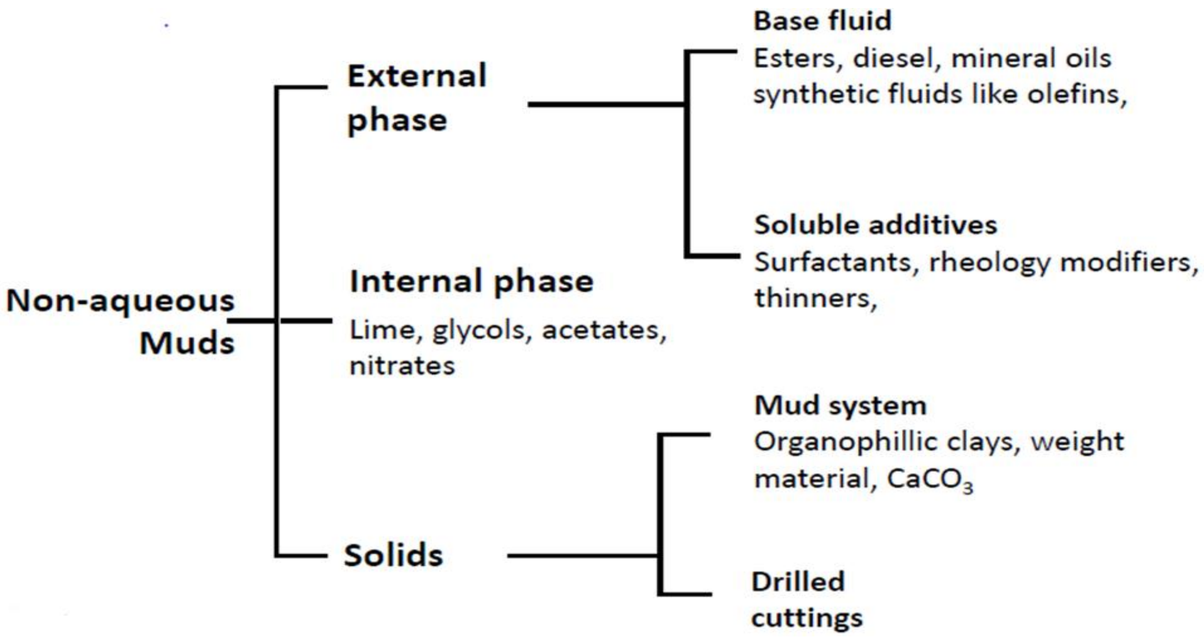

Figure 3. Components of Non-aqueous fluids (Samudra and Sahinidis, 2010)

Oil-based Fluids (OBF)

An oil based fluid can be used as a drilling fluid which has oil as the continuous phase and water presents as the dispersed or internal phase. This type of the drilling fluid consists of water, emulsifiers, weighting agents, mineral oil or diesel and various (often undisclosed), yellow and red chemicals of the list of chemicals[2]. Due to this, OBF is of greater environmental concern than WBF (Bilstad et al., 2014).

All oil fluids have oil as the external phase but they are designed to be free of water when formulated or in use if the water is not quickly emulsified, the solids in the fluid can become water wet and will cause stability problems. The water wet solids will clog the shaker screens and loss of whole fluids will occur. To improve the performance, invert emulsion systems were developed, in which an internal water phase is emulsified into the continuous oil phase (Bilstad et al., 2014).

Oil fluids propose many advantages over water based fluids. Oil based fluid is basically used for improving well stability and also for high pressure or temperature wells. Corrosion of pipe is controlled when oil is the external phase and covers the surface of the pipe. Oil fluids are suitable to be used again, and the oil fluids can be stored for long periods of time (Amoco, 2010).

Different additives need to be added to an oil based fluid to ensure that the emulsion is really stable at high temperatures and with contaminants.

Synthetic Oil-based Drilling Fluids (SBF)

Sometimes OBF are replaced by synthetic oil based fluid which function like OBF but which are free of poly-nuclear aromatic hydrocarbons and have lower toxicity. Since diesel oil in OBF, which is used in OBF, is harmful to the environment. SBF has faster biodegrability and lower bioaccumulation potential. Use of SBF results in a cleaner hole with less sloughing: Also it generates a smaller cutting volume and can be recycled where possible (Onwukwe and Nwakaudu., 2012). The use of palm oil derivatives could be considered as an alternative for oil-based fluids since they are harmless to the environment (Caenn. Darley & Gray., 2011).

At the beginning of the 1990's, three synthetic type materials were found: Esters, Ethers and Poly Alpha Olefins (PAO), which were called as the “first generation”. The marketplace development has created the second generation of SBF, which can be classified as Linear Alpha Olefins (IAOs), Internal Olefins (IOS), and Linear Paraffins (LPs).Typically, the second generation fluids are cheaper and thinner, and more in use worldwide (Friedheim and Conn., 1996).

Emulsifiers, which commonly are metal soaps of fatty acids, are added to the SBF to aid in forming and stabilize the inverted emulsion. The emulsifier (surfactant) packages used in SBF often are

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[2] Black and Red category consists of substances with eco-toxicological properties
Yellow category consists of substances that shall not be defined as red or black (Statoil, 2003).

different from those used in OBF (Neff et al., 2000).

2.1.3 Drilling Fluids Additives

Composition of the fluids can be of different chemicals additives depending on the functions and types of the drilling fluids. Some additives, such as chromium in lignosulfonates used for in fluids have potential contaminates. Also, barite weighting agents may contain concentrations of heavy metals such as cadmium or mercury. Other fluids additives and materials are given in Table 1 (Onwukwe and Nwakaudu., 2012).

Table 1. Drilling Fluids Additives and Substitute Material (Onwukwe and Nwakaudu., 2012)

Additive	Use	Substitute Material
Chrome	Deflocculant	Polyacrylate and/or polyacryamide polymer
Lignosulfonate/lignite		
Sodium chromate	Corrosion control	Sulfites, phosphonates, and amines
Zinc chromate	H2S control	Non-chromium H2S scavengers
Lead-based pipe dope	Pipe thread sealant/lubricant	Unleaded pipe dope
Barite	Mud densifier	Choose barite from sources low in cadmium, mercury and lead.
Arsenic	Biocide	Isothiazolins, carbamates, and gluteraldehydes.

The main additives used in the fluids are presented below.

2.1.3.1 Weighting Materials

Neff said that barite (barium sulfate) is used to increase the weight of the drilling fluids, and overcome formation pressure. The amount of barite added to the fluids is usually increased as both the depth of the well and formation pressure increases (Neff, 2005).

Calcium carbonate and hematite (iron oxide) are also commonly used. These additives may contain heavy metals. This component can increase the density of the drilling fluids, so that the fluid can properly keep the well pressure. Hematite or galena may be added to the system alone with barite to provide hydrostatic pressure.

2.1.3.2 Viscosifiers

Viscosifiers are used in all fluid types. In invert emulsion systems [3](OBF or SBF), the viscosifiers build viscosity through complex interactions with the emulsions. Bentonite clay is usually used in water-based fluids.

2.1.3.3 Fluid Loss Control Agents

These composites are added to reduce the loss of fluid into the drilled formation. the agents include: bentonite clay, lignite and polymers, carboxymethyl cellulose (CMC), polyanionic cellulose (PAC). Bentonite clay is most commonly used as the control agent with very fine particles. One of the important additives for WBF is Lignite as emulsion stabiliser. Various polymers may also be used for OBF and SBF.

2.1.3.4 Emulsifiers

Emulsifiers are added to stabilize oil-in-water emulsions, in OBF and SBF, Two types of emulsifiers are used for more homogenous mixture (Amoco, 2010). Primary emulsifiers include fatty acids (and derivatives) and resin acid (and derivatives). Secondary emulsifiers include amines, lignosulfonates, amides, sulfonic acids, alcohols and related co-polymers. They are especially used at high temperatures in order to improve emulsion stability and wet the drilled solids.

Lime is added to make calcium soaps that aid to emulsification of water in the oil (Amoco, 2010).

2.1.4 Oil based Fluids Additives

Primary Emulsifier

Calcium soaps are the primary emulsifier in oil fluids which are made by the reaction of lime and long chain (C_{16} to C_{22}) fatty acids. Emulsifiers surround the water droplets and prevent their coalescence and help in the formation of fluids (Amoco, 2010).

Secondary Emulsifiers

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[3] Water-in-oil (or invert) emulsion, known as an "invert emulsion mud" (Schlumberger, 2015).

Secondary additives are typically polyamides or imidazolines with powerful oil wetting chemicals. This makes solids oil wet before the emulsion is formed, and is used to simply emulsify any water disturbance simply and quickly (Amoco, 2010).

Organophilic Lignites

This type is used as high temperature fluid loss additives. They also will aid in the emulsification of water especially at high temperatures. Asphaltic fluid loss additives generally consists of gilsonite or asphalt derivatives. Gilsonite has high temperature stability. High concentrations can cause too much viscosity and gelation of the fluids (Amoco, 2010).

Organophilic Attapulgite

Organophilic attapulgite used to improve the suspension properties of fluids without extremely increasing the viscosity (Amoco, 2010). As a drilling-fluid material, it consist of gel salt or brine gel, since that is used as a suspending agent in salt solutions (Nguyen, 2012).

Filtration-Control Agents

Bentonite, different kind of polymers, starches, and deflocculants behaves as filtration-control agents and can reduce the amount of filtrate lost from the drilling fluid into a subsurface formation. In many areas, diesel is used to formulate and maintain oil based fluids.

2.2 Drill Cuttings

During a drilling process, a rotating drill bit attached to the end of drill pipe is used (Cripps et al., 1998).When a drill bit cuts into the rock formation during drilling operation, small pieces of rocks are produced (as shown in Figure 4). When the hole becomes deeper drilling fluid removes the rocks from the hole (Cripps et al., 1998). Then the rocks are mixed with the drilling fluids and transported to the surface of the well (see Figure 5), where the fluid is separated from the mixture. the residue from the mixture, mostly the rocks, is called drill cuttings. So a drill cutting may contain small amount of liquid and solids left from drilling fluid components. The rock type in the cuttings depend on the drilled formation for example, the North Sea usually contains sandstone rock and shale (Gerrard et al., 1999).

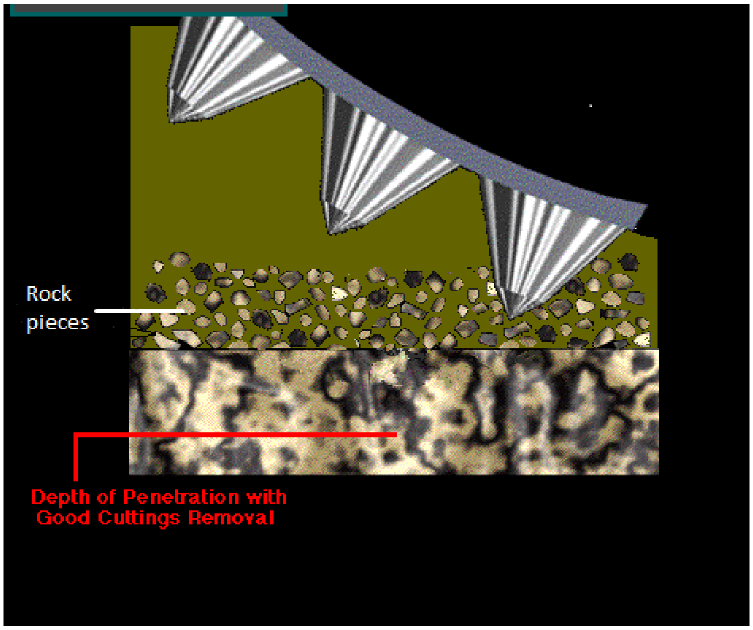


Figure 4. Drilling bitt and produced rock pieces (Schlumberger., 2013)

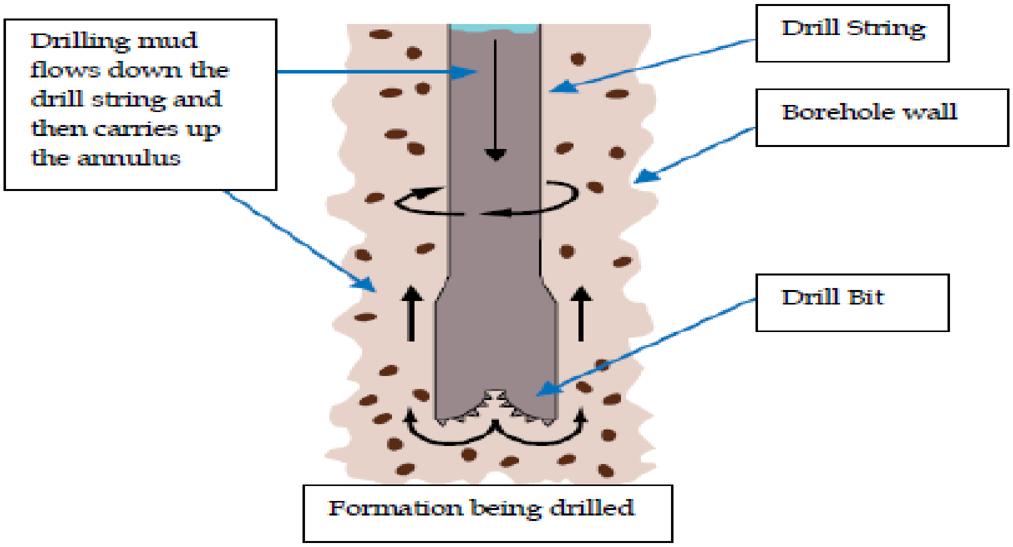


Figure 5. Drilling process and the rocks transportation (Melton et al., 2004)

2.2.1 Drill Cutting Composition

The composition of drilling cutting depends on drilling fluid that has been used for the drilling process (Breuer et al., 2004) and the drilled formation. Similar to the drilling fluids, the cuttings can be divided in to three main types depending on the used drilling fluid in the drilling process: water-based, oil-based and synthetic oil-based (Cripps et al., 1998).

The composition of a drill cutting will vary but it may contain water, oil, chemical residues, salt and metals. The amount of the drilling fluid solids attached to the cuttings depends on grain size of the generated rocks during drilling (Neff, 2005). As a basis for evaluation, it is assumed that cuttings consist of 50% solids, 35% water and 15% oil (or other drill fluid residues) (OLF, 2001). Clay is also found in the cuttings as fine clay is difficult to separate from drill cuttings (Neff, 2005). Oil primary source is OBF and SBF for drilling operation (Breuer et al., 2004).

The cuttings also contain different chemicals originating from the drill fluid including heavy metal, (e.g. Cr, Cu, Ni, Pb and Zn), barite, bentonite, special chemicals, hydrocarbons, organic contaminate and radioisotopes.

Polyaromatic hydrocarbons are found in North Sea due to pyrolytic source such as flare combustion. Barium comes from mineral barite ($BaSo_4$) used in drilling fluid (Breuer et al., 2004). Table 2 shows the quantity of drilling chemicals in OBF and WBF.

Table 2. Drilling chemical use and data up to 1989 (Breuer et al., 2004)

Chemicals	Chemicals (tonnes y-1)	
	OBM	WBM
Weighting agents	1941	12,497
Bentonitic agents	621	7467
Alkaline chemicals	1554	1135
Salinity	2169	9193
Lost circulation	45	317
Lignosulfonates	220	267
Lignites	65	33
Polymers/viscosifier	490	1152
Gilsonite	128	4
Defoamers	NR	143
Biocides	NR	13
Crorrosion inhibitors	NR	30
Scale inhibitor	NR	2
Drilling lubricants	NR	63
Pip- release agents	5	20
Dispersants	NR	NR
Oxygen scavengers	NR	7
Emulsifiers/detergent	1766	178
Cuttings wash	1028	0
Shale inhibitors	NR	26
Weighting agents	34	NR
Base oils	23,693	NR
Total	33,987	33,589

*NR signifies no reported use or discharge.

Table 3 give some information about constituents of drilling waste.

Table 3. Constituents of drilling wastes (Onwukwe and Nwakaudu., 2012)

Type of Waste	Main components	Possible environmentally significant constituents
Waste lubricants	Lube oil, grease	Heavy metals, organics
Spacers	Mineral oil, detergents, surfactants	Hydrocarbon, alcohol, aromatics
Spent/contaminated water based muds (include brine)	Whole mud, mineral oil, biodegradable matters	Heavy metals, inorganic salts, biocides, hydrocarbons, solids/cutting, BOD, organics
Water based muds cutting	Formation solids, water based muds mineral oil	Heavy metals, inorganic salts, biocides, hydrocarbons, solid/cutting
Spent/contaminated oil based muds	Whole mud mineral oil	Hydrocarbons, heavy metals, inorganic salts, solids, BOD, organics, surfactants
Oil based muds cuttings	Formation solids, oil based muds	Heavy metals, inorganic salts, hydrocarbons, solid/cutting
Spent bulk chemical	Cement, bentonite, barites, viscosities, thinners, fluid loss reducers, speciality product	Heavy metals, hydrocarbon, organics, solids
Spent special products	H2S scavengers, defoamers, tracers	Zinc carbonates, iron oxides, hydrocarbons, silicon oils, potassium salts, radioactive material

2.2.2 Environmental Impact

Many of the additives used in drilling fluids are believed to be toxic and should be regulated (Reis, 1996). For example chromium in lignosulfonates, which in the past have been used in drilling fluids or barite weighting agents sometimes contain heavy metals (cadmium or mercury). The use of such additives has been decreased because of environmental impact and the selection of less toxic additives is an ongoing process (Onwukwe and Nwakaudu., 2012). However, drill cuttings are contaminated by drilling fluids and inherit some of toxic additives.

The WBF, due to their water content, cause dispersal of cuttings particles into the drilling fluid. To prevent this problem, the mud is often diluted. Use of WBF hence produces larger amounts of drilling wastes than the OBF (B. Roddie et al., 1999).

As mentioned earlier, diesel oil is used in OBF. The toxicity of diesel oil can be assessed by its high aromatic hydrocarbon content (Daniela et al., 2013).

Non-aqueous fluids can be divided in three groups according to their aromatic content:

Group I – high aromatic content, Group П - medium aromatic content and Group Ш - low aromatic content.

Group I NABF are defined as having PAH levels greater than 0.35%. The PAH content of diesel-oil fluids is typically in the range of 24% and the aromatic content is up to 25%. However, diesel-oil cuttings are not discharged because of their toxicity (this will be discussed in detail in later chapters). Conventional mineral oil (CMO) based fluids are made with crude oil in which total aromatic hydrocarbons are about half that of diesel with PAH contents of 12 %.

Group П fluids usually are defined as Low Toxicity Mineral Oil Based Fluids (LTMBF). NABFs are also developed from refining crude oil in which total aromatic hydrocarbon concentrations (between 0.5 and 5%) are less than those of Group I NABFs and PAH content is less than 0.35% but greater than 0.001%.

Group Ш PAH contents are less than 0.001% and total aromatic contents less than 0.5%. Group Ш can include synthetic hydrocarbons (olefins, paraffins and esters). Broadly speaking, diesel and mineral oils are the base fluids used in NADF.

Group П and Ш NABFs both have lower aromatic content and PAH than diesel oil or mineral oil and contain lower acute toxicity (Melton et al., 2004). Oil based mud refer to group I and synthetic-oil based mud refer to the Group Ш (Melton et al., 2004).

2.2.2.1 Polycyclic Aromatic Hydrocarbons (PAH)

The general formula for aromatic hydrocarbons unsaturated compounds is C_nH_n. They consist of at least one benzene ring. Three double carbon-to-carbon bonds floating around the ring can cause more stability.

Aromatic hydrocarbons are often referred to as polyaromatic hydrocarbon (PAH) if they consist of more than one aromatic ring (Brady,Senese., 2004). PAH are aromatic compounds containing from two to eight conjugated ring systems. They can have a different groups of exchange such as alkyl, nitro, and amino groups in their structure. Figure 6 shows Naphthalene as an example of PAH molecule structure.

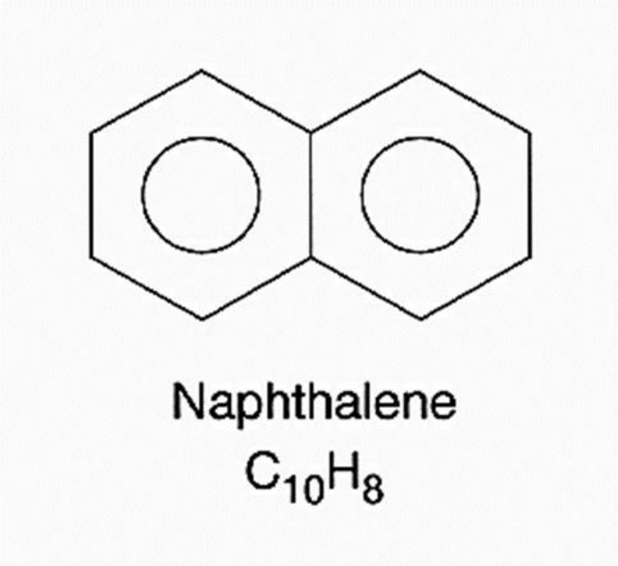


Figure 6. (Mckay et al., 1996)

Polycyclic aromatic hydrocarbons (PAH), are identified by the US Environmental Protection Agency as priority pollutants globally (Yan et al., 2004). PAH are one target component of total polycyclic aromatic hydrocarbons (TPH) and are of concern because some are carcinogenic and may be toxic to the environment (Bojes and Pope., 2007).

Two types of PAH which are in the marine environment are called pyrogenic and petrogenic. Source of pyrogenic PAH is incomplete combustion of organic material, whilst that of petrogenic PAH source is oil (Daniela et al., 2013).

The lower molecular weight unsubstituted PAH compounds, such as naphthalenes, fluorenes, phenanthrenes, and anthracenes, contain two to three rings. They have acute toxicity to some organisms, due to the higher molecular weight for 4- to 7- ring aromatics. However, all known PAH carcinogens, co-carcinogens, and their producers are in the high molecular weight PAH group.

PAHs may reach aquatic environments in domestic and industrial sewage effluents, in surface runoff from land, from release of petroleum and petroleum products into water bodies (Eisler, 1987). In the costal zones PAH enters the water primarily from sewage, runoff from roads, industry and oil spills, while offshore PAH mainly enter the water by oil leak, oil spills, and produced water discharge from offshore (Daniela et al., 2013).

PAH do not easily dissolve in water but they can exist in air as vapors or can stick to surface of solids. They can travel long distances. Most of them settle to the bottoms of lakes or rivers.

PAHs in the soil can contaminate underground water (ATSDR, 1995).

All PAH are solids, and are have low solubility in water. PAH, especially of higher molecular weight, are relatively immobile because of their large molecular volumes, and have low volatility and solubility. After entering water, they quickly become adsorbed by organic and inorganic particulate matter and are mostly deposited in bottom sediments. Most PAH remain relatively near to the point sources, and their concentrations decrease approximately logarithmically with the distance from the source (Tuvikene, 1995).

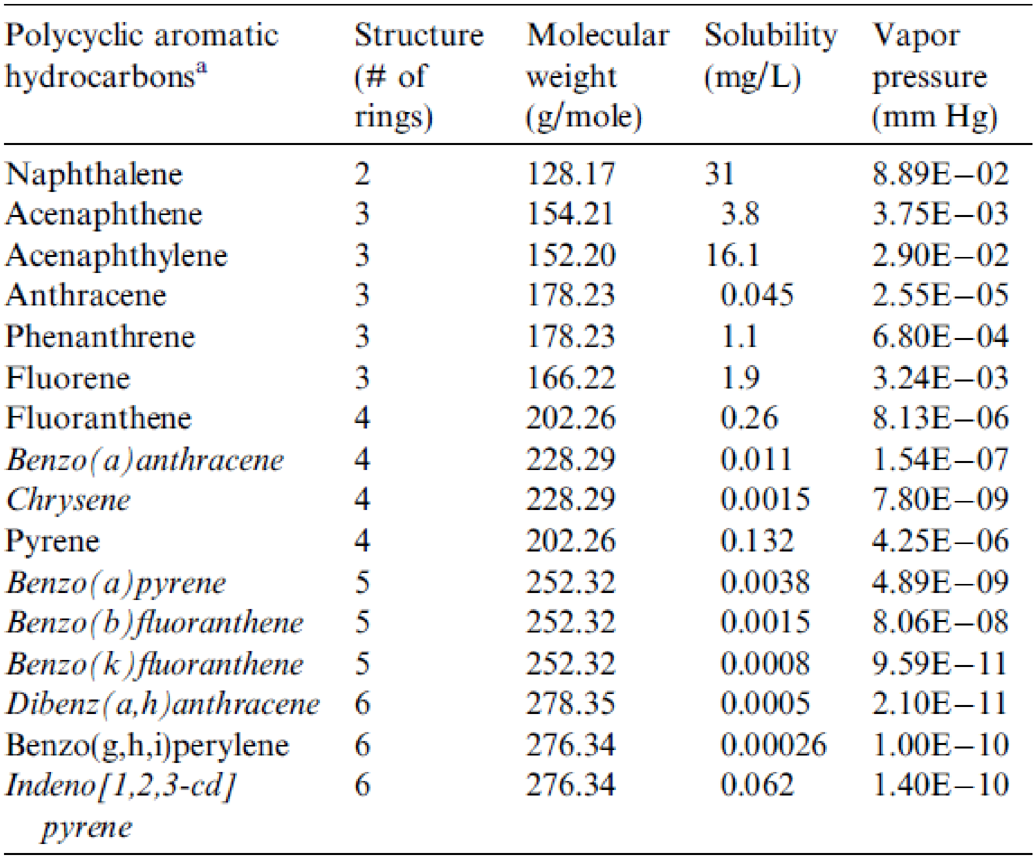
The US EPA has classified 16 PAH as most important and hazardous (Bojes and Pope., 2007). The list is presented in Table 4.

Due to the toxicity of the PAH metabolites the oil industry in some areas of the world are required to monitor their discharges to the aquatic environment (Daniela et al., 2013).

Depending on the quality of OBF, the geological formations and whether drilling is in hydrocarbon reservoir sections, cuttings are coated with different hydrocarbons including PAH, PCB, and heavy metals (Bilstad et al., 2014).

Seven PAH are considered carcinogenic; benzo(a)anthracene, chrysene, benzo(b) fluoranthene, benzo(k) fluoranthene, benzo(a) pyrene (BaP), indeno(1,2,3-cd) pyrene and dibenz(a,h)anthracene. These carcinogenic PAH have a higher molecular weight as well as lower solubility constants and vapour pressure compared to the non-carcinogenic PAH (Bojes and Pope., 2007).Figure 7 illustrated the structure of important PAH.

Table 4. US EPA's 16 priority-pollutant PAH and selected physical-chemical properties



Polycyclic aromatic hydrocarbons[a]	Structure (# of rings)	Molecular weight (g/mole)	Solubility (mg/L)	Vapor pressure (mm Hg)
Naphthalene	2	128.17	31	8.89E−02
Acenaphthene	3	154.21	3.8	3.75E−03
Acenaphthylene	3	152.20	16.1	2.90E−02
Anthracene	3	178.23	0.045	2.55E−05
Phenanthrene	3	178.23	1.1	6.80E−04
Fluorene	3	166.22	1.9	3.24E−03
Fluoranthene	4	202.26	0.26	8.13E−06
Benzo(a)anthracene	4	228.29	0.011	1.54E−07
Chrysene	4	228.29	0.0015	7.80E−09
Pyrene	4	202.26	0.132	4.25E−06
Benzo(a)pyrene	5	252.32	0.0038	4.89E−09
Benzo(b)fluoranthene	5	252.32	0.0015	8.06E−08
Benzo(k)fluoranthene	5	252.32	0.0008	9.59E−11
Dibenz(a,h)anthracene	6	278.35	0.0005	2.10E−11
Benzo(g,h,i)perylene	6	276.34	0.00026	1.00E−10
Indeno[1,2,3-cd] pyrene	6	276.34	0.062	1.40E−10

a US EPA has classified PAH in italics as probable human carcinogens (Bojes and Pope., 2007)

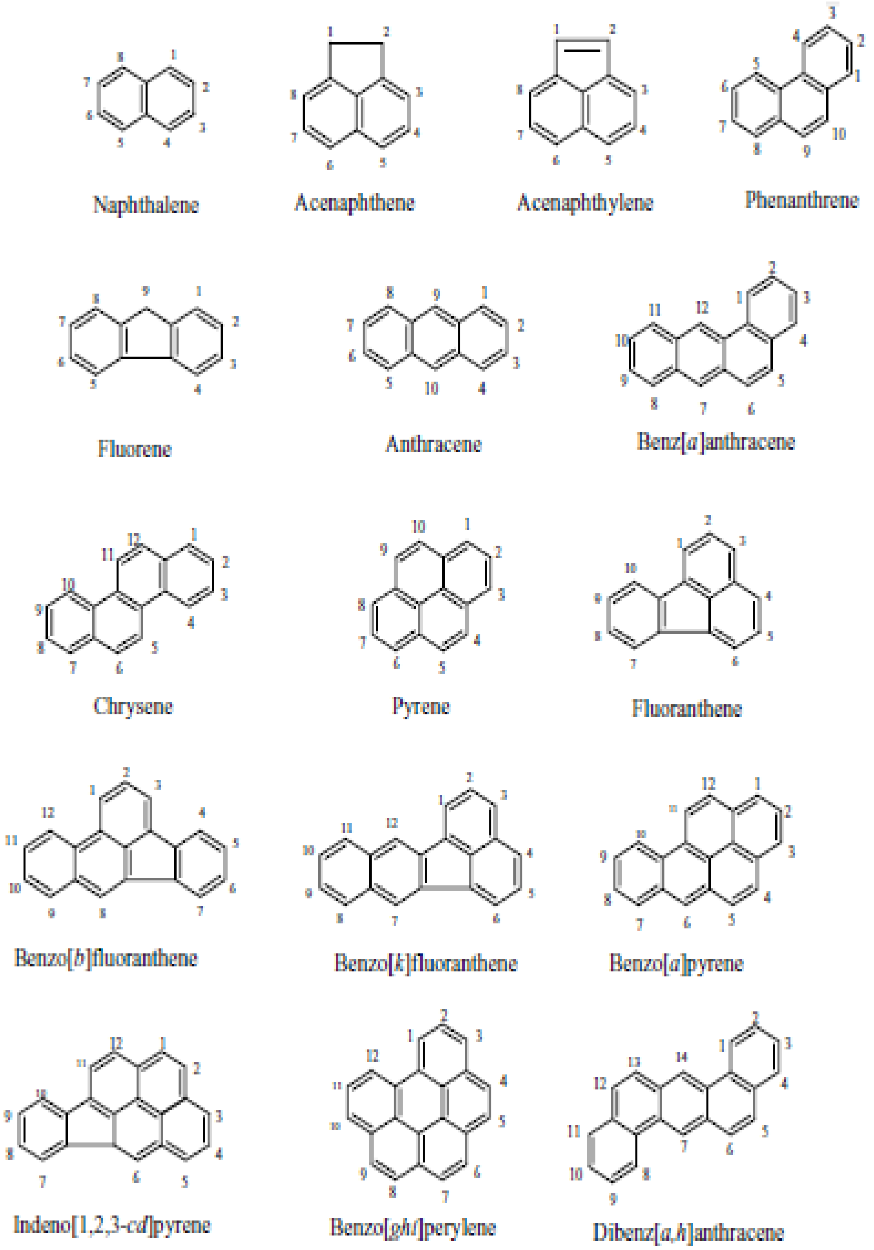
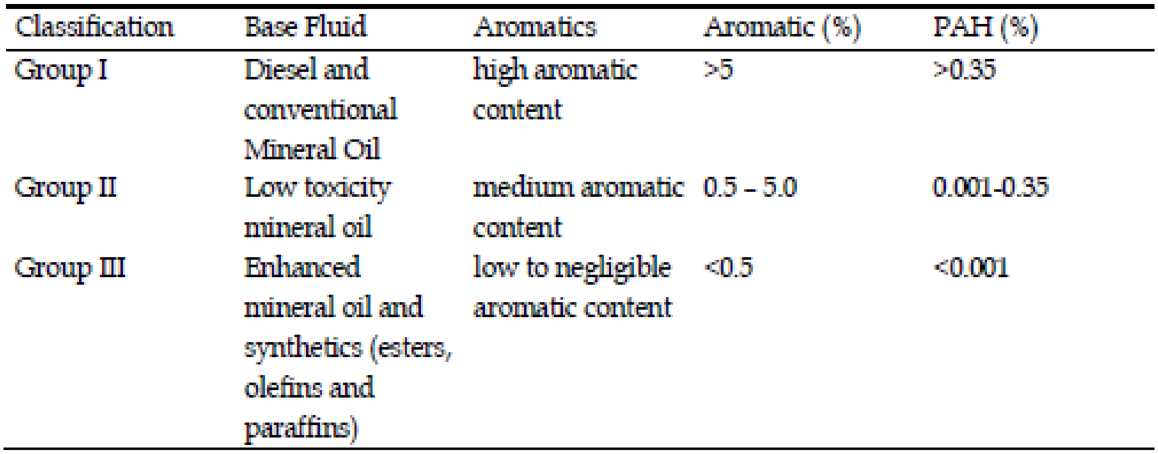


Figure 7. EPA listed structure of priority pollutant PAH (Yan et al., 2004)

Data from offshore oil production platforms in the North Sea has shown that the major aromatic compounds in PW are BTEX (benzene, toluene, ethylbenzene and xylene) (97%), 2- and 3-ring PAH (3%) named NPD (Naphthalenes, Phenanthrenes and Dibenzothiophenes) and greater PAH (<0.2%) (Daniela et al., 2013). The PAH may present in WBM and drill cuttings. They are toxic and carry a risk of bioaccumulation in the marine organisms. PAH are major toxicants in PW (Neff 2005; Neff et al., 2011).

Sediments near offshore oil and gas platforms may contain elevated concentrations of PAH, mainly from drilling discharges. These excess PAH may be toxic to the bottom dwelling species and consumers of benthic fauna, including commercially important fish and shellfish. The main source of PAH in drilling discharges is from drilling muds (particularly OBF and some SBF) and formation oil in the mud system (ERMS, 2006). Table 5 shows NADF classification according to PAH content.

Table 5. NADF Classification Groups and Descriptions (Tullow, 2011)



Classification	Base Fluid	Aromatics	Aromatic (%)	PAH (%)
Group I	Diesel and conventional Mineral Oil	high aromatic content	>5	>0.35
Group II	Low toxicity mineral oil	medium aromatic content	0.5 – 5.0	0.001-0.35
Group III	Enhanced mineral oil and synthetics (esters, olefins and paraffins)	low to negligible aromatic content	<0.5	<0.001

Aromatic Content Test

The aromatic content test includes measurement of the quantity of aromatics or benzene like compounds in the oil. Higher aromatic compounds concentration means higher toxicity of oil fluids. Nowadays the mineral oils used in oil fluids have an aromatic content less than 1% by weight (Amoco, 2010).

“Polymeric materials are used as surfactants, emulsifiers, foaming agents, stuck pipe additives, lubricants, and corrosion inhibitors in addition to functioning as flocculants, deflocculants, viscosifiers, filtration-control agents, and to improve rheological properties of the drilling fluid” (Nguyen, 2012). For a period in the early 80s, the diesel oil was replaced by mineral oils due to their lower toxicity (Bilstad et al., 2014).

2.2.3 Drill cuttings Discharge Regulations

Documentation for the exact quantity of oil contaminated cuttings discharged in to the sea has existed since period of 1983 – 1992, even though the drilling operations started in the 1970s. Environmental monitoring of discharges from the petroleum industry has been conducted since 1973 (Aquateam, 2014). However, 15,500 tons of oil in total attached to drill cuttings has still been discharged to sea during this period. The total weight of cuttings and fluids discharged during the whole period is approximately 695,726 m^3, with a discharge weight of 1,473,282 tons (Cripps et al., 1998).Until the mid-1990s the discharge of cuttings with oil based drilling fluid (OBF cuttings) was the main cause of oil hydrocarbons entering the marine environment from the offshore petroleum industry in the North Sea (Bakkea et al., 2013). Until September 1991 the discharge limit to the sea, of oil attached to cuttings, was 100 g oil per kg dry cuttings. After September 1991, the discharge limits was reduced to 10 g per kg dry cuttings. In the North sea Without contaminated cuttings may be discharged into the sea from 1st January 1994 (Cripps et al., 1998).The National Environmental Protection Act enacted in 1970 was the beginning of numerous federal and state environmental regulations imposed to protect the health and safety people and to protect the environment (Amoco, 2010).Since a worldwide increased activities of upstream oil and gas industry to meet future energy demands which will be associated with more waste generation, zero discharge is considered to be environmentally friendly (Zoveidavianpoor et al., 2012).

The drilling fluids can be recovered, while the drill cuttings should be separated and discharged into the sea if they are of low oil content in order to avoid hazardous impact for environments. The fluid can be used again, but the drill cuttings have been traditionally discharged in to the sea (Gerrard et al., 1999).

Monitoring the level of pollutants such as PAH is necessary because they are chemically quite stable and their lipophilic nature can easily enter biological membranes and accumulate in the organism.

2.3 Drilling Waste Management

The wastes generated during petroleum production can be broadly classified into liquid (i.e produced water & oil) and solid (i.e drilling muds & cuttings) (Ferrari et al., 2000). Drill cuttings are called waste when separated from drilling fluid (Cripps et al., 1998).Drilling waste and its treatment is the most important part of any oil drilling operation (Okeke and Obi., 2013).

The treatment of WBF cuttings is becoming common in more sensitive environments. Well bore fluids are typically hydrocarbon contaminated. Clean-up of fluids will also require the filtering of contaminants before to disposal (Okeke and Obi., 2013).

Untreated drill cutting have special properties and have tendency to settle and cohesive, which makes their transportation difficult.

From the 1990s to the present-day, the drilling industry has witnessed a revolution in OBF and oily-waste management. Less toxic and more environmentally acceptable synthetic-base fluids (SBF) have replaced diesel and mineral-oil fluids in many fields.

Therefore, the operator now has the benefits of nonaqueous drilling fluids coupled with technologies that help to manage cuttings and excess oil- and synthetic-base muds. However, modern SBF offer the nonaqueous qualities of traditional OBF but with less toxicity and higher degrees of biodegradability. In some areas, as result of environmental regulations, cuttings coated with SBF are buried, discharged to the sea or made environmentally benign through bioremediation processes. However, not all areas are suitable for this type of waste management, and more innovative processes are required to protect the environment during drilling process.

An example of stricter environmental discharge regulation occurred in the North Sea in late 1990. Four years prior to regulatory changes, the Norwegian State Pollution Control Agency announced a tightening of regulations for offshore disposal of drilled cuttings. These regulations would be effective on first of January in 1993, and the allowable oil on cuttings disposed by discharge to the sea was reduced from 6 to 1 percent by volume. Technology available at the time could not reduce oil on cuttings to a such as a low level but Amoco Production Company, which began preparing for this regulatory change in the Valhall field by first evaluating the options. Engineers considered transporting oil-wet cuttings to shore for processing, drilling with water-base rather than OBF, processing the cuttings offshore and disposing of cuttings by subsurface injection (MI Swaco, 2013).

Environmentally responsible actions require an understanding of the characteristics of the wastes and how they are generated in order to minimize their environmental impacts by known environmental protection methods. First step for waste management, which is most important, is to reduce or remove generation of the waste at the source. This process is called source reduction.

Another method of minimizing the toxic waste is to use less toxic materials for operation process. There are three major methods for waste management (Onwukwe and Nwakaudu., 2012): waste minimization, treatment reused and disposal.

2.4 Drilling Waste Treatment

2.4.1 Mechanical Separation and Centrifuge Washing

Solid-liquid separation can be used to remove solid contaminants in this case the drill cuttings from the water. This can be achieved through various techniques such as coagulation and centrifugation, sedimentation as well as filtration. However, the first stage in the treatment of oily cuttings is a solids-control system. High efficiency shale shakers are often used to remove as much of the solids as possible before mechanical attrition which can wear the particles down to a smaller size. A shale shaker under favorable condition should be capable of removing around 90 % (by weight) of the oily-drill solids (Cripps et al., 1998).

2.4.2 Distillation and Evaporation

Distillation and evaporation could be used to separate the constituents of liquid mixtures. This works by applying heat to the liquid and extracting the components of that liquid as they evaporate at different temperatures (Cripps et al., 1998).

2.4.3 Stabilisation

Chemical treatment technologies do not necessarily destroy a waste but rather modify the chemical structure of the waste's constituents. These modifications may convert the waste into a useable form, such as a fuel, or render the material less hazardous. Inorganic materials are the most suitable for a technique called solidification (Cripps et al., 1998).

2.4.4 Incineration

Incineration is a relatively inexpensive disposal option, which also is a good alternative for treating retrieved oily drill cuttings. The technique requires high temperature purpose-built plants, and is used for the disposal of organic waste which is highly toxic, highly flammable and resistant to biological breakdown in landfill sites. Except when used for liquid wastes the process normally leaves a solid residue or ash which is then disposed of over land (OLF, 2001).

2.4.5 Thermal Desorption

Thermal desorption process applies heat directly or indirectly to the wastes, to vaporize volatile and semi volatile components without incineration. In some thermal desorption technologies, the off-gases are combusted, and in others, the gases are condensed and separated to recover heavier hydrocarbons. Thermal desorption technologies include indirect rotary kilns, thermal plasma volatilization, hot oil processors, thermal phase separation, thermal distillation, , and modular thermal processors (Onwukwe and Nwakaudu., 2012).

Thermal desorption process uses heat energy to separate contaminants from solids in order to allow safe reused of all phases. Contaminated solids are heated inside a sealed treatment chamber to the point where the hydrocarbon (organic) contaminants are vaporized. Hydrocarbon and water vapors are removed from the treatment chamber condensed and recovered. Dry and clean solids are discharged from the treatment chamber with total petroleum hydrocarbon (TPH) content less than 0.5 %.

Thermal desorption works well at separating organics and certain types of pollution from contaminated solids and effectively removes contaminants and water from the solids so that the solids meet criteria for safe disposal. Recovered contaminants and water can be reused. Thermal desorption can work well where other cleanup methods cannot, for example when a high amount of contamination in the solids exists. It can also be a faster treatment method than others for removing contamination from large volumes of solids (schlumberger, 2013).Figure 8 shows basic process flow of a thermal desorption. One of the commercial examples of the thermal desorption method is TCC (Thermomechanical Cutting Cleaner) which is explained in the next chapter.

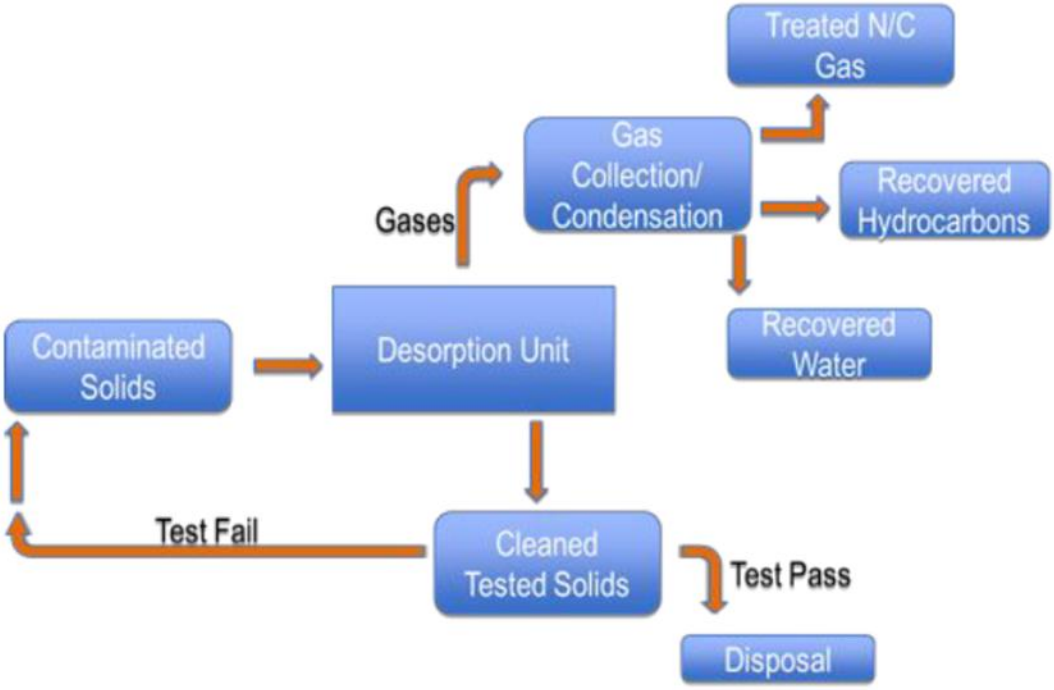


Figure 8. Thermal Desorption process (schlumberger, 2013)

2.5 Thermomechanical Cuttings Cleaner (TCC) Technology

Thermal desorption method has shown relative advantages over other methods and will be discussed in this thesis (Okeke and Obi., 2013).One way of treating oil-based drilling waste is by using TCC technology. A TCC unit is a thermal desorption unit, which separates the incoming waste in streams of water, oil and solids (Thermtech, 2014). The TCC actually is a machine designed for treating drill cuttings in order to convert hazardous oily cuttings into useful products (Bilstad et al., 2014). The oil left in the solids discharged from a TCC unit is acceptable for disposal both onshore and offshore (Halliburton, 2015). Therefore using TCC offshore eliminates the need for transport of cuttings ashore as well as reducing human and environmental exposure to hazard waste thereby improving health and safety (Bilstad et al., 2014).

One of the unique advantages of this technology is its offshore application which began on the

United Kingdom Continental Shelf (UKCS) during the 1990`s. Bikass (2015) claims that discharging TCC-treated OBM cuttings has been accepted on the UKCS since 2003. Bikass says that in 2014 Norwegian Oil and Gas community started to investigate the offshore treatment possibilities of the TCC technology on Norwegian Continental Shelf (NCS) as well.

2.5.1 TCC process

The process starts with screening oversized pieces through a shaker. A feed buffer tank is positioned in the line. The tank contains an agitator that is used to mix the feed material and prevent settling of the feed inside the tank. The cuttings are fed into the unit by a feed pump which is hydraulically powered and allows material to pass into the sealed treatment chamber (so called "process mill") while keeping oxygen out.

The process mill, also known as a Hammer mill, has a barrel shaped chamber (stator) that houses a shaft with a series of hammer arms (rotor) (as shown in Figure 9. Hammermill in TCC). The rotor arms come into contact with a bed of material inside the process mill, where the extreme hammering against the solids by the high speed rotor generates the friction heat. The heat is created within the solids themselves by means of sheer mechanical force from the hammers. This is achieved by whipping and crushing the oil/water-wet solids in such a way that it generates heat in-situ by internal friction and hydrodynamic forces within the reactor. No external heating is necessary.

The rotation of the hammers combined with the motion of the particles in solid-liquid suspension in the reactor breaks down the particles, destroys the capillary forces and reduces the interfacial tension in the solids thereby exposing the fluids for evaporation (OLF, 2001).

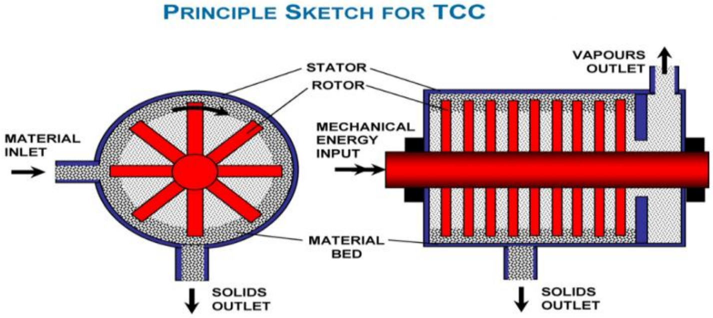
	
(Schlumberger)	(Thermtech)

Figure 9. Hammermill in TCC

The temperature in the process can be kept between $240^{\circ C}$ and $260^{\circ C}$, which is sufficient to evaporate both oil and water (Kirkness, 2008). The vapor will leave the mill and be condensed in two steps (condensers) in order to separate water and oil as well (Thermtech, 2014). A typical TCC process is shown in Figure 10.

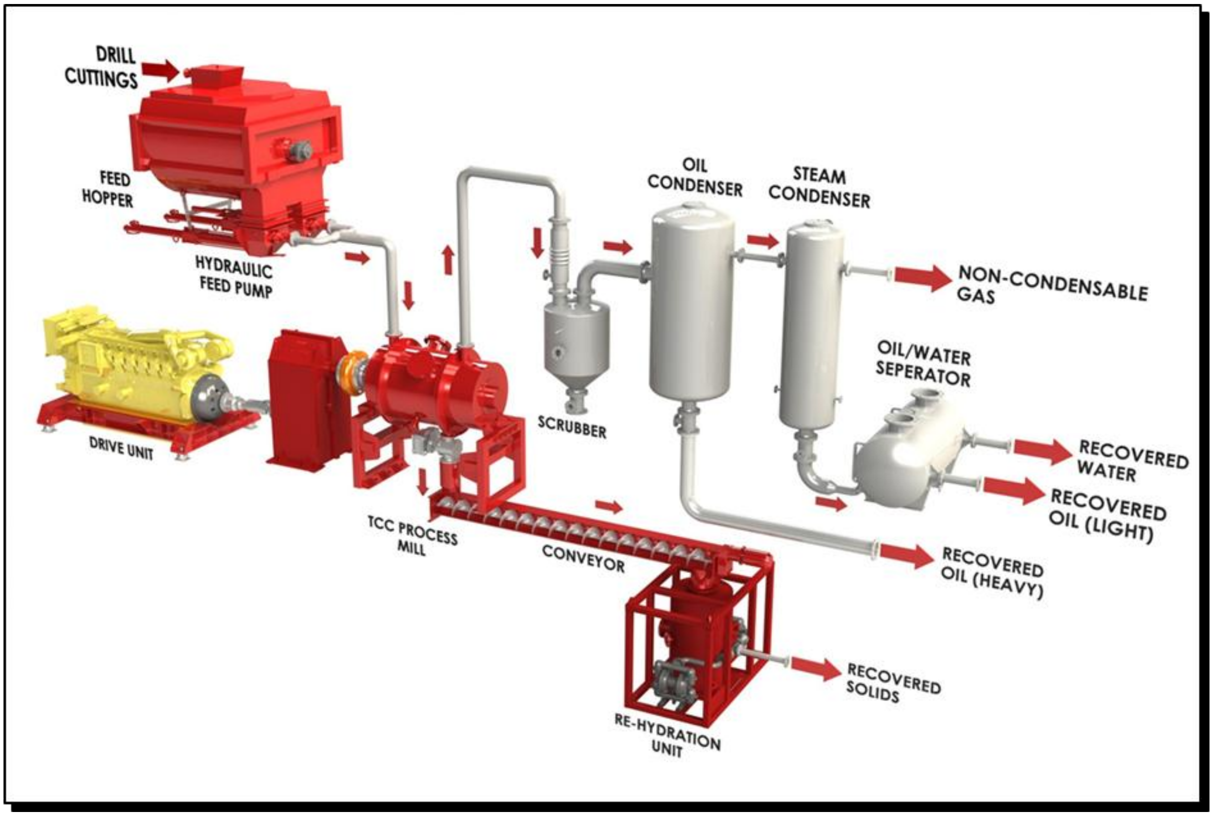


Figure 10. TCC Process (Halliburton, 2015)

2.5.2 Advantages and Disadvantages of TCC Technology

Some advantages of TCC are as explained below:

Performance efficiency of the TCC technology can turn hazardous oily waste material (oily cuttings) into a non-hazardous material, with less than 0.5% hydrocarbons in the solids after treatment. More than 99% base oil recoveries with less than 2% solids are left in recovered oil (Thermtech, 2014). It may even degrade (destroy) added chemicals when operating in a special cracking mode. It is environmentally acceptable technology, with only trace emission of CO_2, SO_2, NO_X and other gases. It is compact with high capacity and small footprint.

Despite these stated advantages this technology can have the following disadvantages:

The TCC technology leaves behind smaller particle sizes of solids in comparison with competitor technologies (e.g. SRD[4] technology) due to a high degree of turbulence (rotational speed > 600 rpm). This does not represent a special problem with cuttings materials as a feed material, but it is a definite challenge when organophilic bentonite or other clay materials make up the main part of the solid feed material. The TCC technology cannot handle non-condensable gases including volatile odor compounds without an added burner or filter as the SRD technology does by routing them back into the gas boiler for incineration (OLF, 2001).

Recovered Oil

The recovered oil quality is dependent upon the temperatures developed in the mill and on the processing time before the oil is leaves the system (Thermtech, 2014). If one of these factors is too high, the oil can be degraded. In the TCC the oil is subjected to high temperatures only for a couple of seconds before it is evaporated and leaves the system. In comparison to other thermal desorption technologies the TCC process temperature is moderate and the evaporation more gentle resulting in a high quality of the recovered oil. Figure 11 shows a gas chromatography / mass spectrometry (GC/MS) profile of used base oil before and after TCC treatment. This particular base oil's most abundant hydrocarbons are C_{11}, C_{12}, C_{13} and C_{14}. These are also present after TCC treatment. Although the abundance of C_{11}-C_{14} decreases slightly, the recovered oil can be instantly re-used as base oil for new muds (MI Swaco, 2013).

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[4] The SRD (Soil Recovery Denmark) unit is a process unit based on distillation and evaporation with a large rotary heat exchanger.

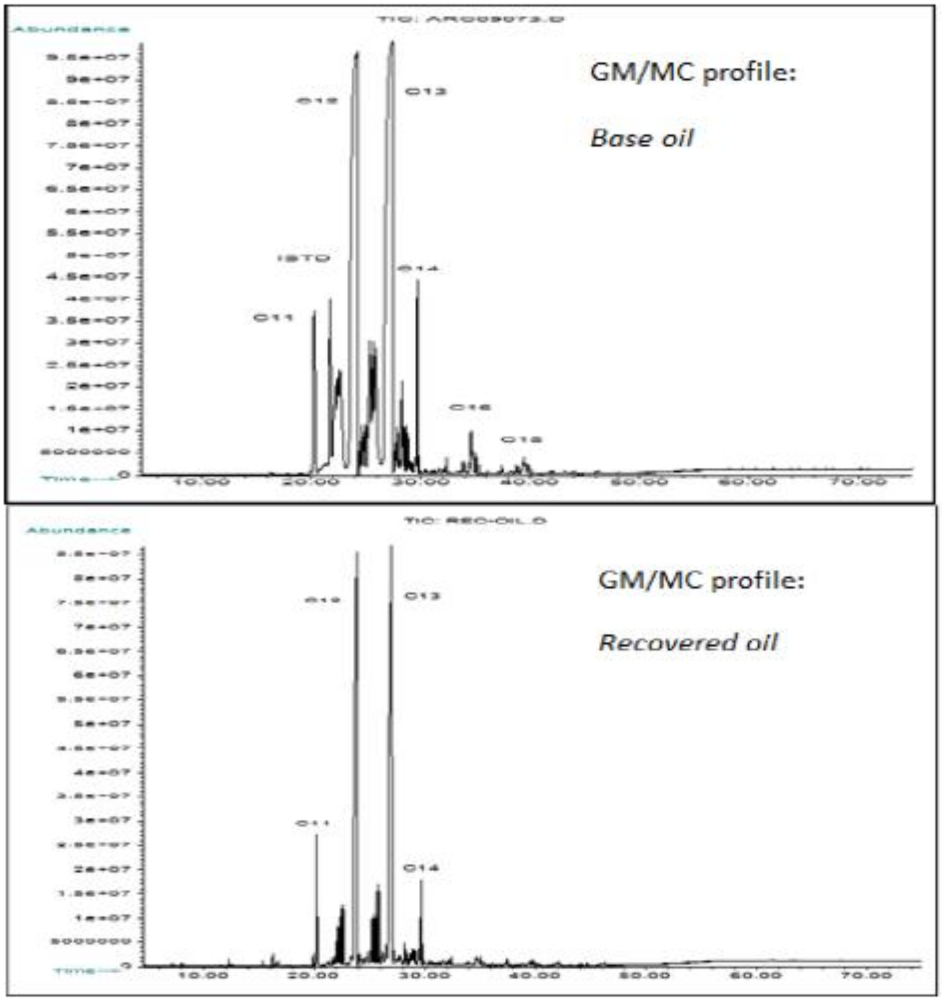

Figure 11. GM/MC profile of base oil and by TCC recovered oil (MI Swaco, 2013)

Recovered Solid Cuttings Material

In terms of reuse of the solid residue, it can be important to remove as much salt as possible associated with the cuttings, as salt is identified as an important hindrance for most reuse opportunities.

Recovered Water

The water recovered from the thermal distillation processes is a waste stream that must be treated either for reuse or disposal. Furthermore, the quantity of water recovered is equal to that entering the process with the cuttings. The water quality obtained indicates the ability of the process to destroy the chemicals on the oily cuttings. Therefore, the best results are obtained with the TCC technology operating in a plasma mode, leaving behind non-emulsified water, which is relatively easy to treat (OLF, 2001).

Chapter 3: Research Method

3 Research Method

The goal of the experimental procedure was to trace the PAH substances through the TCC process and also to determine TCC treatment efficiency for the removal of PAH from drill cuttings from Thermtech AS and samples studied include:

- ✓ Drill cuttings before TCC
- ✓ Recovered solids after TCC
- ✓ Recovered water after TCC
- ✓ Recovered oil after TCC.

The measurements of density and solid content were done based on the methodology provided by Thermteck AS.

The research was oriented to check traces of 16 hazardous PAH[5] (Table 6) in samples of oil, water, cuttings and TCC treated solids. Three trials of each sample were prepared and tested.

Table 6. 16 EPA PAH

#	CAS number	Name	#	CAS number	Name
1	(91-20-3)	Naphthalene	9	(56-55-3)	Benzo(*α)*anthracene
2	(208-96-8)	Acenaphthylene	10	(218-01-9)	Chrysene
3	(83-32-9)	Acenaphthelene	11	(205-99-2)	Benzo(*b*)fluoranthene
4	(86-73-7)	Fluorene	12	(207-08-9)	Benzo(*k*)fluoranthene
5	(85-01-8)	Phenanthrene	13	(50-32-8)	Benzo(*α*)pyrene
6	(120-12-7)	Anthracene	14	(215-58-7)	Dibenz(*α,h*)anthracene
7	(206-44-0)	Fluoranthene	15	(191-24-2)	Benzo(*ghi*)perylene
8	(129-00-0)	Pyrene	16	(193-39-5)	Indeno(*1,2,3-cd*)pyrene

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[5] In this research the difference between the categorized PAHs is that component Methylnaphthalene (CAS# 90-12-0) is not present in the EPA table, while component number 12 present in EPA table but we did not have in our standard sample.

3.1 Materials

The equipment and chemicals used for the experiment are presented in Table 7.

Table 7. List of chemicals and equipment used for the experiment

Equipment		Chemicals
Gas Chromatograph Agilent 5975	Amber screw cap teflon	N-pentane (C_5H_{12})
Volumetric Flask 5,10 ml	Pipet serological	Florisil (0.15 – 0.2 mm) MgO*3.75 SiO_2x H_2O
Ultrasonic bath Branson 5510	Standard wide mouth bottle	Na_2SO_4
Separatory funnels 500 ml and 250 ml	Filter paper	Iso-octane ((CH_3)$_3$CCH_2CH (CH_3)$_2$) Dichloromethane (DCM)
TLD Separatory Funnel Kit	Funnels	
Mortar and pestle	Erlenmeyer flask	
TLD weighing dishes	Hamilton syringe	
Hoses for air up-concentration	Pressurized air	Standard :polynuclear aromatic hydrocarbons mix,1*1 ml,2000 µg/ml in benzene:CH2C12(50:50)

3.2 Methods

The experiment included two parts: 1) Sample preparation part, which consisted of extraction for solids, dilution, clean-up and up-concentration processes, and 2) Gas Chromatography analysis (GC). To prepare samples for CG analysis the extraction of semi-volatile compounds needs to be done both for liquids and solids (liquid-liquid extraction and solid-liquid extraction). Detailed description of each step is presented below (Figure 12).

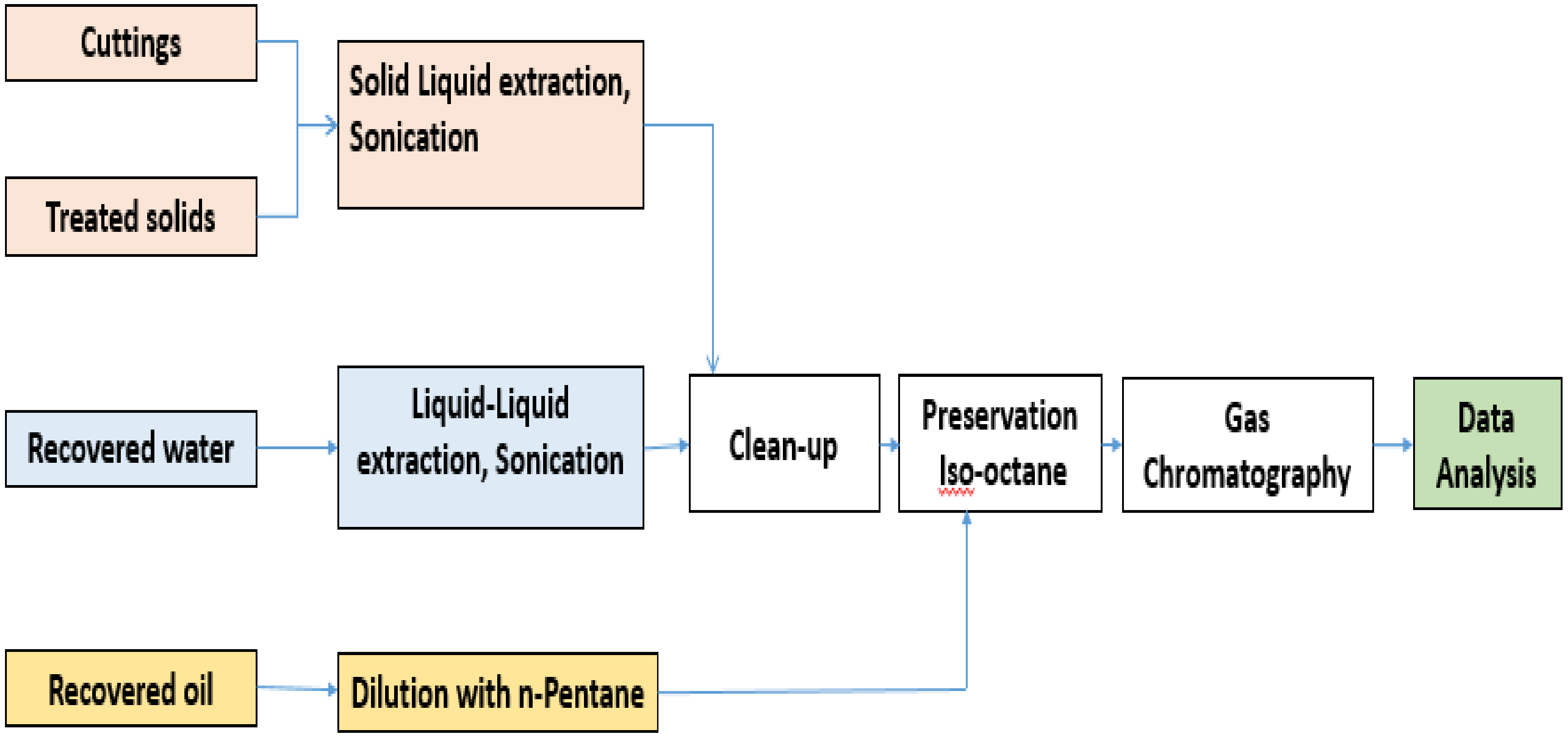

Figure 12. Flow chart due to lab work

3.2.1 Solid Liquid Extraction

Extraction is a critical sample preparation step for the analysis of PAH in soil samples because these hydrophobic compounds are strongly combined to the soil material (Cole-Parmer, 2015).

There are three methods for the extraction of semi-volatile compounds:
1) Soxhlet extraction, 2) extraction after mechanical mixing such as shaking, homogenisation, or stirring, and 3) ultrasonic extraction.

For solid-liquid extraction of organic compounds Soxhlet is the most common method. These are extracted from the matrix by continuously washing the solid with a volatile solvent in a specialized piece of glassware (Soxhlet extraction apparatus). However, Soxhlet extraction takes a long time to achieve high extraction efficiency and it is not suitable for those organic compounds which are thermally unstable. Due to these limitations Soxhlet could not be used for this experiment.

Sonication extraction (EPA Method SW-846 3550) can also be used for semi-volatiles. This method involves the use of sound waves to enhance analyte transfer from sample to solvent. Sonication is a faster extraction technique than Soxhlet and also it may require less solvent (Criteria Group, 1998). For this research sonication extraction was carried out for solid-liquid extraction.

3.2.1.1 Sonication

The ultrasonic agitation, also known as sonication, is a technique which involves the acoustic energy, causing rapid compression and rarefaction of fluid movement. This agitation can be performed or by placing the sample solvent mixture directly into a sonication bath. The desired ultrasound is generated by means of piezoelectric ceramic attached either to the ultrasonic horn or to the walls of the sonication bath (Government of Japan, 2001).

The sonication method is, in some degree, preferable to the Soxhlet since it provides higher extraction efficiencies; is more economical and is more easily operated. However, the level of extraction efficiency was observed to be highly dependent on the sample matrix and concentration of contaminants in the samples (E. V. Lau et al., 2010). Figure 13 shows schematic of Ultrasonic bath.

Figure 13. Ultrasonic cleaner (Cole-Parmer, 2015)

Solid extraction procedure was carried out in the following steps:

1) For treated solids a drying procedure needed to be done beforehand to remove all the water. For this 10 g of recovery solids was placed in the oven over night for drying. Figure 14 shows solids samples before and after TCC being stirred.

2) 5 gr of cuttings and TCC recovery solids were weighed; 50 ml of pentane was added to each sample and the samples were stirred overnight (each sample was done with 3 trials).

3) After stirring, each sample was placed in sonicated bath for 1 hour[6].

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[6] Some samples after sonication was evaporated due to caps not being sealed enough and that is why the experiments was repeated.

3.2.1.2 Clean-up Method

After sonication the filtration procedure and clean-up took place. The usual filters were used to remove some suspended particles from the sonicated liquid (Figure 15 a). a Chromatographic Column was used for clean-up procedure, where 2 g florisil[7] (0.15 – 0.2 mm) and 2g Na_2SO_4 were located into the Chromatographic Column in order to separate aliphatic and aromatic hydrocarbons from the sonicated liquid (Figure 15 b)

When the clean-up procedure had been completed 1.5 ml of Isooctane was added to preserve the Samples since Iso-octane prevents evaporation (Government of Japan, 2001).

3.2.1.3 Extraction for Solid Sample (Lab experiments for Solid extraction)

5 gr of solid was weighed before and after TCC; 50 ml of pentane was added to each sample and they were stirred overnight.

The third sample cuttings was mixed with the pentane but another sample recovery solids was very sticky. This sample did not mix and stuck to the wall of glass bottle. 10 gr of this solid was placed in the oven overnight for more drying. Figure 14 shows recovery solids sample when stirring.

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[7] Florisil is the commercial name for a magnesium silicate with an acidic character. This material is mostly used for clean-up of samples for GC containing pesticides, organochlorine compounds, esters, ketones, phthalic esters, organophosphate pesticides (which include a phosphorus - oxygen bond which can decompose on florisil), separating aliphatic and aromatic hydrocarbons (Government of Japan, 2001).

Figure 14. Step 2 in solid-liquid extraction

After stirring, the samples were placed in the sonicated bath for 1 hour (some samples had lost all their liquid after being sonicated due to having faulty caps so these experiments were repeated).
After that the solids were filtrated with the chromatographic column (with 2 g florisil (0.15 – 0.2 mm) and 2g Na_2SO_4) as shown in Figure 15.
Filtration took some time and the filter had sometimes to be changed due to it becoming clogged. Then 1.5 ml Isooctane was added for storage of the samples because Isooctane prevents evaporation. The experiments continued with the up concentration test. The next chapter will explain this method.

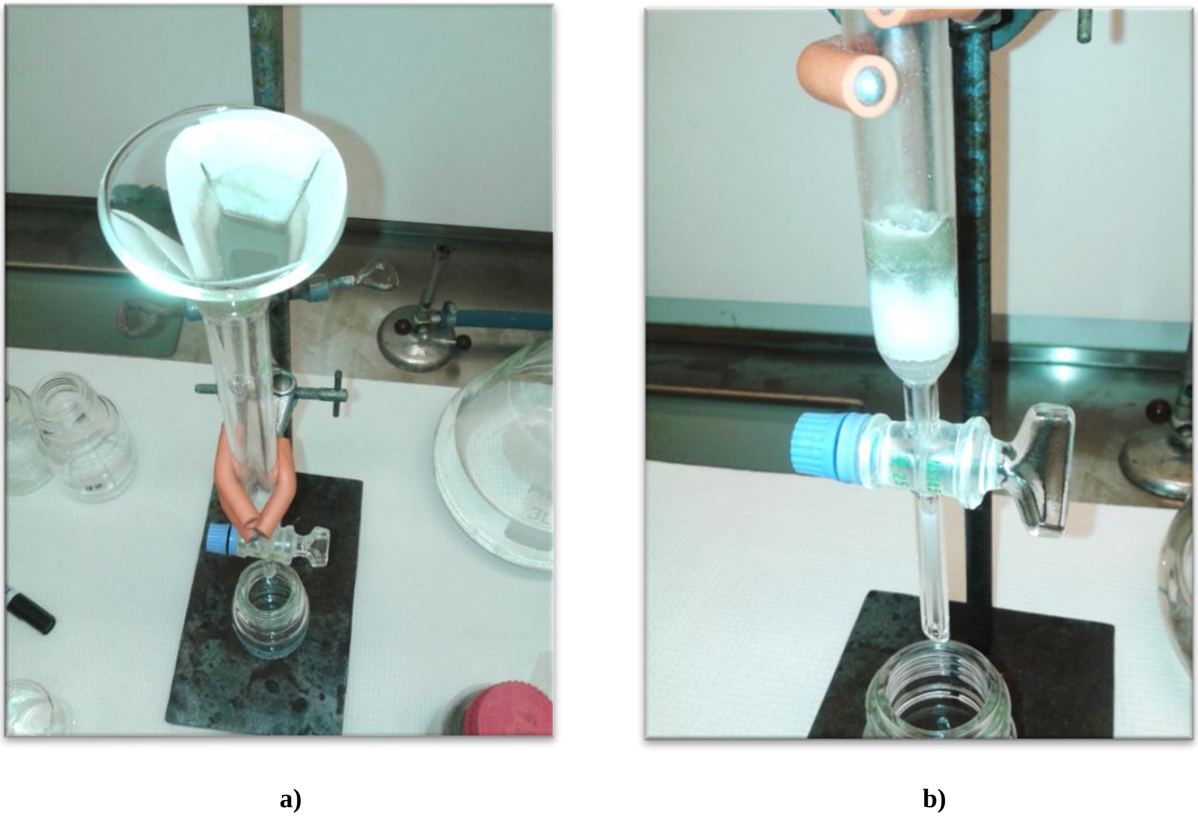


Figure 15. Chromatographic Column

3.2.2 Liquid-Liquid Extraction

For the purposes of this thesis the liquid-liquid extraction (solvent extraction method) was implemented for the extraction of water and oil samples. Solvent extraction methods use non-polar solvents, which are miscible with water, to extract the target compound from water by using the greater solubility of the target compound in the solvent than in the water. Volatile solvents such as hexane, pentane, benzene, ether, ethyl acetate, and dichloromethane are usually used for the extraction of semi-volatile compounds from water. Hexane is suitable for extraction of non-polar compounds such as aliphatic hydrocarbons; benzene is suitable for aromatic compounds, and ether and ethyl acetate are suitable for relatively polar compounds containing oxygen.

For this research the pentane was used for liquid-liquid extraction due to availability.
Extraction is commonly achieved by shaking the water sample and solvent in a separating funnel.

However, occasionally large amounts of emulsion are formed, and it is difficult to separate the solvent from the aqueous phase. Continuous liquid-liquid extraction methods repeatedly circulate solvent in special glassware.

An example of a liquid–liquid extraction using a separatory funnel is shown in Figure 16. Funnel (a) represents solutions before the extraction where 100% of the analyte is in phase 1. Funnel (b) shows solutions after the extraction where most of the analyte is in phase 2, although some insignificant amount of analyte remains in phase 1. Although one liquid–liquid extraction can result in the complete transfer of analyte, a single extraction is not usually sufficient (Larsenr, 2011).

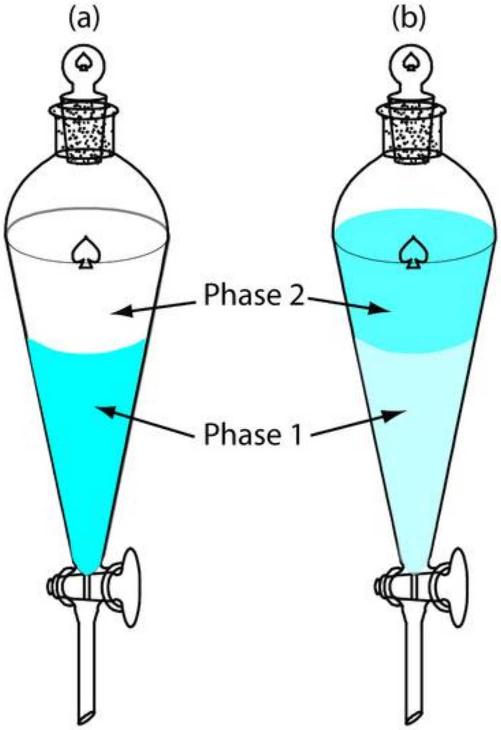


Figure 16. Separatory funnel

3.2.2.1 Liquid- Liquid Extraction for Water Sample

The liquid-liquid extraction for water was carried out in the following steps:

Three 500 ml separatory funnels were set up (Figure 17 b).

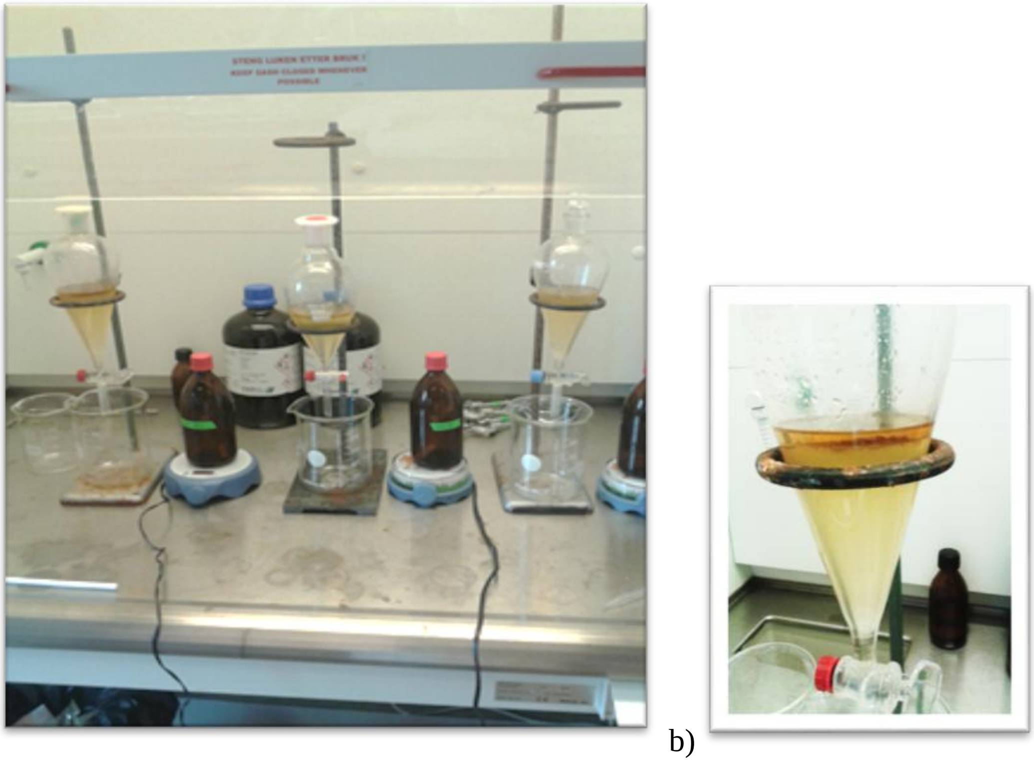
20 ml pentane was added to a 200 ml sample in a glass bottle and stirred for 30 minutes. After that the mixture was put into a 500 ml separatory funnel and shaken.

The water and organic phase were separated into layers.

The organic phase was put into a 250 ml separatory funnel and the water remain into a 500 ml funnel. 20 ml pentane was added to the water sample bottle and well shaken. This mixed liquid was then put into the 250 ml separatory funnel with the organic phase. This phase separation was repeated three times Figure 17 a).

After phase separation the clean-up procedure was done (see 3.2.1.2) using 3 florisil columns filled with 2 g florisil (0.15 – 0.2 mm) and 2g Na_2SO_4 Figure 18.

1.5 ml isooctane was added and the samples stored until the next process.



a) b)

Figure 17. Separatory funnel and water samples

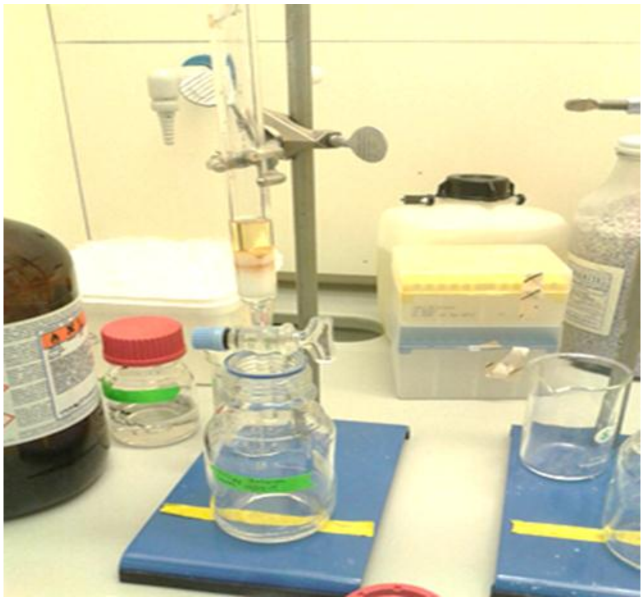


Figure 18. Chromatographic Column

3.2.2.2 *Liquid- Liquid Extraction for Oil Sample*

The liquid-liquid extraction for oil was carried out using a different method since that used for the water sample extraction would not be effective in this case. The following steps for oil extraction were followed:

- ✓ 200 ml of oil was mixed with 20 ml of pentane and stirred for 30 minutes;
- ✓ Using a Hamilton syringe 10 µl of the mixture was taken in order to prepare a 10 ml solution with n-pentane;
- ✓ Trial samples of 1 ml each were put into the GC vials for further GC analysis.

3.2.3 Up- Concentration Test

The purpose of the up-concentration procedure is to remove excessive amount of the solvent (in this case is n-pentane). During this procedure pressurized air was used (see Figure 19).
To reduce excessive amount of pentane in samples of water and solids (cutting and recovery solid), achieving volume of approximately 1 ml ready for GC analysis. The oil samples did not need up-concentration since the amount of n-pentane used was limited.

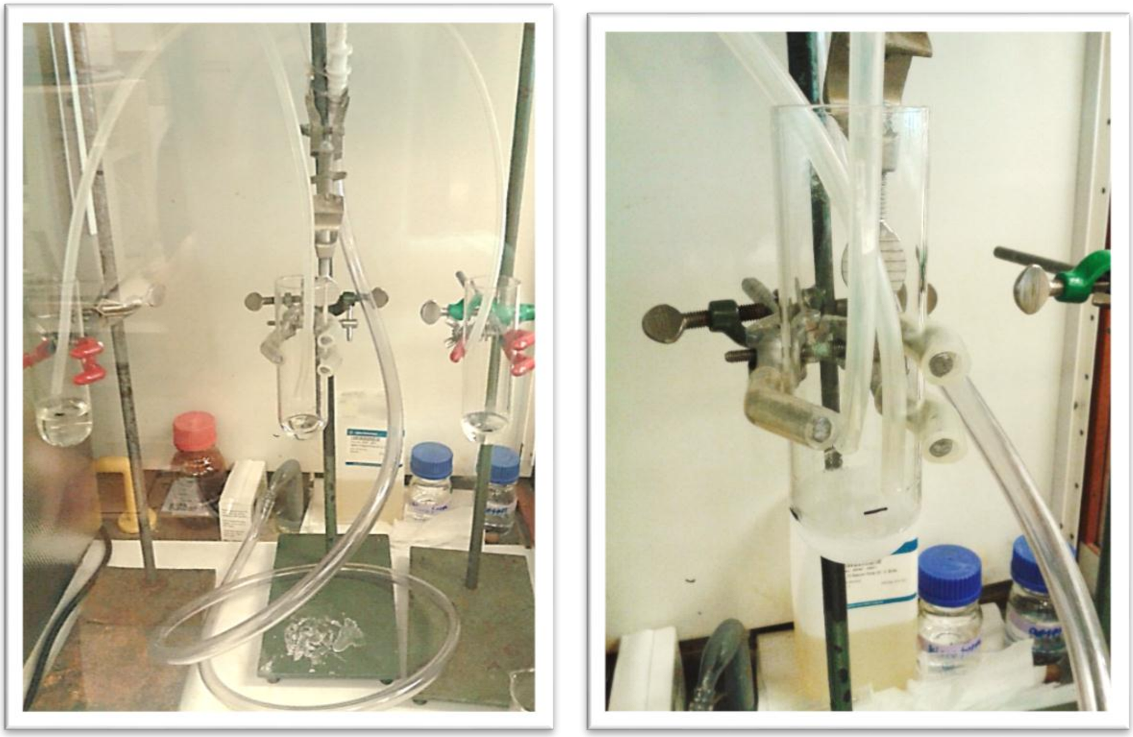


Figure 19. Up concentration with pressurized air

3.2.4 Gas chromatography

After the preparation stage, 12 samples were ready for the Gas Chromatography. The main components of the CG are carrier gas, flow controller, injector port, chromatographic column, column oven, detectors and recorder. Figure 20 shows the connections between all the components of GC, while Figure 21 shows the GC equipment used in the UiS lab.

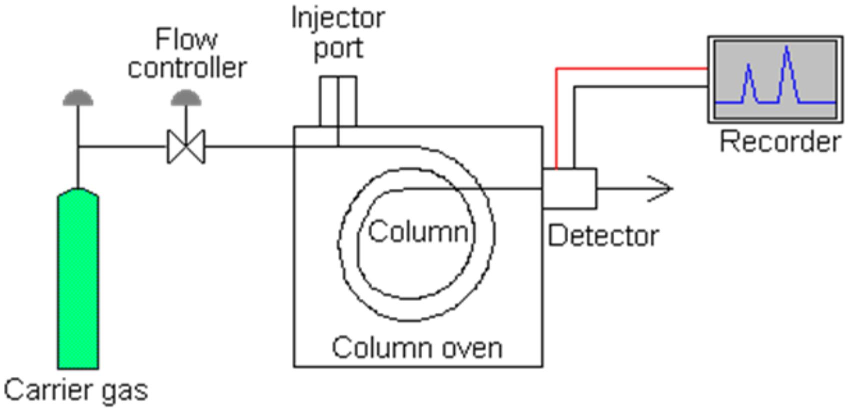


Figure 20. Gas chromatograph (schematic diagram) (Sheffield Hallam University., 2013)

Figure 21. Gas chromatograph

The main functions of GC analysis are:

1. Effective separation of the sample into its components;
2. Identification of these components (qualitative analysis);
3. Estimation of the amounts in which they are present (quantitative analysis).

Description of CG functionality as well as a method for data calculation is provided below.

3.2.4.1 Gas Chromatograph Functionality

The chromatographic separation method involves the movement of a sample mixture through a column of, for example, stationary phase. The usual analysis method used in gas chromatography is elution whereby a small sample of the volatile mixture which is to be separated is introduced into the front end of the column.

A carrier gas is then passed through the column in a constant current and the column is kept at a consistent temperature. The carrier gas acts as an eluent which serves to transport the different components of the sample mixture (as gas or vapor) through the chromatography column. As these substances pass through the stationary phase they are retained by it to varying intensities and this ensures that the rates at which they pass through will also differ. The stationary phase may retain the components of the sample mixture by adsorption, by solubility or by chemical bonding. As they move along the length of the chromatographic column, the components are distributed (due to equilibrium differences) between the stationary and the moving phase and become separated.

The rate at which each component moves will depend upon its partition coefficient: K. Since individual components in a sample have different partition coefficients they will become separated. This is shown in Figure 22 where the individual components are represented by the letters A, B, C, D and E.

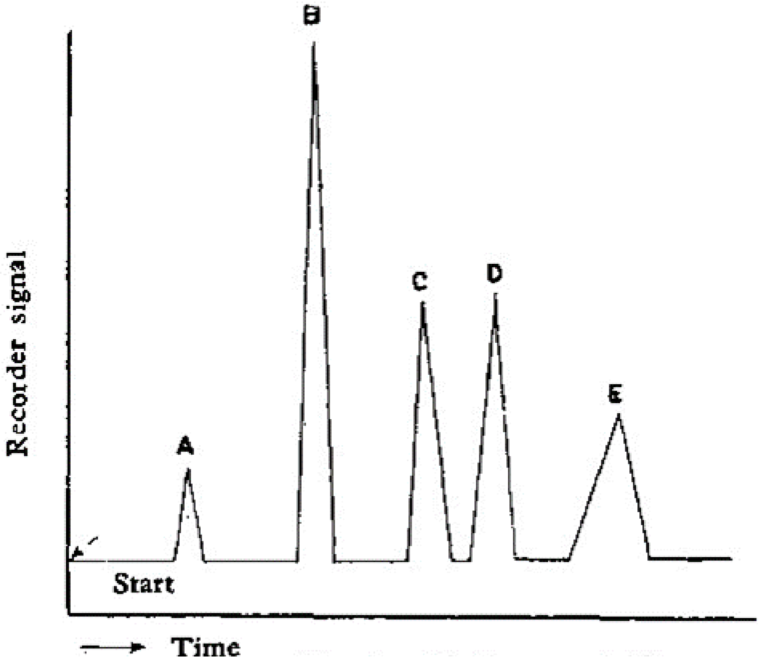


Figure 22. Elution analysis (ORHUN, 1968)

The different components of the sample emerge from the chromatography column at different times and in the form of individual bands which are separated by zones of the carrier gas.

A delicate detector at the end of the column senses the order in which these components emerge and can therefore give an analysis of both what the components are (a qualitative analysis) and of the amounts in which they are present (a quantitative analysis).

The time between the beginning of the analysis and when a component emerges from the column (and the peak maximum occurs in the chromatogram) is known as the retention time. The volume of carrier gas (measured at, or corrected to, both column temperature and column outlet pressure) which passes through the column between the beginning of the analysis and the peak maximum is known as the retention volume. The detector sends signals to the recorder and the relative strength of these signals indicates the relative amounts of the individual components within the sample substance. This means that the peak maximum in the chromatogram gives a quantitative measure of each component.

3.2.4.2 PAH Standard Preparation

The PAHs standard was opened and all of it put into a 10 ml flask using a syringe. The syringe was then washed with dichloromethane (DCM) and series dilution performed three times with DCM. The final dilution had no yellow color.

2.5 ml of this final dilution was then put into a 5 ml flask and filled up with DCM Series dilution was repeated four times.

10 µl was then put into an amber screw cap teflon for GC analysis.

3.2.4.3 Chromatographic Column

The column information used for GC in this thesis is following:

Capillary Column

- Max temperature: 350 °c.
- Nominal length: 30.0 m.
- Nominal diameter: 250.00 µm.
- Nominal film thickness: 0.25 µm.
- Initial pressure: 102 k pa.
- Initial time: 19.00 min.
- Nominal initial flow: 1.6 ml/min.
- Outlet pressure: vacuum.

GC Method

Gas chromatography methods used is:

Control information

- Mass Hunter \ GC MS\ methods\ PAH SIM.M.
- Injection Source: external device.
- Injection location: front.

Oven

- Maximum temp: 350 °c.

- Initial temp: 70 $^{\circ c}$.
- Initial time: 0.5 min.

Figure 21 shows GC instruments used in the UiS lab.

3.2.5 Measuring the Density of Components

In this thesis measured density of cuttings and recovered oil, water and solids. The quantity of density used for calculated the PAH percentage in recovered oil, water and solids.

Measured the density following steps:

- ✓ Oil: a sample volume was taken and weighed. This formula was used to calculate density:

$$\rho\_oil = Mass/ volume$$

- ✓ Cutting: a 100 gr cutting was taken and mixed with 400 gr water (400 ml). This mixture was then measured using this formula:

$$\rho\_cutting = Mass\ cutting / volume\ total - (Mass\ water/ \rho\ water)$$

- ✓ Solids: the same procedure was followed as for cuttings with adjustments made for solvability.

3.2.6 Measuring Solid Content

We also measured the solids content. And also the ratio quantity used for PAH calculation in recovered oil, water and solids.

50 gr of cutting was taken and put in the oven at 300 $^{\circ c}$ for 30 min. The dried solid was weighed and the weight ratio calculated thus:

Ratio: Mass solids/ Mass cuttings

Chapter4: Results and Discussion

4 Results and Discussion

This Chapter presents the experimental results with the discussion of PAH removal efficiency of the TCC technology. The 16 hazardous PAH listed in Table 6 are focused on. The discussion includes quantitative analysis.

Recalculation of raw GC results in ppm into mg/L

The results from Gas chromatography originally were presented in ppm units. To convert data for oil and water into mg/l (and cuttings and recovered solids into mg/kg) the following calculations were done:

Oil sample:

1) 200 ml oil +20 ml pentane = 91% oil in this sample.
2) In result GC for example 0.16684 ppm or gr/1000 ml naphthalene in oil sample.
3) The GC vial is 10 ml. In the vial for GC analyze we have 10 µl from mix number 1.
4) To calculated the naphthalene in 1ml then 0.16684 ppm/1000 ml=1.6684*10^{-4} mg/ml
5) Then 1.6684*10^{-4} mg/ml naphthalene is in 9.1µl oil. We calculate in 1000 ml or 1L. 166.84*10^{-6} mg/ml /9.1 µl=18.334 mg/l naphthalene is in the oil.

Water sample:

1) 0.468 ppm or mg/1000 ml naphthalene is in the result.
2) To know in 1ml: 0.468 ppm/ 1000 ml=0.468*10^{-3} mg/ml in the 1 ml.
3) 0.468*10^{-3} mg/ml is amount of naphthalene in 200 ml water.
4) In 1000 mL: 0.468*10^{-3} mg/ml *1000 ml /200 ml =2.34 *10^{-3} mg/l naphthalene in the water sample.

Solid sample for example:

1) 1.75926 mg naphthalene in 1000 ml.
2) 1.75926 *10^{-3} in 1 ml vial GC.

3) $1.75926 * 10^{-3}$ in 5 g of solids.

4) We calculate in 1kg then

$1.75926 * 10^{-3} * 1000$ g/5 g = 0.352 mg/kg.

4) 0.352 mg/kg naphthalene in solids.

4.1 Overall Results

The overall results from Gas Chromatograph test are summarized in Table 8 and Table 9. As is clear from the tables, none of the samples contained *Acenaphthene* component. Table 8 shows that *Naphthalene* and *Phenanthrene* were higher than other components in recovered oil. In the recovered water, most of the PAHs showed very low values. The total value for the recovered water was 0.0493 mg/l while this value for the recovered oil was 72.28 mg/l.

Table 8. PAH concentrations in the recovered oil and water

Compound Name		Recovered Oil	Recovered Water
PAH		mg/l	mg/l
1	Naphthalene	18.7802	0.0017
2	Methylnaphthalene	7.9277	0.0011
3	Acenaphthylene	3.4555	0.0046
4	Acenaphthene	0	0
5	Fluorene	8.2067	0.0096
6	Phenanthrene	17.1252	0.0121
7	Anthracene	5.2236	0.0152
8	Fluoranthene	1.2655	0.0020
9	Pyrene	2.0273	0.0022
10	Benzo(a)anthrascene	1.8178	0.0001
11	Chrysene	0.9483	0
12	Benzofluoranthene	1.2322	0
13	Benzo(a)pyrene	3.1334	0.0003
14	Indeno(1,2,3-CD)pyrene	0.2359	0.0001
15	Dibenzo(a,h)anthrascene	0.5046	0.0001
16	Benzo(g,h,i)perylene	0.3973	0.0001
	Total PAH	72.2811	0.0493

Table 9 illustrates the results for the cuttings and the recovered solids from TCC. The concentration of the samples was calculated in a 1 ml vial in the GC equipment. Table 9 shows that *Phenantrene* component which had a highest value before TCC treatment has been successfully decreased to almost zero after TCC in the solids. This component was remove partially by TCC and partially went to the recovered oil (17.1252 mg/l) as mentioned earlier. *Methylnaphthalene* was also mostly recovered from the cutting and decrease also from 0.68 mg/kg to 0.011 mg/kg in the solids and was traced in the recovered oil.

Naphthalene decreased from 0.33 mg/kg to 0.18 mg/kg representing an approximate decrease of 45% after TCC. Other components like, *Anthracene*, *Fluorene* and *Pyrene* decreased by more than 95% in the cleaned solids after TCC.

Overall by comparing total PAH in the cutting before TCC (2.81 mg/kg) with the recovered solids after TCC (0.35 mg/kg), the results demonstrate that the TCC process decreases PAH in the solids by 87%.

Table 9. Data comparison the quantity of PAH in the cuttings and the recovered solids after TCC

(Blue color is lowest and green color is highest)

Compound Name		Cuttings	Recovery solids
PAH		mg/kg	mg/kg
1	*Naphthalene*	0.3327	0.1847
2	*Methylnaphthalene*	0.681	0.011
3	*Acenaphthylene*	0.0979	0.0803
4	*Acenaphthene*	0	0
5	*Fluorene*	0.2079	0.0067
6	*Phenanthrene*	0.8764	0
7	*Anthracene*	0.3338	0.0018
8	*Fluoranthene*	0.0787	0.0057
9	*Pyrene*	0.1195	0.0203
10	Benzo(a)anthrascene	0.0168	0.0155
11	*Chrysene*	0.002	0
12	Benzofluoranthene	0.0108	0.0013
13	Benzo(a)pyrene	0.0391	0.0191
14	Indeno(1,2,3-CD)pyrene	0.0029	0.0007
15	Dibenzo(a,h)anthrascene	0.0028	0.0057
16	*Benzo(g,h,i)perylene*	0.0039	0.0011
	Total PAH	2.8062	0.3539

Another method was used for the calculation of the percentage PAH in water, oil and solid after TCC by using data from GC and considering the amount of cutting as 100%. Water, oil and solid percentages were calculated using the same unit of measurement (mg/kg) by considering oil and water density and the weight percentage of the recovered water, oil and solids in the cutting sample. More explanation is in chapter (4.5).

Table 10 shows that the percentage of PAH components with this method. The Rest column shows the remaining percentage which was not found after TCC process and had mostly evaporated scaped through the sludge return line or the non-condensable gas line during TCC procedure.

Table 10. PAH percentage calculated according to density

Comp #	PAH	Percentage Calculated				
		Cutting	Water	Oil	Solid	Rest
1	Naphthalene	100%	0.05%	35.32%	22.87%	41.76%
2	Methylnaphthalene	100%	0.02%	7.28%	0.67%	92.03%
3	Acenaphthylene	100%	0.47%	22.07%	33.76%	43.69%
4	Acenaphthene	0%	0%	0%	0%	0%
5	Fluorene	100%	0.46%	24.70%	1.33%	73.51%
6	Phenanthrene	100%	0.14%	12.22%	0.00%	87.64%
7	Anthracene	100%	0.45%	9.79%	0.22%	89.53%
8	Fluoranthene	100%	0.26%	10.07%	2.99%	86.69%
9	Pyrene	100%	0.18%	10.61%	7.01%	82.20%
10	Benzo(a)anthrascene	100%	0%	0%	0%	0%
11	Chrysene	100%	0%	0%	0%	0%
12	Benzofluoranthene	100%	0.01%	71.70%	4.98%	23.31%
13	Benzo(a)pyrene	100%	0.07%	50.14%	20.17%	29.61%
14	Indeno(1,2,3-CD)pyrene	100%	0.23%	51.22%	9.63%	38.92%
15	Dibenzo(a,h)anthrascene	100%	0%	0%	0%	0%
16	Benzo(g,h,i)perylene	100%	0.28%	64.49%	12.03%	23.19%

4.2 PAH Traced in Recovered Oil

Figure 23 shows the concentration of PAH in recovered oil. The results show that *Naphtalene* and *Phenanthrene* had the highest values in the oil recovered from TCC While *Acenaphthene,* had the lowest value at almost zero (see Appendix A).

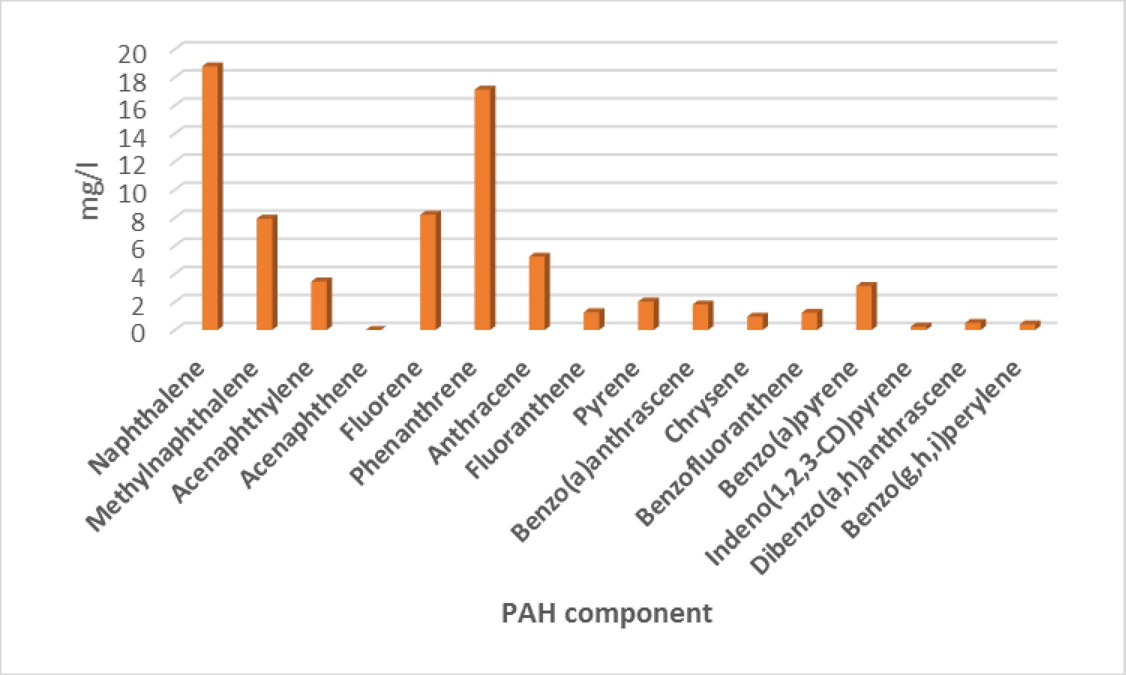


Figure 23. PAH quantity in recovered oil

4.3 PAH Traced in the Recovered Water

Figure 24 shows the concentration of PAH in the recovered water. *Anthracene* component had the highest value which was about 0.015 mg/l. *Naphthalene, Methylnaphthalene, Fluoranthene* and *Pyrene* all had a quantity between 0 – 0.002 mg/l. *Anthracene* is more soluble in water than *Chrysene* (see Appendix A).

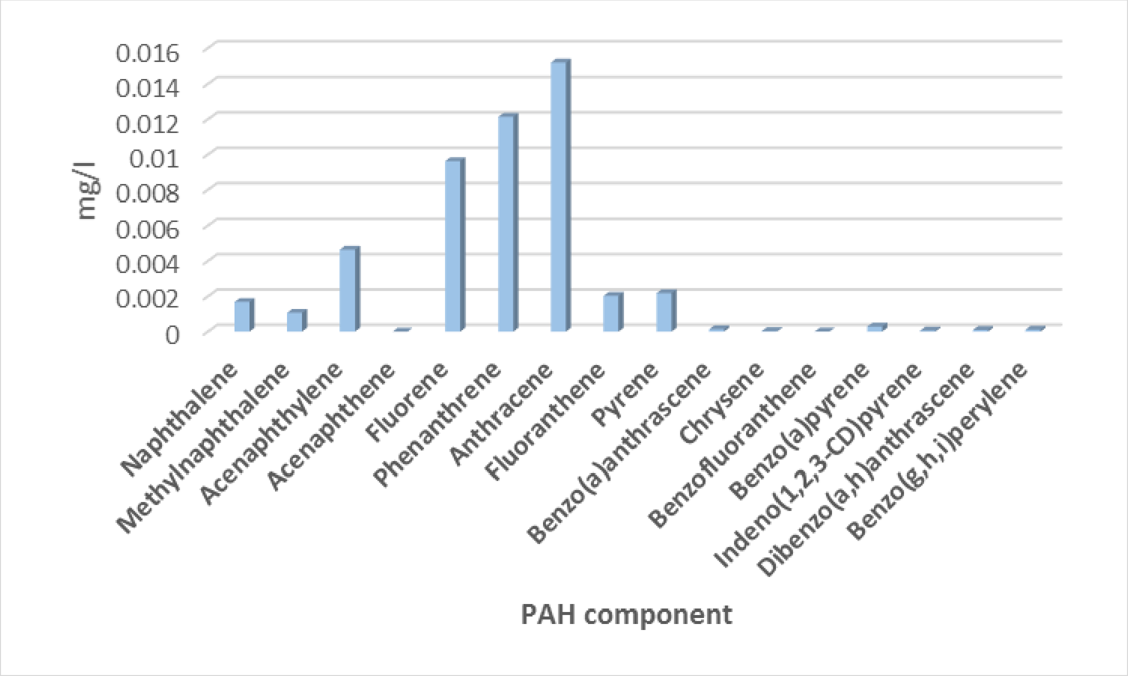


Figure 24. Quantity of PAH in the recovered water

The limits given by the EPA for PAH concentrations allowed to be released into water are presented in Table 11. After TCC the amounts of PAH in recovered water were below these limits, which means that the TCC process is sufficient for water treatment.

Table 11. Standards for PAH

Agency	Focus	Level
U.S. EPA	Water	*0.0001 mg/L (Maximum contaminant level for Benzo(α)anthracene)*
		0.0002 mg/L (Maximum contaminant level for Benzo(α)pyrene, Benzo(b)fluoranthene, Benzo(k)fluoranthene and Chrysene)
		0.0003 mg/L (Maximum contaminant level for Dibenz(α,h)anthracene)
		0.0004 mg/L (Maximum contaminant level for Indeno(1,2,3-cd)pyrene)

Comparing the results for recovered water with the requirement given in Table 11, one can see that the concentrations of components (*Benzo(a)anthrascene, Chrysene, Benzofluoranthene, Benzo(a)pyrene*, *Indeno(1,2,3-CD)pyrene*, *Dibenzo(a,h)anthrascene*, *Benzo(g,h,i)perylene*) in the recovered water are extremely low and within the requirements.

Due to this it can be concluded that TCC recovered water satisfies the requirements for discharged water, what proving efficiency of TCC.

4.4 PAH Traced in the Cuttings and the Recovered Solids

The results also shows that the total PAH16 (sum of all PAH) in the solid samples was reduced by 87% due to the TCC treatment. Figure 25 shows a comparison of the PAH levels between the cuttings and the recovered solids see Appendix A.

Phenanthrene had the highest value in the cutting samples. *Chrysene* and *Phenanthrene* were almost 100% removed from the TCC treated products (i.e the cleaned solids, the recovered oil and water). However, TCC treatment does not give the same results for the other substances. Some substance did not show such good results after treatment, For examples: *Benzo(a)anthrascene* 7.79% , *Acenaphthylene* 18.05% and *Naphthalene* 44.48 %

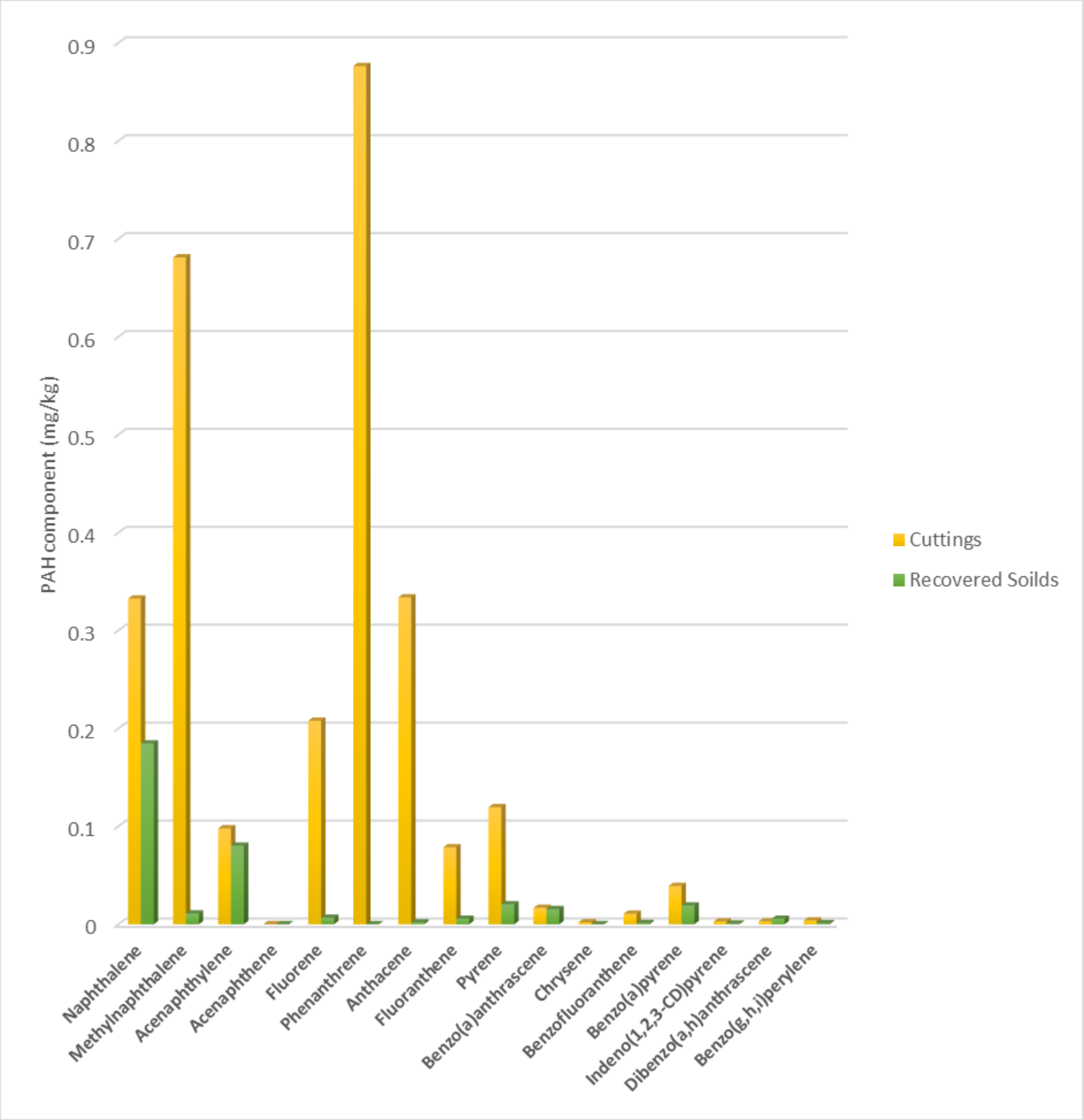


Figure 25. PAH concentration in cuttings and recovered solids

The results show that, the concentrations of PAH on the treated solids were much lower than their concentrations in the cuttings samples.

The amounts of *Fluorene*, *Phenanthrene* and *Chrysene* on solids after TCC were decreased to almost zero. *Methylnaphthalene* was decreased by 98.38 % and *Anthracene* by 99.46 % after treatment. Figure 26 shows the total quantity of PAH in the cuttings and the treated solids which was decreased significantly.

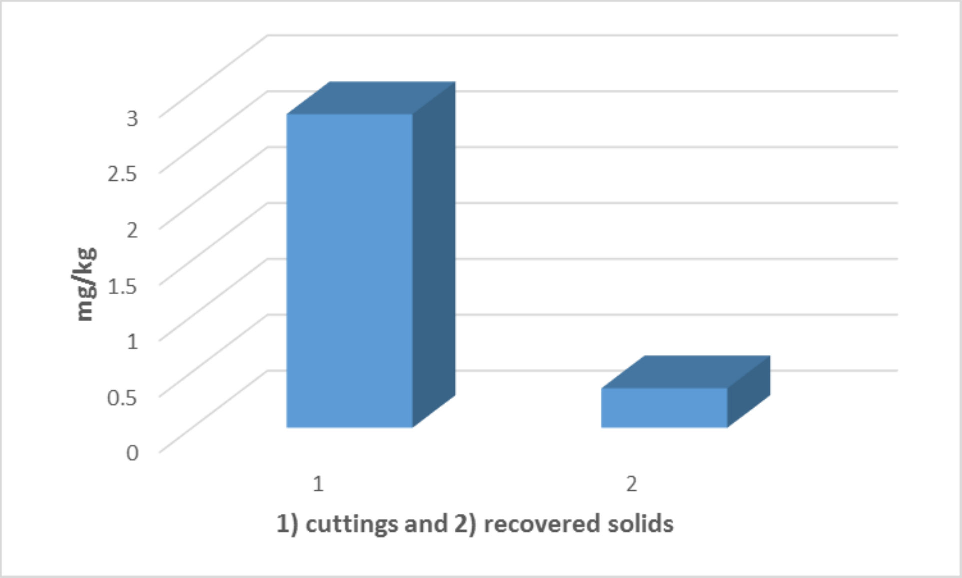


Figure 26. Total of PAH in cuttings and recovered solids

It was proven that TCC is able to remove a high quantity of PAH in cuttings and recovered solids.

4.5 PAH Percentage Calculation Based on Density and Weight

This chapter explains how PAH percentage in cuttings and recovered oil, water and solids after TCC were calculated. The calculation was done in explained below:

The first step was to consider the amount in the cutting sample prior to TCC as 100%.

The methods used to measure the density of samples and solids content was explained in chapter 3.2.5.

Table 12 shows the density and weight percentage results of the cutting composition.

$$\left\{ \begin{array}{c} V\_solid = \dfrac{Mass\_solids}{Mass\_cuttings} \times \dfrac{\rho\_cutting}{\rho\_solid} \\ V\_water + V\_oil + V\_solid = 1 \\ \rho\_water \times V\_water + \rho\_oil \times V\_oil + \rho\_solid \times V\_soild = \rho\_cuttings \end{array} \right\}$$

The methods used for measured the density of samples and solids content has already been explained in part explained in part 3.2.5.

Table 12 shows the percentage of PAH components with this method. The “Rest” column shows the remaining percentage, which evaporated during TCC procedure and was therefore not found in the treated samples. Measurement of the density of components used the following calculations:

ρ_ Oil = Mass_ oil/ volume_ oil

ρ_ Oil = 39 g / 50 ml = 0.78 g /cm3

ρ_ Cutting = Mass_ cutting / volume_ total – (Mass_ water/ ρ_ water)

ρ_ Cutting = 50 g / 240ml – (201.24ml/1) = 1.3 g /cm3

ρ_ Solid = 100 g / 450 ml – (399ml/ 1)= 1.996 g /cm3

Measure Solid Content

Ratio=Mass_ solids / Mass_ cuttings

Solid content Ratio = 31.6g/ 50.1g= 0.6307

Table 12. Density of cuttings and recovered oil, water and solids

Cutting composition	weight per-cent	Density gr/cm3
water	10.0%	1
Oil	48.8%	0.78
Solid	41.2%	1.99
Cutting	100.0%	1.30052

For absolute calculation of recovered substances (oil, water and solids), all the sample units had to be the same. The units for cuttings and recovered solids samples were already mg/kg but the oil and recovered water units needed to be converted to mg/kg from mg/l.The Rest column is the remaining percentage which was not found after TCC process and mostly evaporated during TCC procedure.

Table 13 shows that in recovered water *Fluorene* component had the highest percentage value. *Benzo(a)anthrascene, Chrysene and Dibenzo(a,h)anthrascene* components had zero percentage in the recovered water.

Benzofluoranthene in the recovered oil had a highest value among the PAH components.

Acenaphthylene in the recovered solids had a highest value than the other PAH components.

Table 13. Percentage –calculated recovered substance (oil, water and solids)

PAH	Test result (Average)				Absolute_Calculated at 1kg (mg)				Percentage_Calculated				Rest
	Cutting mg/kg	**Water mg/l**	**Oil mg/l**	**Solid mg/kg**	**Cutting**	**Water**	**Oil**	**Solid**	**Cutting**	**Water**	**Oil**	**Solid**	**Rest**
Naphthalene	**0.3327**	**0.0017**	**0.1878**	**0.1847**	**0.3327**	**0.0002**	**0.1175**	**0.0761**	**100%**	**0.05%**	**35.32%**	**22.87%**	**41.76%**
Methylnaphthalene	**0.6810**	**0.0011**	**0.0793**	**0.0110**	**0.6810**	**0.0001**	**0.0496**	**0.0045**	**100%**	**0.02%**	**7.28%**	**0.67%**	**92.03%**
Acenaphthylene	**0.0979**	**0.0046**	**0.0346**	**0.0803**	**0.0979**	**0.0005**	**0.0216**	**0.0331**	**100%**	**0.47%**	**22.07%**	**33.76%**	**43.69%**
Acenaphthene	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0%**	**0%**	**0%**	**0%**	**0%**
Fluorene	**0.2079**	**0.0096**	**0.0821**	**0.0067**	**0.2079**	**0.0010**	**0.0513**	**0.0028**	**100%**	**0.46%**	**24.70%**	**1.33%**	**73.51%**
Phenanthrene	**0.8764**	**0.0121**	**0.1713**	**0**	**0.8764**	**0.0012**	**0.1071**	**0**	**100%**	**0.14%**	**12.22%**	**0%**	**87.64%**
Anthracene	**0.3338**	**0.0152**	**0.0522**	**0.0018**	**0.3338**	**0.0015**	**0.0327**	**0.0007**	**100%**	**0.45%**	**9.79%**	**0.22%**	**89.53%**
Fluoranthene	**0.0787**	**0.0020**	**0.0127**	**0.0057**	**0.0787**	**0.0002**	**0.0079**	**0.0023**	**100%**	**0.26%**	**10.07%**	**2.99%**	**86.69%**
Pyrene	**0.1195**	**0.0022**	**0.0203**	**0.0203**	**0.1195**	**0.0002**	**0.0127**	**0.0084**	**100%**	**0.18%**	**10.61%**	**7.01%**	**82.20%**
Benzo(a)anthrascene	**0.0168**	**0.0001**	**0.0182**	**0.0155**	**0.0168**	**0**	**0.0114**	**0.0064**	**100%**	**0%**	**0%**	**0%**	**0%**
Chrysene	**0.0020**	**0**	**0.0095**	**0**	**0.0020**	**0**	**0.0059**	**0**	**100%**	**0%**	**0%**	**0%**	**0%**
Benzofluoranthene	**0.0108**	**0**	**0.0123**	**0.0013**	**0.0108**	**0**	**0.0077**	**0.0005**	**100%**	**0.01%**	**71.70%**	**4.98%**	**23.31%**
Benzo(a)pyrene	**0.0391**	**0.0003**	**0.0313**	**0.0191**	**0.0391**	**0**	**0.0196**	**0.0079**	**100%**	**0.07%**	**50.14%**	**20.17%**	**29.61%**
Indeno(1,2,3-CD)pyrene	**0.0029**	**0.0001**	**0.0024**	**0.0007**	**0.0029**	**0**	**0.0015**	**0.0003**	**100%**	**0.23%**	**51.22%**	**9.63%**	**38.92%**
Dibenzo(a,h)anthrascene	**0.0028**	**0.0001**	**0.0050**	**0.0057**	**0.0028**	**0**	**0.0032**	**0.0024**	**100%**	**0%**	**0%**	**0%**	**0%**
Benzo(g,h,i)perylene	**0.0039**	**0.0001**	**0.0040**	**0.0011**	**0.0039**	**0**	**0.0025**	**0.0005**	**100%**	**0.28%**	**64.49%**	**12.03%**	**23.19%**

Figure 27 shows the percentage of PAH in the recovered solids samples according to measurement of the density. *Acenaphthylene* substance had the highest percentage; about 33.76% compared to the other PAH components in the solid.

Some substance were close to zero in the solids samples such as (*Acenaphthene*, *Phenanthrene*, *Benzo (a)anthrascene*, *Chrysene*, *Dibenzo(a,h)anthrascene).*

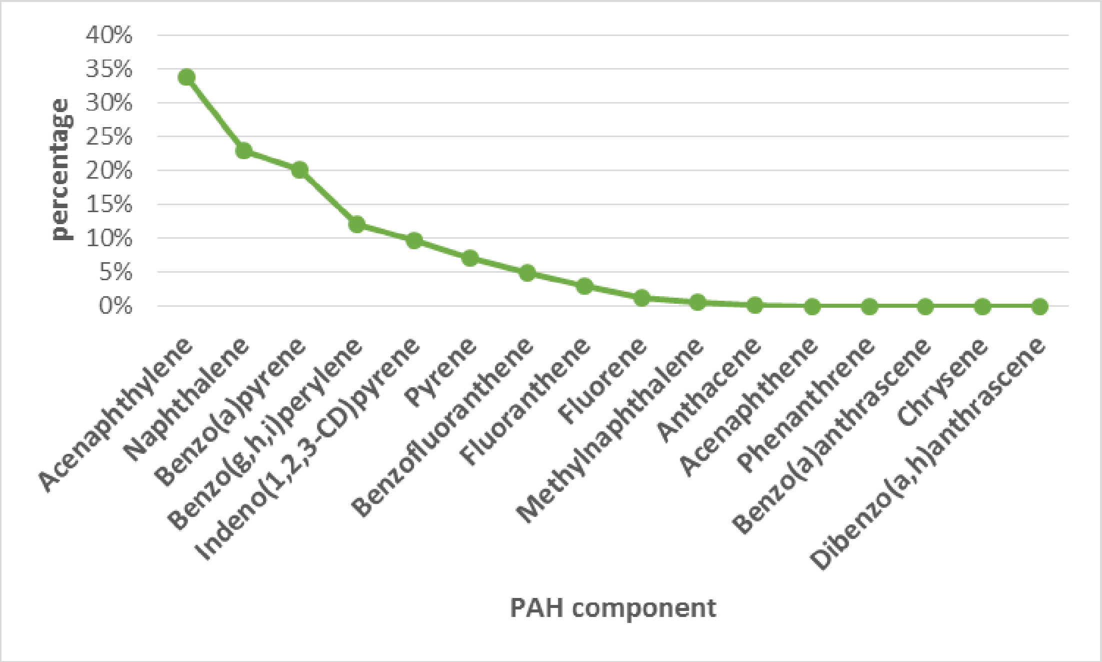


Figure 27. Percentage of PAH in recovered solids

]

The Figure 28 shows percentage of *Naphthalene* in the TCC products (i.e. the recovered oil, the recovered water and the treated solids). As is illustrated in the figure, 35% of the substance went to the recovered oil, 23% went to the treated solids while almost nothing is traced to the recovered water. 42 % of the Rest of *Naphthalene* is missing in the products. As it is heaviest substance (molecular weight 128.1705 g/mol), is most probably escaped through the sludge system from the oil scrubber.or, as *Naphthalene* has a boiling point 217.97 °C (424.35 °F; 491.12 K) and the temperature in the TCC process can be kept between 240 °C and 260 °C. Therefore it is possible to conclude that *Naphthalene* evaporated during TCC treatment.

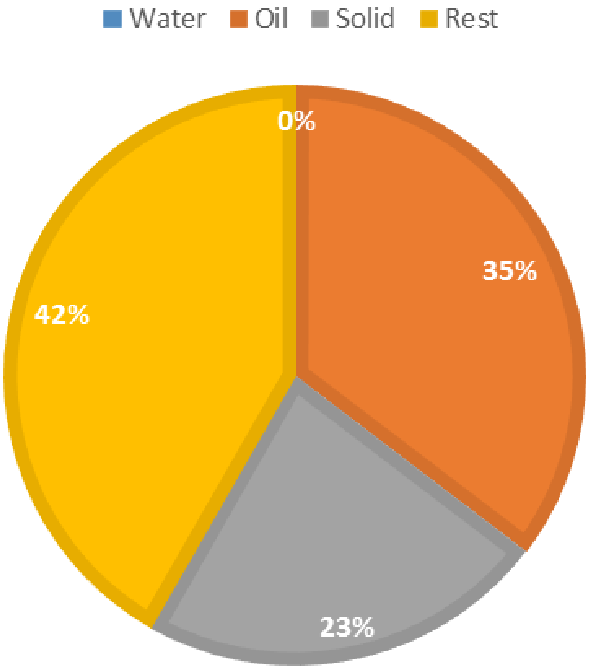


Figure 28. Percentage of Naphthalene in recovered oil, water and solids

Figure 29 shows *Benzo (a) pyrene* percentage in recovered substance (oil, water, solids) The highest amount(about 50%) of *Benzo (a) pyrene* went to the recovered oil; 20% went to the treated solids and 30%(shown as "rest") disappeared during the TCC process.

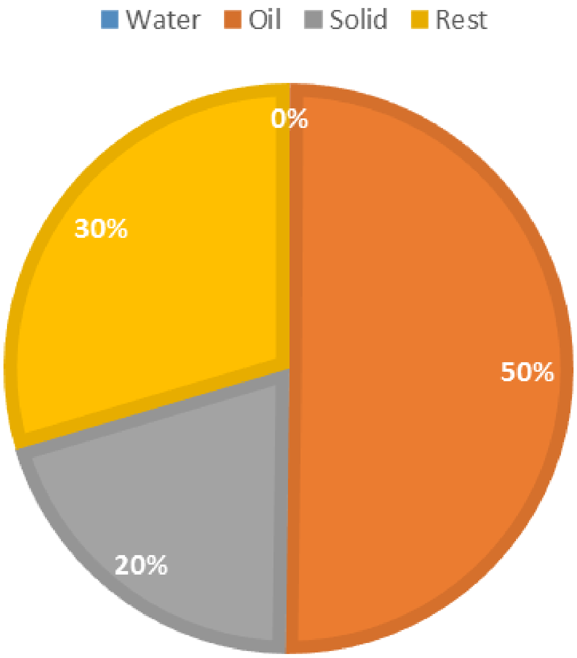


Figure 29. Benzo (a) pyrene percentage in recovered oil, water, solids

Among the PAH substances 92% of *Methylnaphthalene* and 89.5% of *Anthracene* was removed (rest) from the products during the TCC process.

4.6 Comparison with Other PAH Research

Information on PAH concentrations in cuttings before and after different types of treatment can be found in other reports. Table 14 shows comparison between this thesis and Hara thesis and Aquateam Cowi report.

Comparison of the cuttings sample results with Aquateam Cowi (Report No: 14-028), *Acenaphthene* was the largest compound found in the untreated samples by Aquateam Cowi while the results from this thesis show that the samples did not have *Acenaphthene*. The total of PAH in Aquateam Cowi samples was reduced by 92.2% through treatment, while this research has 87 %. According to master thesis by Carolina Hara the total PAH in samples was reduced by 97% through the TCC treatment (Hara, 2014) while, in this study, it was reduced by 87% during TCC treatment. The Concentration of *Naphthalene* in cuttings samples in Hara' results was highest compared with the results of the order two studies. *Naphthalene* showed a reduced amount in Hara's thesis as well as in Aquateam Cowi and this thesis, respectively by 99 %, 95 %, and 44 % during TCC process. *Anthracene* removal efficiency in Hara, Aquateam Cowi, and our results was respectively 96 %, 82 %, and 99 % during TCC process.

Table 14. Comparison the PAH concentration results (Hara, Aquateam Cowi, this thesis)

Compound Name		**Cuttings**			**Recovered solids**		
results from		**Hara**	**Aquateam**	**Thesis**	**Hara**	**Aquateam Cowi**	**Thesis**
PAH		**mg/kg dm**	**mg/kg dm**	**mg/kg**	**mg/kg dm**	**mg/kg dm**	**mg/kg**
1	***Naphthalene***	**5**	**0.6**	**0.3327**	**0.043**	**0.029**	**0.1847**
2	***Methylnaphthalene***	**NA**	**NA**	**0.681**	**NA**	**NA**	**0.011**
3	***Acenaphthylene***	**1.7**	**0.76**	**0.0979**	**<0.05**	**0.0079**	**0.0803**
4	***Acenaphthene***	**3.3**	**2.9**	**0**	**<0.01**	**0.01**	**0**
5	***Fluorene***	**2**	**NA**	**0.2079**	**0.038**	**NA**	**0.0067**
6	***Phenanthrene***	**2.1**	**0.26**	**0.8764**	**0.13**	**0.016**	**0**
7	***Anthracene***	**0.37**	**0.017**	**0.3338**	**0.014**	**0.0029**	**0.0018**
8	***Fluoranthene***	**0.26**	**0.056**	**0.0787**	**0.021**	**0.008**	**0.0057**
9	***Pyrene***	**1.2**	**0.093**	**0.1195**	**0.061**	**0.017**	**0.0203**
10	**Benzo(a)anthrascene**	**0.26**	**0.019**	**0.0168**	**0.028**	**0.022**	**0.0155**
11	***Chrysene***	**0.3**	**0.022**	**0.002**	**0.046**	**0.021**	**0**
12	**Benzofluoranthene**	**NA**	**NA**	**0.0108**	**NA**	**NA**	**0.0013**
13	**Benzo(a)pyrene**	**0.12**	**<0.005**	**0.0391**	**0.031**	**0.03**	**0.0191**
14	**Indeno(1,2,3-CD)pyrene**	**0.037**	**0.07**	**0.0029**	**0.022**	**0.07**	**0.0007**
15	**Dibenzo(a,h)anthrascene**	**0.031**	**0.01**	**0.0028**	**0.015**	**0.02**	**0.0057**
16	***Benzo(g,h,i)perylene***	**0.16**	**0.01**	**0.0039**	**0.098**	**0.1**	**0.0011**
	Total PAH	**17**	**5**	**2.8062**	**0.59**	**0.39**	**0.3539**

*NA not available.

Chapter 5: conclusion

5 Conclusions

In this study, tracing of the PAH substances in the TCC treatment was considered. In order to get the study objectives samples from TCC feed (i.e. the drill cutting) and products (i.e. cleaned solids, recovered oil and water) were collected and tested by GC.
The following points can be concluded from the results:

- Concentration of PAH in the recovered water was closed to zero, for components (*Benzo(a)anthrascene*, *Chrysene*, *Benzofluoranthene*, *Benzo(a)pyrene*, *Indeno(1,2,3-CD)pyrene*, *Dibenzo(a,h)anthrascene*, *Benzo(g,h,i)perylene*) these values were less than required 0.0002 mg/L presented in Table 11. Values for other compounds (*Naphthalene, Methylnaphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene*) were slightly higher. Based on observed results, it can be concluded that TCC treatment is effective for water recovery.

- TCC process can remove approximately 87 % of total PAH in the solids. Other research papers have shown TCC efficiency more than 90 % for cuttings treatment. But the shape of solids shape and their porosity affect oil removal from the solid surface, this causes some deviation in data.

- In cuttings, component *Phenanthrene* had 100 % removal and components *Methylnaphthalene* and *Anthracene* also showed the high level of removal. *Naphthalene*, at only 44 %, was the component which was least removed.

- The main amount of PAH during the TCC treatment went to recovered oil, while some percentage of PAH after TCC process was concluded to be evaporated or removed with sludge.

- The results obtained from this research prove the high efficiency of TCC process for drilling fluids and cuttings treatment with high quality of recovered water and oil, as well as sufficient oil removal from solids. TCC method is an efficient and promising solution for oil industry waste treatment.

Chapter 6: Recommended future study

6 Recommended Future Study

For future research it would be useful to evaluate what happens to other hazardous chemical substances during the TCC process. Focusing on hazardous chemicals could provide information useful for TCC treatment of mud. Another interesting area of research would be PAH dynamics and distribution during TCC treatment. Additional experiments could be undertaken for tracing PAH in different OBF implemented in oil production. This type of research would help to protect the environment from the disadvantages of oil and gas production.

7 Reference

Amoco Production Company. (2010) *Drilling fluid manual*. [Online] betakorbo. Available at: <http://www.scribd.com/doc/38525394/Amoco-Drilling-Fluid-Manual#scribd >

Aquateam. (2014) *Characterising Thermal Treated 08M Drill Cuttings*. Sampling, characterisation, environmental analysis and risk assessment of offshore discharges. [Online] Available from :< https://www.norskoljeoggass.no/Global/NOROG>

ATSDR. (1995) *Public Health Statement for Polycyclic Aromatic Hydrocarbons (PAH).* [Online] Available at: < http://www.atsdr.cdc.gov/PHS/PHS.asp?id=120&tid=25>

B. Roddie (ERT), A. Skadsheim (RF), D. Runciman (ERT), G. Kjeilen (RF). (1999) *Cuttings Pile Toxicity Environment & Resource Technology Ltd RF*. [Online] p.62 Available at: <http://www.anp.gov.br/brasil>

Bikass, S. (2015) *From Environmental Hazard to Zero Impact*. Environment & technology conference. Stavanger, March 2015.

Bilstad, T. (2014) *Offshore Drilling Waste Management: The Gulf of Mexico and the North Sea*. Paper presented at the Summit 2014 State of the Gulf of Mexico, Texas A&M University - Corpus Christi, Houston, USA.

Bojes, H. K. and Pope, P. G. (2007) *Characterization of EPA's 16 priority pollutant polycyclic aromatic hydrocarbons (PAH) in tank bottom solids and associated contaminated soils at oil exploration and production sites in Texas.* Regulatory Toxicology and Pharmacology. 47 (3) [Online] pp. 288-295. Available online at : <http://dx.doi.org/10.1016/j.yrtph.2006.11.007>

Breuer, E., Stevenson, A. G., Howe, J. A., Carroll, J. & Shimmield, G. B. (2004) *Drill cutting accumulations in the Northern and Central North Sea: a review of environmental interactions and chemical fate*. Marine Pollution Bulletin, 48 (1-2), 12-25.

Brady, James E., Fred Senese. (2004) *General Chemistry*. [Online] p 1205. Available at : < http://antoine.frostburg.edu/chem/senese/101/features.shtml>

Caenn,R. HCH Darley & George R. Gray. (2011) *Composition and Properties of Drilling and Completion Fluids*. p 720.

Campbell, J.A. (1998) An E&P Industry Perspective on Acceptability Criteria for the Marine Discharge of Cuttings Drilled with Synthetic Based Drilling. Society of Petroleum Engineer.in *SPE International Conference on Health, Safety, and Environment in Oil and Gas Exploration and Production*, Caracas, 7-10 June. Venezuela: Society of Petroleum Engineers.

Cole-Parmer. (2015) *Cole-Parmer Instrument Company*. Fluid handling and analysis [Online] Available at :< http://www.coleparmer.com/Site-Support>. [Accessed 2015].

Conney, H. (1982) Induction of microsomal enzymes by foreign chemicals and carcinogenesis by polycyclic aromatic hydrocarbons: G. H. A. American Association for Cancer Research.

Cripps, S. J., Aabel, J. P., Picken, G., Andersen, O. K., Heyworth, C., Jakobsen, M., Kristiansen, R., Marken, C., Paulsen, J. E., Shaw, D., Annand, A., Jacobsen, T. G. & Henriksen, I. B. (1998). *Disposal of oil-based cuttings*. Rogaland Research, The Norwegian Oil Industry Association (OLF). Report RF-98/097. 146 pp. ISBN: 82-7220-894-6.

Criteria Group. (1998) *Analysis of Petroleum Hydrocarbons is Environmental*. Total Petroleum Hydrocarbon Criteria Working Group Series. In: W. Weisman, Massachusetts: Amherst Scientific, p. 97.

Daniela M. Pampanin and Magne O. Sydnes (2013) Polycyclic Aromatic Hydrocarbons a Constituent of Petroleum: Presence and Influence in the Aquatic Environment, Hydrocarbon, Dr. Vladimir Kutcherov (Ed.), ISBN: 978-953-51-0927-3, InTech, DOI: 10.5772/48176. Available from: <http://www.intechopen.com/books/hydrocarbon/polycyclic-aromatic-hydrocarbons-a-constituent-of-petroleum-presence-and-influence-in-the-aquatic-en>

E. Breuer a,*, A.G. Stevenson b, J.A. Howe a, J. Carroll c, G.B. Shimmield a. (2004) *Drill cutting accumulations in the Northern and Central North Sea. Issue Drill cutting accumulations in the Northern and Central North Sea*, p. 25.

E. V. Lau, S. Gan, and H. K. Ng. (2010) *Extraction Techniques for Polycyclic Aromatic Hydrocarbons in Soils*. International Journal of Analytical Chemistry [Online]. Volume 2010 (2010), p 9. Available at :< http://dx.doi.org/10.1155/2010/398381>

Eisler, R. (1987) *Polycyclic aromatic hydrocarbon hazards to fish, wildlife and invertebrates: a synoptic review*. Biological report 85 (1.11) [Online] Laurel: U.S. Fish and Wildlife Service Patuxent Wildlife Research Center. Available at: <http://www.pwrc.usgs.gov/oilinla/pdfs/chr_11_PAH.pdf>

Environmental Protection Agency Washington, 2008. Polycyclic Aromatic Hydrocarbons (PAH). United States Office of Solid Waste. p 3.

Environment Risk management system (ERMS). (2006) EIF drilling discharges, Risk assessment, PEC/PNEC ratio, Sediment toxcicity, SSD, Sediment Toxicity review, Water column, Partioning coefficient (Kp), EU Technical Guidance Document (TGD).

Ferrari G, Ceccini F and Xiao L. (2000) *Drilling wastes treatment and management practices for reducing impact on HSE: ENI/AGIP experiences*. College of Environmental Resources Management University of Agriculture, P.M.B 2240, Abeokuta: Nigeria. P 189.

Friedheim, J. E. & H. L. Conn. (1996) *Second Generation Synthetic Fluids in the North Sea: Are They Better?*. SPE/IADC Drilling Conference, Louisiana, 12-15 March. Orleans: Society of Petroleum Engineers.

Gagnon, M. M. and Bakhtyar, S. (2003). Induction of Fish Biomarkers by Synthetic-Based Drilling Muds. Public Library of Science (PloS). [Online]. ONE, 8 (7). Available at: <http://dx.doi.org/10.1371/journal.pone.0069489>

Gerrard, S., Grant, A., Marsh, R. & London, C. (1999). "*Drill Cuttings Piles in the North Sea: Management Options During Platform Decommissioning*" Report no 31. Centre for Environmental Risk, University of East Anglia. Norwich, 224 pp. ISBN 1-873933-11-8.

Government of Japan. (2001) *Standard Guidelines for the Environmental Monitoring of Chemicals*. [Online] Available at :< https://www.env.go.jp/en/index.html>. [Accessed 2015].

Halliburton. (2015) *Thermomechanical Cuttings Cleaner (TCC).* [Online]
Available at :< http://www.halliburton.com/en-US/ps/baroid/drilling/solids-control-equipment-and-services>

Halliburton. (2004). *Thermal Desorption of Oil from Oil-Based Drilling Fluids Cuttings: Processes and Technologies*. SPE Asia Pacific Oil and Gas Conference and Exhibition, 18-20 October, Perth. Australia: Society of Petroleum Engineers.

Halliburton (2013) *Thermomechanical Cuttings Cleaner (TCC)*. [Online]. Available at: <http://www.halliburton.com/en-US/ps/baroid/fluid-services/waste-managementsolutions/waste-treatment-and-disposal/thermal-processing-systems/thermomechanicalcuttings-cleaner-tcc.page#> [Retrieved 22.10.2013]

Hara Carolina. (2014) *Study of treated and untreated oil-based drilling waste exposure in Atlantic salmon (Salmo salar) using a biomarker approach: EROD and oxidative stress parameters*, A Thesis Submitted in Stavanger University for the Degree of MSc Environmental Technology / Offshore Environmental Engineering.

Jay P. Simpson, J.C. Cowan & A.E. Beasley Jr. (1961) *The new look in oil-mud technology*. Petroleum technology, Issue petroleum technology 13[Online] P 1,177 - 1,183. Available at: < http://dx.doi.org/10.2118/150-PA>

Kirkness, Alister James. (2008). *Treatment of Nonaqueous-Fluid-Contaminated Drill Cuttings-Raising Environmental and Safety Standards*.in IADC/SPE Drilling Conference, Orlando, Florida, USA 4-6 March 2008. Society of Petroleum Engineers p. Paper IADC/SPE 112727.

Larsenr (2011) ChemWiki. [Online]Available from :< http://chemwiki.ucdavis.edu/>

Melton, H. R., Smith, J. P., Mairs, H. L., Bernier, R. F., Garland, E., Glickman, A. H., Jones, F.

V., Ray, J. P., Thomas, D. & Campbell, J. A. (2004). "*Environmental Aspects of the Use and Disposal of Non-Aqueous Drilling Fluids Associated with Offshore Oil & Gas Operations*" SPE International Conference on Health, Safety, and Environment in Oil and Gas Exploration and Production. Society of Petroleum Engineers. Alberta, Canada. 10 pp, ISBN: 978-1-55563-9815

MI Swaco. (2013) *Base Oil GC/MS scan*. Example from Bautino, Kazakhstan. Word-file.

Neff, J.M. S. McKelvie .R.C. Ayers, Jr. (2000) *Environmental Impacts of Synthetic Based Drilling Fluids*. U.S. Department of the Interior Minerals Management Service Gulf of Mexico OCS Region. p. 118 pp.

Neff, M, Lee, K. Deblois, E. (2011) *Produced water: overview of composition, fate, and effects*. Centre for Offshore Oil, Gas and Energy Research: Fisheries and Oceans Canada, P _ O. Box.

Neff, J. M. (2005). "*Composition, Environmental Fates, and Biological Effect of Water Based Drilling Muds and Cuttings Discharged to the Marine Environment: A Synthesis and Annotated Bibliography*" Battelle, Petroleum Environmental Research Forum (PERF) and American Petroleum Institute. Duxbury, 83 pp.

Okeke P. N , Obi C. (2013). *Treatment of Oil Drill Cuttings Using Thermal Desorption Technique*. ARPN Journal of Systems and Software 02009-2013 AJSS Journal. [Online] VOL. 3, NO 7, November. P 6. Available at:
< http://scientific-journals.org/journalofsystemsandsoftware/archive/vol3no7/vol3no7_2.pdf>

OLF. (2001). "*Disposal of Oil Contaminated Drill Cuttings- Summary Report*" The Norwegian Oil Industry Association (OLF). Stavanger, 12 pp.

Onwukwe, S. I. and Nwakaudu, M. S. (2012) *Drilling Wastes Generation and Management Approach*. International Journal of Environmental Science and Development, 3 (3), pp. 252257.

ORHUN, F. (1968) *Gas chromatography, experimental studies on the flow rate effects of carrier gas and application of the method to hydrocarbon analysis of some natural gases in turkey*. Mineral Research and Exploration Institute of Turkey. P. 37.

Reis. (1996) *Drilling and Drilling Fluids Waste Management. In: Environmental Control in Petroleum Engineering*. Houston: s.n., p. 156.

Sheffield Hallam University. (2013) [Online].Available at:
< http://www.shu.ac.uk/prospectus/subject/biosciences-chemistry>

Samudra,A. Sahinidis,N. (2010) *Design of High Performance Drilling Fluids: Challenges And Future Directions for HP/HT Fluids*. Kickoff Meeting: Energy Systems Initiative (ESI) Center for Advanced Process Decision-making. p 16.

Schlumberger. (2013) *Oil Well Drilling- introduction to drilling fluids* [CD].

Schlumberger. (2012) *Drilling Fluid properties*. ES Certification Chapter 2— Drilling Fluid Properties.

Schlumberger. (2013) *Oil field review*. USA: Schlumberger journals. (ISSN 0923-1730)

Schlumberger. (2015) *Oilfield Glossary*. [Online]
Available at: <http://www.glossary.oilfield.slb.com/en/Terms/e/emulsion.aspx>

Statoil. (2003) *The most important chemicals used in the petroleum industry*. The statistics include discharges from all fields with production facilities on the Norwegian continental shelf. P 20.

Thermtech. (2014) *How does a TCC work*. [Online]. Available at: <http://www.thermtech.no/home/the_tcc/how-does-a-tcc-reg_-work>

Torgeir Bakkea. Jarle Klungsøyrb &Steinar Sannic. (2013) *Environmental impacts of produced water and drilling waste discharges from the Norwegian offshore petroleum industry*. Marine Environmental Research 92 (2013). [Online] p 154-169. Available at:
< http://www.sciencedirect.com>

Total Petroleum Hydrocarbon Criteria Working Group Series. (1998) Massachusetts: Amherst Scientific. (ISBN 1-884-940-14-5 ed).

Tullow Ghana Limited. (2011) *Summary of Development Drilling Impacts and Assessment of Drill Cuttings Disposal Options*. Environment resources management.

Tuvikene, A. (1995) *Responses of fish to polycyclic aromatic hydrocarbons (PAH)*. [Online] 32. Tartu, Estonia: Institute of Zoology and Hydrobiology, University of Tartu, EE-2400. (1/7). Available at :< http://www.annzool.net/PDF/anzf32/anz32-295-309.pdf>

Walker, C. H., Sibly, R. M., Hopkin, S. P. and Peakall, D. B. (2012) *Principles of ecotoxicology*. Fourth Edition. Florida, USA: Taylor & Francis, Boca Raton.

Walker, C. H.; Hopkin, S. P.; Sibly, R. M.; Peakall, D. B. (2006) *Principles of ecotoxicology*. Boca Raton. Third Edition. Florida, U.S.A: Taylor & Francis, Boca Raton.

Walker, C. H. (2008) *Organic pollutants an ecotoxicological perspective*. USA: Taylor & Francis Group.

Yan, J., Wang, L., Fu, P. P. and Yu, H. (2004) *Photomutagenicity of 16 polycyclic aromatic hydrocarbons from the US EPA priority pollutant list. Mutation Research/Genetic Toxicology and Environmental Mutagenesis*. 557 (1), pp. 99-108. Available online at: <http://dx.doi.org/10.1016/j.mrgentox.2003.10.004>

Zoveidavianpoor,M. Samsuri,A & Shadizadeh,R. (2012) *Overview of Environmental Management* *by Drill Cutting Re-Injection Through Hydraulic Fracturing in Upstream Oil and Gas Industry*. August 1: CC BY.

Appendix A

Table 15. Results of Gas chromatography (recovered oil and recovered water)

Comp #	Compound Name	recovered Oil					Recovered water				
		Sample 1	Sample2	Sample3	Average	Recalculate	Sample 1	sample 2	Sample3	Average	Recalculate
	PAH	ppm (mg/l)				mg/l	ppm				mg/l
1	*Naphthalene*	0.1668	0.3278	0.0181	0.1709	18.7802	0.4677	0	0.5407	0.3361	0.0017
2	*Methylnaphthalene*	0.0535	0.1556	0.0073	0.0721	7.9277	0.0805	0.4558	0.1031	0.2131	0.0011
3	*Acenaphthylene*	0.0177	0.0693	0.0073	0.0314	3.4555	0	1.8747	0.9088	0.9278	0.0046
4	*Acenaphthene*	0	0	0	0	0	0	0	0	0	0
5	*Fluorene*	0.1730	0.0434	0.0077	0.0747	8.2067	0.7428	3.8680	1.1635	1.9248	0.0096
6	*Phenanthrene*	0.1947	0.2257	0.0471	0.1558	17.1252	6.3184	0.7264	0.2382	2.4277	0.0121
7	*Anthracene*	0.1317	0.0109	0.0000	0.0475	5.2236	5.1716	0	3.9387	3.0368	0.0152
8	*Fluoranthene*	0.0113	0.0155	0.0077	0.0115	1.2655	0.2067	0.2092	0.7979	0.4046	0.0020
9	*Pyrene*	0.0158	0.0300	0.0095	0.0184	2.0273	0.4426	0.1769	0.6860	0.4351	0.0022
10	Benzo(a)anthrascene	0.0185	0.0232	0.0080	0.0165	1.8178	0	0.0809	0	0.0270	0.0001
11	*Chrysene*	0.0097	0.0105	0.0057	0.0086	0.9483	0	0	0.0153	0.0051	0
12	Benzofluoranthene	0	0.0336	0	0.0112	1.2322	0	0.0054	0	0.0018	0
13	Benzo(a)pyrene	0.0185	0.0651	0.0019	0.0285	3.1334	0.0557	0.0700	0.0472	0.0576	0.0003
14	Indeno(1,2,3-CD)pyrene	0.0064	0	0	0.0021	0.2359	0.0087	0.0304	0	0.0130	0.0001
15	Dibenzo(a,h)anthrascene	0.0138	0	0	0.0046	0.5046	0.0057	0.0330	0.0153	0.0180	0.0001
16	*Benzo(g,h,i)perylene*	0	0.0108	0	0.0036	0.3973	0.0121	0.0535	0	0.0219	0.0001
	Total PAH					72.2811					0.0493

Table 16. Results of Gas chromatography (cuttings and recovered solids)

Comp #	Compound Name	Cuttings					Solid after TCC					Deference percentage
		Sample 1	sample 2	Sample3	Average	Recalculate	Sample 1	sample 2	Sample3	Average	Recalculate	
	PAH	ppm				mg/kg	ppm				mg/kg	
1	*Naphthalene*	1.7593	1.8994	1.3312	1.6633	0.3327	1.6744	0.9994	0.0962	0.9233	0.1847	44.49
2	*Methylnaphthalene*	3.6053	1.6941	4.9162	3.4052	0.6810	0.0901	0.0502	0.0249	0.0551	0.0110	98.38
3	*Acenaphthylene*	0.0000	0.0000	1.4691	0.4897	0.0979	0.8498	0.3540	0	0.4013	0.0803	18.06
4	*Acenaphthene*	0	0	0	0	0	0	0	0	0	0	0
5	*Fluorene*	1.3113	1.1296	0.6778	1.0396	0.2079	0.0300	0.0710	0	0.0337	0.0067	96.76
6	*Phenanthrene*	4.8593	4.7525	3.5349	4.3822	0.8764	0	0	0	0	0	100
7	*Anthracene*	2.3172	2.3416	0.3483	1.6690	0.3338	0.0147	0.0122	0	0.0090	0.0018	99.46
8	*Fluoranthene*	0.4882	0.2089	0.4828	0.3933	0.0787	0.0176	0.0576	0.0104	0.0285	0.0057	92.75
9	*Pyrene*	0.8689	0.3686	0.5554	0.5976	0.1195	0.0526	0.2131	0.0392	0.1016	0.0203	83.00
10	Benzo(a)anthrascene	0.0415	0.0549	0.1555	0.0840	0.0168	0.0144	0.1887	0.0292	0.0774	0.0155	7.80
11	*Chrysene*	0.0000	0.0160	0.0142	0.0101	0.0020	0	0	0	0	0	100
12	Benzofluoranthene	0.0124	0.0441	0.1048	0.0538	0.0108	0	0.0195	0	0.0065	0.0013	87.92
13	Benzo(a)pyrene	0.0272	0.2706	0.2887	0.1955	0.0391	0.1206	0.1454	0.0212	0.0957	0.0191	51.03
14	Indeno(1,2,3-CD)pyrene	0	0.0432	0.0000	0.0144	0.0029	0	0.0101	0	0.0034	0.0007	76.64
15	Dibenzo(a,h)anthrascene	0	0.0197	0.0230	0.0142	0.0028	0.0644	0.0213	0	0.0286	0.0057	0
16	*Benzo(g,h,i)perylene*	0	0.0337	0.0241	0.0193	0.0039	0	0.0169	0	0.0056	0.0011	70.79
	Total PAH					2.8062					0.3539	87.39

Appendix B

Table 17. Raw results of cuttings (samples 1) due to GC

Comp #	Compound Name	RT (min)	Area	Amount	Units	Qvalue
1	Naphthalene	4.432	8375772	1.75926	ppm	69
2	Methylnaphthalene	5.454	32690046	3.60532	ppm	20
3	Acenaphthylene	0	0	0	ppm	0
4	Acenaphthene	0	0	0	ppm	0
5	Fluorene	7.424	5368607	1.31129	ppm	18
6	Phenanthrene	8.79	16008838	4.85932	ppm	63
7	Anthacene	8.927	11574601	2.31719	ppm	62
8	Fluoranthene	10.549	2757162	0.488203	ppm	60
9	Pyrene	10.885	5637623	0.868874	ppm	59
10	Benzo(a)anthrascene	13.395	122104	0.041503	ppm	56
11	Chrysene	0	0	0	ppm	0
12	Benzofluoranthene	15.557	132141	0.012352	ppm	56
13	Benzo(a)pyrene	16.536	136909	0.027189	ppm	56
14	Indeno(1,2,3-CD)pyrene	0	0	0	ppm	0
15	Dibenzo(a,h)anthrascene	0	0	0	ppm	0
16	Benzo(g,h,i)perylene	0	0	0	ppm	0

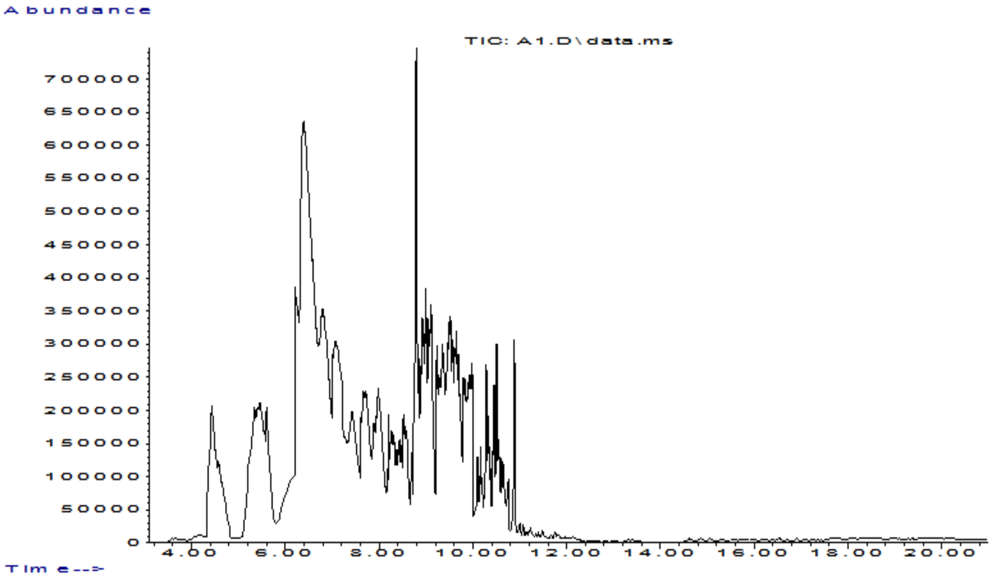


Figure 30. Results of cuttings (sample 1) due to GC

Table 18. Raw results of cuttings (samples 2) due to GC

Comp #	Compound Name	RT (min)	Area	Amount	Units	Qvalue
1	Naphthalene	4.425	9042869	1.89937	ppm	69
2	Methylnaphthalene	5.447	15360226	1.69405	ppm	20
3	Acenaphthylene	0	0	0	ppm	0
4	Acenaphthene	0	0	0	ppm	0
5	Fluorene	7.424	4624606	1.12956	ppm	18
6	Phenanthrene	8.79	15656918	4.7525	ppm	63
7	Anthacene	8.928	11696613	2.34162	ppm	62
8	Fluoranthene	10.603	1180026	0.208944	ppm	60
9	Pyrene	10.994	2391563	0.368589	ppm	59
10	Benzo(a)anthrascene	13.58	161528	0.054903	ppm	56
11	Chrysene	13.58	115563	0.015991	ppm	54
12	Benzofluoranthene	15.607	471861	0.044109	ppm	56
13	Benzo(a)pyrene	16.542	1362726	0.270621	ppm	56
14	Indeno(1,2,3-CD)pyrene	18.585	173445	0.043214	ppm	56
15	Dibenzo(a,h)anthrascene	18.584	61878	0.019685	ppm	1
16	Benzo(g,h,i)perylene	19.099	138879	0.033702	ppm	54

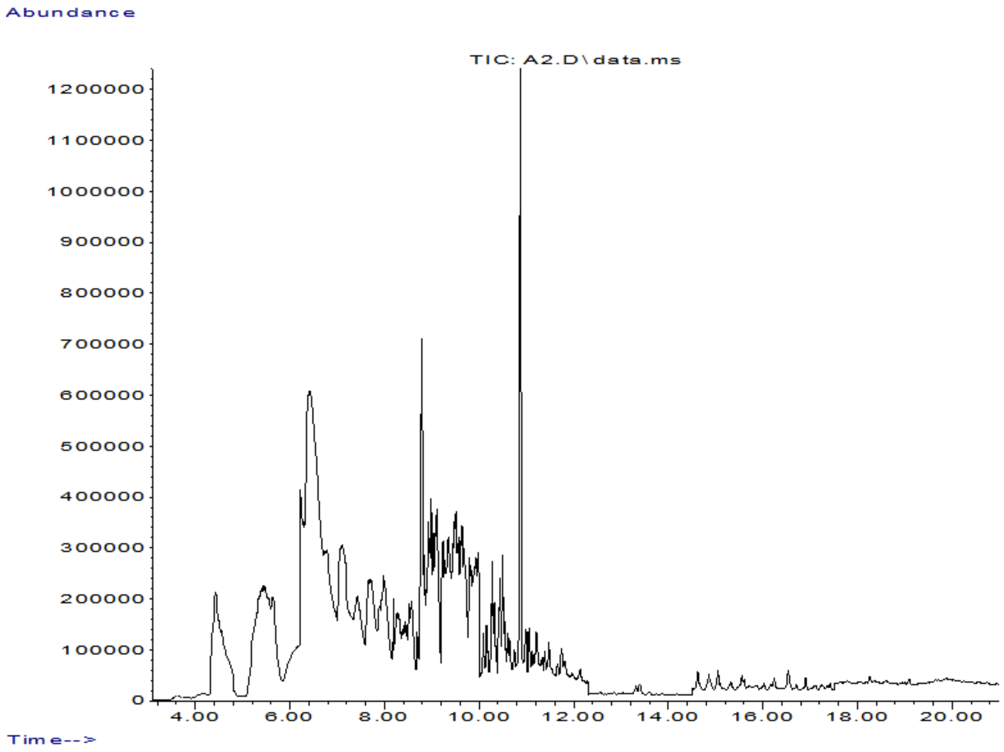


Figure 31. Results of cuttings (samples 2) due to GC

Table 19. Raw results of cuttings (samples 3) due to GC

Comp #	Compound Name	RT (min)	Area	Amount	Units	Qvalue
1	Naphthalene	4.432	6337672	1.33117	ppm	69
2	Methylnaphthalene	5.396	44575994	4.9162	ppm	20
3	Acenaphthylene	6.516	6747418	1.4691	ppm	63
4	Acenaphthene	0	0	0	ppm	0
5	Fluorene	7.493	2775031	0.677804	ppm	18
6	Phenanthrene	8.841	11645531	3.53489	ppm	63
7	Anthacene	8.884	1739580	0.348257	ppm	62
8	Fluoranthene	10.556	2726695	0.482808	ppm	60
9	Pyrene	11.008	3603833	0.555425	ppm	59
10	Benzo(a)anthrascene	13.382	457394	0.155466	ppm	56
11	Chrysene	13.577	102689	0.01421	ppm	54
12	Benzofluoranthene	15.556	1121283	0.104816	ppm	56
13	Benzo(a)pyrene	16.539	1453690	0.288685	ppm	56
14	Indeno(1,2,3-CD)pyrene	0	0	0	ppm	0
15	Dibenzo(a,h)anthrascene	18.569	72154	0.022954	ppm	40
16	Benzo(g,h,i)perylene	19.1	99342	0.024107	ppm	54

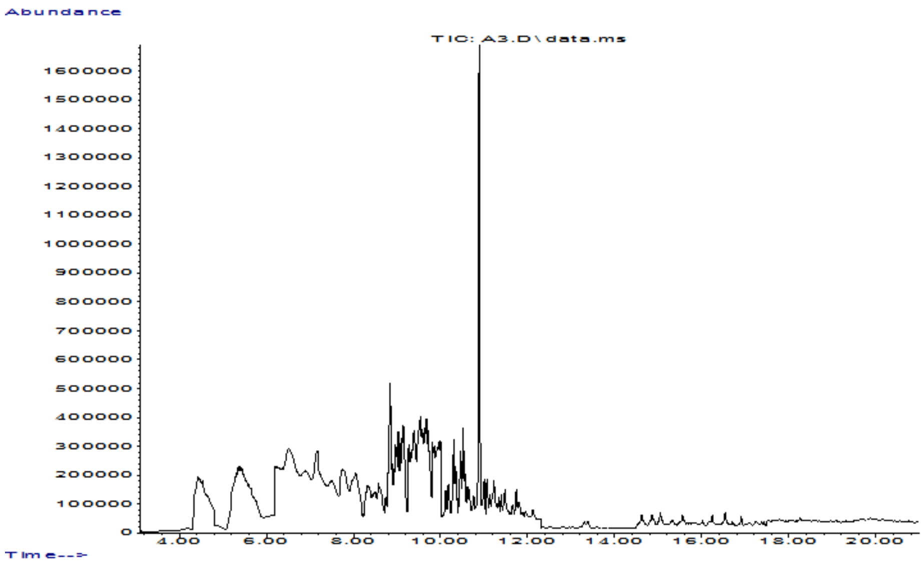


Figure 32. Results of cuttings (samples 3) due to GC

Table 20. Raw results of recovered solids (sample 1) due to GC

Comp #	Compound Name	RT (min)	Area	Amount	Units	Qvalue
1	Naphthalene	4.357	7971725	1.67439	ppm	69
2	Methylnaphthalene	5.525	817158	0.090123	ppm	20
3	Acenaphthylene	6.57	3903076	0.84981	ppm	63
4	Acenaphthene	0	0	0	ppm	0
5	Fluorene	7.37	122898	0.030018	ppm	18
6	Phenanthrene	0	0	0	ppm	0
7	Anthacene	8.857	73541	0.014723	ppm	62
8	Fluoranthene	10.513	99143	0.017555	ppm	60
9	Pyrene	10.898	341433	0.052622	ppm	59
10	Benzo(a)anthrascene	13.419	42430	0.014422	ppm	56
11	Chrysene	0	0	0	ppm	0
12	Benzofluoranthene	0	0	0	ppm	0
13	Benzo(a)pyrene	16.532	607221	0.120587	ppm	56
14	Indeno(1,2,3-CD)pyrene	0	0	0	ppm	0
15	Dibenzo(a,h)anthrascene	18.671	202451	0.064406	ppm	59
16	Benzo(g,h,i)perylene	0	0	0	ppm	0

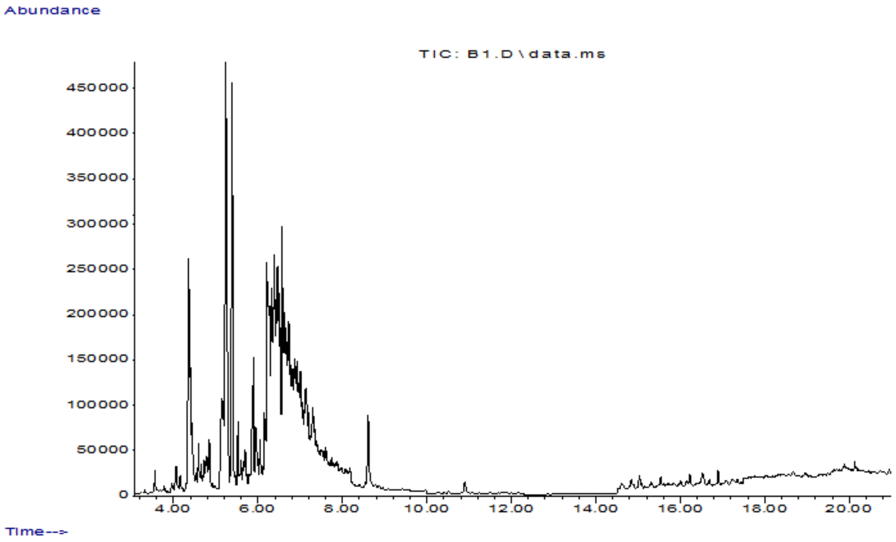


Figure 33. Results of recovered solids (sample 1) due to GC

Table 21. Raw results of recovered solids (sample 2) due to GC

Comp #	Compound Name	RT (min)	Area	Amount	Units	Qvalue
1	Naphthalene	4.362	4758102	0.999397	ppm	69
2	Methylnaphthalene	5.513	455566	0.050244	ppm	20
3	Acenaphthylene	6.561	1626050	0.354037	ppm	63
4	Acenaphthene	0	0	0	ppm	0
5	Fluorene	7.332	290664	0.070995	ppm	18
6	Phenanthrene	0	0	0	ppm	0
7	Anthacene	8.849	61038	0.01222	ppm	62
8	Fluoranthene	10.487	325211	0.057584	ppm	60
9	Pyrene	10.879	1382361	0.21305	ppm	59
10	Benzo(a)anthrascene	13.392	555026	0.188651	ppm	56
11	Chrysene	0	0	0	ppm	0
12	Benzofluoranthene	15.609	208395	0.019481	ppm	56
13	Benzo(a)pyrene	16.541	731981	0.145362	ppm	56
14	Indeno(1,2,3-CD)pyrene	18.577	40524	0.010096	ppm	56
15	Dibenzo(a,h)anthrascene	18.586	66893	0.021281	ppm	49
16	Benzo(g,h,i)perylene	19.1	69573	0.016883	ppm	54

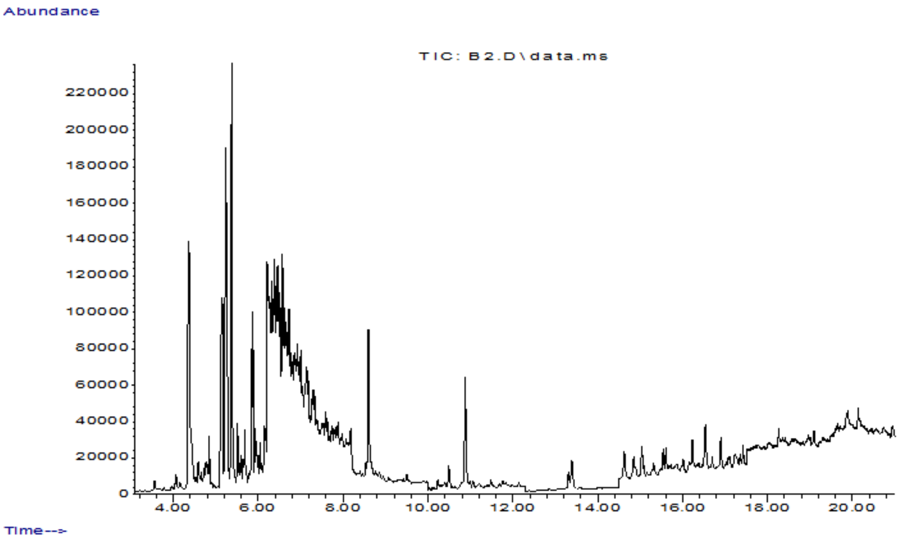


Figure 34. Results of recovered solids (sample 2) due to GC

Table 22. Raw results of recovered solids (sample 3) due to GC

Comp #	Compound Name	RT (min)	Area	Amount	Units	Qvalue
1	Naphthalene	4.357	457819	0.096161	ppm	69
2	Methylnaphthalene	5.361	226060	0.024932	ppm	20
3	Acenaphthylene	0	0	0	ppm	0
4	Acenaphthene	0	0	0	ppm	0
5	Fluorene	0	0	0	ppm	0
6	Phenanthrene	0	0	0	ppm	0
7	Anthacene	0	0	0	ppm	0
8	Fluoranthene	10.487	58600	0.010376	ppm	60
9	Pyrene	10.877	254346	0.0392	ppm	59
10	Benzo(a)anthrascene	13.395	85776	0.029155	ppm	56
11	Chrysene	0	0	0	ppm	0
12	Benzofluoranthene	0	0	0	ppm	0
13	Benzo(a)pyrene	16.539	106950	0.021239	ppm	56
14	Indeno(1,2,3-CD)pyrene	0	0	0	ppm	0
15	Dibenzo(a,h)anthrascene	0	0	0	ppm	0
16	Benzo(g,h,i)perylene	0	0	0	ppm	0

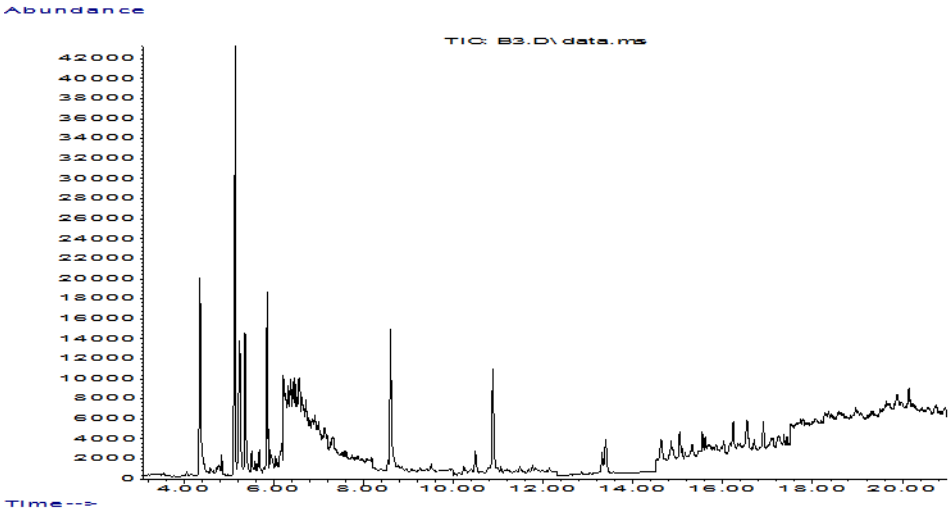


Figure 35. Results of recovered solids (sample 3) due to GC

Table 23. Raw results of recovered oil (sample 1) due to GC

Comp #	Compound Name	RT (min)	Area	Amount	Units	Qvalue
1	Naphthalene	4.363	794318	0.16684	ppm	69
2	Methylnaphthalene	5.369	485085	0.053499	ppm	20
3	Acenaphthylene	6.552	81148	0.017668	ppm	63
4	Acenaphthene	0	0	0	ppm	0
5	Fluorene	7.329	708190	0.172976	ppm	18
6	Phenanthrene	8.965	641448	0.194705	ppm	63
7	Anthacene	8.965	658007	0.13173	ppm	62
8	Fluoranthene	10.623	64076	0.011346	ppm	60
9	Pyrene	11.017	102565	0.015807	ppm	59
10	Benzo(a)anthrascene	13.589	54483	0.018518	ppm	56
11	Chrysene	13.589	70035	0.009691	ppm	54
12	Benzofluoranthene	0	0	0	ppm	0
13	Benzo(a)pyrene	16.336	93135	0.018496	ppm	56
14	Indeno(1,2,3-CD)pyrene	18.563	25845	0.006439	ppm	56
15	Dibenzo(a,h)anthrascene	18.628	43301	0.013776	ppm	59
16	Benzo(g,h,i)perylene	0	0	0	ppm	0

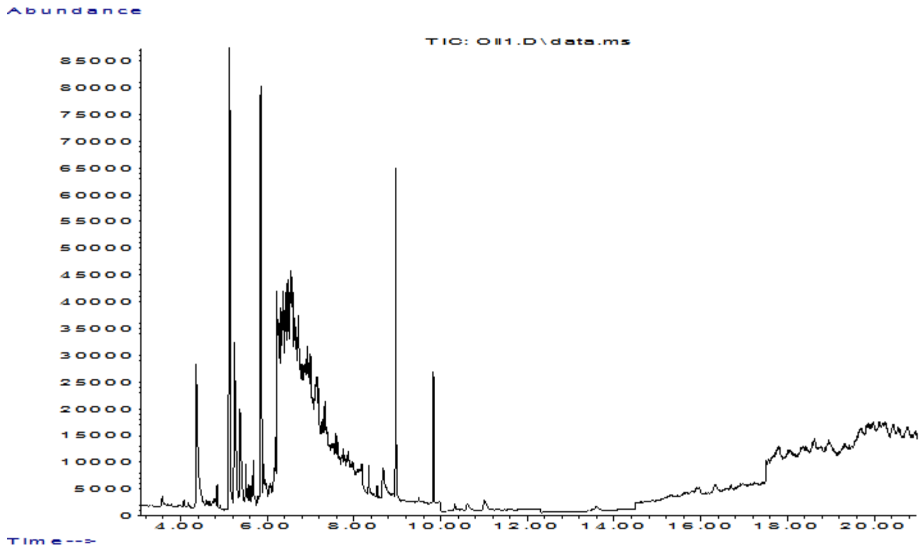


Figure 36. Results of recovered oil (sample 1) due to GC

Table 24. Raw results of recovered oil (sample 2) due to GC

Comp #	Compound Name	RT (min)	Area	Amount	Units	Qvalue
1	Naphthalene	4.347	1560563	0.327783	ppm	69
2	Methylnaphthalene	5.357	1410744	0.155588	ppm	20
3	Acenaphthylene	6.552	318378	0.06932	ppm	63
4	Acenaphthene	0	0	0	ppm	0
5	Fluorene	7.58	177504	0.043356	ppm	18
6	Phenanthrene	8.644	743474	0.225674	ppm	63
7	Anthacene	8.891	54319	0.010875	ppm	62
8	Fluoranthene	10.602	87359	0.015468	ppm	60
9	Pyrene	10.996	194727	0.030011	ppm	59
10	Benzo(a)anthrascene	13.604	68134	0.023159	ppm	56
11	Chrysene	13.604	75886	0.010501	ppm	54
12	Benzofluoranthene	15.604	359864	0.03364	ppm	56
13	Benzo(a)pyrene	16.534	327800	0.065097	ppm	56
14	Indeno(1,2,3-CD)pyrene	0	0	0	ppm	0
15	Dibenzo(a,h)anthrascene	0	0	0	ppm	0
16	Benzo(g,h,i)perylene	19.088	44690	0.010845	ppm	54

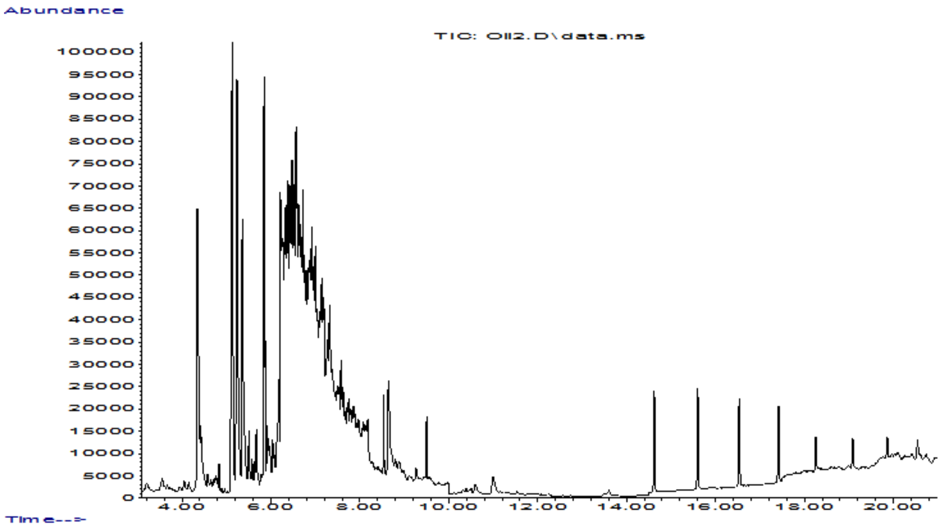


Figure 37. Results of recovered oil (sample 2) due to GC

Table 25. Raw results of recovered oil (sample 3) due to GC

Comp #	Compound Name	RT (min)	Area	Amount	Units	Qvalue
1	Naphthalene	4.366	86056	0.018075	ppm	69
2	Methylnaphthalene	5.507	66551	0.00734	ppm	20
3	Acenaphthylene	6.551	33743	0.007347	ppm	63
4	Acenaphthene	0	0	0	ppm	0
5	Fluorene	7.576	31567	0.00771	ppm	18
6	Phenanthrene	8.711	155299	0.047139	ppm	63
7	Anthacene	0	0	0	ppm	0
8	Fluoranthene	10.654	43681	0.007734	ppm	60
9	Pyrene	11.048	61809	0.009526	ppm	59
10	Benzo(a)anthrascene	13.624	23390	0.00795	ppm	56
11	Chrysene	13.624	41172	0.005697	ppm	54
12	Benzofluoranthene	0	0	0	ppm	0
13	Benzo(a)pyrene	16.529	9810	0.001948	ppm	56
14	Indeno(1,2,3-CD)pyrene	0	0	0	ppm	0
15	Dibenzo(a,h)anthrascene	0	0	0	ppm	0
16	Benzo(g,h,i)perylene	0	0	0	ppm	0

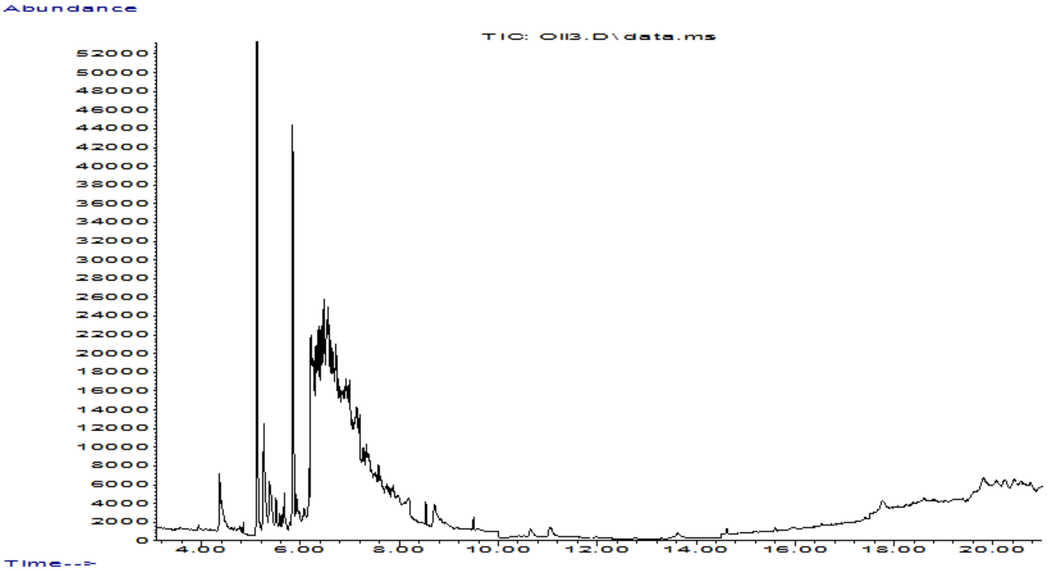


Figure 38. Results of recovered oil (sample 3) due to GC

Table 26. Raw results of recovered water (sample 1) due to GC

Comp #	Compound Name	RT (min)	Area	Amount	Units	Qvalue
1	Naphthalene	4.361	2226828	0.467726	ppm	69
2	Methylnaphthalene	5.538	729665	0.080473	ppm	20
3	Acenaphthylene	0	0	0	ppm	0
4	Acenaphthene	0	0	0	ppm	0
5	Fluorene	7.357	3041180	0.742811	ppm	18
6	Phenanthrene	8.818	20815695	6.3184	ppm	63
7	Anthacene	8.82	25832407	5.17155	ppm	62
8	Fluoranthene	10.595	1167203	0.206673	ppm	60
9	Pyrene	10.981	2871489	0.442556	ppm	59
10	Benzo(a)anthrascene	0	0	0	ppm	0
11	Chrysene	0	0	0	ppm	0
12	Benzofluoranthene	0	0	0	ppm	0
13	Benzo(a)pyrene	16.475	280577	0.055719	ppm	56
14	Indeno(1,2,3-CD)pyrene	18.587	35086	0.008742	ppm	56
15	Dibenzo(a,h)anthrascene	18.583	17962	0.005714	ppm	1
16	Benzo(g,h,i)perylene	19.077	49993	0.012132	ppm	54

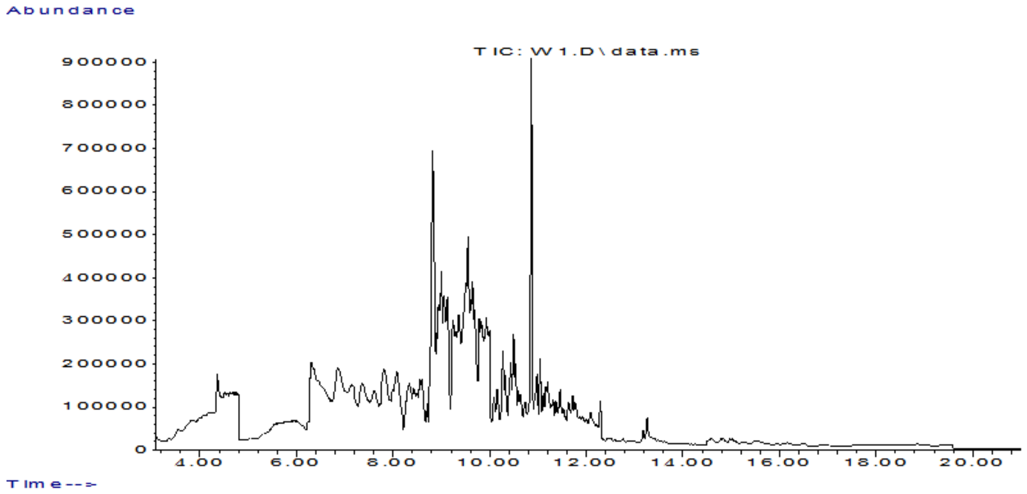


Figure 39. Results of recovered water (sample 1) due to GC

Table 27. Raw results of recovered water (sample 2) due to GC

Comp #	Compound Name	RT (min)	Area	Amount	Units	Qvalue
1	Naphthalene	4.365	2574226	0.540693	ppm	69
2	Methylnaphthalene	5.513	934644	0.10308	ppm	20
3	Acenaphthylene	6.505	4174031	0.908805	ppm	63
4	Acenaphthene	0	0	0	ppm	0
5	Fluorene	7.511	4763584	1.16351	ppm	18
6	Phenanthrene	8.785	784652	0.238173	ppm	63
7	Anthacene	8.925	19674296	3.93872	ppm	62
8	Fluoranthene	10.57	4506207	0.797901	ppm	60
9	Pyrene	11.012	4451069	0.686002	ppm	59
10	Benzo(a)anthrascene	0	0	0	ppm	0
11	Chrysene	13.621	110800	0.015332	ppm	54
12	Benzofluoranthene	0	0	0	ppm	0
13	Benzo(a)pyrene	16.477	237493	0.047163	ppm	56
14	Indeno(1,2,3-CD)pyrene	0	0	0	ppm	0
15	Dibenzo(a,h)anthrascene	18.672	48193	0.015332	ppm	59
16	Benzo(g,h,i)perylene	0	0	0	ppm	0

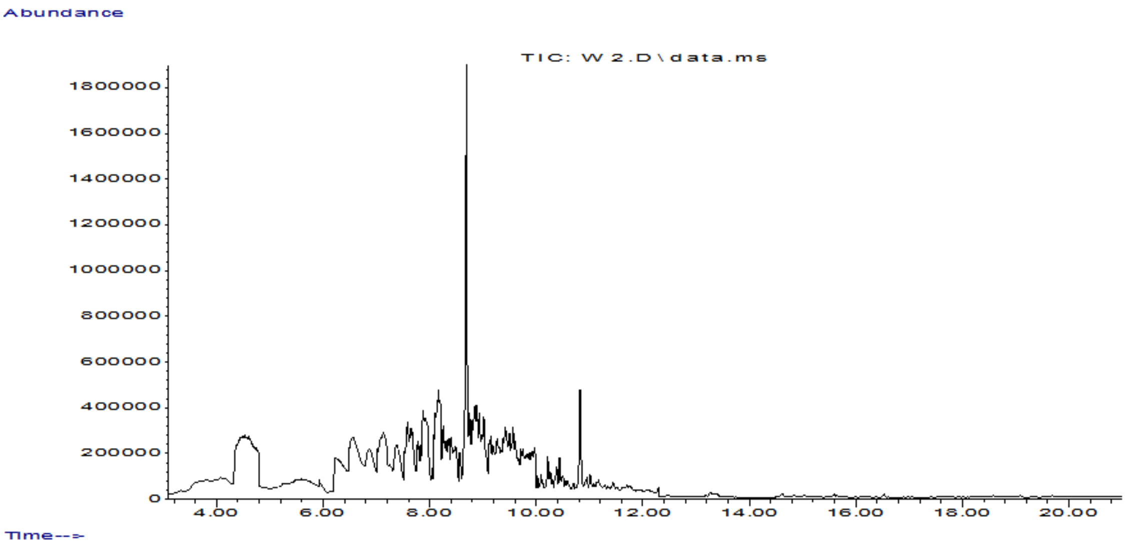


Figure 40. Results of recovered water (sample 2) due to GC

Table 28. Raw results of recovered water (sample 3) due to GC

Comp #	Compound Name	RT (min)	Area	Amount	Units	Qvalue
1	Naphthalene	4.365	2574226	0.540693	ppm	69
2	Methylnaphthalene	5.513	934644	0.10308	ppm	20
3	Acenaphthylene	6.505	4174031	0.908805	ppm	63
4	Acenaphthene	0	0	0	ppm	0
5	Fluorene	7.511	4763584	1.16351	ppm	18
6	Phenanthrene	8.785	784652	0.238173	ppm	63
7	Anthacene	8.925	19674296	3.93872	ppm	62
8	Fluoranthene	10.57	4506207	0.797901	ppm	60
9	Pyrene	11.012	4451069	0.686002	ppm	59
10	Benzo(a)anthrascene	0	0	0	ppm	0
11	Chrysene	13.621	110800	0.015332	ppm	54
12	Benzofluoranthene	0	0	0	ppm	0
13	Benzo(a)pyrene	16.477	237493	0.047163	ppm	56
14	Indeno(1,2,3-CD)pyrene	0	0	0	ppm	0
15	Dibenzo(a,h)anthrascene	18.672	48193	0.015332	ppm	59
16	Benzo(g,h,i)perylene	0	0	0	ppm	0

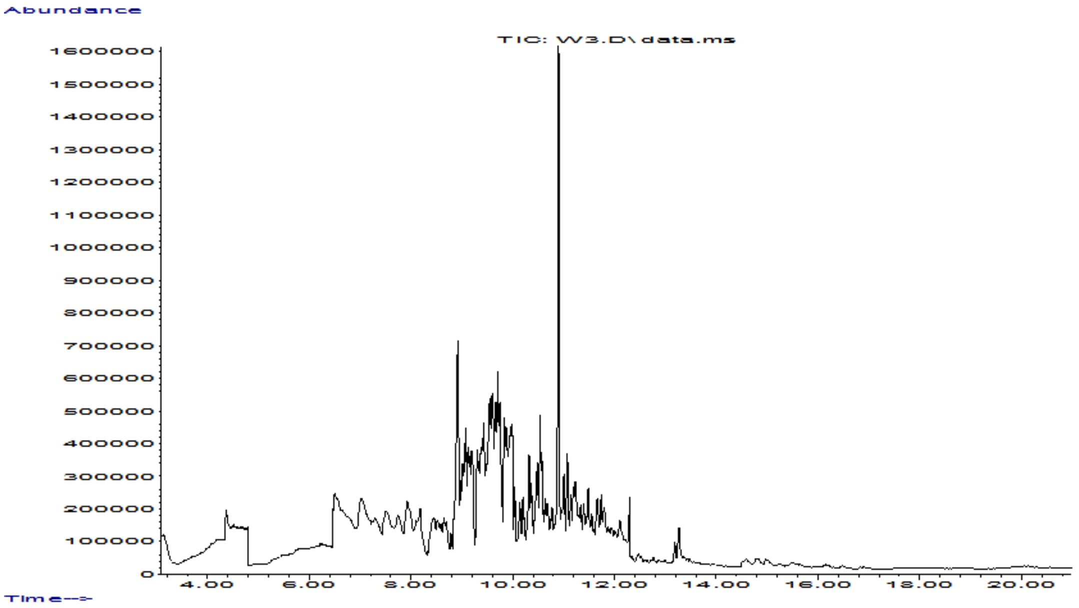


Figure 41. Results of recovered water (sample 3) due to GC