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Treatment of Oily Drill Cuttings Slurries Using Supercritical Carbon Dioxide

by

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Abstract

Research was conducted into using supercritical fluid extraction (SFE) for removing hydrocarbons from drill cuttings slurries, which will be used in a pilot-scale continuous SFE system currently under development. A laboratory-scale batch SFE system employing supercritical carbon dioxide (CO_2) was used in this research. Based on the measured hydrocarbon solubility and apparent hydrocarbon solubility in supercritical CO_2, conditions of 14.5 MPa and 40°C were selected for SFE treatment. The slurries require a minimum water to drill cuttings ratio of 1:1 (mass basis) to be "free-flowing" and therefore suitable for treatment in a continuous system. Water in the slurries leads to lower hydrocarbon extraction efficiencies during SFE treatment compared to the treatment of drill cuttings without slurrying. However, effective mixing and introduction of the supercritical CO_2 at the bottom of the extraction vessel resulted in treated slurries containing less than 1% hydrocarbons (dry mass basis).

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List of Abbreviations

AAFRD	-	Alberta Agriculture, Food and Rural Development
AARD	-	Average absolute relative deviation
AE	-	Alberta Environment
AEUB	-	Alberta Energy and Utilities Board
CCME	-	Canadian Council of Ministers of the Environment
CNOPB	-	Canada-Newfoundland Offshore Petroleum Board
CNSOPB	-	Canada-Nova Scotia Offshore Petroleum Board
CO_2	-	Carbon dioxide
D822	-	Distillate 822 (base oil)
FID	-	Flame ionization detector
GC	-	Gas chromatography
MSDS	-	Material safety data sheet
MT	-	Metric tonne
OBM	-	Oil-based (drilling) mud
PAH	-	Polycyclic aromatic hydrocarbon
RSD	-	Relative standard deviation
SBM	-	Synthetic-based (drilling) mud
SCF	-	Supercritical fluid
SFE	-	Supercritical fluid extraction

USD	-	United States dollars
US EPA	-	United States Environmental Protection Agency
WBM	-	Water-based (drilling) mud

List of Symbols

A - Constant in Chrastil equation (K)

A_i - GC/FID area count for compound i (no units)

B - Constant in Chrastil equation (no units)

b_0 - Constant in modified Chrastil equation (no units)

b_1 - Constant in modified Chrastil equation (K)

b_2 - Constant in modified Chrastil equation (mL/g)

b_3 - Constant in modified Chrastil equation (no units)

C_i - Concentration of compound i (mg/L)

F_i - Mass fraction of compound i (no units)

k - Constant in Chrastil equation (no units)

m_i - Mass of compound i (g)

η - Extraction efficiency of SFE process (%)

P - Pressure (MPa)

ρ - Density of a supercritical fluid (g/mL)

ρ_w - Density of water (g/mL)

RF - GC/FID response factor (mL/g)

RF_{avg} - Average GC/FID response factor (mL/g)

S - Solubility concentration (g/g or g/mL)

T - Temperature (K)

V - Volume (mL)

W - Weight of drill cuttings or slurry (g)

y - Solubility mole fraction (no units)

Chapter 1: Introduction

1.1 Problem Scenario

As the world continues to rely on energy from oil and gas for our homes, cars, and countless other applications, exploration for new oil and gas, and the exploitation of known reservoirs, will continue. Exploration and production of oil and gas resources requires operators to drill into the subsurface to access reservoirs. In 2008, there were over 20,000 new wells, totaling almost 23 million metres, drilled in Canada alone [1]. This drilling process produces significant quantities of waste, known as drilling waste. One type of waste, which accounts for a significant fraction of drilling waste, is known as "drill cuttings" or simply referred to as "cuttings" [2]. Cuttings are produced during the drilling process itself. While drilling a well, a mixture called drilling mud is pumped down through the drill pipe to the drill bit, and back to the surface through the annulus [3]. The drilling mud can be aqueous-based (water-based) or non-aqueous-based (oil-based or synthetic-based), depending on the type of base fluid used in the mud [3,4]. The drilling mud serves many purposes including lubricating and cooling the drill bit, carrying the solids from the wellbore back to the surface, and stabilizing the walls of the wellbore, among others [2-6]. When the drilling mud is returned to the surface, it is mixed with rock cuttings from the wellbore being drilled. This mixture is usually sent through solids control equipment, such as shale shakers and/or centrifuges, to separate the rock cuttings from the drilling mud [3,7]. However, even with the most efficient separation equipment, the cuttings contain residual mud coated on their surface [3,7,8]. These drill cuttings, which contain residual drilling mud, are a significant waste stream in oil and gas exploration and production.

In recent decades, environmental regulations have become increasingly stringent regarding the disposal of drill cuttings. These regulations are particularly concerned with the disposal of cuttings containing oil-based drilling mud, because of the potential environmental impacts associated with the hydrocarbons in the drill cuttings. Decades ago, there were little or no regulations for the disposal of drill cuttings. Cuttings produced from onshore drilling operations were disposed of directly to the land, and cuttings produced in offshore operations were dumped into the sea without treatment [9]. However, regulations have been introduced and developed throughout the past decades, and today these regulations govern the amount of oil that can be present on the cuttings prior to disposal to land or sea. In many cases, the use of water-based mud over oil and synthetic-based mud is advantageous because water-based mud poses less of an environmental threat, and therefore regulations on the disposal of cuttings containing water-based mud are less strict. However, oil and synthetic-based muds have several technical advantages that lead to enhanced drilling operations, lower overall cost, and safe operation [3,10]. Therefore, despite the strict environmental regulations governing their use and the disposal issues related to the cuttings produced, oil and synthetic-based muds are prevalent in the drilling industry today [11,12], and are expected to increase in popularity as oilfields mature and more challenging wells are drilled [6].

Since the advent of environmental regulations governing the disposal of drill cuttings born from the use of oil and synthetic-based muds, many techniques have been developed to reduce the hydrocarbon content of the cuttings to below regulatory levels. These techniques include biological treatment, thermal treatment, and subsurface reinjection [3,13]. However, these techniques have shortcomings, such as long treatment times for biological treatment [14], high energy input and air emissions for thermal treatment [11,15], and concerns over waste containment integrity for subsurface reinjection [3]. Furthermore, stringent regulations in many parts of the world require oil-containing cuttings produced during offshore drilling to be shipped to land for treatment and disposal [2,16,17], and this shipping is a costly process [3,5,16]. With the increasingly stringent environmental regulations, and the limitations of current treatment and disposal methods, there is a need to develop a new technology that can remove the hydrocarbons from oily drill cuttings in a timely, inexpensive, and environmentally friendly manner.

Supercritical fluid extraction (SFE) is a novel technique for the treatment of drill cuttings. SFE is a solvent extraction process that uses a supercritical fluid as the solvent, rather than potentially harmful and toxic organic solvents. For several decades SFE has been used in other applications, such as the decaffeination of coffee beans, hops extraction, and the production of fine oils and essences [18-20]. In recent years, the lower toxicity of supercritical fluids, compared to organic solvents, has lead to the use of SFE in the food and pharmaceutical industries [20-22], and in soil remediation [23-27]. Supercritical carbon dioxide (CO_2) is the most commonly used supercritical fluid because it is cheap, readily available in high purities, non-toxic and environmentally-friendly [24,28,29].

SFE has been recently tested as a technology to effectively remove hydrocarbons from oil-laden drill cuttings, potentially enabling the safe disposal of the cleaned solids and the reuse of the recovered oil or synthetic-based drilling mud [5,8,16,30-37]. However, to date, all work on the use of SFE for the treatment of oily drill cuttings has been in laboratory-scale, batch studies, and according to a recent literature review, a continuous system has not yet been developed. The technology has not been tested on a large scale or established in industry. Batch SFE systems are cumbersome and expensive to operate in high-throughput situations [38,39], such as drill cuttings treatment. In order for SFE to be economically feasible for such an application, a continuous system should be developed. Continuous systems are less expensive to operate and more efficient on a per-ton basis than batch systems [20,22,23,40]. However, feeding a mostly solid waste stream, such as drill cuttings, into a high pressure extractor in a continuous fashion is one major challenge for the development of a continuous system [39]. Adding water to the drill cuttings, to create a slurry that can be pumped through a continuous extractor, is a solution that is being proposed. A similar solution has been proposed for the treatment of solid matrices contaminated with organic compounds [38], and this method was successful at treating contaminated soil [41].

1.2 Research Objectives

As mentioned previously, SFE has been proven to be effective for removing oil for drill cuttings. However, to date no studies have been conducted to test the effectiveness of SFE in removing oil from drill cuttings slurries. It is therefore the objective of the research described herein to investigate the possibility of using water as a slurrying agent and a transportation medium for pumping drill cuttings through a high pressure extraction vessel. In particular, the hydrocarbon extraction efficiency, already known to be high for plain drill cuttings, will be investigated for drill cuttings slurries. Other parameters that will aid in the design of a continuous SFE treatment system will also be studied, such as the solubility of a typical base oil in supercritical CO_2, and diffusion effects during the extraction process. The results, obtained using a laboratory-scale batch SFE system, will be used as a basis from which a pilot-scale continuous system for the treatment of drill cuttings can be designed and operated.

The specific objectives of this project are:

1. Measure the solubility of Distillate 822, the base oil found in the drill cuttings, in supercritical CO_2 between 35 and 50^oC, and 10.3 and 17.2 MPa, in order to determine suitable conditions of temperature and pressure that will be used during the SFE treatment of the drill cuttings.

2. Determine the parameters for the Chrastil and modified Chrastil equations in order to predict the solubility of Distillate 822 in supercritical CO_2.
3. Determine the apparent solubility of Distillate 822 in supercritical CO_2 in the presence of drill cuttings and drill cuttings slurries.
4. Investigate the feasibility of producing drill cuttings slurries that are suitable for feeding continuously through a continuous SFE column. In particular, the “flowability”, “pumpability” and solids settling characteristics of the slurries, both before and after SFE treatment, will be qualitatively observed.
5. Determine the hydrocarbon extraction efficiency during the SFE treatment of oily drill cuttings slurried with water in varying ratios.
6. Select a water ratio for further testing, based on the results of objectives 4 and 5 above.
7. Attempt to maximize the extraction efficiency from the selected slurry by the use of additives and/or equipment modifications. A hydrocarbon content of less than 1% on a dry mass basis in the extracted slurry was set as the goal.

This research will provide information that can be used as a basis from which a continuous pilot-scale SFE system for the treatment of drill cuttings can be developed. The solubility and apparent solubility are required for the design and optimization of such a system. The research on drill cuttings slurries will aid in determining an appropriate water to drill cuttings ratio to start experimentation on the continuous system.

Successful development of the pilot-scale continuous system should lead to the future commercialization of a continuous SFE system for the removal of hydrocarbons from oily drill cuttings, and would potentially offer a new treatment technology to meet the stringent regulations regarding the disposal of such cuttings. Although the technology can be used on both onshore and offshore drilling rigs, the most benefit would likely be realized in offshore operations, where the implementation of a continuous SFE system on offshore drilling rigs could eliminate the need to store the oily drill cuttings on the rig and to transport them to shore, resulting in substantial cost savings.

1.3 Thesis Organization

This thesis is divided into five chapters. Chapter 1 provides an introduction to the challenge of drill cuttings management in the oil and gas industry, a summary of the background information, and includes a list of the specific objectives of the project. Chapter 2 provides a more in depth literature review of drilling waste disposal regulations, treatment techniques, and the history and theory of SFE for use in drilling waste treatment and similar applications. Chapter 3 outlines the procedures, equipment, and materials used to conduct the research. Chapter 4 presents the solubility, apparent solubility, and SFE results, and includes a discussion of the obtained results. Finally, Chapter 5 summarizes the key conclusions of the research project, and provides some recommendations for the development of the pilot-scale continuous SFE system.

Chapter 2: Literature Review

2.1 The Drilling Process

This section will provide some general information regarding the operations carried out while drilling oil and gas wells. The operations discussed include the drilling process itself, the drilling mud used, the solids control equipment used to recover the drilling mud, and the generation and characteristics of drill cuttings.

2.1.1 Drilling and Drilling Muds

Drilling for oil and gas can be done on onshore or offshore drilling rigs. Generally, drilling involves the use of a drill bit attached to a drill string to penetrate the subsurface. As the drill bit penetrates the rock in the subsurface, drill cuttings are generated. A typical drilling operation, including the flow of drilling mud, is shown in Figure 1. An offshore drilling rig is pictured in Figure 2 and an up-close image of the drill bit and drill string is shown in Figure 3.

Drilling mud is a complex mixture of liquids and solids that is circulated down through the drill string and drill bit, and returned to the surface through the annulus (between the outside of the drill string and the wellbore walls) [3,7], as shown in Figure 1. Drilling mud is vital to the drilling process, since without it, only shallow, low pressure formations could be exploited effectively and safely [3]. In general, drilling mud is composed of a base fluid (aqueous or non-aqueous), a solid phase dispersed in the base fluid (to control the density and viscosity), and other additives (to control such properties as pH, thermal stability, etc.) [2,12].

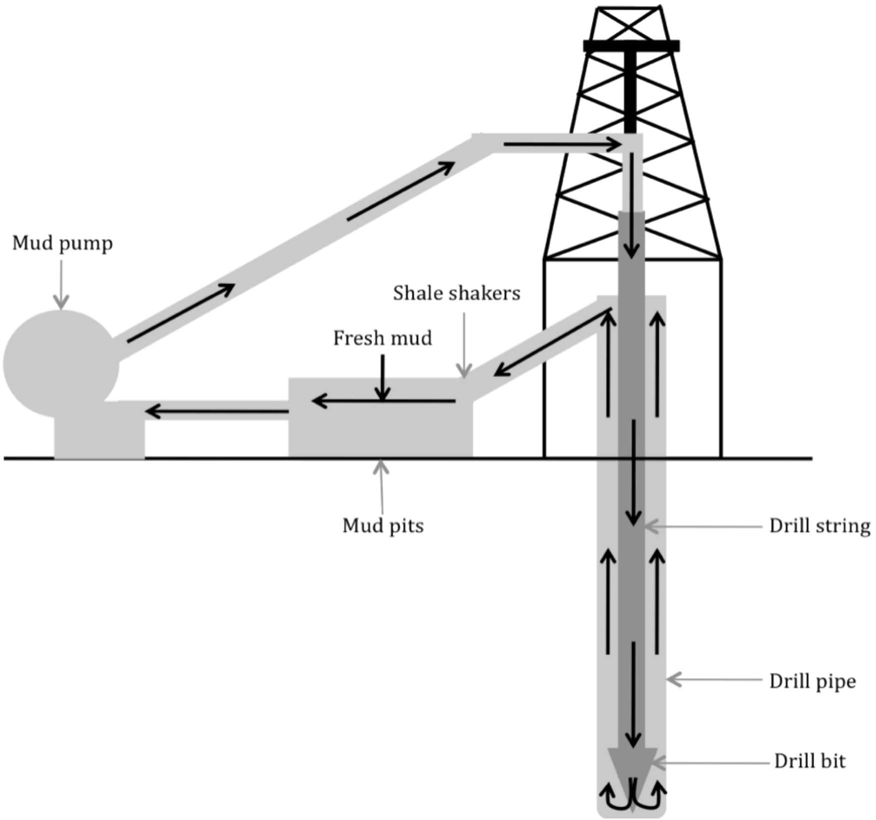


Figure 1: Drilling rig and drilling mud circulation, indicated by the black arrows (modified from [3]**)**

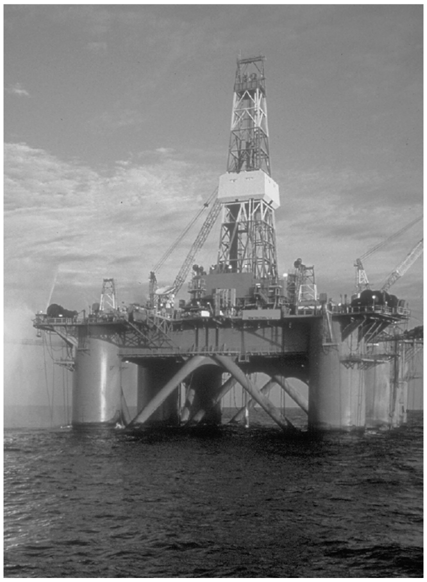


Figure 2: An offshore drilling rig (taken with permission from [3]**)**

Figure 3: Drill bit and drill string (taken with permission from [3]**)**

Drilling mud performs a variety of tasks, including lubricating and cooling the drill bit and drill string, carrying drill cuttings to the surface, maintaining a balanced pressure between the formation and borehole, sealing the permeable formation, and stabilizing the borehole walls to prevent collapse [2-4,6,7]. In order to perform these functions, the drilling mud must possess some specific properties, such as ample lubricity to lubricate the drill bit and drill string, sufficient viscosity to suspend cuttings and transport them to the surface, sufficient thermal stability, adequate density to control formation pressures, and good filtration properties to allow the formation of a thin cake that will create a seal between the formation and the borehole [3]. Using a drilling mud with the appropriate properties is absolutely vital for safe and efficient drilling operations. Most downtime and extra expenses incurred during drilling are associated with problematic interactions between the drilling mud, borehole and cuttings [2]. As the pressure, temperature and geology of each formation varies, the operator must select a mud with the necessary properties for that specific situation. Typically, the mud is selected and fine-tuned based on the formation conditions and applicable environmental regulations [42].

There are three types of drilling mud, classified according to the type of base fluid in the continuous phase (liquid phase) of the mud. The three classes are water-based mud (WBM), oil-based mud (OBM) and synthetic-based mud (SBM) [4,14], but the latter two can be classified under the general term of non-aqueous mud [3,43]. The following sections will describe the components of each type of mud, and the advantages and disadvantages of their use, from both an operational and environmental standpoint. Table 1 provides a simple comparison between WBM, OBM and SBM. Of interest is one study that found that in offshore operations, SBM is the preferred mud in many situations, followed by WBM and then OBM [42]. These results are based on a risk-based approach that considered technical operations, resource use, liability, and economics associated with drilling, and the transportation and discharge of the resulting wastes, including cuttings [42].

Table 1: Comparison of WBM, OBM and SBM

Property	WBM	OBM	SBM	References
Lubricity	Lower	Higher	Higher	[6]
Wellbore Stability	Lower	Higher	Higher	[6,43]
Thermal Stability	Lower	Higher	Higher	[3,43,44]
Mud Cost	Low	Moderate	High	[2,6]
Drilling Time / Costs	Higher	Lower	Lower	[3,42]
Environmental Concerns	Low	High	Moderate	[3,42]
Occupational Hazards	Low	High	Moderate	[42]

2.1.1.1 Water-Based Mud

WBM is the most common type of mud used in drilling [6]. For example, about 90% of offshore rigs operating in the Gulf of Mexico used WBM as of 1995 [2]. The continuous phase of WBM is water or brine, with small amounts of emulsified oil to increase the lubricity [42]. Barite, a solid mineral, is added to WBM in significant amounts to increase the density. Other additives include bentonite to increase the viscosity and prevent large filter cake build-up; lignosulfate to act as a dispersing agent to control the density and viscosity from becoming too high when the cuttings become hydrated; pH-controlling substances; foaming control agents; and chemicals to boost the thermal stability of the WBM [3,6].

The advantages of WBM are mostly related to their low impact on the environment. Because the continuous phase is mostly water, with only a small amount of oil, the disposal of the drill cuttings produced when WBM is used is easier and less expensive compared to OBM and SBM [6]. For example, in Alberta, Canada, drill cuttings produced with WBM have fewer restrictions in terms of the treatment and disposal options available, and less government approvals for disposal are required for WBM disposal, compared to OBM and SBM. Provided that the cuttings meet salinity, hydrocarbon, and other elemental guidelines, and that the appropriate government agency is notified, drill cuttings containing WBM can be disposed of in burial pits or directly onto the land via land spreading. In contrast, the disposal of drill cuttings containing OBM are subject to *preapproval* by various government agencies prior to land treatment, reinjection, or other disposal methods [45]. At sea, spent WBM and the associated drill cuttings can often be discharged to the sea directly, as they pose little, if any, adverse threats to the sea floor or aquatic communities [2]. Another advantage of WBM is that it is cheaper on a per-ton basis [6], but as will be noted in the following paragraph, the lower initial cost can sometimes be offset by increased operating costs.

The disadvantages of WBM are mainly the result of their poor performance as compared to OBM and SBM. Compared to their non-aqueous-based counterparts, WBM has lower lubricity, lower drill penetration rates, and is more reactive with shale that is often found in the subsurface [2,3,6]. The greater reactivity of WBM with shale in the subsurface in turn leads to lower wellbore stability [6]. WBM generates between 1000 and $2000m^3$ of waste per well drilled, of which 220 to $450m^3$ are drill cuttings. This amount of waste is significantly more than the amount of waste generated with OBM [2]. The increased waste associated with WBM use is due to the fact that most spent WBM is simply disposed of (owing to the cheap cost of the base fluid: water) [2]. Also, the lower wellbore stability causes hole enlargement and collapse in some cases, increasing the volume of cuttings generated [3].

In summary, WBM has significant environmental advantages related to the relative ease of disposal of the generated wastes and cuttings, but WBM suffers from several operational disadvantages.

2.1.1.2 Oil-based Mud

OBM was introduced in the 1960s, when diesel oil was typically used as the continuous phase. In more recent decades, some operators have switched to lower toxicity mineral oils for the continuous phase, but diesel oil remains popular in many parts of world, including Alberta [11,12]. Often, water or brine is emulsified into the oil (in this case, the water or brine is known as the internal or dispersed phase) in amounts ranging from 5 to 50% water or brine [12,42,43]. The water is added to increase the viscosity of the mud [3]. OBM also contains barite, bentonite, and other chemical additives that achieve the required density, viscosity, pH, thermal stability, and emulsifiers that stabilize the oil-water emulsion needed for drilling in each unique formation [2,12,43].

The advantages of OBM are primarily a result of its operational advantages over WBM. In general, OBM reduces the overall cost of drilling by minimizing operational problems, and OBM can sometimes be necessary for safe operations [3,10]. The increased lubricity, higher thermal stability, and lower reactivity of OBM relative to WBM improve drilling operations [3,13,42,43]. The non-polar molecules that make up the oil phase in OBM render them non-reactive with shale [42], and therefore promote higher wellbore stability. The higher lubricity of OBM is evidenced by their coefficient of friction that is up to

50% lower than that of WBM [3]. This higher lubricity can help increase the drilling penetration rate of OBM as compared to WBM [2,3,43], reducing the time and cost of well completions. These advantages allow OBM to be used in more challenging formations or drilling scenarios, such as high temperature formations, formations containing hydratable shale, high angle and extended reach wells (including horizontal drilling), and salty formations [2,6]. For example, in Alberta where the oil fields are mature, many new projects use horizontal and inclined drilling through sensitive shale, and OBM is being used to prevent wellbore collapse, stuck pipe and other operational difficulties [12]. Similarly, the United States Environmental Protection Agency (US EPA) notes that although WBM is still used in many cases in the United States, there is a trend towards deeper wells as the more easily extracted oil and gas becomes depleted, and therefore OBM (and SBM) will likely continue to become more important [6].

The disadvantages of OBM are mainly related to the disposal of the wastes, including drill cuttings, generated when they are used. The use of OBM results in significantly less generated waste (300 to 1300m^3 per well drilled) than when WBM is used [2] because much of the mud is separated from the drill cuttings and reused. However, the waste and cuttings that are produced pose a greater environmental threat because of the oil present in the waste. For example, when oil laden cuttings and drilling waste are dumped into the sea, the sea-floor communities suffer from persistent drill cuttings piles that accumulate [2]. The toxicity of OBM and the associated drill cuttings is of concern both from an occupational health and safety standpoint and an environmental standpoint [3]. Some oil-based base fluids, including diesel, contain 20-30% aromatic hydrocarbons [14,43], which are known to be toxic to workers and organisms in the environment. Of the roughly 25% aromatic hydrocarbons found in diesel, between 2 and 4% are polycyclic aromatic hydrocarbons (PAHs) [43], which are of particular concern because they are often carcinogenic and mutagenic. More recent advances in drilling mud technology have lead to the use of mineral oils that contain about half the amount of PAHs that diesel contains. Even more recently, low-toxicity mineral oils have been developed which contain only 0.5 to 5% aromatics and less than 0.35% PAHs [43]. Nonetheless, the cuttings, which contain residual OBM, still pose a concern to ecological and human health, and thus are subject to more strict regulations on their treatment and disposal, which, in turn, can sometimes restrict their use.

2.1.1.3 Synthetic-based Mud

SBM is a more recent advance in drilling mud technology. Although SBM was developed for use offshore, more stringent legislation for onshore operations worldwide is leading to its use on land as well [13]. SBM was first introduced in Europe's North Sea in the mid and late 1980s due to increased restrictions on the disposal of oil-laden cuttings to the sea [11]. SBM was later introduced into Gulf of Mexico operations in the early 1990s as an alternative to OBM [13], which was being more heavily regulated under new US EPA regulations [42]. SBM was developed to have similar operational advantages as OBM, but with less negative environmental impacts and occupational risks [2,9,13,42,43,46]. By definition, SBM contains a base fluid that is produced from a reaction of specific and pure feedstocks, as opposed to OBM that contains base fluids that are produced by a separation process such as distillation, or by cracking. The other requirements of SBM are that the base oil must contain less than 10mg/kg PAHs, have low toxicity, and must easily biodegrade under aerobic conditions [4,43]. Base oils that meet these criteria include esters, ethers, acetals, olefins, paraffins and mixtures of the above [3,6,43].

Because SBM contains highly refined base oils, the cost is higher than OBM and WBM. In general, the cost of non-aqueous base fluids, including OBM and SBM ranges between $300 and $3000 (USD) per cubic metre [3]. SBM costs about 4 to 5 times more than OBM [2]. SBM has all of the technical advantages of OBM such as high lubricity, high drill bit penetration rate, low reactivity, and high thermal stability, and therefore leads to less problems during drilling, particularly in difficult drilling situations such as those encountered in deep, directional and horizontal drilling [2]. In addition, the environmental impacts and occupational health issues associated with SBM are significantly lower, owing to its lower toxicity and higher biodegradability than OBM [3,42,43,47]. As a result, the cost required to dispose of cuttings and other wastes generated from SBM is lower. These environmental advantages over OBM, and the operational advantages over WBM, mean that the overall cost of drilling a well is often significantly less (up to 50% less) when SBM is used [2,42,48].

The disadvantages of SBM are similar to those of OBM. There is still concern over soil and groundwater pollution from land disposal of drill cuttings containing residual SBM due to the high salt content in the waste and organic loading from the base fluid [13,47]. Investigations have been conducted into the effects of dumping SBM-contaminated cuttings directly into the sea, and their accumulation on the seafloor [13,44]. Accumulation of the cuttings on the seafloor results in the burial of seafloor communities and the depletion of dissolved oxygen caused by the biodegradation of the hydrocarbons remaining in the cuttings. However, the extent of such problems appears to be small, and the seafloor can recover [43].

To summarize, SBM is the most costly drilling mud, but operational, occupational and environmental benefits mean that SBM is often overall cheaper when operation and disposal costs are considered, and therefore more appealing for use in difficult drilling situations. However, the trend of legislation in recent decades indicates that greater restrictions will be placed on how SBM-laden cuttings can be disposed of, and the more stringent regulations may limit the widespread use of SBM in the future, unless better drill cuttings treatment techniques are developed.

2.1.2 Solids Control

Solids control is a mechanical separation process to separate the drill cuttings from the drilling mud before the mud is reused. Since WBM is often immediately discarded after use along with the drill cuttings [2], solids control equipment is more important when OBM and SBM are used. Solids control is used to reduce the amount of drilling mud on the cuttings, and to reduce the amount of cuttings in the drilling mud prior to reuse. However, this process is not 100% efficient, so inevitably some cuttings end up in the recycled drilling mud, and some OBM or SBM will end up on the cuttings [3,7,8]. The residual non-aqueous mud (OBM or SBM) present on the cuttings after they pass through the solids control equipment is the reason that the disposal of drill cuttings is heavily regulated and is costly and challenging for oil and gas operators.

The fact that some cuttings remain in the drilling mud also leads to an operational challenge, in that the recovered mud must often be reconditioned prior to reuse. Extra solids present in the mud lead to an undesirable viscosity increase, which is corrected by adding additional drilling fluid to the mud. However, this action leads to a higher drilling mud volume and forces the wasting of spent drilling mud, increasing the volume of oil-laden waste [3]. Thus, operators must maintain an efficient solids control operation in order to minimize drilling waste, limit the residual OBM or SBM on the drill cuttings prior to treatment and disposal, and to maintain drilling mud with acceptable properties. In general, an efficient solids control system will reduce costs. The following sections describe some common equipment used for solids control.

2.1.2.1 Shale Shakers

Shale shakers are the primary equipment used to remove drill cuttings from the mud. They consist of a series of vibrating screens that screen out the rock cuttings and allow the drilling mud to pass through. Therefore, the mud is collected below the screens and sent for reconditioning and reuse, and the cuttings are collected on top of the screens and sent for storage prior to treatment and disposal [3,7]. Often, two sets of screens are used: a primary screen to remove coarse cuttings, and a secondary screen to remove finer cuttings [7]. Figure 4 shows the basic operation of a shale shaker.

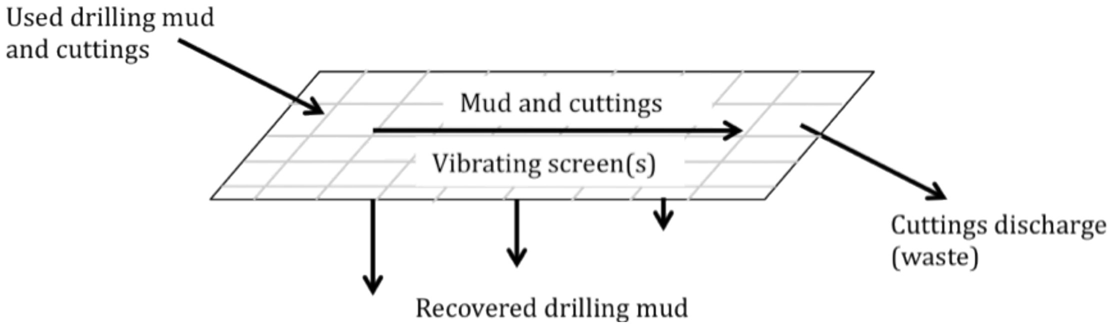


Figure 4: Shake shaker assembly, showing the vibrating screens which separate the cuttings from the used mud (based on information from [3]**)**

The vibrating screens on shale shakers contain openings that can vary in size from screen to screen. Coarse screens contain large openings and remove only larger cuttings. The oil content of larger cuttings is often less than that of finer cuttings, because the larger cuttings have a smaller surface area to which OBM and SBM can adhere, and the coarse screens retain less drilling mud [3]. However, the downfall of coarse screens is that they also allow more cuttings to pass through, which is harmful to the reused mud [3]. The opposite is true for fine screens. Therefore, operators must achieve a balance between the advantages and disadvantages of using coarse and fine screens that is specific to the well being drilled and the mud being used. In general, cuttings from shale shakers may contain as much mud as they do rock cuttings on a volumetric basis [7], resulting in as much as 15% (mass basis) oil content in the cuttings [3,16].

2.1.2.2 Additional Solids Control Equipment

In some cases, operators may choose to employ additional techniques for reducing the residual mud adhered to drill cuttings. Additional equipment is used if the next cuttings treatment step requires a lower residual hydrocarbon content in the cuttings, or if the drilling mud used is valuable enough to warrant further recovery [7]. Hydrocyclones, centrifuges and specially designed cuttings dryers are a few of the options used in the industry. Hydrocyclones are often used to recover WBM. Centrifuges are used to separate very fine (colloidal) solids from the mud to prevent these fines from causing a deterioration in mud performance upon reuse [3,7]. Cuttings dryers can be very effective at recovering residual mud from the cuttings, and reducing the cleaned cuttings to a fine powder [7]. In one example, the hydrocarbon content of cuttings collected after shale shakers was reduced from 12% to 2% using a cuttings dryer [43].

2.1.3 Drill Cuttings Generation and Characteristics

Drill cuttings are produced when any oil or gas well is drilled, as a result of the rock cuttings removed from the wellbore by the drilling mud. As mentioned previously, the cuttings themselves are separated from the drilling mud by shale shakers and other solids control equipment. However, in many cases the cuttings still contain a significant quantity of oil, and as a result of stringent environmental regulations, can be costly to treat and dispose of.

Oil and gas operators benefit when cuttings generation and the oil content of the generated cuttings are minimized, because cuttings represent a significant portion of all drilling-related wastes generated [2]. The oil content is minimized by using solids control equipment, and then is sometimes further reduced by other techniques prior to final disposal (to be discussed in Section 2.3). Efforts have also been made to reduce cuttings volume. Firstly, smaller diameter wells, the use of directional or horizontal wells, and the use of pneumatic drilling (which employs gaseous drilling fluids) can all greatly reduce the volume of cuttings generated [3,7]. These and other efforts have lead to a dramatic drop in cuttings volume in recent decades, and operations today produce about one third of the volume of drilling wastes of earlier projects [3].

The amount of drilling waste (including drill cuttings) generated depends on the depth of the well, the geologic formation being penetrated, the type of drilling mud and the effectiveness of the solids control equipment being used. Therefore, there are several estimates of the amount of drill cuttings and other wastes that are produced when drilling a well. One estimate suggests that drilling operations produce between 1 to 2m^3 of drilling waste per vertical metre of well drilled [49]. The US EPA estimates that between 0.1 and 1m^3 of waste are produced per vertical metre drilled [6]. This lower estimate of the amount of waste produced could reflect more modern drilling practices. The US EPA also estimates that the average depth of a well drilled in the United States is 1700m deep [6]; such a well could generate as much as 1700m^3 of drilling waste. WBM has been known to generate even more waste: up to 2000m^3 per well drilled [2].

Drill cuttings have a variety of physical and chemical properties, and these properties can have implications for appropriate treatment methods and end use applications of the cuttings [50]. Possibly the most important property of the cuttings is the oil, or hydrocarbon content. Estimates of the oil content of cuttings, after being treated by the solids control equipment, range from 5 to 20% by mass [3,11,50]. This oil could be present in the cuttings as free oil coating the surface of the solid particles, as oil emulsified in the water phase, or as oil trapped in the pores of the solid particles found in the cuttings [51]. This oil can contain a variety of compounds, including toxic PAHs and other aromatics, depending on the type of base oil in the drilling mud. Along with these high oil contents, another concern is the salt content of cuttings [12,13,47]. Cuttings also contain rock cuttings from the subsurface, water (the salts will be dissolved in this phase), cavings and metal fragments, oil from the formation, bentonite, barite and other additives from the drilling mud [12,43,51].

The physical properties of drill cuttings also vary. The solid particles in drill cuttings can range from 10μm to 20mm in diameter [50]. Typically, the density of untreated cuttings is about 1.65 metric tonnes per cubic metre (MT/m^3), and the density of mostly oil-free treated cuttings ranges from 2.2 to 2.7 MT/m^3 [50]. Cuttings are typically sludge-like in character with a liquid (oily) phase and a solid porous phase.

2.2 Drill Cuttings Disposal Regulations

This section will describe the evolution of regulations regarding the safe treatment and disposal of hydrocarbon-contaminated drill cuttings resulting from OBM and SBM use. Because the regulations vary from one jurisdiction to another [52], only the regulations from relevant or important regions will be discussed. Offshore regulations in two major oil-producing regions including the Gulf of Mexico and Europe's North Sea, along with Canadian legislation regarding offshore drilling on Canada's East Coast, will be discussed first. Next, regulations for onshore drilling waste management, as they apply to Alberta, Canada, will be highlighted. In general, and particularly in offshore drilling, the limits on the hydrocarbon content of drill cuttings being discharged are becoming increasingly stringent [17,52], and, as a result, waste and cuttings management is an important aspect in the oil and gas industry today [53,54]. The increasingly stringent environmental regulations worldwide are one major driving force for the development of a commercially viable SFE system for treating oily drill cuttings.

2.2.1 Offshore Regulations

In the past, wastes, including drill cuttings, generated during offshore oil and gas exploration were discharged directly to sea without any treatment [9]. Direct disposal of oil-laden drill cuttings to the sea can result in organic loading on the sea floor leading to exposure of organisms to toxic compounds, burial of ocean-floor ecosystems, and reduced oxygen caused by the biodegradation of the hydrocarbons remaining in the disposed cuttings [2,7,13,43,44]. As a result, in recent decades, regulations have been placed on the offshore disposal of drill cuttings, and governments have mandated reporting and monitoring of such disposal. These regulations vary from one area to another, but in general all have become increasingly more stringent in recent decades [17,52]. The following sections will briefly describe the regulations for offshore-generated drill cuttings management in different parts of the world.

2.2.1.1 North Sea

Perhaps the most stringent regulations for offshore drill cuttings management are found in Europe's North Sea [53]. Operators drilling in the North Sea spend more money to comply with drill cuttings management regulations than operators anywhere else in the world [53]. The tightening of regulations in the North Sea began in the mid 1980s, when regulators mandated that operators monitor and report discharges of drilling wastes, and that they reduce the amount of oil on the cuttings before discharge [11]. Later, the direct discharge of oil-contaminated cuttings was banned and the limit for oil-on-cuttings prior to discharge was set at 1% under OSPAR (an intergovernmental commission to protect the Northeast Atlantic Ocean in Europe) regulations [55]. More recently in 2005, some areas of the North Sea, including the Norwegian Sea, have implemented a "zero discharge regime" [15,56]. With these regulations in effect, most of the drill cuttings generated have been shipped to shore for landfill disposal since most current treatment technologies cannot meet the mandated residual oil level to allow offshore disposal [50]. Also, many of the local formations are not suitable for cuttings reinjection [56]. Since shipping waste to shore is a costly endeavor, a new treatment technique is needed that can fulfill the legislated requirements for drill cuttings treatment and disposal to the North Sea.

2.2.1.2 Gulf of Mexico

The US EPA regulates drilling waste management and disposal in the Gulf of Mexico. However, in some cases, states or other jurisdictions have been granted permission to administer the US EPA's regulations [7]. As with the North Sea, the trend has been towards more strict regulations. In 1993, the US EPA introduced regulations requiring that "no free oil" be present on the cuttings and that the cuttings meet toxicity and metal concentration criteria prior to their discharge to sea. Cuttings containing diesel oil were not allowed to be discharged to sea [7]. Cuttings which did not meet this criteria had to be shipped to shore for land disposal or reinjected into the formation [2]. In 2000, the US EPA concluded that the use of SBM was the best approach [3,15]. Currently, cuttings containing such synthetic base oils must have either 6.9% or 9.4% total petroleum hydrocarbons by weight, depending on the type of SBM used, if they are to be discharged to the Gulf of Mexico. These levels can be obtained with good solids control equipment [7,51,57]. Because of these regulations permitting certain cuttings to be discharged to sea, drilling waste management costs in the Gulf of Mexico are nearly 5 times lower than those in the North Sea [53]. Still, the trend is for ever-increasing regulation on the disposal of drill cuttings in the future.

2.2.1.3 Canada's East Coast

The National Energy Board (NEB) has written the Offshore Waste Treatment Guidelines [4], which regulate the use and disposal of drilling mud and cuttings on Canada's East Coast. The Canada-Newfoundland Offshore Petroleum Board (CNOPB) and the Canada-Nova Scotia Offshore Petroleum Board (CNSOPB) are responsible for administering the NEB's regulations [3]. The guidelines state that WBM should be used whenever possible. However, SBM can be used if WBM is impractical. Furthermore, OBM should not be used, and will only be permitted if the use of SBM or WBM is not feasible [4]. Drill cuttings containing OBM cannot be discharged to sea, and the method for their treatment and disposal requires preauthorization. Drill cuttings containing SBM should be reinjected into the formation. If reinjection is not technically feasible, drill cuttings containing SBM can be discharged to sea if they contain less than 6.9g of hydrocarbons per 100g of wet solids [4].

2.2.2 Onshore Regulations

In the past, when regulations were less stringent or non-existent, drilling waste generated onshore was simply dumped on lease sites or nearby properties without any treatment [9]. However, as with the offshore industry, onshore operations have been subject to increasing regulations regarding drilling waste treatment and disposal, as issues regarding soil and groundwater contamination and dangers to human and ecological health have been raised as a result of poor management of oil field wastes. The following is a discussion of regulations applicable in Alberta, Canada. However, onshore regulations vary around the world.

According to Alberta Environment (AE), the regulations regarding drilling waste management, disposal and reporting are found in the Alberta Energy and Utilities Board's (AEUB) Directive 50 published in 1996 [58]. Directive 70, also published by the AEUB, deals with the inspection of drilling waste disposal practices in Alberta [59]. In Directive 50, three agencies are responsible for regulating drilling waste management and disposal in Alberta: the AEUB is responsible for drilling waste disposal on private lands, the Public Lands Department of Alberta Agriculture, Food and Rural Development (AAFRD) is responsible for disposal on "white" public lands including farmland, and the Land and Forest Service of AE is responsible for disposal on "green" public lands including forests [45]. Each of these agencies has helped in developing Directives 50 and 70.

Directive 50 provides the requirements for reporting each instance of drilling waste disposal, both before and after disposal [45]. Prior to disposal, the waste must be analyzed for major ions, toxicity, hydrocarbon content, and other properties. Based on these results, the disposal method is selected from a list of approved techniques. The receiving soils must be analyzed if land treatment is to be used. The disposal of oil-laden drill cuttings and other oil-containing wastes is considered "non-routine" and requires pre-approval from the appropriate regulatory body ("routine" disposals apply mainly to WBM and their cuttings, and do not require preapproval according to Directive 50). Land treatment, reinjection and landfill disposal are among the possible options that can be considered for oil-laden cuttings [45].

2.3 Current Drill Cuttings Treatment and Disposal Methods

This section will cover the treatment and disposal methods currently being used for drill cuttings. Methods for offshore-generated cuttings include direct discharge to sea, transportation to shore for disposal on land, cuttings reinjection, and treatment prior to discharge to sea. Onshore methods include burial, biological treatment, thermal treatment and stabilization/solidification. Each technique has advantages and disadvantages, which will be discussed. In addition, the Drilling Waste Management Information System provided by Argonne National Laboratories [7] provides an excellent resource for each type of treatment and disposal method shown below.

2.3.1 Offshore Treatment and Disposal Options

With the advent of more stringent regulations in the North Sea, Gulf of Mexico and elsewhere, operators have been forced to use a variety of treatment and disposal methods. Unfortunately, several of the options available onshore are not technically feasible offshore due to space and time limitations, so offshore options are somewhat limited. Below is a brief discussion of the methods that offshore operators use for managing drill cuttings and other drilling wastes.

2.3.1.1 Direct Discharge to Sea

Direct discharge to sea is becoming less common due to prohibitive legislation, but was common years ago [9]. Cuttings containing SBM can still be discharged to sea in the Gulf of Mexico if the hydrocarbon content meets US EPA standards, which is often the case after the cuttings are discharged from shale shakers or other solids control devices [7,57]. Discharge to sea is inexpensive because storage, transportation, and treatment of the drill cuttings beyond solids control devices are not required, and the method is technically easy to apply [43]. If regulations permit this practice, then most operators will choose this disposal method because of the aforementioned advantages [7]. Operators in

Newfoundland, the Gulf of Mexico, Indonesia, Malaysia, and other places still dispose of their drill cuttings overboard [43]. However, in the case of Newfoundland (Canada) and the Gulf of Mexico, this practice is only permitted if the cuttings contain low toxicity SBM and if the hydrocarbon concentration is below the applicable regulatory limit [3,7].

One significant disadvantage of discharge to sea is that a large amount of base oil (found in the drilling mud which coats the cuttings) is lost when drill cuttings are discharged overboard. As a result, additional base oil is needed to make up for this loss, which results in increased costs for operators. In one example, an offshore operator was discharging between 50,000 and 75,000 metric tonnes (MT) of drill cuttings containing low toxicity base oil to the sea. The environmental impacts were acceptably low due to the SBM being used, but an estimated 12,500 to 18,000 m^3 of the expensive base oil was being lost annually. This loss lead the company to investigate the use of thermal desorption to recover the oil prior to cuttings discharge [57].

2.3.1.2 Transportation to Shore for Treatment and Disposal

With the advent of stricter environmental regulations, a significant amount of offshore drilling waste, including cuttings, is being shipped to the shore for landfill disposal [2,16,17,49]. Although other onshore treatment and disposal methods could be used once the drill cuttings reach shore, landfill disposal is the most common [49,60]. For example, in the Gulf of Mexico, most cuttings containing OBM are transported to shore, where there are several companies that accept the waste at the dock, and transport it to nearby landfills using barges [60]. In the North Sea, where OSPAR regulations are strict and can't be met by most treatment methods, a large amount of cuttings is shipped to shore. At one time, there was concern that the large cost associated with this practice would limit exploration in the North Sea [61]. However, exploration and production did continue, and in 2003, nearly 100,000 MT of oily cuttings were shipped to shore, mostly in Norway and the United Kingdom [62].

There are several large disadvantages with this technique as compared to direct discharge to sea. First, the cost can be high due to the use of ships to transport the waste to shore, and the need to store batches of cuttings on offshore rigs between shipments [3,5,16]. If the rig is located a great distance from shore, the cost to ship cuttings to shore can result in the operation being entirely unaffordable [3]. Second, there are air emissions that occur during the long range transport of drill cuttings to shore [2]. Third, there must be sufficient infrastructure present onshore to handle the waste being received. As mentioned, there is infrastructure in place along the Gulf Coast of the United States, but such systems are not as common in Norway [15]. Therefore, cuttings are being shipped even greater distances to ports that can accept the waste [15]. Finally, the transport of drill cuttings to shore can be technically challenging due the use of cranes to load and unload waste to ships in rough seas [15].

In one example from Norway, the transport of drill cuttings to shore required a 78 hour one-way trip by boat. The cost was large, and the environmental costs due to energy consumption and carbon dioxide emissions were also substantial [15].

2.3.1.3 Cuttings Reinjection

Cuttings reinjection involves pumping the drill cuttings back into the formation through the annulus of the well being drilled, or into a dedicated reinjection well nearby [9]. The cuttings and other waste are first slurried with water, and then mixed vigorously to break up solid chunks [54,63]. The slurry is sent through a mesh to remove large chunks prior to being pumped into the subsurface [63]. The pumps pressurize the slurry, causing the formation in which the waste is being injected to crack, permitting the waste to enter the formation for storage [46,64]. The stored cuttings are then confined by either natural geological formations or by cement casings. Reinjection can be used when there is a suitable formation for the confinement and storage of the drill cuttings, and when the well being used for reinjection is intact [3]. Reinjection is a common method in the

Gulf of Mexico [11] and in the North Sea, where about 119,000 MT of drill cuttings were reinjected in 2003 [62].

There are several advantages of reinjection. This technology eliminates the need to ship the drill cuttings to shore, has no impact on the water column or sea floor as with direct discharge, and is a proven technology [3]. Furthermore, the cost is normally relatively low [63,64], and is estimated to be under \$50/MT (US) [65].

Cuttings reinjection also has disadvantages. First, there is a risk of loss of containment resulting in formation communication or the release of drill cuttings into the sea [3]. Second, the pumping of cuttings for reinjection requires a significant amount of energy [3]. Finally, reinjection is difficult in deep water and requires substantial knowledge of the subsurface geology, since not all formations or wells are suitable [3]. The most common problem with reinjection is the inability to pump the drill cuttings slurry down the hole due to overpressure in the formation, or the plugging of the annulus of the reinjection well by solids [3]. Furthermore, in many regions, permits are required for reinjection, potentially resulting in more challenges for operators [64]. The operator is also required to carefully monitor for accidental releases and to have a contingency plan in the case of accidental releases [3].

Reinjection can also be used for disposing of drill cuttings produced in onshore operations. For example, in Alberta, Canada, reinjection of oil-laden drill cuttings is allowed following regulatory approval, if the disposal zone is deeper than the deepest potable water zone [45].

2.3.1.4 Treatment Prior to Discharge to Sea

There are limited options available for treating drill cuttings prior to discharge of the cleaned cuttings to sea, and include the hammermill. Of course, shale shakers and other solids control equipment fall in this category, but since they are unable to remove nearly all of the mud and base oil from the cuttings, they will not be discussed further in this section. Most advanced drill cuttings treatment methods require too large an area, or are not technically feasible for use on an offshore rig.

Although technically classified as a thermal treatment option, which will be discussed in a later section, hammermills will be discussed here because they can be used on offshore rigs due to their small footprint [51]. Pulverized drill cuttings are heated in the hammermill, where the oil vapours are removed and condensed, and the cleaned solids drawn off in a cyclone device [51]. One major advantage is that the cleaned solids can often be discharged to the sea without worry of environmental harm [51,56]. Furthermore, the base oil is condensed and collected, and can be reused, further reducing operating costs [56]. One study suggested that the use of a hammermill constituted the "best available technology" for meeting the strict North Sea regulations on cuttings disposal [56]. Furthermore, hammermills are the only commercial treatment method approved for use in the North Sea (Norway and the United Kingdom) prior to discharge of the cleaned cuttings; all other waste must be reinjected or transported to shore [51].

A disadvantage of using a hammermill is the large amount of energy needed to heat the drill cuttings to between 275 and 300°C that is required to volatilize the larger hydrocarbons found in the base oil [56].

2.3.2 Onshore Treatment and Disposal Options

There are many options for the onshore treatment and disposal of oily drill cuttings. The following subsections will describe some of the common techniques, and their advantages and disadvantages.

2.3.2.1 Burial in Pits and Landfills

Burial of wastes in pits and landfills is the most common onshore method for drilling waste disposal [7]. In Alberta, most drill cuttings and other similar wastes are transported to landfills for disposal [66]. Both pits and landfills must be placed in a suitable area where spillage and migration of hydrocarbons and other contaminants from the containment area will not occur [7]. Both low permeable geological barriers and synthetic liners, in combination with covers and leachate collection systems, are used to prevent migration of hydrocarbons and other contaminants into the soil and groundwater [54]. Burial in caverns at abandoned salt mines is a less common technique that has been used in the United States and Canada [9,48].

The advantages of landfill disposal and onsite burial are that they are often simple and cheap disposal techniques, particularly when onsite burial pits are used [7]. Transportation to offsite landfills increases the cost [7], but landfill disposal is still estimated to cost around $50/MT (USD) and is one of the cheaper options [65].

One downfall of these techniques is that the base oil is not recovered, meaning a significant lost cost. Furthermore, environmental impacts such as contaminant migration into soil and groundwater can occur, introducing large liability costs [3,7]. Also, the waste and surrounding environment must often be monitored for long periods of time, which is not favourable to oil and gas operators using burial pits, or to commercial operators of landfills [7].

2.3.2.2 Biological Treatment

Biological treatment, or biotreatment, is defined as the conversion of hydrocarbons into non-toxic products such as water, carbon dioxide and cell mass, using microorganisms [17,67]. There are many types of biotreatment used for treating oily drill cuttings, including land treatment, land farming, composting, phytoremediation, vermiculture, and bioreactors. A full discussion the biotreatment of drilling waste is beyond the scope of this thesis; therefore, only a brief discussion of the techniques and their advantages and disadvantages will be given below. In all cases, the biodegradability of the base oil used in the mud is the most important factor in determining the effectiveness of biotreatment techniques [65].

Land treatment and land farming are similar approaches, in which drill cuttings are spread onto a parcel of land and natural biological processes are used to reduce the hydrocarbon content of the drill cuttings over a period of time. Land treatment involves a single application of drilling waste to the soil, whereas land farming involves multiple applications to the same soil [7]. The drill cuttings are applied in an amount that will not overload the soil with hydrocarbons or other contaminants such as salts. For example, in Alberta, Canada, the hydrocarbon content in the initial mixture of soil and drill cuttings must not exceed 3% on a dry mass basis [45]. The soil containing the drill cuttings is then tilled to promote aeration, which is needed for the aerobic biodegradation of hydrocarbons [10,14,68]. In many cases, nutrients are added to promote biodegradation, as microorganisms require nutrients such as nitrogen and phosphorous to metabolize hydrocarbons [14,43,49]. The final hydrocarbon concentration is often regulated by local government, and varies from one jurisdiction to another. In Alberta, Canada, the land treatment site can be closed when the hydrocarbon content reaches 0.1% in subsoil, or 0.5% in topsoil, on a dry mass basis [45]. The advantages of land treatment and land farming are that these treatment methods are relatively inexpensive due to their low energy requirements and natural attenuation [7,65,68]. The cost is estimated at under $20/MT (USD) of drill cuttings treated [65]. Disadvantages include concerns over migration of the contaminants offsite [7], long treatment times (especially in cold climates such as Alberta) [10,66], large areas of land required for treatment [54,66], and potential negative effects on flora and fauna due to hydrocarbon and salt loading [10,47].

Composting is another form of biotreatment, and can take place in static piles, windrows (piles which are mechanically mixed), or aerated piles [7,67]. A bulking agent, such as wood chips or straw, is often added to the piles to increase aeration in order to promote more rapid biodegradation [65]. Because the drill cuttings are placed in piles, the space required for this biotreatment technique is must lower than land treatment or land farming [54,66]. Also, composting often requires less time than land treatment or land farming because the nutrient level, moisture content, heat loss and pH of the piles are easier to control [7,67]. The cost is relatively low at $50/MT (USD) or less [65]. The increased cost over land treatment and land farming is because composting is a more active approach, involving oxygen, nutrient, moisture and pH control [14,65].

Vermiculture and phytoremediation are two techniques applied to increase the rate of biodegradation. In the case of vermiculture, worms are used to biodegrade the hydrocarbons in the drill cuttings, and the treated cuttings/soil mixture can be used as a value-added soil fertilizer [15]. Vermiculture is ineffective in cold climates [15]. In phytoremediation, plants are used for biotreatment. Plants can directly uptake pollutants, and also promote more rapid biodegradation near the roots because roots emit chemicals which promote microorganism metabolism of hydrocarbons [14].

Bioreactors involve the same aerobic biodegradation as in land treatment, land farming, or composting, but the process takes place in a highly controlled stirred and aerated vessel [7]. The main advantage of bioreactors is that treatment is fast and requires a small area, unlike land treatment, land farming and composting. Because the temperature, aeration, pH, mixing, and nutrient levels are highly controlled, and because bioreactors have a high capital cost, treatment of drill cuttings using bioreactors can be expensive and can cost up to $300/MT (USD) [65], which is the main disadvantage.

2.3.2.3 Thermal Treatment

Thermal treatment is a good technique to treat oily drill cuttings when the base oil is not biodegradable, and treatment can be optimized to remove nearly all of the oil contamination [7]. Thermal treatment can fall into two main categories: incineration and thermal desorption. In incineration, drill cuttings are heated in a chamber to between 1200 and 1500^{o}C which burns off most of the oily residue [49,54]. The disadvantages of incineration are the high energy cost (owing to the high temperature) and the air emissions, although most modern incinerators have equipment to capture products of incomplete combustion [7]). Also, the base oil is destroyed in the incineration process.

Thermal desorption involves the heating of drill cuttings to remove the oil by volatilization [7,69]. The temperatures are much lower than for incineration, at approximately 220 to 350°C [69,70]. Because the base oil is not oxidized, the base oil can be condensed and recovered for reuse, which is one of the main advantages of this technology [51]. The other advantage is that thermal desorption can produce very clean solids, which can be easily disposed of or used in other applications such as asphalt [15]. Studies suggest that thermal desorption can reduce the hydrocarbon content of drill cuttings to well under 1% [51,57,69]. The disadvantages of thermal desorption include high treatment costs that range between \$100 and \$700/MT (USD) (depending on the temperature used) [65], air emissions associated with fuel burning required to produce the heat [69], and the danger of thermally cracking or thermally degrading the base oil hydrocarbons that may limit its reuse (by reducing its performance and increasing its toxicity) [3,51,57]. However, several studies have shown that the change in properties of the base oil after thermal desorption does not affect performance, although thermal desorption can cause a slight odour in the recovered base oil [57,69,70]. Some studies have found that thermal desorption causes trace amounts of dimethyl disulphide and aromatics to be formed (which may explain the odour), but the levels are too low to cause performance, environmental or health risks [57,70].

2.3.2.4 Stabilization and Solidification

Stabilization and solidification involves the addition of various compounds to the oily drill cuttings to form a solid material in which the contaminants (hydrocarbons and others) are trapped and migration is limited [7]. The solid material can then be buried or otherwise disposed of without worry of negative environmental effects. Fly ash, cement, lime, kiln dust and other clays are commonly used to stabilize and solidify drill cuttings [3,7,17].

The advantages of this treatment technique are mainly due to the fact that the additives used are inexpensive and readily available [3,17]. Stabilization is only slightly more expensive than reinjection or most biotreatment techniques, and costs up to \$100/MT (USD) [65]. Furthermore, the end product of stabilization and solidification can sometimes be used in other applications. For example, the use of Portland cement with water and ash to solidify and stabilize oily drill cuttings resulted in a product that could be buried, or used in road materials [12]. Another study suggested that the solidified product could be used as backfill in earthworks operations, building materials or in road foundations [54].

The main disadvantage of stabilization and solidification is that this treatment technique causes an increase in the volume and weight of the waste [3,17]. Long-term stability of the end products of stabilization and solidification, and the future leaching of contaminants due to weathering are also concerns. Some studies have shown that solidified drilling wastes failed leachate tests [7]. Furthermore, unlike thermal desorption, solidification and stabilization does not facilitate the recovery of the base oil, and therefore results in a lost cost to operators. Drill cuttings with very high hydrocarbon content, low solids content, or with very fine or very coarse solids are not suitable for this technique [7].

2.3.3 Summary of Inadequacies of Current Drill Cuttings Management Practices

As was seen in Section 2.1, the use of WBM can eliminate the need for complex treatment and disposal techniques, because the aqueous base fluid in WBM is not environmentally hazardous. However, OBM and SBM provide significant technical advantages over WBM, and are required in many drilling scenarios such as deep wells, reactive formations and directional drilling. Therefore, the use of OBM and SBM is required for future exploration of oil and gas resources.

As was mentioned previously, there are many treatment and disposal options for drill cuttings resulting from OBM and SBM use, but each has disadvantages. For example, direct disposal of oily drill cuttings to sea is prohibited in many areas. If permitted, disposal to sea results in the loss of expensive base oil. Shipping drill cuttings to shore for disposal in landfills from offshore rigs is expensive, and also results in the loss of base oil. Reinjection is relatively cheap, but is prone to technical failure, results in base oil loss, and is only suitable in some geological formations. Most biotreatment options are also relatively inexpensive, but require long times and large spaces for the hydrocarbons to be biodegraded, also resulting in the loss of base oil. Thermal treatment, such as incineration, thermal desorption, and hammermills, requires large energy input, and is prone to releasing harmful air emissions. Stabilization and solidification is also an option to treat oily drill cuttings, but the long-term integrity of the stabilized and solidified products is still unknown. The loss of base oil, that occurs in nearly all of these treatment and disposal options (except for thermal desorption and hammermills), is a major cost for operators. Furthermore, most of these techniques (except hammermills) are not feasible for use on offshore platforms due to space, time and other technical limitations.

In addition to the challenges of current techniques, the cost of drilling waste management has been increasing, and is expected to continue to increase, with the advent of stringent regulations on the treatment and disposal of drilling waste, including drill cuttings [53]. Also, some oil and gas companies have adopted even more stringent standards for drilling waste management that exceed local legislation, in order to increase their “corporate accountability” to manage wastes properly [53]. This push towards corporate accountability has been the result of increased media pressure to be environmentally sensitive [54] and fear by oil and gas companies of long term liability [7].

One survey found that most North Sea oil and gas operators agree that current drilling waste management techniques used to comply with tight regulations are less than optimal, and there is a need for a new solution [53].

Most operators agree that treating drill cuttings offshore and disposing of the cleaned cuttings would be cheaper than shipping oily drill cuttings to shore for treatment and disposal [7]. A previous study on the SFE treatment of drill cuttings was partly motivated by the need to develop an economically feasible system for treating oily drill cuttings on offshore rigs, allowing the continued use of OBM [16]. Therefore, a treatment system that is small enough to fit on an offshore drilling rig, and one that can treat oily drill cuttings to meet the stringent regulations in a cost-effective manner, is preferred.

SFE is a new treatment method for oily drill cuttings that has the potential to meet this need [37]. As early as 1997, SFE was recognized as a key technique for the treatment of oily drill cuttings generated offshore once regulations are tightened [28].

2.4 Supercritical Fluid Extraction

This section will cover the fundamentals of supercritical fluid extraction and will highlight the advantages and disadvantages of the technology as it applies to the treatment of oily drill cuttings. First, a brief description of the evolution of SFE will be given, including the first applications of the technology. Second, the theory of SFE will be discussed, including the properties of supercritical fluids and the mechanisms involved in SFE. Third, a focused discussion of past research on utilizing SFE for oily drill cuttings treatment will be given. Finally, batch and continuous SFE will be discussed, and the technical challenges of continuous SFE will be identified.

2.4.1 Evolution of Supercritical Fluid Extraction

The early applications of SFE were mainly in smaller-scale niche applications [18]. The first large-scale applications included coffee and tea decaffeination and hops extraction, which were pioneered in Germany in the late 1970s [19,20]. The move to supercritical carbon dioxide (CO_2) allowed the technology to expand to other applications [18]. Since CO_2 could replace harsh organic chemicals often used in liquid extractions, and can efficiently extract a variety of solutes from complex matrices, SFE was found useful in other applications such as the extraction of pharmaceuticals, cosmetics [71] and flavours (such as vanilla and ginger) from plants [20,21]. One hindrance to the widespread use of SFE was the fact that liquid extractions were cheaper, and although the final product was of higher quality when SFE was used, some consumers opted for the cheaper products of liquid extractions [21]. Today, SFE has found use in many other niche markets, such as metal and electronic part cleaning and degreasing [28,71], cleaning of foundry sludges [18], as a reaction medium for polymerization or enzymatic reactions [38], and in certain extractions in the food industry such as the removal of fat from potato chips and the concentration of Vitamin E from natural sources [22]. In each case, harsh organic chemicals were replaced by supercritical fluids, which was the main driving force for the use of SFE in the food industry [21].

The literature contains many accounts of successful laboratory-scale studies of the SFE treatment of contaminated soil [23-26,72-82] but there are no reports of full scale use of the technique. An economic analysis on the scale-up of an SFE process for the treatment of contaminated soil found a capital cost of 2.2 million dollars (USD) and an operating cost of \$200/MT (USD) for a semi-continuous process [74]. Recent research has begun on the development of a continuous SFE system for contaminated soil, which is believed to be more economically feasible for full-scale application [41].

2.4.2 Properties of Supercritical Fluids

SFE is a proven effective treatment technique for drill cuttings, and a variety of other applications, because of the unique properties of supercritical fluids (SCFs) themselves. SCFs are excellent solvents for a variety of reasons [83]. Their properties are intermediate of liquid and gas properties, and embody the beneficial solvent characteristics of both. Table 2 summarizes the properties of SCFs relative to the liquid and gas states. The density of a SCF most resembles the density of its liquid state, while the diffusivity and viscosity are intermediate between the liquid and gas states [18,20,22,83-85]. Furthermore, SCFs possess near zero surface tension, meaning that they can easily penetrate into the pores of solid matrices (such as drill cuttings) [38,78,79,85]. These properties mean that SCFs can extract substances from solid matrices more quickly than their liquid counterparts [20,24].

Table 2: Comparison of the properties of a liquid, supercritical fluid and gas (modified from [38]**)**

Property	**Liquid**	**Supercritical Fluid**	**Gas**
Density (kg/m^3)	1000	200-800	1
Viscosity (mPa s)	0.5 – 1.0	0.05 – 0.1	0.01
Diffusivity (cm^2/s)	10^{-5}	$10^{-3} – 10^{-4}$	0.1

In order to obtain a SCF, the temperature and pressure of a substance must be above the critical temperature and pressure, as shown in Figure 5. As the temperature and pressure are raised to near the critical point (but still below the critical point), the thermodynamic properties of the gas and liquid phase begin to merge together. When the critical point is surpassed, the differences in thermodynamic properties between a liquid and a gas disappear, and a single phase is formed [24,37,83,84]. As the substance enters the supercritical phase, there is no sudden change of properties as with any other phase change [22]. For example, when a gas condenses to a liquid, the density suddenly increases by several orders of magnitude, and the viscosity increases. Such a sudden change of properties does not occur when a supercritical fluid is formed.

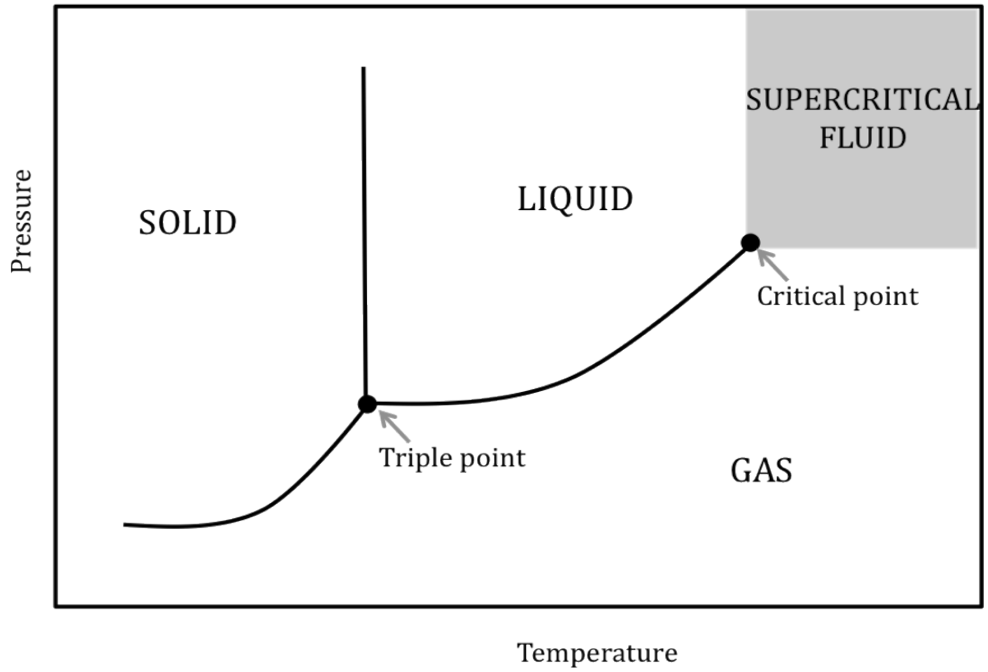


Figure 5: Phase diagram of a substance showing the supercritical fluid region (modified from [83]**)**

The tunability of SCFs is the key to the operation of SFE systems [24,37,38,71]. Near the critical point, a small change in temperature and/or pressure can cause a large change in the density of the SCF [24,84,85]. As will be seen later, the solubility of a compound in a SCF is related to the density of the SCF, and therefore the solubility can be tuned precisely by changing the temperature and pressure [84]. Therefore, the operator can tune the extraction of a specific compound by increasing the pressure in the extraction vessel (an increase of pressure causes an increase in density of the SCF, and subsequently an increase in solubility of most compounds). Then, once the SCF exits the extraction vessel, the pressure can be reduced to allow the extracted compound to precipitate out of solution for the purpose of collecting the compound (a decrease in pressure causes a decrease in density of the SCF, and subsequently a decrease in solubility of most compounds). This cycle of pressurization/extraction followed by depressurization/precipitation forms the basis for the operation of an SFE system [22], which will be explained in greater detail in Section 2.4.4.

2.4.3 Supercritical Carbon Dioxide

Supercritical CO_2 is the most commonly used solvent for SFE systems because supercritical CO_2 possesses the following characteristics [5,20,22,24,28,29,37,38,79,84-86]:

- Relatively easily obtainable critical point of 31.2°C and 7.4 MPa
- Inexpensive
- Readily available in high purity
- Non-toxic
- Non-reactive
- Safe to handle
- Environmentally friendly

CO_2 is considered environmentally benign when used in SFE because it can be recycled in the SFE process and therefore does not contribute to global CO_2 problems [22]. One analysis found that, due to the recycling of CO_2 in SFE systems, SFE using CO_2 is responsible for less than one in one millionth of global CO_2 emissions, and reasoned that this contribution is very minimal and that SFE likely reduces the greenhouse effect because the CO_2 otherwise would have been vented directly to the atmosphere [28]. Furthermore, supercritical CO_2 replaces more harsh organic chemicals which could otherwise be used for the treatment of oily drill cuttings [18,28,79,85,87]. CO_2 also leaves little or no residue on the recovered product [18,79]. The fact that CO_2 is cheap, safe to handle, non-toxic and leaves no significant residue is illustrated by its use in several food applications [22].

In general, supercritical CO_2 can easily dissolve non-polar solutes such diesel, mineral oils and other hydrocarbons [5,37], making it a prime candidate for use in the SFE treatment of oily drill cuttings. For example, supercritical CO_2 can easily solvate n-alkanes in the C_5 to C_{30} range, and some PAHs [25], which are found in many base oils. Because CO_2 has a low critical temperature of just over 31°C, there is no fear of thermal degradation of hydrocarbons during SFE [18,28], and heating requirements are often minimal. For the various reasons discussed above, supercritical CO_2 was selected for use in this research project.

2.4.4 Basics of Supercritical Fluid Extraction

SFE makes use of significant variations in the solubility of the compound being extracted with small changes in temperature, and especially pressure [20,83,85]. The process itself requires two main steps. First, the extraction of solute (in this case, hydrocarbons) from the matrix (in this case, drill cuttings) occurs at a high pressure, that is above the critical pressure, in the extraction vessel. Second, once the SCF, now loaded with solute, exits the extraction vessel, the pressure is reduced, causing separation of the SCF and the extracted compound, allowing the compound to be collected. The SCF can then be repressurized and recycled [22].

For a batch SFE system using supercritical CO_2, the equipment required are a CO_2 tank, a CO_2 pump, an extraction vessel or column, a separation vessel or column, a CO_2 condenser (if necessary for recycling the CO_2), heat exchange equipment to maintain vessels and tanks at their desired temperatures, and auxiliary piping and valves [24]. For a continuous SFE system, the only major additions are a slurry pump, which can deliver the slurry to the high pressure extraction column, and a collection/recycle system at the column exit for the treated slurry [41]. The basic setup of a batch SFE system is shown in Figure 6, and a continuous SFE system for treating a slurry is shown in Figure 7.

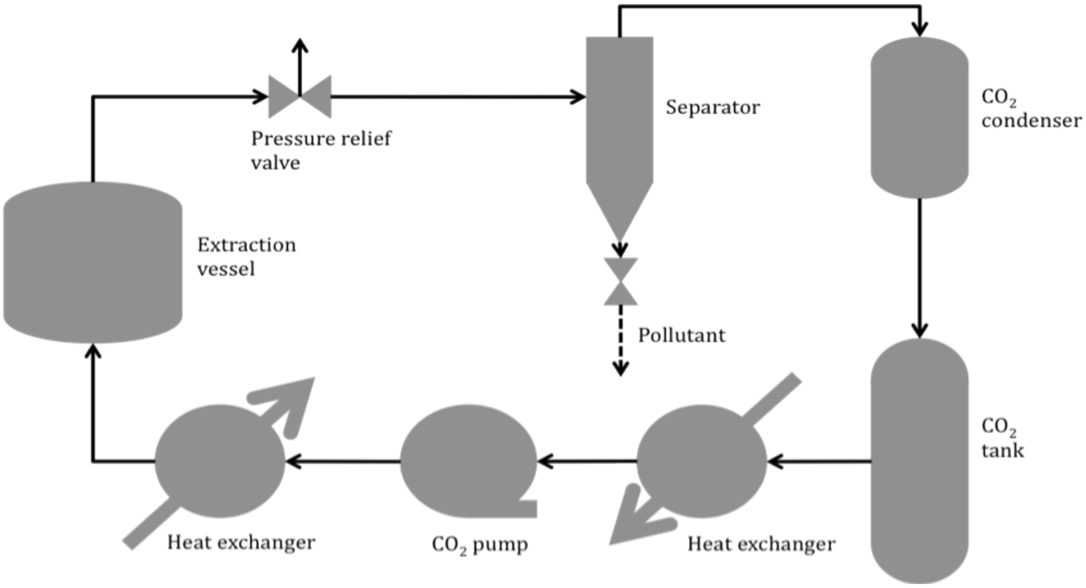


Figure 6: Basic setup of a batch SFE system (modified from [24]**)**

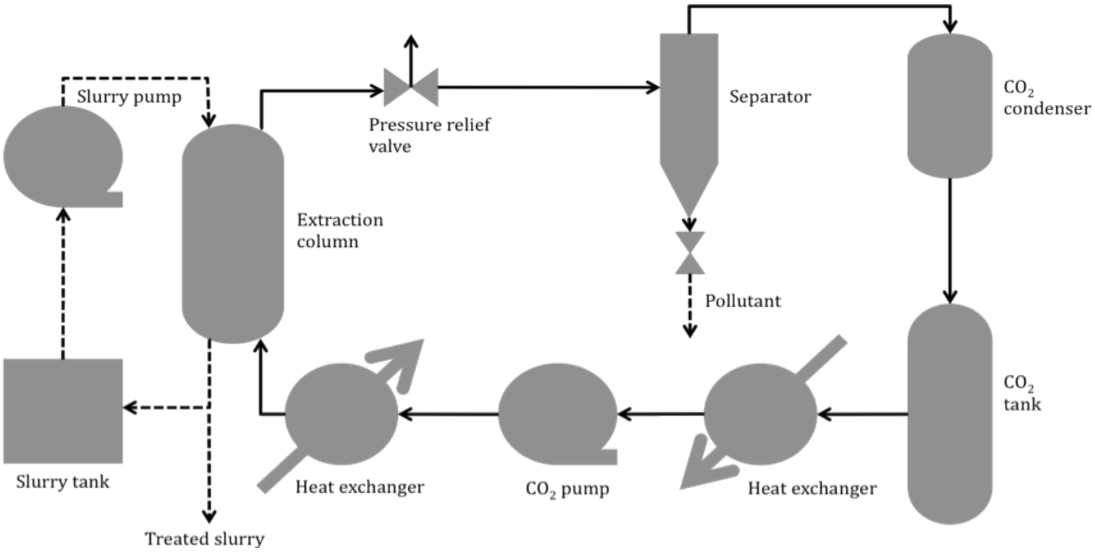


Figure 7: Basic setup of a continuous SFE system for treating a slurry of water and contaminated solids (modified from information found in [24] **and** [41]**)**

The design of SFE systems requires knowledge of thermodynamic concepts relating to the solubility of the component being extracted in the SCF, and component selectivity when there is more than one solute [71,84]. Consideration must also be given to the interactions between the solid phase in the matrix and the solute to be extracted, as the adsorption of the solute on the solid surface may be a limiting factor during SFE treatment [74]. Design also requires awareness of any mass transfer limitations which may hinder the extraction [71,84], such as diffusion limitations.

2.4.5 Theory of Supercritical Fluid Extraction

An in-depth discussion of solubility, adsorption, diffusion and water effects, as they relate to SFE, is found in the following sections.

2.4.5.1 Solubility Concepts in SFE

The solubility of the solute in the SCF may be the most important parameter to measure prior to designing an SFE system [29,88,89]. The kinetics of the direct dissolution of a solute in a SCF are fast [90]. Thus, if there is a free solute phase in the matrix being treated with SFE, then the extraction is normally solubility limited [90]. The solubility represents the maximum amount of solute that can be present in the SCF phase at a given set of conditions (i.e. pressure and temperature), and is therefore related to the maximum obtainable extraction efficiency of an SFE process.

There are two main factors that determine the solubility. First, the solubility of a solute in a SCF is strongly dependent on the density of the SCF, which is determined by the temperature and pressure of a system [84,91,92]. Raising the pressure and lowering the temperature causes the density of the SCF to increase, which in turn increases its solvating power. Second, the solubility is affected by the vapour pressure (volatility) of the solute [82,86,92,93]. Compounds that have a sufficient vapour pressure will experience an increase in volatility with an increase in temperature, promoting a higher solubility [86]. Gasoline-range hydrocarbons are examples of components that have sufficient vapour pressures to be subject to this second effect [76]. Because of these two effects, the solubility is increased with increasing pressure (owing to the increase in SCF density), but can either be increased or decreased with increasing temperature, depending on which of the two factors (decreased SCF density due to increased temperature, or increased solute volatility due to increased temperature) is dominant.

In general, if the pressure is near the critical pressure, a small increase in temperature will cause a large decrease in SCF density. Here, the small increase in temperature does not cause a large enough increase in solute volatility to compensate for the large decrease in SCF density, and the overall result is a lowering of solubility with increasing temperature. However, if the pressure is well above the critical pressure, a change in temperature causes a very minor change in SCF density. Here, the increased volatility of the solute may be dominant over the very small decrease in SCF density, resulting in a higher solubility with increasing temperature [22,92,94]. These competing effects cause what is known as a "crossover pressure". Below the crossover pressure, the solubility decreases with increasing temperature. Above the crossover pressure, the solubility increases with increasing temperature. Several authors have who have studied the solubility of hydrocarbons in SCFs have found a crossover pressure [92,95-97]. In one example, a crossover pressure near 11 MPa was found for the solubility of octacosane ($C_{28}H_{58}$) in supercritical CO_2 [89], as shown in Figure 8.

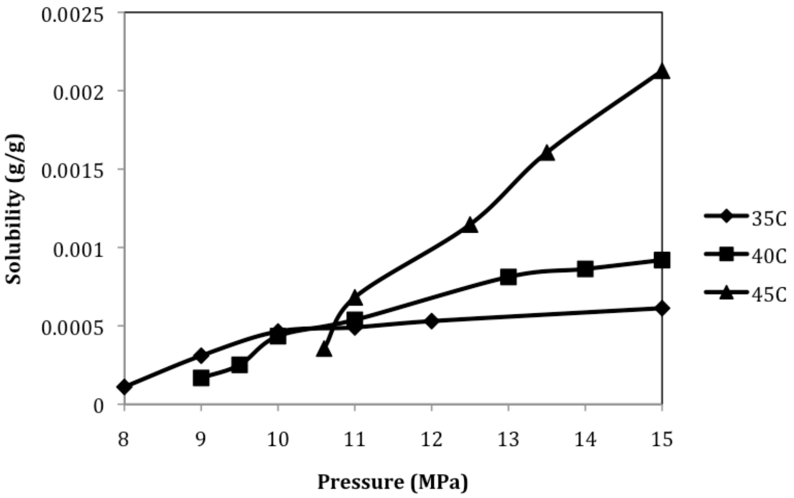


Figure 8: Example of crossover pressure for octacosane, as found by [89]

Relevant to this research is the solubility of n-alkanes in supercritical CO_2, as Distillate 822, the base oil found in the drill cuttings used in this research, is comprised of mainly n-alkanes, with 85% being $C_{15}H_{32}$ or larger [98]. Supercritical CO_2 is best suited to solvate non-polar or slightly polar molecules [22], and therefore can easily dissolve solutes such as diesel, mineral oils and other hydrocarbons [5,37]. The solubility of the diesel oil, which contains n-alkanes among other compounds, in supercritical CO_2 was measured to be about 0.1g/g at 14.5 MPa and 40^oC [31]. Lower molecular weight molecules are the most readily soluble, but the power of CO_2 to solvate larger hydrocarbons is increased by increasing the pressure [22]. As the chain length of n-alkanes increases, the solubility in supercritical CO_2 drops sharply [95,97,99,100]. For example, at 14.5 MPa and 40^oC, the solubility of hexadecane ($C_{16}H_{34}$) is about 0.16 g solute per g CO_2 (g/g) [101] while the solubility of octadecane ($C_{18}H_{40}$) is only about 0.03 g/g [102]. Supercritical CO_2 is a poor solvent for high molecular weight molecules and highly polar molecules [87].

There have been a variety of attempts to formulate theoretical or empirical equations to model the solubility of a particular solute in a SCF. Equations of state, such as the Peng-Robinson or Soave-Redlich-Kwong equations, along with solvation parameters, can be used to predict solubilities in SCFs [103], but these require substantial theoretical knowledge and determination of fugacity coefficients, and are therefore difficult to solve [83]. Furthermore, these equations of state are known to be quite inaccurate near the critical point of a substance [83]. A more common approach to modeling the solubility in a SCF is to use the Chrastil Equation [91]. The parameters in the Chrastil Equation have physical meaning, but in practice the parameters are found by fitting the data, so the model is considered an empirical one [83]. The Chrastil Equation relates the SCF density to the solubility of an individual component, in a logarithmic relationship, as shown in Equation 1. The equation is based on the theory that solute molecules combine with solvent (SCF) molecules to form a complex [91]. The Chrastil equation is:

$$\ln S = k \ln \rho + \frac{A}{T} + B \qquad \text{Equation 1}$$

where S is the solubility (g/mL), ρ is the density of the SCF (g/mL), T is the temperature (K), *k* is equal to association number in the dissolved complex, *A* (K) is related to the heats of vapourization and solvation of the solute, and *B* is related to *k* and the molecular weights of the solute and SCF [91]. The solubilities of octacosane ($C_{28}H_{58}$) and triacontane ($C_{30}H_{62}$) in supercritical CO_2 were successfully modeled using the Chrastil Equation [89].

More recently, a modified Chrastil equation was developed, which includes a pressure parameter in addition to the density parameter (which is of course dependent on pressure) [104]. The modified Chrastil equation is shown in Equation 2:

$$\ln y = b_o + \frac{b_1}{T} + b_2 \rho + b_3 \ln P \qquad \text{Equation 2}$$

where y is the solubility mole fraction of the solute, P is the pressure (MPa), b_o is related to the heats of vapourization and solvation of the solute, b_1 (K) is related to the heats of solvation and vapourization, as well as the molar volume of the solute, b_2 (mL/g) is related to the association number in the dissolved complex, the second virial coefficient of the solute, the second mixed virial coefficient and the molar volume, and b_3 is related to the association number [104,105]. The solubility of uracil in supercritical CO_2 was modeled more accurately using the modified Chrastil equation compared to the original Chrastil equation [105].

In the case of mixtures of solutes, the presence of other solutes may increase or decrease the solubility of a particular solute compared to its solubility as a pure compound. One example is the use of non-polar additives (or non-polar modifiers) to increase the solubility of a particular non-polar solute in a SCF. Non-polar modifiers, when dissolved in the supercritical phase, increase the density of the SCF phase, which in turn causes an increase in solubility of other non-polar solutes [94,106,107]. For example, the presence of isooctane (C_8H_{18}) at an initial mole fraction of 0.08 increased the solubility of a mixture of decane ($C_{10}H_{22}$), dodecane ($C_{12}H_{26}$) and hexadecane ($C_{16}H_{34}$) by two to three times in supercritical CO_2 at 9.7 MPa and 50°C [106]. In another study, the solubility of individual hydrocarbons in supercritical CO_2 was up to 280% higher when in a mixture with similar hydrocarbons compared to that component's solubility in its pure form [108]. Similar result have been found in other studies [92,109,110]. However, not all experiments have found an increased solubility in the presence of other similar compounds. For example, the solubilities of anthracene (a PAH) and carbozole (an aromatic hydrocarbon) in supercritical CO_2 were found to increase in the presence of phenanthrene (a PAH), but the solubility of phenanthrene was reduced in the presence of the other two solutes [29]. Also, a successful model was developed for the solubility of a paraffin wax mixture (mostly n-alkanes in the C_{17} to C_{38} range) in supercritical CO_2 under the assumption that the presence of other n-alkanes in the solution did not affect the solubility of each alkane; this assumption was based on some experimental evidence [111].

Polar modifiers can also be added to increase the solubility of polar solutes. Methanol and ethanol are popular polar modifiers [103]. These modifiers work effectively when there is a much stronger interaction between the modifier and the desired solute, compared to between the pure CO_2 and the desired solute [83,87,94,103].

There are a variety of experimental methods used to measure the solubility of compounds in SCFs. They include static, dynamic and chromatographic methods [29,83]. A detailed description of each is provided elsewhere [83]. The "saturation method", which is a type of dynamic method, will be discussed as this method was used in this research. In the saturation method, an amount of solute is placed in a vessel and the SCF is allowed to flow through. The flow rate must be low enough to ensure sufficient contact time for equilibrium to be reached, and this uncertainty is the primary disadvantage of this technique [83]. At the outlet, the dissolved solute is collected in traps and the amount collected is measured.

This measurement is combined with knowledge of the amount of CO_2 flowing through the vessel to determine the solubility [83]. A technique similar to the saturation method was used to measure the solubility of PAHs and polychlorinated hydrocarbons in supercritical CO_2 [79].

2.4.5.2 Adsorption and Desorption of Solutes from Solid Matrices in SFE

Depending on the strength of interaction between the solute and the solid phase in a contaminated porous matrix (such as contaminated soil or oily drill cuttings), the solute may be strongly bound to the solid particles in the porous matrix, rendering them less mobile, and therefore more difficult to extract during SFE. The desorption of the solute from the solid surface can be instantaneous if the interactions are weak [112]. An example of weak interactions is the extraction of petroleum hydrocarbons from silica beads, where the extraction was solubility limited [76]. In the case of stronger interactions, the desorption of the solute from the solid phase may be the limiting factor in the SFE process, meaning that the solubility concentration in the outlet SCF phase is not reached [76,112]. One example is the SFE treatment of oily foundry sludge (consisting of fine porous and non-porous metal particles coated with lubricating oil), which was limited by the desorption of oil molecules from the metal phase [113]. In another example, a model was developed to describe the SFE treatment of PAH-contaminated soil, based on the assumption that some PAHs were weakly bound and therefore their extraction was solubility limited, and other PAHs (in the same soil sample) were strongly adsorbed and their extraction was desorption limited [114].

There are many cases when desorption limits SFE processes in the treatment of contaminated soil, because soil often contains organic matter to which hydrocarbons, PAHs and other contaminants can be strongly bound [73,79,85,86,115]. In several studies, an increase in organic content of the soil lead to a decrease in recovery of organic solutes using SFE [76,78,81]. Also, older (aged) samples will often contain more adsorbed contaminants than newer (recently spiked) samples, meaning that SFE treatment is less effective on aged samples [26,77,116]. Non-polar contaminants, rather than polar contaminants, are preferentially bound to organic matter in soil [117].

Although the adsorption of contaminants onto the solid phase is normally related to organic matter, inorganic particles made up of silica and aluminas (clays, for example) can also facilitate adsorption [118]. Usually only polar molecules will be adsorbed to such materials [24]. However, n-alkanes can be adsorbed onto some clay surfaces, but are not preferentially adsorbed in the presence of polar resins and asphaltenes [119]. When n-alkanes do become adsorbed onto clay surfaces, larger molecules are adsorbed more strongly due to their stronger Van der Waal interactions with the clay surface [76]. This phenomenon was exemplified in one study that showed the preferential recovery of smaller n-alkanes compared to larger n-alkanes from montmorillonite clay using supercritical CO_2, partially due to their smaller Van der Waal forces [120].

An increase in temperature is often beneficial for SFE efficiency when desorption is the limiting factor, as higher temperatures favour desorption [86,94,118]. In addition to raising the temperature, modifiers can be added to that will preferentially adsorb onto the active sites in the solid phase, and force the desorption of the solute of interest [25,26,86,93]. An example is the use of methanol to preferentially bond and force the desorption of PAHs from marine sediments [25].

2.4.5.3 Diffusion of Solutes in SFE

Solutes can be trapped (but not adsorbed) within the pores of clay and other matrices, and can be difficult to extract [76,118]. This phenomena can occur in drill cuttings, where the base oil can become trapped in the pores of the solid particles found in the cuttings [51]. In addition, non-polar hydrocarbons such as n-alkanes can become trapped when larger polar molecules are adsorbed to the clay surface [119].

In order for a solute molecule that is initially found within the pores of the solid matrix (whether adsorbed or simply trapped) to be extracted, the solute must diffuse from the interior of the solid particle to the exterior (intraparticle diffusion), diffuse into the SCF phase at the solid-fluid boundary, and then diffuse from the boundary layer into the bulk SCF phase [74,79,82,90,112,115]. In the SFE treatment of biphenyl-contaminated soil, the rate limiting step was the diffusion of the solute molecules out of the soil particles [90]. In another study, pore diffusion, along with desorption, was found to control the extraction of hexachlorobenzene from soil [115]. This intraparticle diffusion step is often the rate limiting step [121]. However, in the extraction of hydrocarbons from aged soil, the diffusion of the hydrocarbons into the bulk phase of the CO_2 was found to be the rate limiting step at low solvent flow rates (no mixing) [82]. Another study also found diffusional resistance at low CO_2 flow rates when extracting PAHs from soil [74].

An increase in temperature increases the rate of diffusion of molecules within the porous matrix, increasing the efficiency of an SFE process that is diffusion limited [76,94]. In addition, certain polar modifiers (such as water, alcohols and acetone) added in small amounts can also be adsorbed onto clay particles, causing the matrix to swell and the pores to expand. This phenomena enables trapped solute molecules to more easily diffuse out of the porous matrix (through the enlarged pores) and into the SCF phase [76,94,122].

2.4.5.4 Effect of Water on SFE

In a wet porous matrix, a hydrocarbon (solute) can exist in four phases: free phase, adsorbed on the dry solid, adsorbed on the solid but covered in water, or dissolved in the water itself [85]. There are several studies that show that water can either increase or decrease SFE treatment effectiveness. From an extensive literature review, the following general statement regarding water content and its effect on SFE treatment can be made: small amounts of water may increase the extraction efficiency of SFE processes, while larger amounts of water often decrease the efficiency. According to one author, the water content should be kept under 10% for successful SFE treatment [38]. Of course there are several exceptions to this generalization.

A small amount of water may aid SFE treatment because the water can preferentially adsorb onto active sites in clays, causing an increased recovery of adsorbed solutes [86,123]. This factor lead to the increased removal of phenols from spiked soil when the soil had up to 10% water content [78]. A small amount of water (3-10%) was also beneficial in the removal of PAHs from spiked and aged soils, and the results were attributed to the preferential adsorption of the polar water molecules compared to the non-polar PAH molecules [124]. A similar effect could explain the optimal moisture content of 20% for the removal of petroleum hydrocarbons from soil [125] and the reason why the US EPA recommends a moisture content of 20% when performing analytical SFE for the determination of petroleum hydrocarbons in soil [126].

A small amount of water can also act as a polar modifier to increase the solubility of polar compounds in SCFs [20]. For example, a water content of 16-18% helped the SFE removal of polar chorophenols from soil by acting as a polar modifier [72]. Water contents up to 10% also increased the solubility of phenols in supercritical CO_2 [78].

As mentioned, a small amount of water can also be adsorbed onto clays, causing the matrix to swell and the pores to expand, leading to decreased diffusional resistance and thus an increase in SFE efficiency [76,94,127]. For example, the extraction efficiency of Diuron (an organic chemical) from montmorillonite clay was successfully correlated with the swelling of the clay in the presence of water [127].

There are also many studies indicating that water negatively effects SFE treatment. The dissolution of water into supercritical CO_2 increases the polarity of the CO_2, and thus decreases the solubility of non-polar hydrocarbons such as n-alkanes [38,39]. This effect was used in part to explain the poor recovery of PAHs from soil-water slurries in two separate studies [38,39].

Possibly a more significant negative effect is the "shielding" effect. Water is quite immiscible with supercritical CO_2, as shown by its solubility near $2x10^{-3}$ g/g in CO_2 at 40^oC and 14.5 MPa [128,129]. Thus, water can act as a mass transfer barrier to supercritical CO_2 penetrating the porous matrix [38,123]. Similarly, organic components may become trapped between the solid phase and water coating the solid phase, making them much less accessible to the SCF [118]. Water in the pores of the solid matrix can also increase the diffusional limitations that were discussed in the previous section, since the diffusion in liquids is slower than in SCFs [94]. In general, these negative effects are found in soils with much higher water contents or soil-water slurries.

Several studies show that excess moisture hinders SFE treatment. Lower PAH recoveries from waste sludge using SFE were found at 45% water compared to 2% water [121]. The removal of polychlorinated biphenyls (PCBs) using SFE proceeded more slowly when the soil contained 20% moisture compared to dry soil due to slower desorption and diffusion of the pollutants from the soil caused by water in the pores [81]. A similar result was found in the extraction of dioxins from sediment containing 20% moisture [130] and the extraction of DDT from soil containing 20% moisture [117] using supercritical CO_2 modified with small amounts of methanol. Recovery using SFE of diesel from spiked soil was more efficient at 2% moisture content compared to 8% because the extra water trapped the diesel in the pores of the soil [76]. A soil moisture content of 20% caused the recovery of PAHs using supercritical CO_2 to fall to 20% compared to near 90% in soil containing less than 10% moisture. This observation was attributed to the water causing agglomeration of the soil particles, causing the PAHs to be less accessible to the SCF [124]. Mass transfer coefficients were at least 200 times lower in the SFE removal of naphthalene from soil containing 20% water compared to soil containing 10% or less water, and these findings were attributed to water shielding the solute from the CO_2 [131]. Sufficient mixing to suspend the agglomerate soil particles would likely reduce this mass transfer resistance [131]. A recent study found that SFE using CO_2 was hindered when the soil/rock matrix contained more than 10% moisture [132].

In soil slurries (soil that contains enough water to be free-flowing), SFE treatment is usually hindered by the excess water. One study found very low recoveries (between 11 and 15%) of naphthalene from soil-water slurries (5:1 water to soil ratio) at $47^{o}C$ and within a pressure range of 7.5 to 18 MPa [39]. The pressure had little effect on the recovery of the naphthalene from soil slurries, and a solubility concentration of naphthalene in the supercritical CO_2 was never reached after 24 hours of exposure to excess solvent, due to the water [39]. The same authors reported better recoveries (41-61%) of phenols from similar soil-water slurries over the same pressure range, and reasoned that the partial solubility of phenol in water was the reason for the reduced mass transfer barrier [39]. The SFE removal of PAHs and chlorophenols from soil-water slurries containing up to 50% water was “generally unsuccessful”, with residual pollutant concentrations up to ten times greater in the slurries compared to soils containing only 10% moisture [38]. Recovery of petroleum hydrocarbons from a “bioslurry” was increased two times when the water content was halved [125].

Few exceptions to the poor recoveries seen from soil-water slurries have been noted. The recovery of PAHs from soil slurries using supercritical CO_2 was not affected by the presence of water in a ratio of 2:1 water to soil [94]. Similarly, 70 to 87% of PAHs could be recovered from 2:1 water to soil slurries using CO_2 between 35 and $45^{o}C$ and 13 to 22 MPa [133]. The same researchers also found good SFE recoveries (46-95%) of slightly water soluble phenols from 2:1 water to soil slurries using CO_2 between 35 and $45^{o}C$ and 13 to 22 MPa [133].

2.4.5.5 Apparent Solubility

“Apparent solubility” will be the term used in this thesis to describe the maximum concentration of the solute that is obtainable in the outlet SCF stream during the SFE treatment of a contaminated porous matrix, such as contaminated soil or drill cuttings. The apparent solubility is less than the solubility itself (which is measured using the solute, without the presence of the porous matrix) due to adsorption, diffusion or water-related hindrances, as discussed in the previous sections. For example, the apparent solubility of diesel oil from drilling waste at 14.5 MPa and 40°C was found to be of the order of 0.05g of diesel per gram of CO_2 (g/g), while the diesel solubility at the same pressure and temperature was near 0.1g/g [31].

2.4.5.6 SFE Theory Applied to the Treatment of Oily Drill Cuttings

This section will be briefly describe how solubility, adsorption, diffusion and water content affect the SFE treatment of drill cuttings using supercritical CO_2. Cuttings often contain free oil that is not trapped inside the porous matrix [51]. The free oil is likely easily extracted by the supercritical CO_2. As mentioned, drill cuttings contain barite, bentonite and rock from the formation. Since these are minerals and clays, rather than organic matter, adsorption of the base oil to the solids is not expected to be a significant factor. Furthermore, drill cuttings are not aged the many decades like some contaminated soils, further reducing the chances that the adsorption is significant. Cuttings also contain oil that is trapped in the pores (10- 100 microns in diameter) of the solid phase [51], so diffusion limitations are expected in the extraction of this oil.

The limiting factor in the extraction of hydrocarbons from drill cuttings can change rapidly during the course of SFE treatment [16]. In one study, the first part of the SFE treatment of drill cuttings was solubility limited, and the latter part was diffusion limited [31]. Both solubility and diffusion affected the removal of organic binders from porous ceramic materials using SFE [134], a process similar to the SFE treatment of oily drill cuttings.

Water content will have effects on the SFE treatment of oily drill cuttings that are similar to examples given in the previous section relating to the treatment of contaminated soil. Water can be adsorbed to the clay particles in the drill cuttings, trapping hydrocarbons between the water molecules and the clay surface, like the phenomenon described by Hawthorne et al. [118]. Water could also fill the pores in the solid phase of the cuttings, and act as a barrier to the penetration of supercritical CO_2, as described in [131] for contaminated soil, or cause the supercritical CO_2 phase to become more polar, reducing its solvating capacity for the non-polar hydrocarbons. These factors can be used to explain the reduced SFE recovery of base oil from drill cuttings when the water content was increased to 30% [37].

One study found that a water content of 50% in the drill cuttings did not affect the extraction efficiency during SFE treatment, and reasoned that the water displaced the oil from the solid particles, making the oil more accessible to the supercritical CO_2. However, at water contents between 7 and 20%, the water acted as a mass transfer barrier and reduced the extraction efficiency [31]. The conclusion regarding the high water content (50%) and its effect on SFE efficiency must be questioned because of the method used to judge the extraction efficiency, and this issue will be detailed later in this thesis.

2.4.6 Supercritical Fluid Extraction of Drill Cuttings: Previous Research

This section will summarize the results that have been obtained for the SFE treatment of oily drill cuttings.

2.4.6.1 Previous Research on the SFE Treatment of Drill Cuttings

The first patent for the SFE treatment of drill cuttings was accepted in 1984 [30]. The patent was very general in nature, and covered the liquid or supercritical fluid extraction of hydrocarbon-containing materials, including drill cuttings, using a variety of solvents, including CO_2. A large-scale batch system that involved the the slurrying of the cuttings with water or an oil-based fluid, and the pumping of the slurry to an extraction vessel, and the treatment of that slurry batch with a recirculated supercritical or liquid solvent, was proposed. Although this design is only conceptual and was not tested, several laboratory scale experiments on the treatment of drill cuttings using supercritical and liquid CO_2, among other solvents, were conducted. The best results were cuttings that were "dry, non-oily and free-flowing" after treatment. Treatment was performed with CO_2 at pressures between 9.7 and 22.1 MPa and temperatures between 30 and 55°C, with the better results, based on the mass of oil recovered, at lower temperatures and/or higher pressures [30].

Hydrocarbon extraction efficiencies above 98% were obtained during the SFE treatment of oily drill cuttings using supercritical propane and HFC 134a in a laboratory-scale batch system [16]. Based on these results, a full-scale semi-continuous system, in which drill cuttings were loaded into one of two extractors using augers, was proposed. While one extractor contains drill cuttings being treated with SFE, the other is being loaded, enabling essentially continuous treatment. The economic analysis indicated a capital cost of 4.8 million dollars (US) and an annual operating cost of $120,000 (US) for a system that could handle 12,000 lbs/hour (5.4 MT per hour) of cuttings, which is cheaper than reinjection, transport to shore, or the use of SBM or WBM [16]. However, such a system was never developed based on the recent literature review.

Later, supercritical CO_2 was used to reduce the oil content of drill cuttings to 0.2% (corresponding to over 95% extraction efficiency) using a laboratory-scale batch SFE system capable of treating 200g of cuttings [37]. When scaled up to an apparatus for treating 6kg of cuttings, the residual oil content was 1%. The best conditions for the extraction were 35°C and 10 MPa, and higher pressures did not result in greater hydrocarbon removal. A solvent to drill cuttings ratio of 1:1 was found to be optimal, and the CO_2 was recirculated. When the water content exceeded 15-20%, the hydrocarbon extraction efficiency dropped. At 30% water content, the extraction efficiency dropped to 80% [37].

In 2004, Halliburton experimented with the treatment of drill cuttings using supercritical CO_2, and found the treatment to be effective. However, the technology was not deemed cost effective at the time [51]. Instead, liquefied propane and butane were used to treat oily cuttings because of the higher cost associated with the higher temperature and pressure required to use supercritical CO_2 [11]. The hydrocarbon content of the cuttings was reduced to less than 1%. Mixing was required to obtain these high extraction efficiencies, and the base oil recovered was suitable for reuse. The system pressure was only 1.4 MPa when propane was used, and ambient temperature was sufficient [11]. Their paper did not include any safety concerns about using flammable and explosive gases such as propane.

In 2006, a study investigated the use of supercritical CO_2 to remove oil from cuttings generated in Iran [8]. The study tested pressures of between 16 and 22 MPa and temperatures between 55 and 79.5°C. Testing was performed on a laboratory-scale batch apparatus using less than 6g of cuttings, and the weight loss of the cuttings after SFE treatment was used to assess the extraction efficiency. At 20 MPa, increasing the temperature from 55 to 79.5°C lead to a great increase in extracted oil (at such a high pressure, the crossover pressure was likely exceeded, explaining this trend). An increase in pressure from 18 to 22 MPa at a constant temperature of 60°C only lead to a small increase in extraction efficiency. At 16 MPa and 60°C, almost no oil was extracted [8].

The same year, a patent was published involving the treatment of oily drill cuttings using liquified CO_2 between 3 and 7 MPa and temperatures near ambient conditions [135]. Using a laboratory-scale batch apparatus, residual oil contents near 1% were reported, corresponding to over 90% removal at 6.8 MPa and 20°C [135].

Two very similar patents were published by the same researchers in 2007 regarding the treatment of oily drilling waste (or similar materials) using supercritical or near critical CO_2 and other solvents, in a batch, semi-continuous or continuous scheme [35,36]. In laboratory testing to support the patent, hydrocarbon extraction efficiencies of up to 99% at 24 MPa and ambient temperature using CO_2 were reported. Generally, the extraction improved as the pressure was increased and the temperature decreased, even to below the critical temperature. Temperature had a greater effect on extraction efficiency at lower pressures compared to higher pressures. At 17.2 MPa and 43°C (the conditions which most resemble the 14.5 MPa and 40°C used in this project), the extraction efficiency was 95%. Analysis of the recovered oil indicated a lower kinematic viscosity and higher API gravity number, and a drop in water content of the treated cuttings was also noted [35,36].

In 2008, a small-scale batch SFE system (with CO_2) was used to extract oil from drill cuttings at 20 MPa and temperatures between 55 and 79.5°C [5]. The focus of the paper was on the modeling of a small amount of experimental results. The treated cuttings contained between 13 and $28g/m^3$ of hydrocarbons. Although the density of the cleaned cuttings would need to be known to convert these to mass percentages, the results appear to be very good. The extraction efficiency increased when the temperature was increased owing to the high constant pressure [5].

As can be seen, there have been a wide variety of studies on the use of CO_2, both in the liquid and the supercritical state, as well as other liquid and supercritical solvents, for the treatment of oily drill cuttings. Although the range of temperatures and pressures has been great, all studies have shown that their process can be fine tuned to produce high extraction efficiencies.

2.4.6.2 Previous Research at the University of Alberta on the SFE Treatment of Drill Cuttings

Research on the SFE treatment of drill cuttings and other drilling wastes using supercritical CO_2 has been ongoing in the Department of Civil and Environmental Engineering at the University of Alberta for several years. The evolution of this research is presented in this section.

Research began on the SFE treatment of drilling wastes contaminated with diesel oil using a laboratory-scale batch apparatus [32]. 10g of oily centrifuge underflow (similar to drill cuttings but containing much finer solid particles) was treated between 8.3 and 17.2 MPa and 35 and 60^{o}C, using a 15 minute static period (CO_2 present but not flowing) followed by a 30 minute flow period at a 10mL/min CO_2 flow rate as measured at the pressure used. Mixing was carried out using a simple magnetic mixing bar. At pressures above 13.7 MPa, increasing the temperature lead to only a slight increase in hydrocarbon extraction efficiency, while at 10.3 MPa (closer to the critical pressure), the extraction efficiency dropped when the temperature was increased. At both 35^{o}C and 50^{o}C, an increase in pressure by about 2 MPa (from 8.3 to 10.3 MPa at 35^{o}C and from 10.3 to 12.4 MPa at 50^{o}C) lead to an increase of about two-fold in extraction efficiency. The highest extraction efficiency, near 90%, was found at 12.4 MPa and 50^{o}C. Using a double cycle (two static periods and two flow periods) further increased the extraction efficiency to 97%. The recovered diesel oil had a very similar composition to the untreated diesel, and could potentially be reused [32].

Research continued with the SFE treatment of centrifuge underflow and drill cuttings containing diesel oil using CO_2 and a laboratory-scale batch apparatus [31]. Conditions studied involved pressures between 9.0 and 15.2 MPa and temperatures between 40 and 60^{o}C. The treatment consisted of a 15 minute static period and a 90 minute flow period in which the CO_2 flowed at about 10mL/min measured at the pressure of the system. The longer flow period was presumably due to the fact that 100g of drilling waste was treated in each experiment. Based on the appearance of the treated wastes, the best temperature and pressure were 14.5 MPa and 40^{o}C. Above 14.5 MPa, very little difference in the appearance of the cuttings was noted. The pressure has a greater effect on extraction efficiency compared to the temperature. Above 13.8 MPa, all extractions had hydrocarbon extraction efficiencies of greater than 95%, no matter which temperature was used. At a lower pressure of 9.0 MPa and a temperature of 40^{o}C, the extraction efficiency dropped to between 69 and 77%. The recommended mixing speed was 800rpm using a new helical impeller. SFE treatment during the first 30 minutes of the flow period was solubility limited and the final part of the extraction was diffusion limited. Mixing reduced this diffusional resistance somewhat. The recovered diesel was found to contain less longer-chain hydrocarbons than the untreated diesel, but nonetheless the conclusion was that SFE treatment did not significantly alter the composition of the diesel [31]. The extraction efficiency was also determined at varying moisture contents of the drill cuttings, up to a water to drill cuttings ratio of 1:1. Below 7% moisture content, the extraction is not affected. Between 7 and 20% water, the increased water covers the diesel-coated particles, and acts as a "resistant polar layer", leading to a lower extraction efficiency. Above 20% water, the water may displace the oil from the solid particles, resulting in a greater extraction efficiency [31].

Research continued with the SFE treatment of centrifuge underflow containing an oily base fluid at 14.5 MPa and 40^{o}C using a laboratory-scale batch apparatus [33,34]. Unlike the prior work, treatment of 100g of centrifuge underflow using 800rpm mixing (with the same helical impeller as [31]) resulted in major outlet plugging by solids that had carried over into the outlet lines. To prevent outlet plugging, the mixing speed was reduced to between 50 and 100rpm, the amount of drilling waste treated reduced to between 50 and 75g, and several extraction vessel modifications were made to reduce solids carryover. The CO_2 flow rate was increased to between 30 and 40g/min. The resulting hydrocarbon extraction efficiencies were lower at 72.6 to 79.0%. Use of additives mixed with the drilling waste increased the extraction efficiency. One additive resulted in an extraction efficiency of 98%, equivalent to a residual hydrocarbon content of only 0.25% in the drilling waste. A second additive was used and the extraction efficiency was as high as 97%. Chromatograms indicated that the recovered drilling fluid was not altered by SFE treatment and may be suitable for reuse [33,34].

The lessons learned from previous researchers (temperature and pressure for SFE treatment, mixing speed, vessel modifications, additive use, among others) were used as guidelines in the current research for the treatment of drill cuttings and water slurries.

2.4.7 The Need for a Continuous Supercritical Fluid Extraction System for the Treatment of Oily Drill Cuttings

2.4.7.1 Batch Supercritical Fluid Extraction Cannot Fill the Need

SFE has the potential to meet the need for an effective treatment technology for oily drill cuttings, since SFE is effective [8,16,30,34,37], environmentally friendly [5,28], cost competitive [16,37], appropriate for offshore treatment [16,28], and facilitates the potential reuse of base oil without fear of thermal damage [5,8,34,37]. Although this treatment method has been known for some time now (dating back to an original patent in 1984 [30]), SFE for the treatment of drill cuttings has not yet been commercialized, and all studies to date have been on small-scale batch systems, with 6kg being the maximum amount of drilling waste successfully treated [37].

Several researchers have proposed full-scale semi-continuous systems, where two batch vessels are operated in parallel (one vessel is in the extraction phase while the other is loaded with drill cuttings, and they sequence between extraction and loading phases to effectively allow continuous treatment of cuttings) [16,30,35-37,135], but no such system has actually been developed based on this literature review. Several authors have stated that batch or semi-continuous systems are not economical on a commercial scale where high throughputs of drill cuttings and similar materials are expected [39,74], despite some studies that have indicated economic feasibility of a semi-continuous SFE system for treating drill cuttings [16,37]. Concern over the energy cost to reach the high pressures required to reach the supercritical state of many fluids has been raised [11]. Specifically, the pressurization/depressurization cycles required to first extract the contaminant from the solid matrix, and then separate the extracted contaminant from the SCF, are energy intensive and costly [38,75,82]. In addition, batch and semi-continuous systems are technically awkward to operate in the field [38], due to the constant need to load oily drill cuttings and unload treated drill cuttings from the extraction vessel. Furthermore, this loading and unloading cycle is costly [75]. For these economical and technical factors, batch and semi-continuous SFE systems have not yet been commercialized for the treatment of drill cuttings in the oil and gas industry, despite the fact that the technology has been proven on a laboratory-scale.

2.4.7.2 Continuous Supercritical Fluid Extraction Can Fill the Need

A continuous SFE system can potentially fill the need for a new drill cuttings treatment technique that can be used on offshore and onshore rigs. In a continuous SFE system, both the drill cuttings and SCF are fed continuously into an extraction column, typically in a countercurrent fashion [22], similar to one used for contaminated soil [41]. The use of a continuous SFE system is cheaper on a per ton basis than batch or semi-continuous systems [22,23], and the cost decreases with increasing throughput [21,22].

For the treatment of contaminated soils using SFE, a continuous system can reduce the cost by as much as five times over a batch system [40], and a similar situation can be expected for oily drill cuttings. The lower cost is related to the fact that manual loading and unloading of drill cuttings to an extraction vessel is not required in a continuous system, and a continuous extraction column requires less volume for equivalent treatment than a batch extraction vessel [24].

In addition to its cost advantage, a continuous SFE system could have technical advantages over batch and semi-continuous systems. First, using a continuous SFE system may only require one pressure vessel (or extraction column), reducing the footprint of the equipment. A semi-continuous system requires a minimum of two pressure vessels. Second, a continuous SFE system would allow immediate treatment of oily drill cuttings as they are withdrawn from the wellbore, potentially eliminating the need to store drill cuttings on a rig, as would be the case for a batch SFE system [51]. For these two reasons, a continuous SFE system will require much less space than its batch and semi-continuous counterparts, and therefore it could potentially be more easily placed on an offshore drilling rig. Due to these economical and technical advantages, a continuous system should be easier to develop on a commercial scale.

2.4.7.3 Technical Issues with a Continuous SFE System

There have been several technical issues identified regarding the development of a continuous SFE system for treating oily drill cuttings or other similar materials:

- A method to continuously feed drill cuttings, which are largely solid, through a high pressure extraction column in a continuous manner, is needed [28,39]
- The plugging of lines downstream of the extraction column could reduce the reliability of a continuous SFE system [28]

Slurrying the oily drill cuttings with water is the solution being proposed. Slurrying soil with water has been proposed for the continuous SFE treatment of contaminated soils, which would enable the continuous feed of soil to a high pressure column [38,39], and would presumably prevent solids plugging in downstream lines. A recent study demonstrated that contaminated soil could be fed continuously through a high pressure extraction column when previously slurried with water, although some technical difficulties such as slurry buildup in the bottom of the column were reported [41]. However, this attempt was the first of this kind, and the technical difficulties experienced can likely be solved. Furthermore, transporting slurries containing solids with a large particle size distribution, and that include large solid particles, can be difficult [136]. This issue could affect drill cuttings and water slurries, as drill cuttings can contain particles that are 10μm to 20mm in diameter [50].

The only widespread application of drill cuttings and water slurries is during the reinjection of drill cuttings. Prior to reinjection, the cuttings are slurried with seawater to enable them to be pumped downhole [3,16,64]. Water is added to the cuttings, and the slurry is agitated in a tank to grind up large particles [63]. 90% of the particles in the slurry just prior to reinjection are under 120μm, and screens are used to remove any remaining large particles [63]. Nonetheless, solids settling in the reinjection slurries is sometimes a problem [50,64].

Attempts to treat drill cuttings slurries using SFE have not been presented as of the current literature review. Based on this lack of previous experience in treating drill cuttings and water slurries with SFE, and some of the technical issues related to the SFE treatment of soil slurries and the reinjection of drill cuttings slurries, the following list of possible technical issues regarding the SFE treatment of drill cuttings slurries has been developed, and are reflected in several of the project objectives given in Section 1.2:

- The mixing of oily drill cuttings with water may be difficult due to oil-water immiscibility (the soil slurries produced for continuous SFE treatment by [41] had much lower water-immiscible contaminant concentrations than drill cuttings)
- The cuttings may settle rapidly in the water
- The effectiveness of SFE treatment could be lower when drill cuttings are mixed with water (see Section 2.4.5.4)

The actual feeding of drill cuttings slurries to a high pressure extraction column is outside of the scope of this thesis, but will be investigated in future research involving the design and testing of a pilot-scale continuous SFE system for treating drill cuttings, which will be based on the system used by [41] for continuously treating contaminated soil slurries. Similar problems to those experienced during the continuous treatment of soil slurries, such as slurry build-up in the extraction vessel [41], may need to be solved in this future research. Furthermore, abrasion of piping caused by the flow of slurries containing drill cuttings, and the increased cohesiveness of the solid particles in the presence of water can cause operational difficulties in reinjection processes [50], and these issues may also be present in the continuous SFE treatment of drill cuttings. If these technical limitations can be overcome, then a continuous SFE system for the treatment of oily drill cuttings can be commercialized for use in the oil and gas industry, and particularly on offshore rigs.

Chapter 3: Materials and Method

3.1 Summary of Methodology

Drill cuttings from a local Alberta drilling rig were obtained from MI SWACO's Spruce Grove field office. The cuttings contained a low toxicity mineral oil (trade name: Distillate 822). A sample of plain Distillate 822 (D822) was also obtained. The solubility of D822 in supercritical CO_2 was measured at pressures varying between 10.3 and 17.2 MPa and temperatures between 35 and $50^{o}C$. The apparent solubility of D822 from drill cuttings was then determined at 14.5 MPa and $40^{o}C$ in order to determine if the SFE treatment of drill cuttings was limited by solubility or diffusion. The apparent solubility of D822 from dried drill cuttings and drill cuttings slurried with water was also estimated, in order to assess the effects of water on the SFE treatment of drill cuttings.

Following these measurements, experiments were focused on the SFE treatment of drill cuttings and water slurries. Slurries containing between 0.5 and 5 parts water per part drill cuttings (mass basis) were produced. Hereafter, these slurries will simply be referred to by their water to drill cuttings ratios (e.g. 0.5:1, 1:1, 2:1 and 5:1). The extractions were performed on a laboratory-scale batch apparatus using supercritical CO_2 at 14.5 MPa and $40^{o}C$, conditions that were chosen for further investigation following the solubility and apparent solubility experiments, and that were previously determined as suitable conditions for similar drilling wastes [31]. The CO_2 flow rate was maintained at approximately 38g/min. Between 25 and 40g of drill cuttings, in addition to the water, were treated in each experiment, and most experiments were performed in triplicate. Mixing was carried out using a helical or paddle impeller at 100rpm. The hydrocarbon extraction efficiency from each slurry was determined, and compared to the extraction efficiency from plain drill cuttings (no water added), in order to determine the effect of water on SFE treatment, and to determine the best water to drill cuttings ratio for further investigation. The extraction efficiency was determined by comparing the hydrocarbon content (from the D822) of the drill cuttings before and after SFE treatment. The hydrocarbon content before and after treatment was determined using a Dean-Stark extraction. In addition to determining the extraction efficiency, the "pumpability", "flowability" and settling characteristics were qualitatively assessed for each slurry both before and after SFE treatment.

Once the best water content in the slurry was determined, attempts were made to increase the hydrocarbon extraction efficiency from that slurry by using additives or vessel modifications, based on the determined limiting mechanism (solubility or diffusion) of the extraction.

3.2 Materials

This section will describe the materials, chemicals and apparatus used in this research.

3.2.1 Drill Cuttings

A single batch of drill cuttings was used for all experiments. The drill cuttings were obtained from MI SWACO's Spruce Grove, Alberta field office. The origin of the drill cuttings was a drilling operation in Alberta operated by the Murphy Oil Corporation. The drilling mud used when the cuttings were produced was an oil-based mud with a 90:10 oil to water ratio and an estimated solids content of 7 to 10%. Distillate 822 (D822) was the base fluid used in the continuous phase of the drilling mud.

The drill cuttings were stored in a closed bucket inside a walk-in cooler at approximately 4^{o}C to minimize volatilization of the oil. Subsamples used in the extractions were taken from the main batch after agitation to ensure that the oil and solids in the drill cuttings were well mixed. These subsamples were stored in glass jars in the laboratory refrigerator at 4°C.

3.2.2 Distillate 822 Base Oil

A sample of D822 base oil was supplied by MI SWACO's field office in Spruce Grove, Alberta. According to the Material Safety Data Sheet (MSDS), D822 mainly consists of normal alkanes (n-alkanes) in the range of $C_{11}H_{24}$ to $C_{18}H_{38}$. Another source states that D822 contains 84.7% n-alkanes of $C_{15}H_{32}$ and larger [98]. As a comparison, diesel fuel contains only 49.8% of $C_{15}H_{32}$ and larger n-alkanes, and overall has a lighter fraction of n-alkanes [98]. D822 has a low toxicity, and contains a total of 0.09% aromatics (as compared to diesel which has 1.88%) of which two thirds is benzene, toluene, ethylbenzene and xylenes [98]. The flash point is 77°C, which is higher than that of diesel fuel which has a flash point of 47°C [98]. Advantage Mud Systems Ltd. [98] provides more details on product formulation and properties. Because of the low toxicity, D822 is considered a mineral oil and drilling mud containing D822 is considered oil-based (not synthetic-based because D822 is produced using a distillation process).

The D822 sample was stored in a sealed container in the laboratory refrigerator at 4°C in order to minimize volatilization.

3.2.3 Chemicals

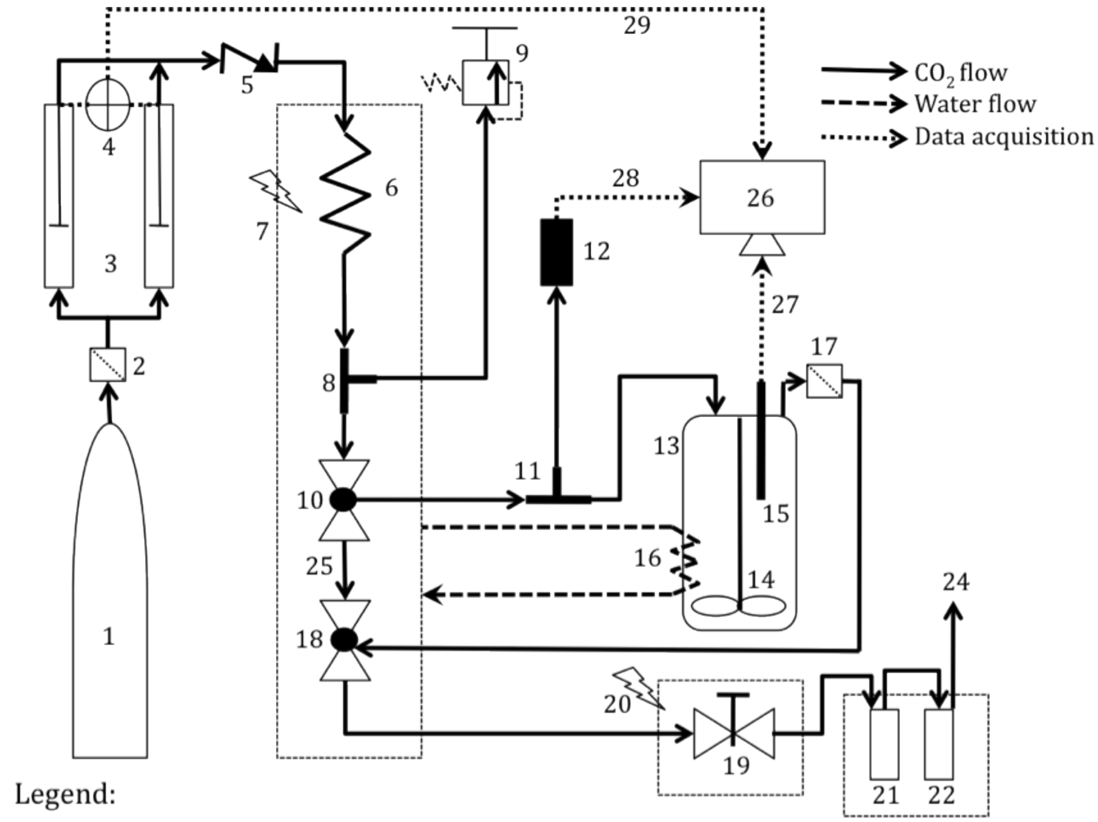
Table 3 shows the purity, grade and supplier of each of the chemicals used in this research.

Table 3: Chemicals specifications, uses and suppliers

Chemical	Primary Use	Manufacturer / Supplier
Carbon Dioxide (3.0 Bone Dry, liquid)	SFE solvent	Praxair
Hexane (HPLC Grade)	Soxhlet extraction	Fisher Scientific
Acetone (99+%)	Soxhlet extraction	Acros Organics
Toluene (HPLC Grade)	Dean-Stark extraction	Fisher Scientific
Methanol (HPLC Grade)	Cleaning	Fisher Scientific
Sodium Sulphate, Anhydrous (10-60 Mesh)	Soxhlet and Dean-Stark extractions	Fisher Scientific
n-Decane (>99%)	GC standard	Sigma-Aldrich Ltd.
n-Hexadecane (99%)	GC standard	Sigma-Aldrich Ltd.
n-tetratriacontane (98%)	GC standard	Sigma-Aldrich Ltd.
n-pentacontane (>97%)	GC standard	Sigma-Aldrich Ltd.
Diesel fuel	GC standard	Commercial gas station
Motor Oil (10W-30)	GC standard	Imperial Oil Ltd.
Silica Gel (70-270 mesh)	Drying agent	Sigma-Aldrich Ltd.
Glass Wool (silane-treated)	Trap vials	Mandel Scientific

3.3 Laboratory- Scale Batch SFE Apparatus

The laboratory-scale SFE apparatus used in this research is designed to treat a single batch of drill cuttings at one time. The apparatus was used for all SFE experiments, and was modified slightly for use in determining the solubility and apparent solubility of D822 in supercritical CO_2. Figure 9 provides a schematic of the apparatus.



Legend:

1. CO_2 Cylinder
2. Particulate Filter
3. Syringe pumps
4. Pump controller
5. Check valve
6. Heating coil
7. Circulating hot water bath
8. Tee
9. Pressure relief valve
10. Inlet Ball valve
11. Tee
12. Pressure transducer
13. Extraction vessel
14. Mixer blade
15. Thermistor
16. Heating jacket
17. Glass wool filter
18. Outlet ball valve
19. Outlet metering valve
20. Hot water bath (70°C)
21. Main trap vial
22. Carryover trap vial
23. Ice bath
24. CO_2 vent to fume hood
25. Vessel bypass
26. Data acquisition computer
27. Data acquisition: temperature
28. Data acquisition: vessel pressure
29. Data acquisition: pump pressure and CO_2 flow rate

Figure 9: Process flow diagram for SFE apparatus

As Figure 9 shows, a CO_2 cylinder (1) feeds CO_2 through a particulate filter (2) to two syringe pumps (3), where the CO_2 is compressed to the desired pressure. The syringe pumps operate in parallel so that a continuous supply of CO_2 is available for the extraction, and are controlled by the pump controller (4). As one pump is refilling (drawing CO_2 from the cylinder), the other is running (supplying CO_2 to the extraction vessel). The pump cylinders are equipped with cooling jackets fed by a refrigerated water bath (not shown), to ensure that the CO_2 remains in the liquid phase that is desired for good pump performance. The CO_2 passes through a check valve (5) (to prevent backwards flow from the extraction vessel back to the pumps) before passing through a heating coil (6) that is submerged in a heated circulating water bath (7), in order to heat the CO_2 to the temperature of the extraction prior to entering the extraction vessel. A tee (8) is placed next that connects to a pressure relief valve (9) set to rupture at 25.9 MPa (the uppermost pressure limit for the syringe pumps). The CO_2 passes through an inlet ball valve (10) before a second tee (11) is placed to connect to the pressure transducer (12), which reads the actual pressure in the SFE system. The CO_2 then flows into the extraction vessel (13) that contains a batch of drill cuttings, slurry or D822, depending on the type of experiment being conducted. The extraction vessel is equipped with a mixing impeller (14) driven by a Magnedrive® motor (not shown) and controlled by a mixer controller (not shown) to provide agitation. A thermistor probe (15) is inserted into the vessel to measure the system temperature. A heating jacket (16) surrounding the vessel is fed by the heated circulating water bath (7) to keep the temperature constant during the extraction. At the outlet of the extraction vessel, the CO_2, now loaded with solute, passes through a glass wool filter (17) (to prevent solids carryover), before passing through the outlet ball valve (18). Next, the loaded CO_2 passes through a heated metering needle valve (19) that is used to control the flow rate of CO_2 through the entire system. Since the CO_2 is expanded back to ambient pressure (it becomes a gas) after passing through the metering valve, rapid cooling occurs. Thus, the metering valve is submerged in a second hot water bath (20) set at $70^{o}C$ to prevent ice build-up (from any entrained water from the slurry), and to prevent solute solidification, both of which plug the outlet line and prevent a continuous flow of CO_2. After expansion at the heated metering valve, the extracted compounds precipitate from the CO_2 gas phase and are collected in two trap vials (21 and 22) submerged in an ice bath (23) to reduce volatilization of the collected compounds. The first trap vial (21) is the main collection vial, while the second trap vial (22) is the carryover vial used to collect any precipitated compounds that are carried over due to entrainment in the CO_2 gas flow. The CO_2 gas is then vented to the fume hood (24). The apparatus is also equipped with a bypass line (25) that is opened by valves (10) and (18) to allow CO_2 to flow through the system, while bypassing the extraction vessel, in order to clean the tubing of any residual solute. The pump controller, thermistor and pressure transducer are all connected to a data acquisition computer (26) used to collected the system temperature (27), system pressure (28), and the CO_2 flow rate and pressure as measured at the pumps by the pump controller (29). The stainless steel tubing used to connect all of the parts is 1/16" OD tubing (inlet lines and bypass line) and 1/8" OD tubing (outlet lines). The apparatus is pictured in Figure 10.

Table 4 shows the supplier and pressure rating (if applicable) of the components in the SFE apparatus. More details on some of the key components of the SFE apparatus are explained in the following sections.

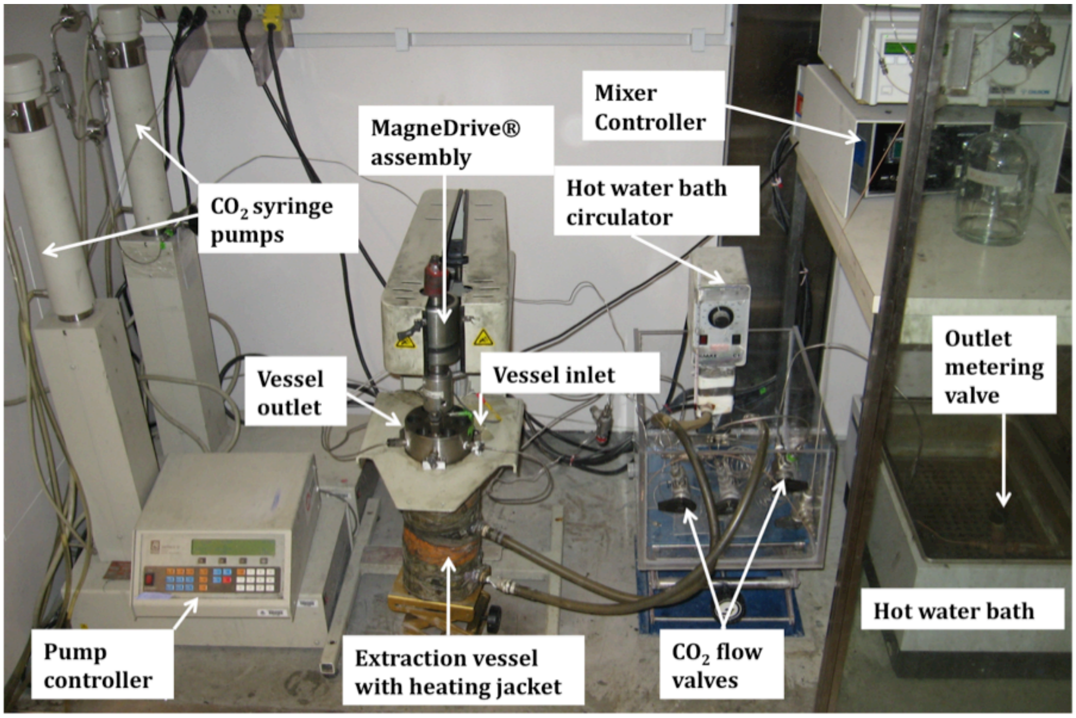


Figure 10: Picture of laboratory-scale batch SFE apparatus

Table 4: SFE apparatus components and their suppliers and pressure ratings (modified from [32]**)**

Component (label in Figure 9)	Manufacturer / Supplier	Pressure Rating (MPa)
CO_2 cylinder (1)	Praxair	
Filter (0.5µm) (2)	Swagelok (NUPRO)	
ISCO syringe pumps (Model 500D) (3) with controller (4)	Canberra Packard	25.9
Check Valve (5)	Swagelok (NUPRO)	
Heated water circulator (Model 002-4175) (7)		
Tees (8,11) and tubing	Swagelok	
Pressure relief valve (Model SS-4R3A with Spring R3A-F) (9)	Swagelok	41.4 (assembly) 27.6 (spring)
Ball valves (SS-83XKS4) (10,18)	Swagelok	41.4
Pressure transducer: Omega PX 502 (12)	Omega	20.7
Extraction Vessel: 300mL (13)	Autoclave Engineers (Division of Snap-tite)	37.9
Impeller (14)	Custom made	
MagneDrive® (II, Series 0.75) (14)	Autoclave Engineers (Division of Snap-tite)	37.9
Thermistor probe: YSI 406 (15)	Labcor Technical Sales Inc.	
Needle metering valve (Model SS-31RS4) (19)	Swagelok	34.5
Hot Water Bath (Isotemp) (20)	Fisher	

3.3.1 Extraction Vessel and MagneDrive® Mixer

The extraction vessel is a 300mL stainless steel enclosure produced by Autoclave Engineers. A diagram of the vessel is given in Figure 11. Not shown is the heating jacket that surrounds the vessel, that allows warm water to circulate around the outside of the vessel, enabling temperature control during the extraction. The vessel is closed by a stainless steel top (Figure 12) that is bolted onto the vessel, with a Teflon o-ring (Zimco Gauge and Valves, Calgary, AB - part number 06-06250385) used to create a pressure seal. The vessel lid contains ports in which the thermistor probe and CO_2 inlet and outlet fit. There are several other ports that are available, but these were sealed since they were not needed.

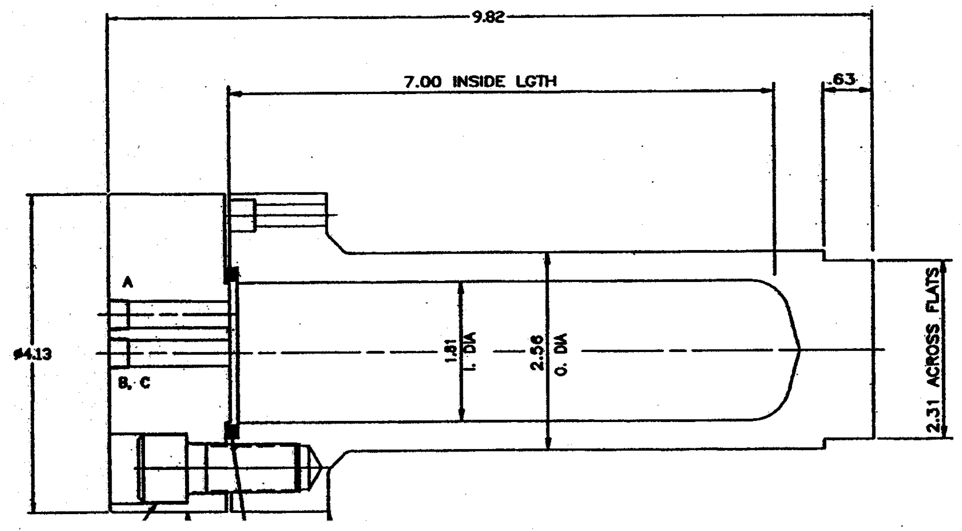


Figure 11: Diagram of 300mL extraction vessel (vessel is pictured on its side, all dimensions in inches) (modified from [137]**)**

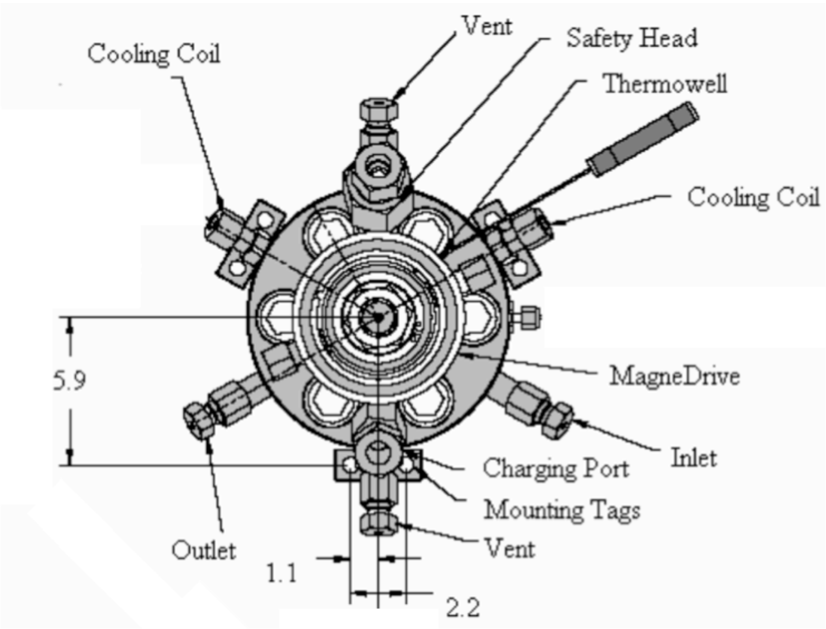


Figure 12: Vessel lid showing inlet, outlet and other connections (all dimensions in cm) (modified from [137]**)**

A MagneDrive® mixer motor drives the impeller inside the vessel by rotating a magnet outside the vessel, thus not compromising the seal between the vessel and the vessel lid. The rotating magnet is driven by a motor and a rubber chain. The entire assembly, comprising of the extraction vessel, vessel lid, and MagneDrive® mixer and motor, is shown in Figure 13.

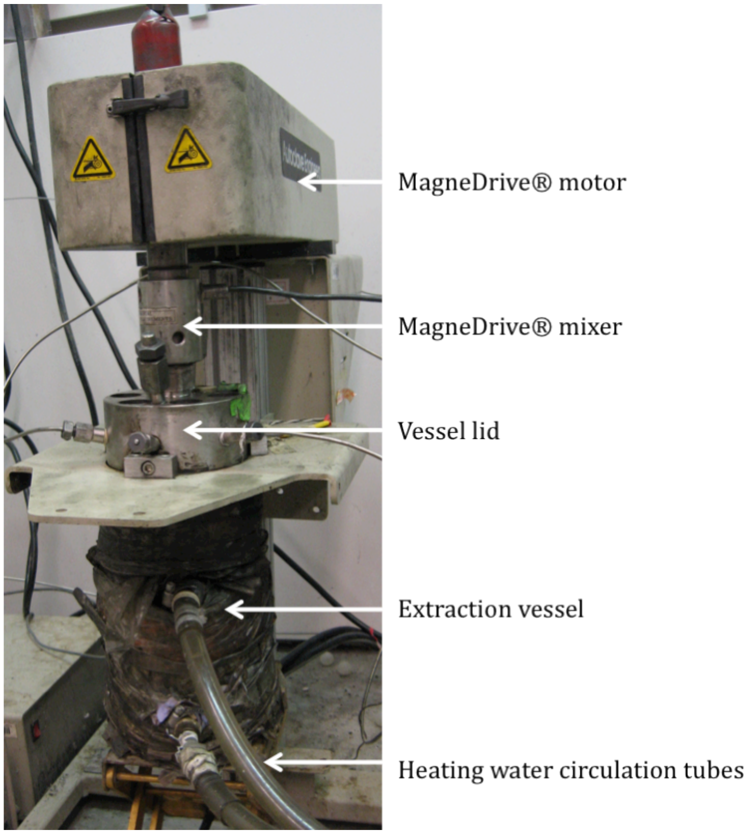


Figure 13: SFE laboratory assembly, including the extraction vessel, vessel lid MagneDrive® motor and mixer and heating water circulation tubes.

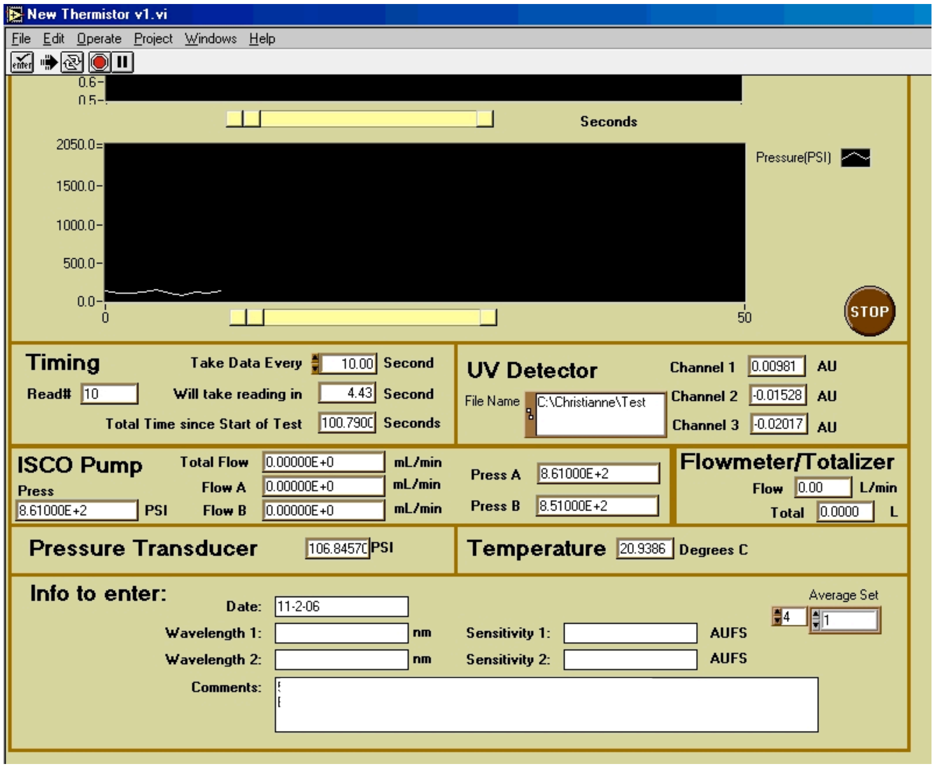
3.3.2 *Mixing Impellers*

Two different styles of mixing impellers were used in the experiments. In most experiments, a helical impeller (Figure 14) was used. The helical impeller was custom made from stainless steel, and the diameter is just slightly smaller than the inside diameter of the extraction vessel. Because of this tight fit, for experiments using this helical mixer, the CO_2 must be introduced above the mixing impeller (about 2.5 inches below the top of the vessel). The other mixing impeller is a simple paddle impeller that extends to near the bottom of the extraction vessel (see Figure 14). Because this paddle impeller does not fit tightly into the extraction vessel, there is room to extend the CO_2 inlet tube to the bottom of the extraction vessel, enabling CO_2 to be delivered to the bottom of the vessel.

Figure 14: Helical mixing impeller (left) that permits CO_2 inlet just above blade, approximately 2.5 inches below the top of the vessel, and paddle impeller (right) that permits CO_2 inlet at bottom of vessel

3.3.3 Labview Data Collection

Labview™ software was used to measure and record the system pressure, temperature, and the CO_2 flow rate as measured by the pump controller, throughout the course of each extraction. Other parameters were also recorded using Labview™, such as the time since the data recording began and the set-point pressure of the pumps. Sample data collected by Labview™ are shown in Appendix E. Figure 15 shows a screenview of the Labview™ software used in this research. The UV detector and flowmeter/totalizer data were not used in these experiments and therefore that data is not relevant to this work.



Timing
Take Data Every 10.00 Second
Read# 10
Will take reading in 4.43 Second
Total Time since Start of Test 100.790C Seconds

UV Detector
File Name C:\Christianne\Test
Channel 1 0.00981 AU
Channel 2 -0.01528 AU
Channel 3 -0.02017 AU

ISCO Pump
Press 8.61000E+2 PSI
Total Flow 0.00000E+0 mL/min
Flow A 0.00000E+0 mL/min
Flow B 0.00000E+0 mL/min
Press A 8.61000E+2
Press B 8.51000E+2

Flowmeter/Totalizer
Flow 0.00 L/min
Total 0.0000 L

Pressure Transducer 106.8457C PSI

Temperature 20.9386 Degrees C

Info to enter:
Date: 11-2-06
Wavelength 1: nm
Wavelength 2: nm
Sensitivity 1: AUFS
Sensitivity 2: AUFS
Comments:
Average Set 4 1

Figure 15: Labview screen used to record temperature, pressure and flow rate data throughout each SFE experiment (modified from [33]**)**

3.4 Solubility and Apparent Solubility Measurements

The apparatus pictured in Figure 9 was used with some slight modifications for both the determination of the solubility of D822 in supercritical CO_2, and the measurement of the apparent solubility of the D822 from drill cuttings and drill cuttings and water slurries. First, owing to the low flow rate of CO_2 used, the second trap vial (carryover vial) was not used. Instead, only one trap vial was used to collect the compound of interest (D822). Second, a mass flowmeter/totalizer (Agilent Technologies Model# 5067-0223) was attached to the CO_2 gas outlet after the trap vial, in order to measure the mass of CO_2 flowing through the trap vial. A summary of the procedure used to measure the solubility and apparent solubility of the D822 in supercritical CO_2 is provided in the following sections. Appendix A contains the detailed procedures.

3.4.1 Measurement of the Solubility of Distillate 822 in Supercritical CO_2

The solubility of D822 in supercritical CO_2 was measured at 10.3, 14.5 and 17.2 MPa and 35, 40 and 50°C, using a method similar to the "saturation method" described in [83], where CO_2 is allowed to flow through the vessel at a rate low enough to ensure the CO_2 at the outlet is saturated with D822. First, about 70mL of D822 was placed in the extraction vessel and the vessel was sealed. The large amount of D822 placed in the vessel was to ensure that there was excess solute in the system. The circulating water bath was set at a temperature about two degrees higher than the desired temperature for the experiment, and the warm water allowed to flow through the heating jacket on the vessel. Once the temperature in the vessel neared the desired temperature at which the solubility was to be measured, the pump was set to the desired pressure and run. CO_2 was introduced into the vessel, marking the beginning of a 60 minute static period, where the system was maintained at the desired temperature and pressure, to ensure equilibrium between the CO_2 and the D822 was reached. During the static period, mixing was carried out with the helical mixer blade (Figure 14) at 20rpm in order to reduce boundary layer diffusional resistance (at the D822/CO_2 interface) that could prevent a solubility concentration of D822 from being realized in the bulk of the supercritical CO_2 phase.

Once the static period was completed, the mixer was turned off and the outlet valves were opened slightly, allowing a flow of about 1 – 1.5mL/min as measured at the pumps (7.5°C and the set pressure). This flow rate was the lowest possible flow rate that could be obtained using the syringe pump, and corresponded to a standard volumetric flow rate (atmospheric pressure and 20^{o}C), as measured using the flowmeter/totalizer after the trap vial, of between 300 and 500mL/min. Note that the flow had to be maintained below 640mL/min (standard) as that is the upper limit for the flowmeter.

A few minutes of flow were allowed to ensure that the flow had stabilized to within the range measureable by the flowmeter. Once a steady flow was obtained, the first trap vial was installed at the outlet. At the same time that the trap vial was installed, the totalizer on the flowmeter was zeroed. The trap vial was used to collect precipitated D822 for a period of five minutes, during which the totalizer measured the total volume of CO_2. After the five minute period, the vial was removed and another was installed. At the same time, the final totalizer volume was recorded, and zeroed for the second measurement. This process was repeated a third time, for a total of three measurements at five minute intervals during 15 minutes of CO_2 flow. After the 15 minute flow period, a second static period (with 20rpm mixing) was carried out for 30 minutes to reestablish equilibrium. Next, a second 15 minute flow period (no mixing) was used to obtain three additional solubility measurements. Therefore, for most pairs of pressure and temperature, six solubility measurements were conducted. At 14.5MPa and 40^{o}C, one experiment used a 60 minute flow period to assess whether equilibrium could be maintained in the vessel for an extended period of time at the flow rate of 1-1.5mL/min as measured at the pumps.

Each trap vial was allowed to dry and degas (to remove extra mass caused by CO_2 dissolving in the D822) before being weighed. The amount of D822 collected during the 5 minute interval was determined by the difference in the weight of the trap vial before and after the five minute period. This weight of D822 was divided by the mass of CO_2 during the same five minute interval to calculate the solubility in grams of D822 per gram of CO_2 (g/g), as shown in Equation 3.

$$S = \frac{m_{D822}}{m_{CO_2}} \qquad \text{Equation 3}$$

where S is the solubility of D822 in CO_2 (g/g), m_{D822} is mass of D822 collected during the five minute interval (g), and m_{CO_2} is the mass of CO_2 used during the five minute interval (g).

During each 5 minute interval, the flow rate, as measured at the pump, was also recorded in Labview™. Following the run, the flow rate was numerically integrated (using the trapezoid rule) over the five minutes to determine the total mass of CO_2 as measured at the pump. Appendix F gives details of this calculation. Because of small leaks in the system, this measurement was expected to be slightly higher than the mass of CO_2 measured at the outlet flowmeter. The pump measurement was simply used to confirm the flowmeter's measurement. The data collected over the range of pressures and temperatures was fitted to the Chrastil and Modified Chrastil equations.

The above procedure was validated by determining the solubility of hexadecane in supercritical CO_2 at 35°C between 9 and 12.4 MPa, and at 40°C between 12.4 and 15.5 MPa, and comparing the determined solubilities to the data collected by Eustiquio-Rincon and Trejo [102], and Nieuwoudt and du Rand [101] at the same conditions.

3.4.2 Measurement of Apparent Solubility

The apparent solubility of D822 from drill cuttings, of D822 from drill cuttings dried with silica gel, and D822 from a 1:1 water to drill cuttings slurry, was also measured at 14.5MPa and 40°C to determine the limiting mechanism (solubility or diffusion) of the extractions. The same procedure was used as the one described in Section 3.4.1 for the measurement of solubility, except drill cuttings (and water for the slurry) were placed in the vessel instead of just D822. Sufficient drill cuttings were placed in the vessel to ensure that there was excess D822 present to reach a solubility concentration in the supercritical CO_2. A 60 minute static period was used, followed by a 150 minute flow period, in which the flow rate was kept near 1-1.5mL/min as measured at the pumps. Mixing at 100rpm, rather than 20rpm, was carried out during the static and flow periods, to mimic the extraction conditions. The trap vial was changed at 5 minute intervals for the first 90 minutes, and then at 15 minute intervals after. The longer flow period was used so that the apparent solubility of the D822 from the drill cuttings could be assessed over the course of the extraction, since the limiting mechanism (solubility or diffusion) can change throughout the course of an extraction [16,31]. The cumulative mass of D822 extracted was plotted against the cumulative mass of CO_2, as measured at the flowmeter/totalizer, and the initial (maximum) slope found that represents the apparent solubility. Duplicate experiments were performed to ensure the validity of the results. The apparent solubility was compared to the solubility determined at the same temperature and pressure to assess which mechanism controlled the SFE removal of hydrocarbons from drill cuttings.

A third experiment was completed on 100g of drill cuttings mixed with silica gel to dry the drill cuttings. The silica gel was added until the cuttings were "free-flowing", indicating that the water had been absorbed by the silica gel. The results of this experiment were compared to the results of the duplicate experiments on plain drill cuttings, to determine the influence of the water present in the drill cuttings.

The apparent solubility of D822 from a 1:1 water to drill cuttings slurry was also determined and compared to the apparent solubility of D822 from plain drill cuttings (no water added). Due to the presence of large amounts of water, a low CO_2 flow rate of 1-1.5mL/min was not possible because water was freezing in the metering valve at these low flow rates. Thus, flow was maintained near 10-15mL/min, which was the lowest flow rate that could be maintained. This flow rate well exceeded the maximum flow rate of the flowmeter, so calculations relied on the pump flow rate data rather than on the flow rate data collected at the flowmeter/totalizer. The pump flow data was numerically integrated (see

Appendix F) over each five minute time interval to determine the mass of CO_2. The static period was still maintained at 60 minutes, with a 90 minute flow period. Mixing was maintained at 100rpm using the helical mixer. Also, since water may have been collected in the trap vials, creating an overestimate of the amount of D822 collected, the mass of D822 in the trap vials was determined by adding 20mL of toluene to the vials, and measuring the amount of D822 using gas chromatography.

3.5 Supercritical Fluid Extraction Procedure

The laboratory-scale batch SFE apparatus shown in Figure 9 and pictured in Figure 10 was used for all of the extractions. A total of 43 extractions were performed using 17 different conditions of water content, drill cuttings mass, slurry volume, mixer impeller type and additive addition. Each extraction was completed at 14.5 MPa and 40^{o}C. For most conditions, triplicate extractions were completed. At some conditions, time permitted only duplicate experiments. In a few cases, only a single extraction was completed if the result of that extraction was poor and did not warrant further time and resource investment. A detailed procedure used in each SFE experiment is given in Appendix B. The following is a brief description of the methodology.

A sample of drill cuttings was placed in a glass jar. The exact amount of drill cuttings (either approximately 25g or 40g) was measured and recorded by using an analytical balance (Mettler Toledo AX205 DeltaRange®). If a slurry was being tested, the appropriate amount of water was measured to the nearest milliliter using a graduated cylinder, and added to the glass jar. The lid was closed and the slurry was subjected to vigorous wrist shaking for one minute. The slurry was then transferred to the extraction vessel.

The vessel, now charged with the drill cuttings and water, was bolted closed using the Teflon o-ring as a seal, as per the manufacturer's instructions. The hot water circulating bath was set to about 42^{o}C in order to obtain a temperature of 40^{o}C inside the vessel. The cooling water for the pumps was turned on and set to 7.5^{o}C, and the hot water bath containing the metering valve was set to 70^{o}C. The mixer was turned on to a speed of 100rpm. Once the vessel temperature was just below 40^{o}C, the syringe pumps were refilled with CO_2, set to 14.5 MPa, and allowed to run. The inlet valve to the extraction vessel was opened, so that the vessel was pressurized to 14.5MPa. A static period, in which the outlet valves remained closed, was carried out for 15 minutes. During this time, the trap vials (main collection vial and carryover vial) were partially filled with glass beads and glass wool, and placed at the outlet, inside an ice bath.

Once the 15 minute static period was complete, the flow period was begun. The outlet valves were opened to allow continuous CO_2 flow, and the metering valve was adjusted to obtain a flow rate of about 40mL/min, as measured at the pumps (14.5 MPa and 7.5^{o}C). This flow rate corresponds to about 38g/min of CO_2. Mixing at 100rpm was continued during the flow period. The main trap vial was changed at 15 minute intervals. By measuring the weight of the vial before and after, the mass of D822 (and water, in the case of the slurries) collected during each 15 minute interval was determined. The flow period was carried out for a total of 90 minutes.

After the flow period, the flow of CO_2 through the vessel was stopped and the vessel allowed to depressurize. Once depressurized, CO_2 was allowed to flow through the bypass line for about 30 seconds in order to clean the outlet lines of any remaining D822. After this bypass period, the final main collection vial and the carryover vial were removed. The vessel was unbolted, and the treated drill cuttings or slurry was poured into a jar and stored at 4^{o}C in the laboratory refrigerator for further analysis.

3.6 Determination of Hydrocarbon Extraction Efficiency

The hydrocarbon extraction efficiency refers to the percentage of D822 that was removed from the drill cuttings during SFE treatment. The extraction efficiency is determined by measuring the hydrocarbon (from D822) content of the drill cuttings before and after SFE treatment. Since the drill cuttings slurries that were tested contained varying amounts of water, all hydrocarbon content measurements were converted to a dry mass basis, to allow valid comparison between the extraction efficiencies from slurries containing varying amounts of water. The hydrocarbon content was measured using a Dean-Stark extraction, followed by analysis of the extract using gas chromatography (GC). The following sections describe the preparation of GC standard solutions used to calibrate the GC, the GC analysis procedure including calibration and daily quality assurance, the Soxhlet extraction procedure that was used as part of the Dean-Stark method validation, and then the Dean-Stark extraction procedure which was adopted as the means of determining the hydrocarbon content of the treated and untreated cuttings.

3.6.1 Standard Solution Preparation

3.6.1.1 n-Alkane Standards

n-Alkane standard solutions were prepared for GC calibration, as prescribed in the Canadian Council of Ministers of the Environment (CCME) guidelines found in *Reference Method for the Canada-Wide Standard for Petroleum Hydrocarbons in Soil – Tier 1 Method* [46], which was followed to calibrate the GC. The procedure described in [46] was used for GC calibration as it is a Canada-wide recognized analytical method, and the determination of petroleum hydrocarbons in soil is similar to the determination of the same hydrocarbons in drill cuttings.

As prescribed in the guideline [46], six n-alkane standard solutions in toluene were produced, each containing approximately equal amounts of decane ($C_{10}H_{22}$), hexadecane ($C_{16}H_{34}$) and tetratriacontane ($C_{34}H_{70}$). The six standard solutions contained approximately 5, 10, 25, 100, 250 and 500mg/L of each n-alkane. The 500mg/L solution was prepared by measuring approximately equal masses of each n-alkane into a 250mL volumetric flask using the analytical balance. The solution was placed in an ultrasonic bath for 60 minutes to ensure dissolution of all of the n-alkanes, in particular the tetratriacontane, which due to its larger molecular weight, is less soluble in toluene than the two lighter n-alkanes. Next, a series of dilutions was made to generate the 250, 100, 25, 10 and 5mg/L solutions. Using the exact amount of each n-alkane added to the original 500mg/L solution, the exact concentration in each standard solution was calculated. In addition, the CCME guidelines require a standard solution of pentacontane in toluene with a maximum concentration of 15mg/L [46]. To fulfill this requirement, a standard solution containing 6.4mg/L pentacontane ($C_{50}H_{102}$) in toluene was made. This solution was also subjected to the ultrasonic bath for 60 minutes to ensure complete dissolution of the pentacontane, which is relatively insoluble in toluene. No additional solutions of pentacontane were prepared due to the solubility limitation. The standard solutions were stored in a refrigerator at $4^{o}C$ between uses.

3.6.1.2 Diesel/Motor Oil Standards

As described in the CCME procedure [46], diesel and motor oil standards must also be prepared in order to check the linearity of the GC response factor. The standards must represent the entire range of concentrations that will be measured using the GC. The standard solutions made for this research project contained 1000, 5000, 10000 and 50000mg/L of total hydrocarbons, comprised of approximately one part diesel fuel and three parts motor oil (by mass) in toluene. The 50000mg/L solution was made by measuring approximately 1.25g of diesel fuel and 3.75g of motor oil into a 100mL volumetric flask and bringing to volume with toluene. By weighing the flask before and after the chemicals were added, the exact amount of oil and diesel added was determined. Appropriate dilutions were made to produce the 10000, 5000 and 1000mg/L standard solutions. These standards were also stored in the refrigerator at $4^{o}C$ between uses.

3.6.1.3 Distillate 822 Standards

Although not prescribed in the CCME method, D822 standard solutions in toluene were also made in order to assess both the linearity and accuracy of the GC for D822. Solutions containing approximately 1000, 5000, 10000 and 50000mg/L of D822 were made. The 50000mg/L solution was made by adding approximately 5g (the exact amount was measured and recorded) of D822 into a 100mL volumetric flask and bringing to volume with toluene. The 10000, 5000 and 1000mg/L solutions were made by diluting the 50000mg/L solution. These standards were also stored in the refrigerator at 4^{o}C between uses.

3.6.2 Gas Chromatography

3.6.2.1 Gas Chromatography Method

The CCME procedure for the determination of total petroleum hydrocarbons requires the use of a poly(dimethylsiloxane) low bleed column of at least 15m in length and an inner diameter not exceeding 0.53mm, in combination with GC/FID detection [46]. In this research, a Varian CP-3800 (Varian Inc., Palo Alto, California, USA) GC was used that was equipped with a Flame Ionizing Detector (FID), a CP-8410 autoinjector with a capacity to hold ten 2mL sample vials, and a CP-1177 split/splitless injector system. Varian's *Star Chromatography Workstation* (*Version 5.5*) was used to analyse GC results. The column was a Restek (Fisher Scientific, Edmonton, AB) 100% poly(dimethylsiloxane) 30m long column that has an internal diameter of 0.32mm. The column had a maximum temperature of 350^{o}C and a minimum bleed temperature of 330^{o}C. The operational parameters that were used in the GC method are shown in Table 5. The method was based on that used by Street [33], but with an increased injector temperature in order to increase the detection of the heavier n-alkanes.

Table 5: GC operational parameters for total petroleum hydrocarbon analysis of drill cuttings

Parameter	Details
Injection temperature	325°C
Oven temperature	• Hold at 40°C for 2 minutes • Ramp to 320°C at a rate of 20°C per minute • Hold at 320°C for 8 minutes
FID temperature	340°C
Split/Splitless	• Start with split on at a split ratio of 10 • At 0.01 seconds, split is turned off • At 0.75 seconds, split is turned on to a ratio of 50 • At 2 minutes, split ratio reduced to 10
Hydrogen carrier gas	• 18mL/min • Ultra high purity grade • Supplied by Praxair (Edmonton, Alberta)
Nitrogen make-up flow	• 12mL/min • Ultra high purity grade • Supplied by Praxair (Edmonton, Alberta)
Detector hydrogen flow	• 11mL/min • Ultra high purity grade • Supplied by Praxair (Edmonton, Alberta)
Detector air flow	• 487mL/min • Extra dry grade • Supplied by Praxair (Edmonton, Alberta)
Injection Volume	2μL

3.6.2.2 Gas Calibration Procedure

The CCME procedure [46] was used to calibrate the GC/FID. According to this procedure, a minimum three-point calibration is required using standards containing approximately equal concentrations of n-decane, n-hexadecane and n-tetratriacontane, that incorporates the entire range of concentrations which will be measured. The FID response factor for each of these n-alkanes must be within 10% of each other. An n-pentacontane standard of a maximum concentration of 15mg/L must also be injected, and its response factor must be within 30% of the average response factor from the three smaller n-alkanes. The linearity of the detector must be assessed using diesel and motor oil standards. The r^2 value of a plot of area count versus concentration must not be lower than 0.85.

In this research, a six-point calibration using the aforementioned n-alkane standards was carried out, and covered the range of 5mg/L to 500mg/L. All injections were made in triplicate using the GC method described above (the same method to be used for the drill cuttings hydrocarbon content analysis). The response factor for each n-alkane at each concentration was found using Equation 4. Note that the area count of each individual n-alkane was corrected by subtracting the average area count for the same n-alkane found in the toluene blank injections. The average response factors for each n-alkane were compared to ensure that each was within 10% of the others. The n-pentacontane standard was also injected and its response factor found using Equation 4:

$$RF = \frac{A_{alkane} - A_{alkane,blank}}{C_{alkane}} \qquad \text{Equation 4}$$

where RF is the response factor in (L/mg), A_{alkane} is the area count for an individual n-alkane, $A_{alkane,blank}$ is the average area count of an individual n-alkane in the toluene blanks and C_{alkane} is the concentration of the n-alkane in standard solution (mg/L).

Using the response factor of each individual n-alkane at each concentration, the average response factor (RF_{avg}) was determined. In addition, the average retention time of each n-alkane was found, in order to determine the retention times that separate the F2 (C_{10}-C_{16}), F3 (C_{16}-C_{34}) and F4 (C_{34}-C_{50}) hydrocarbon fractions, as defined by the CCME [46]. The F2 hydrocarbon fraction is defined as the hydrocarbons that appear in the GC chromatogram between the top (apex) of the decane peak and the apex of the hexadecane peak. Similarly, the F3 fraction includes hydrocarbons appearing between the apex of the hexadecane peak and the apex of the tetratriacontane peak, and the F4 fraction includes hydrocarbons appearing between the apex of the tetratriacontane peak and the apex of the pentacontane peak [46]. These hydrocarbon fractions were developed by the CCME so that guidelines regarding the concentration of hydrocarbons in soil could be issued with regard to groupings of similar hydrocarbons, instead of individual hydrocarbons [46]. The concentration of F2, F3 and F4 n-alkanes in the drill cuttings was determined separately, in order to check for the preferential extraction of light n-alkanes (i.e. F2 n-alkanes) during SFE treatment.

In addition, the linearity of the FID response was determined by injecting the diesel and motor oil standards (1000, 5000, 10000 and 50000 mg/L) in triplicate using the same GC method. A plot of total area count for each fraction (F2, F3 and F4) versus concentration was produced and the r^2 value found, in order to assess compliance with the CCME's FID linearity requirement.

Although not required by the CCME procedure, the D822 standards (1000, 5000, 10000 and 50000 mg/L) were also injected in triplicate. The concentration of the D822 standards was found using the GC/FID analysis (using a rearrangement of Equation 4), and compared to the known concentrations in each standard, in order to assess the accuracy of the GC/FID for determining the concentration of D822.

3.6.2.3 GC Quality Assurance Checks

The CCME procedure also requires the use of daily quality assurance checks, by injecting the low and mid-point n-alkane standards. The daily response factor of the low concentration standard must be within 20% of the response factor determined during calibration. The daily response factor of the mid-point concentration standard must be within 15% [46].

In this research, the low concentration standard was the 5mg/L n-alkane standard, and the mid-point standard was taken to be the 100mg/L standard. Because the GC was not operated each day, triplicate samples of both of these n-alkane standards were injected at the end of each GC run to ensure that the FID response was normal. In the cases where the response factor did not meet the

CCME’s requirements, troubleshooting took place to fix the problem, and the samples were reinjected. In most cases when the daily response factors were outside of the 20% and/or 15% windows, changing the septa on the GC injector was required to fix the problem.

In addition, the entire series of D822 standards was periodically injected to ensure the continued accuracy of the GC/FID response. These calibration checks were not required by the CCME procedure, but were carried out when the GC had not been used for a long period of time.

3.6.3 Soxhlet Extraction

The CCME procedure [46] requires that Soxhlet Extraction be used for the determination of petroleum hydrocarbons in soil and this procedure was used successfully for drilling waste without using the prescribed silica gel cleanup, because drilling waste is not expected to contain any polar compounds [33]. The Soxhlet extractions performed in this study, to determine the hydrocarbon content of the untreated drill cuttings, were done using the same method described in [33] except that sodium sulphate was not used to dry the drill cuttings prior to Soxhlet extraction. The Soxhlet extraction requirements are given in [46] and a brief description will be given here.

About 5g of drill cuttings were placed in a cellulose extraction thimble (Whatman 33mm x 94mm, Fisher Scientific, Edmonton, Alberta) and the thimble was placed in a Soxhlet flute. The extraction was carried out using a 1:1 mixture (by mass) of n-hexane and acetone for 16 to 24 hours at a reflux rate of about 4-6 cycles per hour, as required in the CCME procedure [46]. Once the extraction was complete, the collected solvent (now containing the D822 base oil) was passed through a column containing about 9g of sodium sulphate, in order to remove any traces of water that could damage the GC column. Next, a rotary evaporator was used to evaporate the solvent and 25mL of toluene was used to dilute the concentrated D822. The toluene/D822 solution was transferred to 2mL GC vials for GC/FID analysis. The concentration of F2, F3 and F4 n-alkanes was found using the following equations 5, 6 and 7 respectively, as given in [33]. Equation 8 was used to find the total hydrocarbon content of the cuttings. Note that, as with the calibration standards, the area counts for each hydrocarbon fraction were corrected by subtracting the average toluene blank area count for the same fraction. The equations are as follows:

$$C_{F2} = \frac{(A_{C10-C16})(V)}{(RF_{avg})(W)} \qquad \text{Equation 5}$$

$$C_{F3} = \frac{(A_{C16-C34})(V)}{(RF_{avg})(W)} \qquad \text{Equation 6}$$

$$C_{F4} = \frac{(A_{C34-C50})(V)}{(RF_{avg})(W)} \qquad \text{Equation 7}$$

$$C_{total} = C_{F2} + C_{F3} + C_{F4} \qquad \text{Equation 8}$$

where *C* is the concentration of the given n-alkane fraction (F2, F3, F4 or total) in mg of hydrocarbon per kg of drill cuttings (mg/kg) on a wet basis, *A* is the area count of the given hydrocarbon fraction (average of triplicate injections), corrected by subtracting the average toluene blank area count for the same fraction, *V* is the volume of toluene dilution (mL), RF_{avg} is the average GC/FID response factor from the calibration and *W* is the drill cuttings weight. The total mass fraction (easily convertible to a percentage) of hydrocarbons in the drill cuttings, on a wet basis, was found by the simple unit conversion in Equation 9:

$$F_{h,wet} = \frac{C_{total}(mg/kg)}{1000000 mg/kg} \qquad \text{Equation 9}$$

where $F_{h,wet}$ is the total mass fraction of hydrocarbons in the cuttings on a wet basis.

The Soxhlet procedure, as described above, can only calculate the concentration of hydrocarbons in the drill cuttings on a wet basis, as it does not factor in the water content of the drill cuttings. Treated drill cuttings were not analyzed for hydrocarbon content using Soxhlet extraction, because of the variable amount of water present in the treated drill cuttings slurries. The CCME procedure states explicitly that Soxhlet extraction is not valid for liquids or slurries [46]. The US EPA's standard procedure for Soxhlet extraction states that any free water should be decanted prior to analysis [138]. In one test, the water content in some cases was found to significantly affect Soxhlet extraction results [125]. Given this evidence, Soxhlet extraction was not used to determine the extraction efficiency of SFE treatment. Instead, the results of Soxhlet extraction on untreated drill cuttings were used as a comparison for the results (i.e. hydrocarbon content of the drill cuttings) of the Dean-Stark extraction, as part of the validation of the Dean-Stark extraction. Since Soxhlet extraction had been used successfully by in previous research on drilling wastes [31,33], Dean-Stark extraction should yield similar hydrocarbon content results, in order for valid results comparison between the different research studies.

3.6.4 Dean-Stark Extraction

Dean-Stark extraction was selected as a possible replacement for Soxhlet extraction because it can be carried out on the drill cuttings slurries. The Dean-Stark extraction is used in the oil and gas industry to determine the oil/water/solids content of a given sample. Its ability to determine the water content was the motivation for its use in this research, because knowledge of the water content allows the determination of the hydrocarbon content on a dry basis, enabling valid comparison of SFE extraction efficiencies between drill cuttings and water slurries containing variable amounts of water. Another advantage is that the Dean-Stark extraction is carried out using toluene as the solvent, so that rotary evaporation and solvent exchange, which must be performed during Soxhlet extraction, is not required.

3.6.4.1 Dean-Stark Extraction Procedure

The detailed Dean-Stark extraction procedure is given in Appendix C. The following is a summary. First, about 15g of drill cuttings slurry, or about 10g of untreated drill cuttings, was placed in a 100mL flat-bottom extraction flask. In the case of a slurry, stirring was used to ensure slurry uniformity prior to being added to the extraction flask. About 100mL of toluene was added to the extraction flask. A Dean-Stark trap and a condenser were attached to the flask. The assembly was placed on a heating plate, and the toluene-slurry mixture was boiled for five hours. Since toluene boils at about 111^{o}C, the water in the sample evaporates, condenses in the condenser, and is collected in the Dean-Stark trap, as shown in Figure 16. After the extraction, the volume of water collected in the trap was recorded. The contents of the flask were filtered to separate the toluene solution from the solids. Clean toluene was used to rinse the flask and the solids and this toluene was added to the toluene solution from the Dean-Stark extraction. The final volume of the toluene/D822 solution was recorded. This solution was then poured through a column containing about 9g of sodium sulphate in order to remove any residual water not collected in the trap. A portion of the solution was then filtered into a 2mL GC vial for GC/FID analysis.

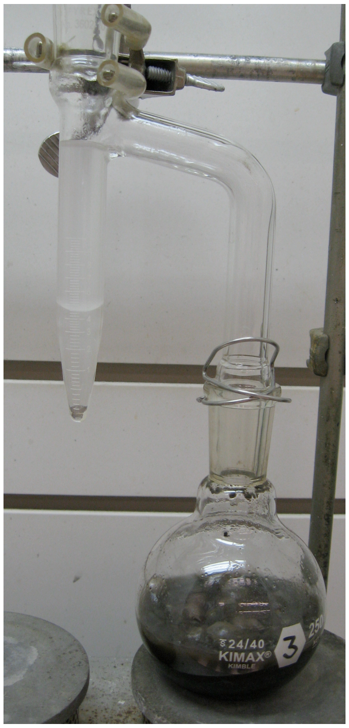


Figure 16: Dean-Stark extraction set-up. The toluene and drill cuttings are placed in the flask (bottom right), and the water is collected in the Dean-Stark trap (upper left)

The F2, F3 and F4 hydrocarbon content of the drill cuttings or slurry, on a wet basis, was found using Equations 10, 11 and 12:

$$C_{F2} = \frac{(A_{C10-C16})(V_f)}{(RF_{avg})(W)} \qquad \text{Equation 10}$$

$$C_{F3} = \frac{(A_{C16-C34})(V_f)}{(RF_{avg})(W)} \qquad \text{Equation 11}$$

$$C_{F4} = \frac{(A_{C34-C50})(V_f)}{(RF_{avg})(W)} \qquad \text{Equation 12}$$

where V_f is the final toluene solution volume (mL) and W is the drill cuttings or treated slurry weight (g). Equations 8 and 9 were then used to find the total hydrocarbon concentration, and the hydrocarbon mass fraction on a wet basis.

In order to compare the hydrocarbon content of the treated slurries and the SFE extraction efficiency from the treated slurries, the concentration of hydrocarbons must be converted to a dry basis, because each treated slurry contained different amounts of water. First, the mass fraction of water in the cuttings or slurry was found using Equation 13:

$$F_w = \frac{V_w \rho_w}{W} \qquad \text{Equation 13}$$

where F_w is the mass fraction of water in the slurry or untreated drill cuttings, V_w is the volume of water collected in the Dean-Stark trap (mL) and ρ_w is the density of water at ambient conditions (0.9982g/mL). Next, the solids fraction of the slurry was found using Equation 14:

$$F_s = 1 - F_w - F_{h,wet} \qquad \text{Equation 14}$$

where F_s is the mass fraction of solids in the slurry or untreated drill cuttings. Finally, the hydrocarbon fraction on a dry basis was found using Equation 15:

$$F_{h,dry} = \frac{(F_{h,wet})}{(F_{h,wet} + F_s)} \qquad \text{Equation 15}$$

where $F_{h,dry}$ is the mass fraction of hydrocarbons in the slurry or untreated cuttings on a dry basis.

The hydrocarbon extraction efficiency of any given SFE experiment, expressed as the percentage of hydrocarbons removed during the extraction, was found by comparing the mass fraction of hydrocarbons (dry basis) of the treated slurry (or cuttings) to the mass fraction of hydrocarbons (dry basis) of the untreated cuttings, as shown in Equation 16:

$$\eta = \left(\frac{F_{h,dry,untreated} - F_{h,dry,treated}}{F_{h,dry,untreated}} \right) \times 100 \qquad \text{Equation 16}$$

where η is the SFE hydrocarbon extraction efficiency (%), $F_{h,dry,untreated}$ is the mass fraction of hydrocarbons in the untreated cuttings (dry basis) and $F_{h,dry,treated}$ is the mass fraction of hydrocarbons in the treated slurry or cuttings (dry basis).

The F2 to F3 ratio, as determined by the ratio of corrected area counts, was found for the treated slurries and the untreated cuttings, to determine if the lighter hydrocarbons (i.e. F2 n-alkanes) were being preferentially extracted.

3.6.4.2 Dean-Stark Extraction Method Validation

The Dean-Stark extraction procedure was developed in-house, and was validated in two ways. First, the hydrocarbon content of untreated drill cuttings determined using Dean-Stark extraction was compared to the results obtained using Soxhlet extraction, a method proven to work on dry drilling wastes [31,33]. In this case, the results were compared on a wet basis because Soxhlet extraction cannot be used to directly determine the water content of the drill cuttings [33]. Second, the hydrocarbon content, on a dry basis, was determined for spiked barite slurries using Dean-Stark extraction. Barite, the main solids component in drilling mud, was spiked with D822 in ratios of approximately 1, 5 and 15% barite (on a dry mass basis), allowed to age for several months, and then slurried with water in a ratio of 1:1 water to spiked barite. These concentrations were thought to represent the range of hydrocarbon contents that would be encountered in the untreated and SFE-treated drill cuttings. The hydrocarbon content of the spiked slurries was determined using Dean-Stark extraction and compared to the known dry concentrations, in order to assess the accuracy of the Dean-Stark procedure.

3.7 Liquid-Liquid Extractions to Determine Mass of D822 Collected

Both D822 and water were visually present in the trap vials following each SFE experiment when a drill cuttings slurry was being treated. Thus, the mass collected in the trap vials during each 15 minute interval during SFE treatment was the sum of the mass of water and D822 collected. In order to determine the amount of D822 being collected, liquid-liquid extraction were performed on the vials from selected SFE runs, and the solvent extract was injected into the GC/FID for analysis. The following is a description of the procedure used, with a detailed procedure given in Appendix D.

First, exactly 30mL of toluene was added to each vial, and the vial was vigorously shaken. For vials where large amounts of D822 was collected, the solution from this vial was further diluted to 100mL with toluene to ensure that the concentration was within the calibrated range of the GC/FID. The vials were then left overnight in order to allow for water/toluene phase separation. The following day, a syringe was used to take a sample of the toluene phase, and this sample was filtered through a syringe filter to remove any solids that may be present (such as glass wool). The toluene sample was further passed through sodium sulphate to remove any residual water that could damage the GC column and then placed into a 2mL GC vial for GC/FID analysis. After GC injection, the mass of D822 collected in the trap vial was determined using Equation 17:

$$m_{D822} = \frac{(A_{total})(V_t)}{RF_{avg}}\left(\frac{1L}{1000mL}\right)\left(\frac{1g}{1000mg}\right) \qquad \text{Equation 17}$$

where m_{D822} is the mass of D822 in the trap vial (g), A_{total} is the total area count (F2+F3+F4), corrected for the average total area count (F2+F3+F4) of the toluene blanks, and V_t is the toluene volume (mL).

Chapter 4: Results and Discussion

4.1 Solubility of Distillate 822 Base Oil in Supercritical CO_2

The solubility of D822 in supercritical CO_2 at various pressures and temperatures was measured. These results were correlated to the Chrastil and modified Chrastil equations. The data collected will be used in the design of the pilot-scale continuous SFE system, since knowledge of the solute solubility in the SCF is vital in the design of such systems [88,89].

4.1.1 Solubility of D822 in Supercritical CO_2 between 10.3 and 17.2 MPa, and 35 and 50°C

The solubility of D822 in supercritical CO_2 was measured at pressures of 10.3, 14.5 and 17.2 MPa, and temperatures of 35, 40 and 50°C. The average solubility at each condition of pressure and temperature is shown in Table 6 along with the CO_2 density at the stated conditions.

Table 6: Solubility of D822 in supercritical CO_2

Pressure (MPa)	Temperature (°C)	CO_2 Density (g/mL)[a]	Average Solubility (g/g)[b]
10.3	35	0.72	0.058 +/- 0.022 [c]
10.3	40	0.65	0.041 +/- 0.006
10.3	50	0.43	0.002 +/- 0.001
14.5	35	0.81	0.089 +/- 0.014
14.5	40	0.77	0.092 +/- 0.009
14.5	50	0.69	0.058 +/- 0.011
17.2	35	0.84	0.105 +/- 0.008
17.2	40	0.81	0.092 +/- 0.024
17.2	50	0.74	0.097 +/- 0.006

[a] According to [139]

[b] Average solubility at the 95% confidence level, based on at least 6 measurements unless otherwise noted

[c] Based on four measurements

The solubility data from Table 6 is shown in Figure 17 as a function of pressure, and in Figure 18 as a function of CO_2 density.

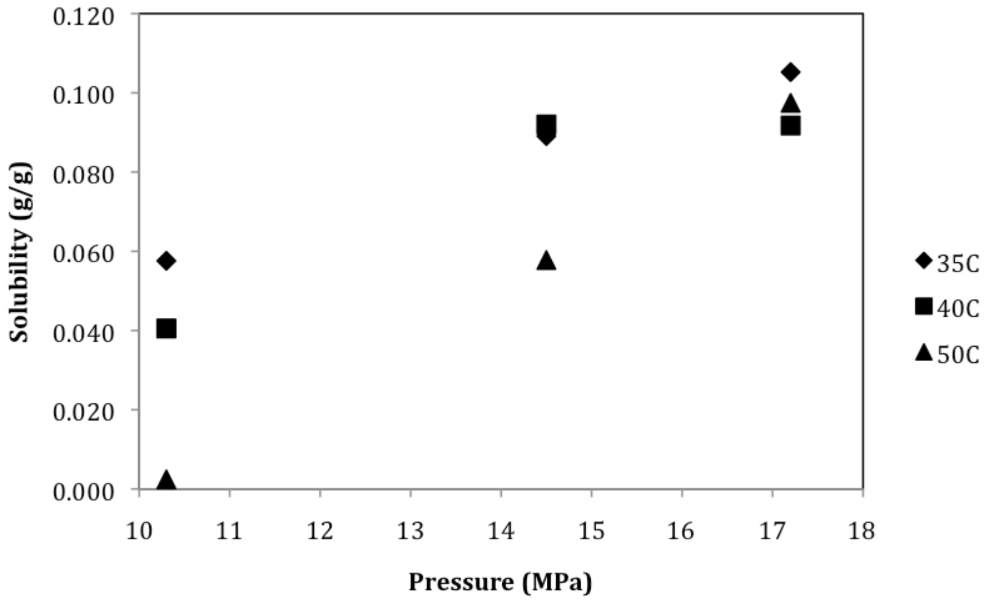


Figure 17: Solubility of D822 in supercritical CO_2 versus pressure

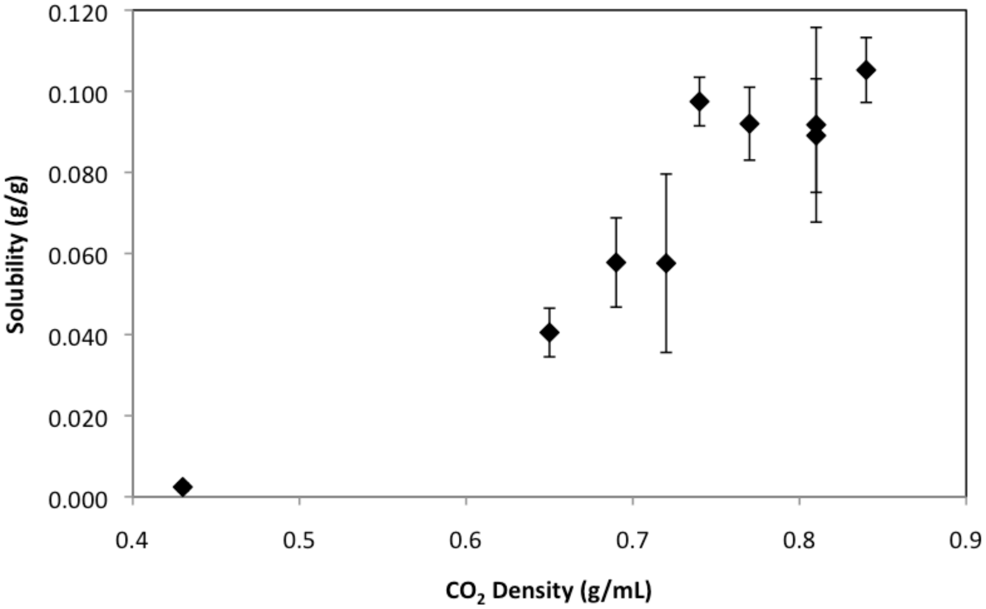


Figure 18: Solubility of D822 in supercritical CO_2 versus CO_2 density, with 95% confidence intervals shown

Figure 17 shows that at the lower pressure (10.3 MPa), the solubility decreases with increasing temperature. This result is consistent with the observation that, at pressures near the critical pressure and moderate temperatures, the solvent density has a greater effect on the solubility than the volatility of the solute, and the solubility decreases as the temperature increases (and the CO_2 density decreases) [22,92,94]. As the pressure is increased from 10.3 MPa to 14.5 and 17.2 MPa, the D822 solubility increases to near 0.100 g/g, and temperature has less of an effect on the solubility. At 17.2 MPa, all solubility measurements are near 0.100g/g, and are not significantly different at the 95% confidence level. This observation indicates that a crossover pressure likely occurs near 17 MPa, above which the solubility likely increases with increasing temperature, as the increase in solute vapour pressure is dominant over the decrease in CO_2 density. Several authors have also found crossover pressures that are well above the critical pressure for hydrocarbons and other organic solutes [89,92,95-97].

Figure 18 shows that the solubility of D822 in supercritical CO_2 increases with increasing CO_2 density, which is consistent with literature [84,91,92]. However, above a CO_2 density of 0.74g/mL the solubility appears to plateau at values near 0.100g/g, and there is no statistically significant difference in the measured solubilities at or above that density at the 95% confidence level.

Based on the 95% confidence intervals presented in Table 6, there is no significant difference between the solubilities measured at 17.2 MPa and 35, 40 or 50^oC, and those measured at 14.5 MPa and 35 or 40^oC. Therefore, the pressure chosen for further investigation during the SFE experiments was 14.5 MPa due to the lower energy requirements compared to the use of 17.2 MPa. Because diffusion limitations might occur during the SFE treatment of drill cuttings, the higher temperature of 40^oC was chosen (rather than 35^oC) for further investigation. Higher temperatures are favourable for SFE systems that are limited by diffusion [76,94]. Furthermore, conditions of 14.5 MPa and 40^oC have been proven effective for the SFE treatment of drilling wastes, including drill cuttings, contaminated with similar base oils [31,33,34].

There is no evidence of any solubility enhancement caused by the mixture of n-alkanes in D822, which agrees with the assumption made by Chartier [95]. The solubility of D822 lies between the solubilities of hexadecane ($C_{16}H_{34}$) and octadecane ($C_{18}H_{38}$) found by other authors [101,102], as seen in Figure 19. Because these two n-alkanes are among the main components in D822, the solubility of D822 would likely be larger than both of these n-alkanes if the presence of similar n-alkanes in the mixture caused an increase in the solubility of the mixture as a whole, as found by Llave et al. [106].

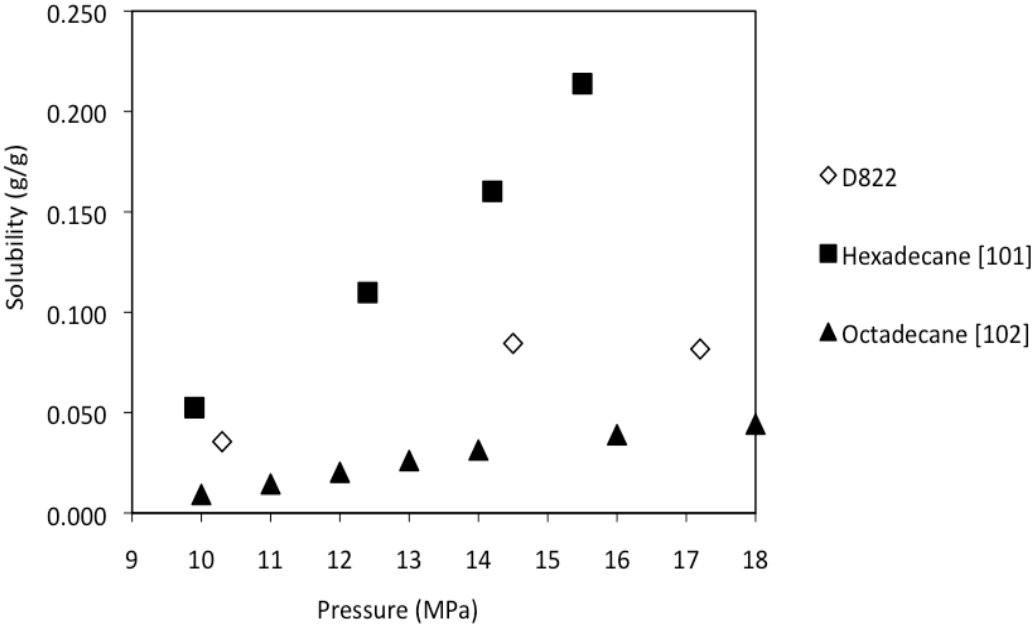


Figure 19: Solubility of D822 compared to the solubility of hexadecane [101] **and octadecane** [102] **at 40°C**

4.1.2 Validation of the Solubility Procedure

The procedure used to measure the solubility of D822 in supercritical CO_2 was validated by measuring the solubility of hexadecane ($C_{16}H_{34}$) in supercritical CO_2 and comparing the measured results to literature values.

The solubility results for hexadecane are shown in Figure 20. At 35^{o}C, the measured solubilities are systematically higher than those found by Eustaquio-Rincon and Trejo [102]. However, as seen in Figure 20, the solubility at 12.4 MPa and 35^{o}C, as measured by [102], is lower than the solubility at 12.4 MPa and 40^{o}C as measured by Nieuwoudt and du Rand [101] and in this study. Thus, the measurements made by [102] could be underestimates, because at 12.4 MPa the solubility at 35^{o}C is expected to be higher that at 40^{o}C owing to the decreased CO_2 density at 40^{o}C. At 40^{o}C, there is good agreement between the solubility measurements in this study and those made by [101], especially at the low and moderate pressures investigated. In all cases, the differences between the solubility measurements in this study and those reported in the literature are within the deviation commonly seen in the literature [101,102], due to the various techniques used to measure solubility. Thus, the procedure used in this research to measure the solubility of D822 in supercritical CO_2 is considered valid.

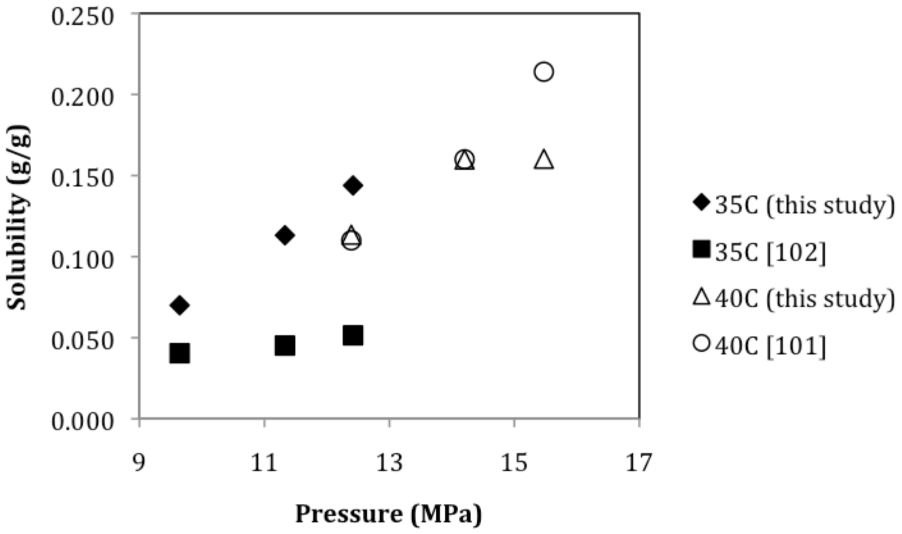


Figure 20: Solubility of hexadecane ($C_{16}H_{34}$) found in this study. Literature values at 35^{o}C found by [102] **and at 40^{o}C by** [101]

In addition, the solubility of D822 at 14.5 MPa and 40^{o}C is in agreement with the solubility of diesel oil in supercritical CO_2 measured by Lopez Gomez

[31] at the same conditions using the same apparatus and a similar method. The solubility of diesel was found to be 0.10g/g [31] and the solubility of D822 is 0.092g/g. The fact that diesel contains a lighter fraction of n-alkanes can explain the slightly higher measured solubility for diesel, because the solubility of n-alkanes in supercritical CO_2 increases with decreasing molecular weight [95,97,99,100].

The CO_2 flow rate measured using the flowmeter during the solubility experiments at 14.5 MPa and $40^{o}C$ was compared to the flow rate as measured at the pumps, in order to check the accuracy of the flowmeter. The CO_2 flow rate measured by the flowmeter was 0.71 +/- 0.12 g/min at the 95% confidence level, while the CO_2 flow rate measured at the pumps was 0.78 +/- 0.10 g/min. The confidence intervals for the flow rates measured at the pumps and at the flowmeter overlap, indicating no significant difference at the 95% confidence level. Thus, the accuracy of the flowmeter is confirmed.

4.1.3 Modeling of Solubility Data

The solubility of D822 in supercritical CO_2 was modeled using the Chrastil and modified Chrastil equations. Both models are presented in the following sections. Predictive models are important because the solubility of D822 and similar base oils in supercritical CO_2 can be predicted at different temperatures and pressures, which can reduce the number of solubility experiments needed in case the extraction conditions are modified when testing the pilot-scale continuous SFE system.

4.1.3.1 Chrastil Model

The Chrastil equation [91] was used to model the solubility results. Using a multiple linear regression analysis in Microsoft Excel™, the constants for the Chrastil model were found to be: k=7.183, A=-2952K and B=8.562 when the solubility data in Table 6 were used. The adjusted r^2 is 0.979, indicating a good fit for the model. Figure 21 shows the modeled and measured solubility values.

The average absolute relative deviation (AARD) between the modeled and measured values is 15.8%. As observed in Figure 21, the Chrastil model does not predict a crossover pressure near 17 MPa.

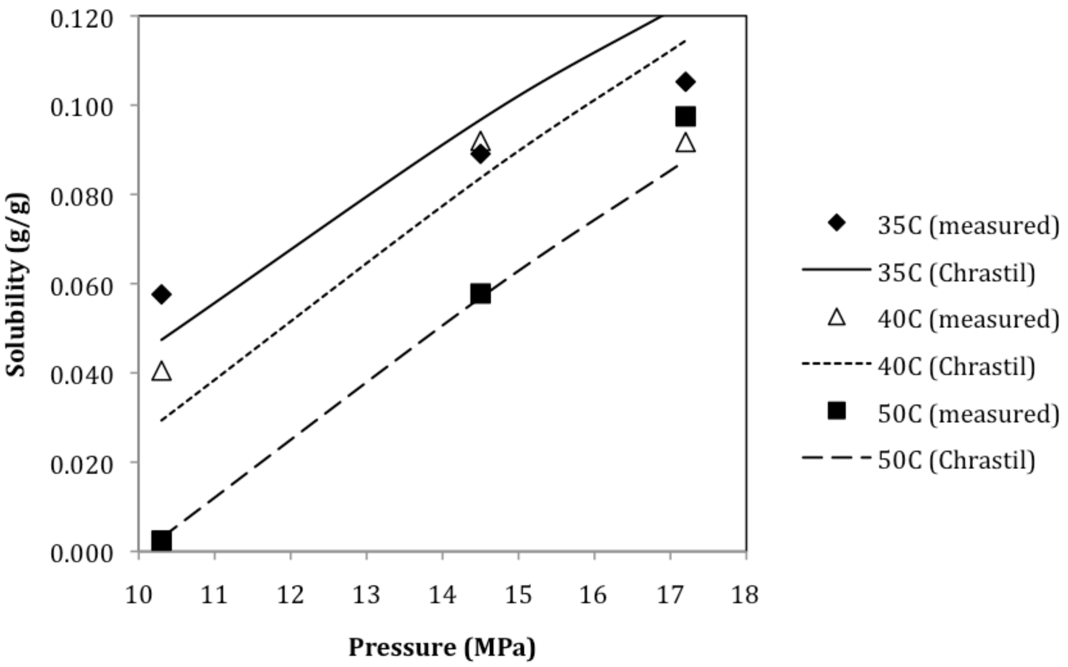


Figure 21: Comparison of the measured solubilities of D822 in supercritical CO_2 to those predicted by the Chrastil model

4.1.3.2 Modified Chrastil Model

The modified Chrastil equation [104] was also used to model the solubility of D822 in supercritical CO_2. Since the molecular weight of D822 is not known, solubilities in g/mL were used (as for the Chrastil model). The constants for the modified Chrastil model were found to be: b_0=25.33, b_1=-10561K, b_2=17.99mL/g and b_3=-3.057 using the data in Table 6. The adjusted r^2 value was 0.992, indicating an excellent fit for the data. Figure 22 shows the modeled solubility values for different temperatures and pressures, compared to the measured values. The AARD for the modified Chrastil model is 9.9%. The modified Chrastil model predicts a crossover pressure near 17 MPa, as was observed in this study.

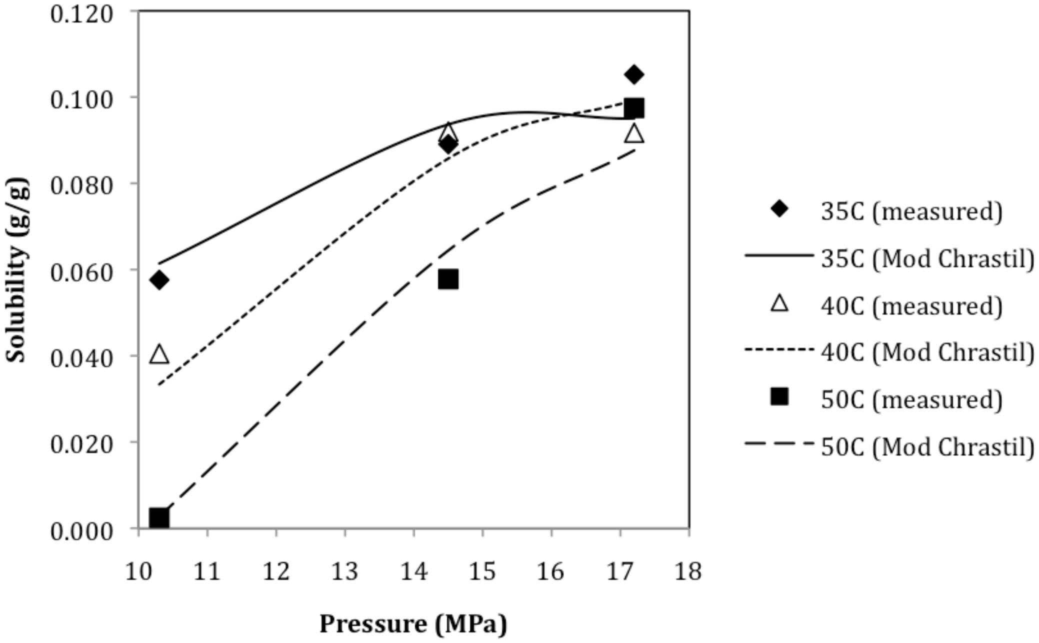


Figure 22: Comparison of the measured solubilities of D822 in supercritical CO_2 to those predicted by the modified Chrastil model

The modified Chrastil model is a better predictor of the solubility of D822 in supercritical CO_2, rather than the Chrastil model, based on the higher adjusted r^2 value and lower AARD of the modified Chrastil model, and based on the fact that the modified Chrastil model can account for the crossover pressure. Another study, in which the solubility of uracil in supercritical CO_2 was measured and modeled, also found that the modified Chrastil model was a better predictor than the original Chrastil model [105].

4.1.4 Solubility Measurement over an Extended Time Period

The solubility of D822 in supercritical CO_2 at 14.5 MPa and 40°C was measured at 5 minute intervals over a 60 minute flow period, to determine if equilibrium could be maintained in the vessel over an extended period of time. The average CO_2 flow rate was 0.72 +/- 0.02 g/min at the 95% confidence level. The solubility, as measured during each 5 minute interval, is shown in Figure 23.

The average solubility throughout the 60 minute experiment was 0.089 +/- 0.003 g/g. This confidence interval overlaps with the solubility obtained using 15 minute flow periods (see Table 6), indicating no significant difference at the 95% confidence level. Therefore, equilibrium was maintained for the 60 minute flow period at the aforementioned CO_2 flow rate. More evidence of this conclusion is the relatively flat trend in Figure 23. If equilibrium in the vessel had not been maintained over the course of the 60 minute flow period, the trend in Figure 23 would exhibit decreasing solubility measurements as the flow period proceeded.

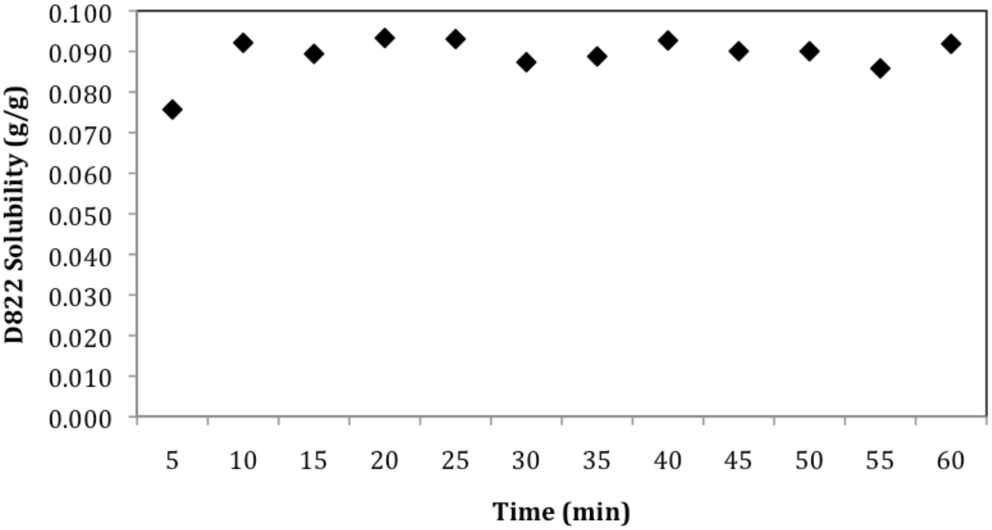


Figure 23: Solubility of D822 in supercritical CO_2, measured over an extended time interval

4.2 Apparent Solubility of D822 from Drill Cuttings in Supercritical CO_2

4.2.1 Apparent Solubility at 14.5 MPa and 40°C

The apparent solubility of D822 from drill cuttings in supercritical CO_2 was measured to determine the limiting mechanism of SFE. The experiments were conducted at the conditions chosen for further investigation (14.5 MPa and 40°C). Figure 24 shows the cumulative mass of D822 collected versus the cumulative mass of CO_2 for D822 (during the 60 minute solubility experiment) and D822 from drill cuttings.

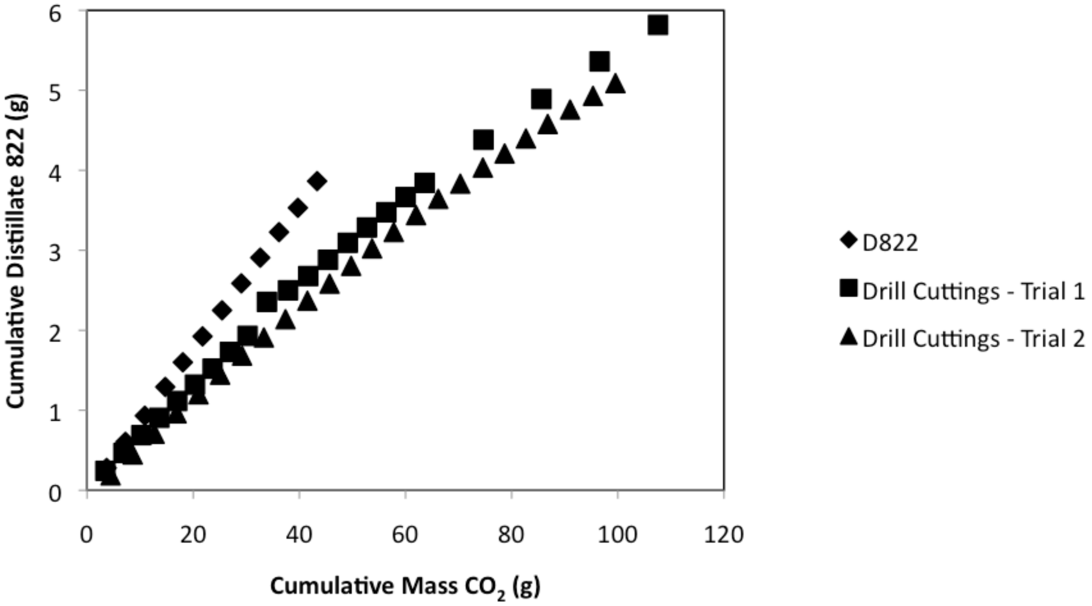


Figure 24: Cumulative mass of D822 extracted versus cumulative mass of CO_2 used for D822 (from the 60 minute solubility experiment) and D822 from drill cuttings at 14.5 MPa and 40°C

The apparent solubility is determined from the maximum slope of the data presented in Figure 24, which occurs near the beginning of the flow period. The initial slopes of the two trials are 0.070g/g and 0.063g/g, with an average apparent solubility of 0.067g/g at 14.5 MPa and 40°C. Recall that the solubility of D822 in supercritical CO_2 at the same conditions, measured over a 60 minute flow period, is 0.089g/g. Because the apparent solubility is less than the solubility (which is evident in Figure 24 because the drill cuttings lines lie below the D822 line), the SFE treatment of oily drill cuttings is not solubility limited. As discussed in section 4.1.4, equilibrium can be maintained in the extraction vessel over an extended flow period at the low CO_2 flow rates (near 0.7g/min) used in these experiments. Therefore, the lower apparent solubility is not a result of a loss of equilibrium in the vessel.

Other than solubility, SFE can be limited by adsorption/desorption or diffusion, as discussed in Section 2.4.5. Since drill cuttings, unlike soil, contain negligible organic matter, and D822 contains mainly non-polar n-alkanes, strong adsorption of D822 onto the solid phase of the cuttings is not likely the cause of the reduced apparent solubility. Although non-polar n-alkanes can sometimes become adsorbed to the surface of clays [119], which are often found in drill cuttings [43,51], this phenomenon is not expected to be significant in drill cuttings since the drill cuttings are not aged.

Instead, D822 may become trapped in the pore space of the solid phase in the drill cuttings [51], rendering the hydrocarbons more difficult to extract by SFE [76,118]. In this case, the limiting mechanism of SFE treatment is likely the diffusion of hydrocarbons from the interior of the solid phase to the exterior of the solid phase. Transfer of solute from the exterior surface of the solid phase to the CO_2 phase is likely rapid [90], and the 100rpm mixing was likely sufficient to eliminate the diffusional resistance of the solute traveling from the boundary layer to the bulk of the CO_2 phase.

As seen in Figure 24, the slopes of the apparent solubility (drill cuttings) lines decrease as the mass of CO_2 used increases. Near the end of each apparent solubility experiment, the apparent solubility dropped to between 0.04 and 0.05g/g. This observation indicates increasing diffusion resistance as more D822 is extracted from the drill cuttings, likely because the hydrocarbons that are trapped in the solid phase to a greater extent are removed after the more easily extractible hydrocarbons. Previous research has also lead to the conclusion that the SFE treatment of oily drill cuttings is increasingly diffusion limited as the flow period proceeds [31].

4.2.2 Effect of Water on the Apparent Solubility of D822 from Drill Cuttings in Supercritical CO_2

The drill cuttings used in this research were assumed to contain a small amount of water (this assumption was confirmed when the drill cuttings were analyzed for moisture content, as will be discussed later). The apparent solubility of D822 from drill cuttings that were pre-treated with silica gel was used to assess the effect of this water on SFE. Silica gel is used to remove polar compounds, including water, from various media [46]. Thus, drill cuttings should contain no free water after treatment with silica gel. The treated drill cuttings were "free flowing" after adding 0.15g of silica gel per gram of drill cuttings, indicating that the water had been removed.

Figure 25 shows the cumulative mass of D822 collected versus the cumulative mass of CO_2 used, for the "dried" drill cuttings and the plain drill cuttings. The slope of the curve for the "dried" drill cuttings is approximately the same as for the plain drill cuttings, indicating that the small amount of water present in the drill cuttings has a negligible effect on the extraction of hydrocarbons from those drill cuttings.

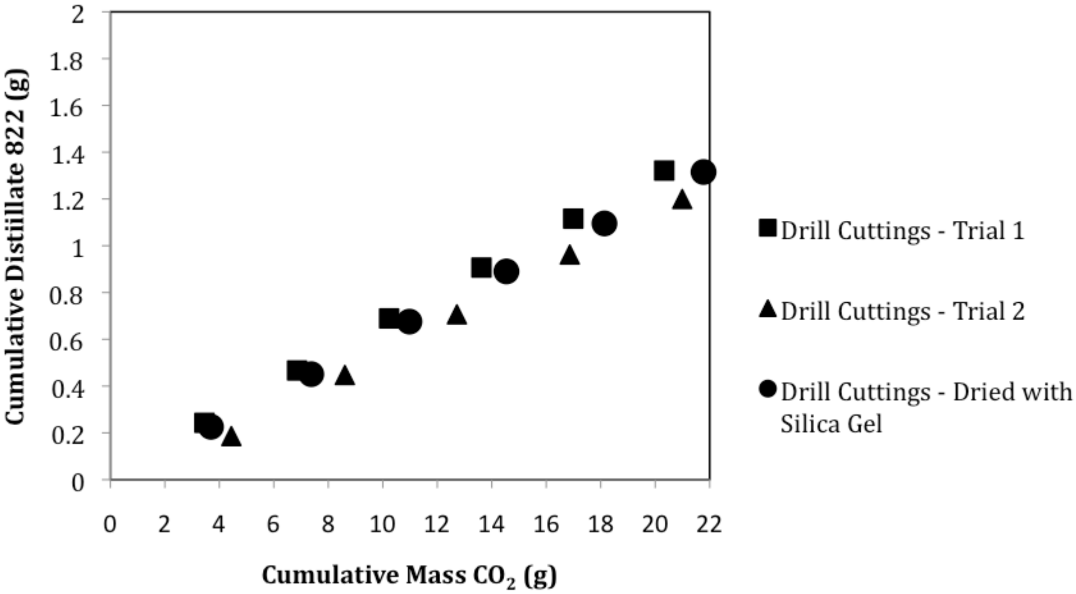


Figure 25: Cumulative D822 extracted versus cumulative CO_2 used for plain drill cuttings and "dried" drill cuttings at 14.5 MPa and 40°C

The apparent solubility of D822 from drill cuttings slurried with water (1:1 ratio of water to drill cuttings) was also determined at 14.5 MPa and 40^{o}C. However, as mentioned in Section 3.4.2, the procedure had to be modified (higher CO_2 flow rate, CO_2 flow rate measured at pumps, and toluene extraction of the collected D822 to separate the D822 from collected water). The higher CO_2 flow rate may have resulted in an underestimate of the apparent solubility, because the CO_2 may have been purged from the vessel before equilibrium was reached. The apparent solubility of the D822 from the slurry was estimated to be less than 0.001g/g (data not shown), which is almost two orders of magnitude less than the solubility of D822 at the same pressure and temperature, and significantly less than the apparent solubility of D822 from plain drill cuttings. The large amount of water added to the drill cuttings likely acts as a barrier to CO_2 penetration by filling the pores of the solid phase, and decreases the diffusion of the hydrocarbons out of the solid phase of the drill cuttings. Water dissolved in the CO_2 phase may also decrease the solvating power of the CO_2 for non-polar hydrocarbons.

4.3 Gas Chromatography Calibration Results

The calibration of the GC/FID was carried out using the CCME's *Reference Method for the Canada-Wide Standard for Petroleum Hydrocarbons in Soil – Tier 1 Method* as a guideline [46]. The first calibration was carried out in August, 2008, at the beginning of the study. A second calibration was completed in March, 2009, following some routine GC maintenance. The results of both of these calibrations are presented in the following sections.

4.3.1 Alkane Standard Solutions

Six n-alkane standard solutions in toluene were produced, each containing approximately equal amounts of decane ($C_{10}H_{22}$), hexadecane ($C_{16}H_{34}$) and tetratriacontane ($C_{34}H_{70}$). The concentration of each n-alkane in each solution is noted in Table 7. These standard solutions were used in both GC calibrations.

Table 7: n-Alkane standard solution concentrations in toluene

$C_{10}H_{22}$ Concentration (mg/L)	$C_{16}H_{34}$ Concentration (mg/L)	$C_{34}H_{70}$ Concentration (mg/L)
5.00	5.22	5.03
10.00	10.45	10.06
25.01	26.12	25.15
100.02	104.47	100.62
250.06	261.18	251.54
500.12	522.36	503.04

As required by the CCME [46], a 6.4mg/L pentacontane ($C_{50}H_{102}$) standard solution in toluene was produced, and used in both calibrations.

4.3.2 Diesel and Motor Oil Standard Solutions

Four diesel and motor oil standard solutions were used to assess the linearity of the GC/FID response, as required by the CCME guidelines [46]. The standards were used in both calibrations. Table 8 shows the concentrations of both motor oil and diesel, and the total hydrocarbon concentration in toluene.

Table 8: Hydrocarbon concentration in diesel and motor oil standard solutions

Motor Oil Concentration (mg/L)	Diesel Concentration (mg/L)	Total Hydrocarbon Concentration (mg/L)
751	252	1003
3755	1258	5013
7509	2516	10,025
37,546	12,582	50,128

4.3.3 Distillate 822 Standard Solutions

Four D822 standard solutions were used to assess the accuracy of the GC/FID in determining the concentration of this base oil. The solutions were used in both calibrations. The concentrations of D822 in toluene in the standard solutions were 1003, 5013, 10025 and 50127mg/L.

4.3.4 GC/FID Response Factor Determination

The n-alkane standards shown in Table 7 were used to determine the average response factor of the GC/FID. A typical chromatogram of an n-alkane standard solution is shown in Figure 26, and a chromatogram from the n-pentacontane solution is shown in Figure 27. The average response factors, as calculated using Equation 4, and the average retention times for the first calibration are shown in Table 9. The average response factor from the first calibration was used in all GC runs on or before March 3, 2009.

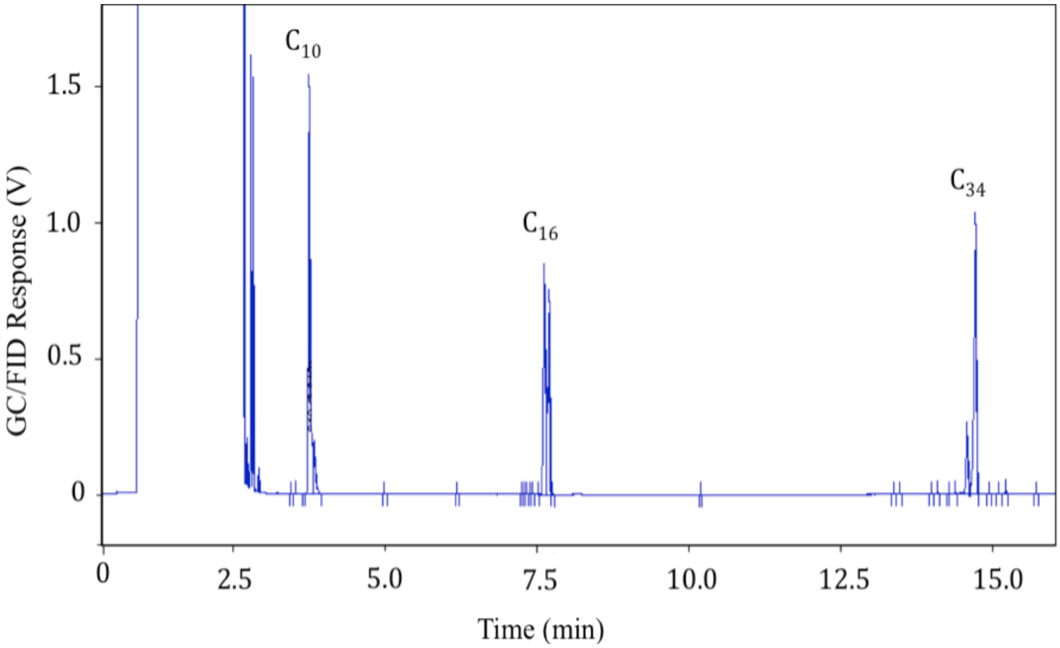


Figure 26: Typical GC/FID chromatogram for the n-alkane standard solutions. This particular chromatogram is for the 500mg/L standard solution.

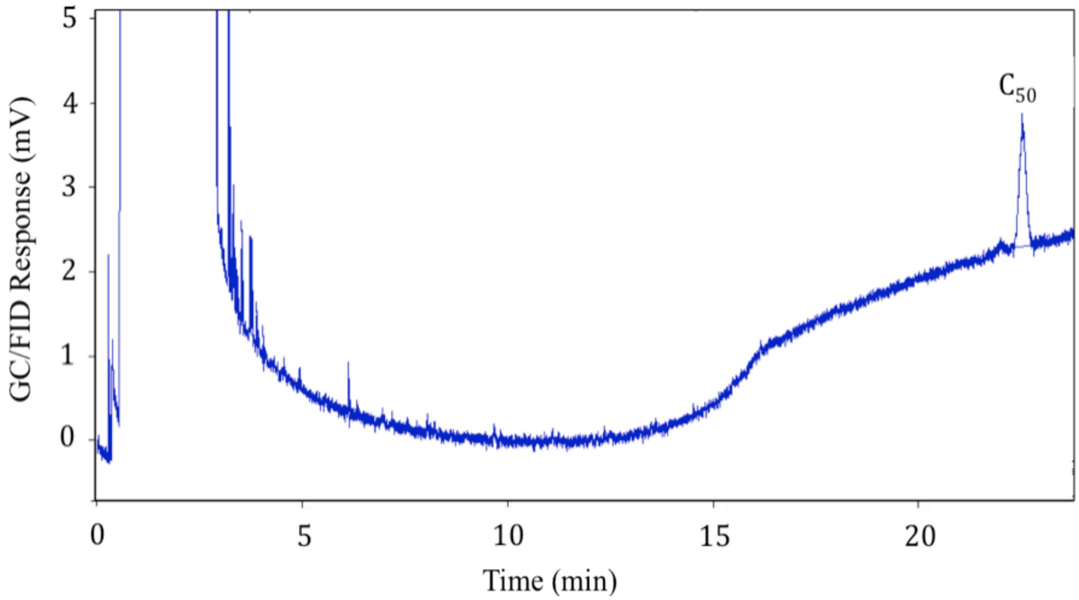


Figure 27: Chromatogram for the 6.4mg/L n-pentacontane standard solution

Table 9: GC/FID response factors and retention times for August 2008 calibration. The average response factor and retention time for each n-alkane is based on triplicate injections of the 5, 10, 25, 100, 250 and 500mg/L standard solutions.

n-Alkane	Average Response Factor $(mg/L)^{-1}$	Average Retention Time (min)
n-Decane	6967	3.77
n-Hexadecane	6789	7.63
n-Tetratriacontane	6251	14.59
Average	**6669**	N/A

The maximum deviation between response factors occurred between the decane and tetratriacontane response factors. The response factor for tetratriacontane is 10.3% lower than the response factor for decane, which is very close to the CCME's criteria of 10% [46]. The hexadecane response factor is 2.6% less than the decane response factor, and the tetratriacontane response factor is 7.9% lower than the hexadecane response factor; both are within the CCME's criteria. Although the maximum deviation (10.3%) was slightly outside of the 10% criteria set by CCME, the calibration was considered successful.

The n-pentacontane response factor was 5339, which is 20% less than the average response factor of the three lighter n-alkanes and well within the CCME's criteria of 30% [46]. The average retention time for n-pentacontane was 22.96 minutes.

The response factors for the second calibration are shown in Table 10, and the average response factor from that calibration was used for all GC runs after March 3, 2009.

Table 10: GC/FID response factors and retention times for March 2009 calibration. The average response factor and retention time for each alkane is based on triplicate injections of the 5, 10, 25, 100, 250 and 500mg/L standard solutions

n-Alkane	Average Response Factor $(mg/L)^{-1}$	Average Retention Time (min)
n-Decane	6707	3.72
n-Hexadecane	6813	7.58
n-Tetratriacontane	6018	14.56
Average	**6513**	N/A

The maximum deviation between response factors occurred between the hexadecane and tetratriacontane response factors. The response factor for tetratriacontane is 11.7% lower than the response factor for hexadecane, which again is slightly outside of the CCME's criteria [46]. The decane response factor is 1.6% less than the hexadecane response factor, and the tetratriacontane response factor is 10.3% lower than the decane response factor. It seemed as though the response factor for tetratriacontane had dropped somewhat since the previous calibration for unknown reasons. However, as will be seen, D822 contains all hydrocarbons that are smaller than tetratriacontane, and so its slightly lower response factor was not of great concern. Therefore, the calibration was deemed acceptable.

The n-pentacontane response factor was only 3083, which is 53% less than the average response factor from the three lighter n-alkanes, and well outside of the CCME's 30% criteria [46]. As explained, D822 contains no hydrocarbons larger than tetratriacontane, so the low response factor for n-pentacontane was not seen as an important issue. However, this observation further supports the theory that the GC/FID response for heavy hydrocarbons had been diminished since the first calibration.

4.3.5 GC/FID Response Linearity

The linearity of the GC/FID response for each hydrocarbon fraction (F2, F3, F4) was assessed using the diesel and motor oil standard solutions that are described in Table 8. The linearity was assessed in both calibrations, and the results from each test are shown in Figure 28 and Figure 29.

As seen in Figure 28 and Figure 29, the r^2 values for each hydrocarbon fraction, in both calibrations, are well above the minimum CCME requirement of 0.85 [46]. Thus, the GC/FID response exhibits good linearity.

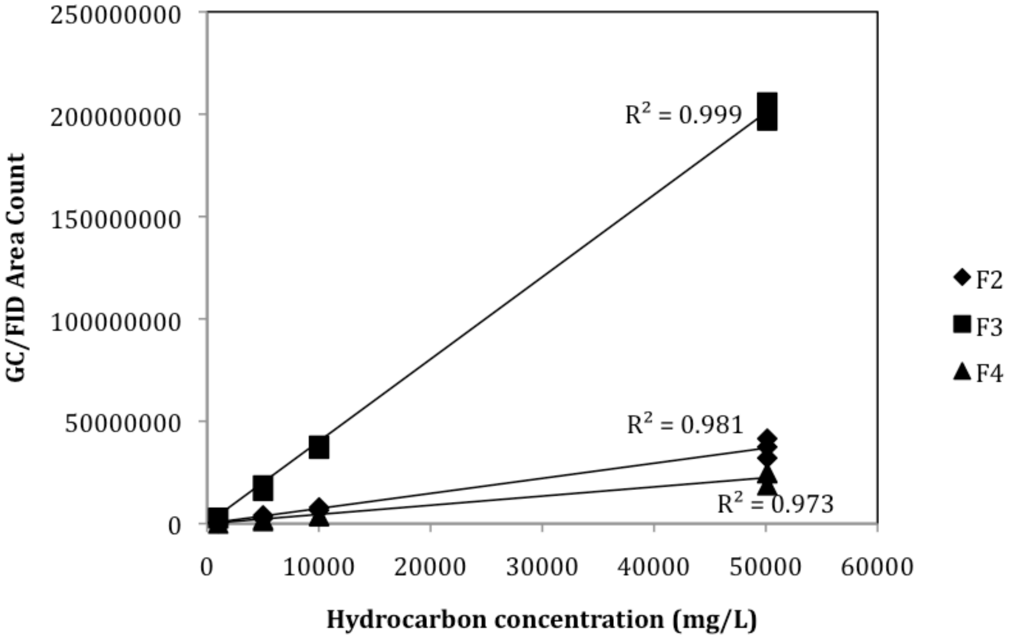


Figure 28: GC/FID response linearity assessment using diesel and motor oil standard solutions for the August 2008 calibration

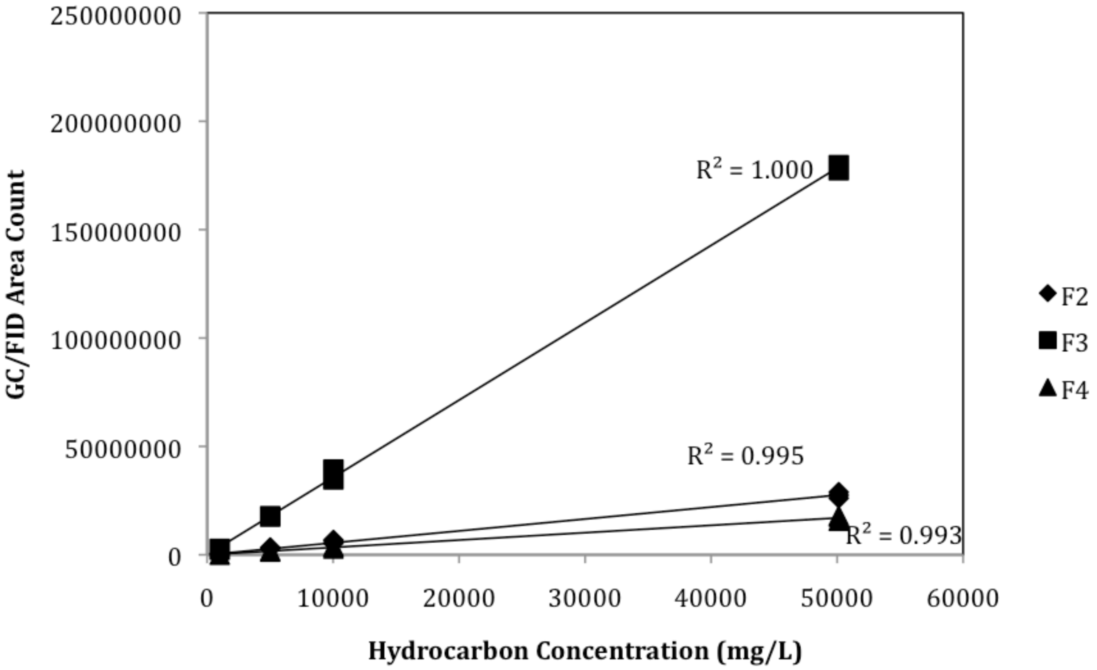


Figure 29: GC/FID response linearity assessment using diesel and motor oil standard solutions for March 2009 calibration

4.3.6 GC/FID Accuracy for Distillate 822

The D822 standard solutions were injected in triplicate in order to assess the accuracy of the GC/FID for determining the concentration of D822. The results from both calibrations are found in Table 11 and Table 12.

Table 11: GC/FID determination of the concentration of D822 in standard solution for August 2008 calibration

Hydrocarbon Concentration (mg/L)	GC/FID Determined Concentration (mg/L)[a]	Percent Error (%)
1003	961	-4.2
5013	5003	-0.21
10,025	9997	-0.30
50,127	49,879	-0.51
	Average Error:	**-1.3**

[a] GC/FID concentration found using a rearrangment of Equation 4

Table 12: GC/FID determination of the concentration of D822 in standard solution for March 2009 calibration

Hydrocarbon Concentration (mg/L)	GC/FID Determined Concentration (mg/L)[a]	Percent Error (%)
1003	971	-3.1
5013	5246	3.9
10,025	10,063	-0.33
50,127	48,121	-4.7
	Average Error:	**-1.1**

[a] GC/FID concentration found using a rearrangment of Equation 4

The results shown in Table 11 and Table 12 show that the GC/FID analysis provides very accurate concentration measurements for D822, as the absolute error in each calibration run is just over 1%. The D822 accuracy verification for March 2009 confirms that the observed drop in GC/FID response for heavier hydrocarbons (tetratriacontane and pentacontane) did not affect the GC/FID response for D822.

4.4 Dean-Stark Extraction Validation

Dean-Stark extraction was used to determine the hydrocarbon (from D822) and water content of drill cuttings and drill cuttings slurries prior to and after SFE treatment, in order that the hydrocarbon extraction efficiency could be determined on a dry mass basis. The Dean-Stark procedure was validated first using barite slurries spiked with D822, to ensure that the method produced accurate results for drill cuttings slurries. Second, the hydrocarbon content of drill cuttings (no water added) determined using Dean-Stark extraction was compared to the hydrocarbon content determined using Soxhlet extraction, which is a proven method for determining the hydrocarbon content of drill cuttings [31,33]. Soxhlet extraction was not used in this research because the method is not valid for slurries [46].

4.4.1 Dean-Stark Analysis of Spiked Slurries

Three spiked slurries, containing 1.1, 4.8 and 14.6% D822 on a dry mass basis, were analysed in triplicate using Dean-Stark extraction followed by GC/FID analysis, to determine the accuracy of the procedure. The results of these analyses are shown in Table 13.

The average error in the hydrocarbon content, on a dry mass basis, was 3.0%, and the AARD was 7.6%. The maximum absolute error was 18.2%, obtained on the slurry containing 1.1% D822 (the measured hydrocarbon content was 1.3%, so the larger percent error is due to the low hydrocarbon concentration).

The Dean-Stark extraction on the spiked slurry containing 1.1% (dry mass basis) D822 yielded a hydrocarbon content of 1.23 +/- 0.16% at the 95% confidence level. This confidence interval includes 1.1%, so there is no statistical difference between the measured and actual hydrocarbon content. The same was true for the slurries containing 4.8 and 14.6% D822. For the 4.8% slurry, the measured hydrocarbon content was 4.87 +/- 1.17%. For the 14.6% slurry, the measured hydrocarbon content was 14.0 +/- 1.21%. Therefore, Dean-Stark extraction and subsequent GC/FID analysis can accurately determine the hydrocarbon content in drill cuttings slurries.

The average error for solids content was 5.7%, with an AARD of 7.3%, indicating that Dean-Stark analysis can accurately determine the solids content of slurries. The greatest errors were 17.4 and 36.1%. These large errors occurred on two samples that were the last remaining slurry, and so these samples were likely not representative of the overall slurry. If these two samples are not considered, all absolute errors were less than or equal to 3.2%.

The average error for the water content was -5.4%, with an AARD of 7.1%. The greatest errors occurred in the same samples as the large errors in the solids content. Again, these large errors were likely due to slurry heterogeneity in the last remaining slurry. If these two samples are not considered, all absolute errors were less than 3%.

Based on these results, the Dean-Stark extraction is capable of determining the hydrocarbon, solids and water content of slurries accurately.

Table 13: Dean-Stark analysis of barite slurries spiked with D822

Trial	Component	Known concentration (mass%)	Calculated concentration (mass%)	Percent Error (%)
1	Hydrocarbons[a]	1.1	1.30	18.2
	Solids	49.5	48.1	-2.8
	Water	49.9	51.3	2.8
2	Hydrocarbons[a]	1.1	1.22	10.9
	Solids	49.5	48.2	-2.6
	Water	49.9	51.2	2.6
3	Hydrocarbons[a]	1.1	1.17	6.4
	Solids	49.5	48.7	-1.6
	Water	49.9	50.7	1.6
4	Hydrocarbons[a]	4.8	4.45	-7.3
	Solids	47.0	48.5	3.2
	Water	50.6	49.3	-2.6
5	Hydrocarbons[a]	4.8	4.77	-0.6
	Solids	47.0	47.6	1.3
	Water	50.6	50.0	-1.2
6	Hydrocarbons[a]	4.8	5.38	12.1
	Solids	47.0	55.2	17.4
	Water	50.6	41.7	-17.6
7	Hydrocarbons[a]	14.6	14.1	-3.2
	Solids	43.2	43.3	0.2
	Water	49.4	49.6	0.4
8	Hydrocarbons[a]	14.6	14.4	-1.6
	Solids	43.2	43.1	-0.2
	Water	49.4	49.6	0.4
9	Hydrocarbons[a]	14.6	13.4	-8.0
	Solids	43.2	58.8	36.1
	Water	49.4	32.1	-35.0

[a] Hydrocarbon content was measured on a dry mass basis

4.4.2 Dean-Stark versus Soxhlet Extraction of Untreated Drill Cuttings

The hydrocarbon content of untreated drill cuttings (no water added), measured using Dean-Stark extraction, was compared to the hydrocarbon content measured using Soxhlet extraction. A wet mass basis was used for comparison because Soxhlet extraction cannot determine the water content directly.

The Dean-Stark extractions yielded a hydrocarbon content of 15.1 +/- 1.5% at the 95% confidence level on a wet mass basis. The Soxhlet extractions yielded a hydrocarbon content of 13.8 +/- 1.6%. These two confidence intervals overlap, indicating that Dean-Stark extraction is equivalent to Soxhlet extraction for plain drill cuttings at the 95% confidence level.

4.5 Drill Cuttings Characterization

A total of 14 Dean-Stark extractions were carried out on untreated drill cuttings in order to determine the hydrocarbon (from D822), solids and water content. The extractions were performed throughout the entire course of the research, so that the measured composition of the drill cuttings is representative of the entire batch of cuttings used. Table 14 shows the composition of the untreated drill cuttings used in this research.

Table 14: Composition of untreated drill cuttings

Component	Basis	Mass Percentage (%)[a]
Hydrocarbon	Dry	17.7 +/- 1.4
Hydrocarbon	Wet	17.2 +/- 1.3
Solids	Wet	79.9 +/- 1.5
Water	Wet	3.0 +/- 0.23

[a] Calculated at the 95% confidence level, based on 14 measurements

A chromatogram of the extract from untreated drill cutting is shown in Figure 30, along with the decane, hexadecane and tetratriacontane peaks, which divide up the F2 and F3 hydrocarbon fractions. The chromatograms show that D822, the base oil found in the drill cuttings, contains only F2 and F3 hydrocarbons. The ratio of F2 to F3 hydrocarbons is 0.642 +/- 0.017 at the 95% confidence level.

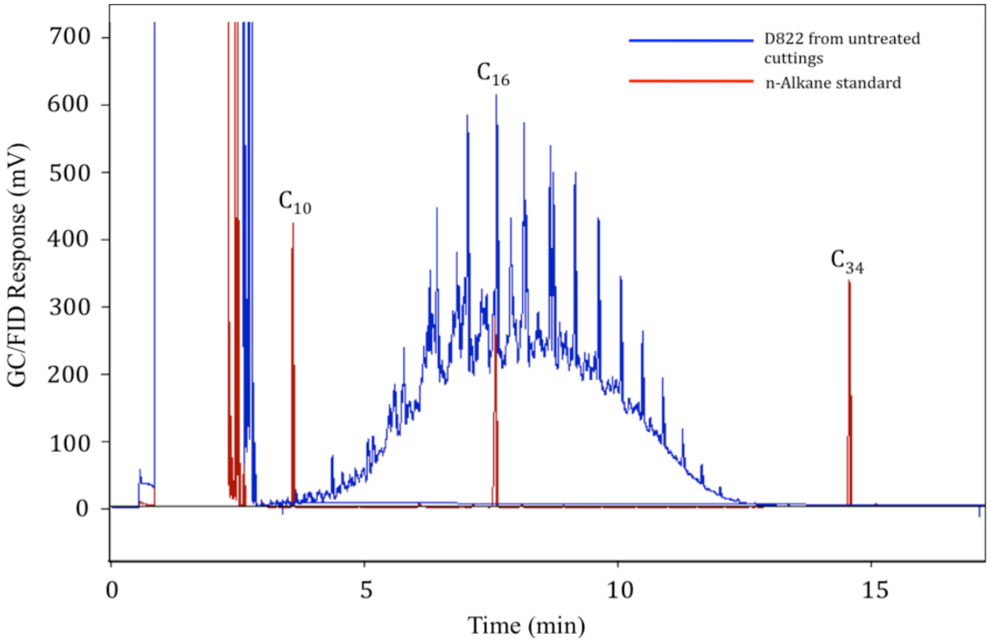


Figure 30: Chromatogram of D822 extracted from untreated drill cuttings, and the n-alkanes that divide the F2 and F3 hydrocarbon fractions

The specific gravity of the untreated oily drill cuttings was estimated to be 1.67. The untreated drill cuttings have the consistency of a thick sludge, with oil coating solid chunks that are no bigger than about 5mm in diameter. The drill cuttings were not free flowing (they did not take the shape of the container they were in unless left for an extended period of time). They are dark brown to black in colour, and have a distinctive hydrocarbon odour. Figure 31 shows a picture of the untreated drill cuttings.

Figure 31: Untreated drill cuttings containing D822 base oil

4.6 Drill Cuttings Slurries Prior to SFE Treatment

Slurries containing 0.5:1, 1:1, 2:1 and 5:1 water to cuttings ratios were produced. In all cases, the drill cuttings and water were immiscible upon contact, owing to the immiscibility of the D822 and water. Prior to agitation or stirring, the drill cuttings were present at the bottom of the slurry, with a separate water phase on top.

Stirring with a laboratory spoonula did little to mix the oily drill cuttings with the water. Any oily drill cuttings that did become suspended during stirring immediately settled when stirring was stopped, and the distinct cuttings and water phases reformed rapidly.

Vigorous wrist action shaking of the slurries was required to effectively mix the drill cuttings and water. After one minute of vigorous shaking, a dark grey slurry was formed. However, once shaking was halted, the drill cuttings rapidly settled to the bottom and the water and cuttings phases reformed. After shaking, stirring with a spoonula revealed that the slurry could be easily re-suspended again. However, large chunks of drill cuttings were persistent throughout the slurry and settled rapidly after stirring.

Figure 32 shows the slurries after they have been left to settle for several minutes.

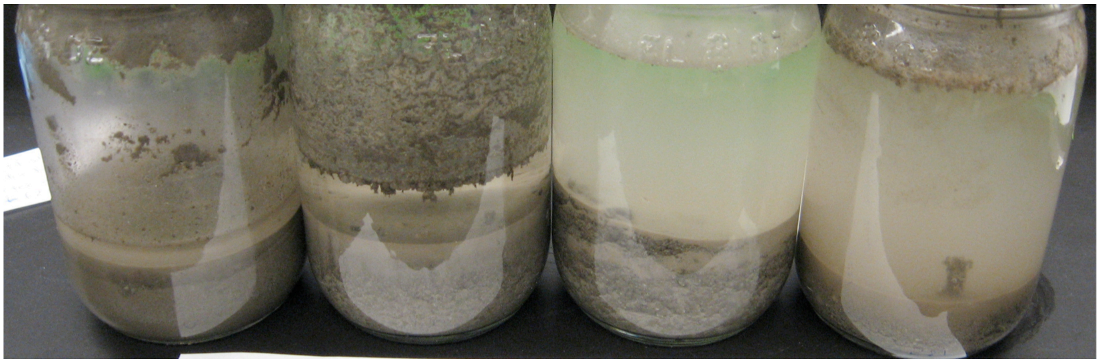


Figure 32: Drill cuttings slurries prior to SFE treatment, after being left to settle for several minutes (from left to right: 0.5:1, 1:1, 2:1 and 5:1 slurry)

All slurries produced were suitable to be pumped because they were “flowable” and “pourable” despite the solids settling issue. During pumping, the solids should remain suspended due to turbulence in the flow.

An attempt was made to grind the drill cuttings by mashing them with the spoonula. However, chunks of drill cuttings quickly reformed, and the technique was deemed ineffective at producing a well-mixed, non-settling slurry.

4.7 SFE of Drill Cuttings Slurries

The drill cuttings slurries (with water to drill cuttings ratios of 0.5:1, 1:1, 2:1 and 5:1) were treated by SFE to assess how the water content affected the hydrocarbon (D822) extraction efficiency. All SFE experiments were conducted at 14.5 MPa and 40°C. Mixing was carried out at 100rpm and the CO_2 flow rate was maintained near 38g/min during the 90 minute flow period, which followed an initial 15 minute static period. Further details on the extraction conditions are found in Section 3.5. Initially, a total of 25 SFE experiments were conducted on the aforementioned slurries. The extraction efficiency of each SFE experiment was determined by comparing the hydrocarbon content of the slurries before and after SFE treatment, as determined by Dean-Stark extraction and subsequent GC/FID analysis.

4.7.1 Slurries with Constant Drill Cuttings Mass

In the first set of experiments, each slurry was produced by maintaining a fixed mass of drill cuttings (approximately 25g) and varying the volume of water added. Therefore, the overall slurry volume varied for each water to cuttings ratio tested. The 0.5:1, 1:1, 2:1 and 5:1 slurries had approximate volumes of 27, 40, 65 and 140mL, respectively. In addition, drill cuttings (no added water) were also treated using SFE and the extraction efficiency determined. The helical impeller was used.

The average hydrocarbon extraction efficiencies for each slurry and plain drill cuttings are shown in Figure 33. Each experiment was conducted in triplicate, except for the 1:1 slurry experiment, where four experiments were conducted.

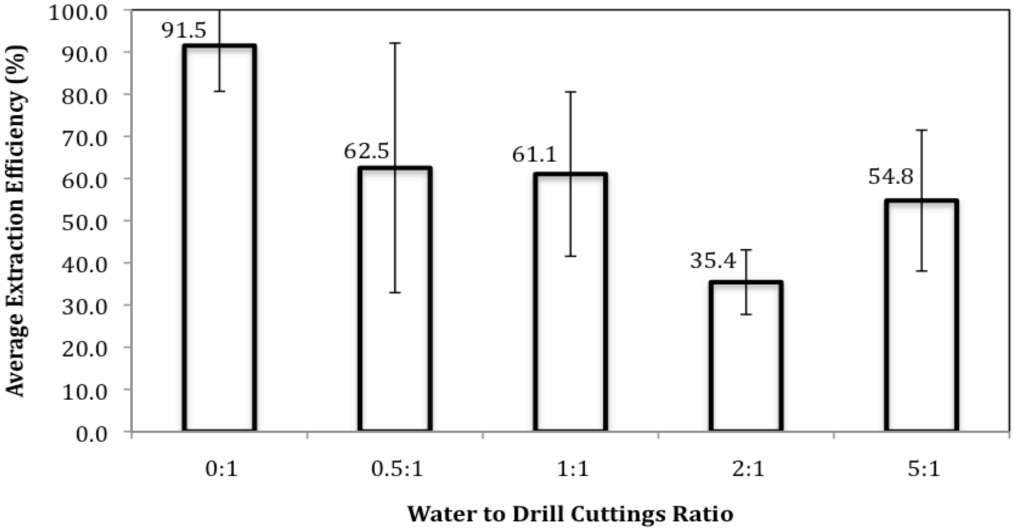


Figure 33: The average hydrocarbon extraction efficiency from 25g of drill cuttings slurried with water at 14.5 MPa, 40^{o}C, and 100rpm mixing with the helical impeller. The error bars represent the two-sided 95% confidence interval.

The hydrocarbon extraction efficiencies from drill cuttings slurries are lower than that of plain drill cuttings, as indicated in Figure 33. On average, over 90% of the hydrocarbons were removed from plain drill cuttings. When water was added to make 0.5:1 and 1:1 slurries, the average extraction efficiency fell to just over 60%. Only about 35% of the hydrocarbons were removed from the 2:1 slurries. However, further water addition up to a ratio of 5:1 lead to a slight increase in extraction efficiency over that of the 2:1 slurry, with about 55% of the hydrocarbons removed. Statistically speaking, the hydrocarbon extraction efficiencies from the 1:1, 2:1 and 5:1 slurries are lower than the extraction efficiency from drill cuttings (no water added) at the 95% confidence level. However, the extraction efficiency from the 0.5:1 slurry is not significantly lower. These lower extraction efficiencies from drill cuttings slurries with higher water contents (i.e 1:1 ratio and greater) are consistent with the results obtained from previous researchers who studied the SFE treatment of soil slurries [38,39].

There is no statistical difference between the extraction efficiencies from the 0.5:1, 1:1, 2:1 and 5:1 slurries at the 95% confidence level. The lack of statistical difference (at the 95% confidence level) of the extraction efficiency from the 2:1 slurry compared to the other slurries is assumed to be a result of the low number of samples (i.e. three in most cases), which increases the confidence interval width. A statistical difference between the extraction efficiency from the 2:1 slurry and the extraction efficiencies from the other slurries exists at the 91% confidence level. Therefore, the extraction efficiency from the 2:1 slurry is assumed to be lower than the extraction efficiencies from the other slurries.

The lower hydrocarbon extraction efficiencies from the slurries relative to the extraction efficiency from drill cuttings (no water added) can be explained. First, excess water may act as a barrier to CO_2 penetration (the “shielding” effect), as described by other researchers [38,123], because supercritical CO_2 and water are not miscible with each other (water solubility in supercritical CO_2 at 14.5 MPa and 40°C is of the order of 10^{-3}g/g) [128,129]. Second, excess water in the pores may further hinder the diffusion of the hydrocarbons out of the drill cuttings, which has been shown to be the most likely limiting factor during SFE treatment (even before water is added). Third, water dissolved in the CO_2 phase increases the polarity of the CO_2 phase, and therefore reduces the solubility of non-polar species such as the hydrocarbons found in D822. However, since the process is not solubility limited, this factor is assumed to be less than the other factors.

The reason for the increase in SFE efficiency when the water to cuttings ratio is increased to 5:1 is not clear. One possible explanation is that the drill cuttings particles are more dispersed when the water content is high, as in the 5:1 slurry, resulting in greater contact of the oil-laden solid particles with the CO_2. Another possible explanation is that the 5:1 slurry volume was higher, and therefore the slurry filled more of the extraction vessel. Since the interface of the 5:1 slurry with the CO_2 phase occurred closer to the CO_2 inlet to the vessel (which was a few inches below the vessel lid), better CO_2-drill cuttings contact may have occurred in the 5:1 slurry as compared to the other slurries.

The results above suggest that, for a fixed mass of drill cuttings, the 0.5:1, 1:1 and 5:1 slurries result in the highest hydrocarbon extraction efficiencies.

4.7.2 Slurries with Constant Volume

To check the possibility that the slurry volume had an effect on the extraction efficiency, a second set of experiments was conducted using a constant slurry volume. Only slurries containing 1:1, 2:1 and 5:1 water to cuttings ratios were tested, each in triplicate. In each case, the slurry volume was approximately 60mL, meaning that a varying mass of drill cuttings was used in each. The 1:1, 2:1 and 5:1 slurries contained approximately 38, 23 and 11g of drill cuttings, respectively. The extraction efficiencies from each of the slurries are shown in Figure 34.

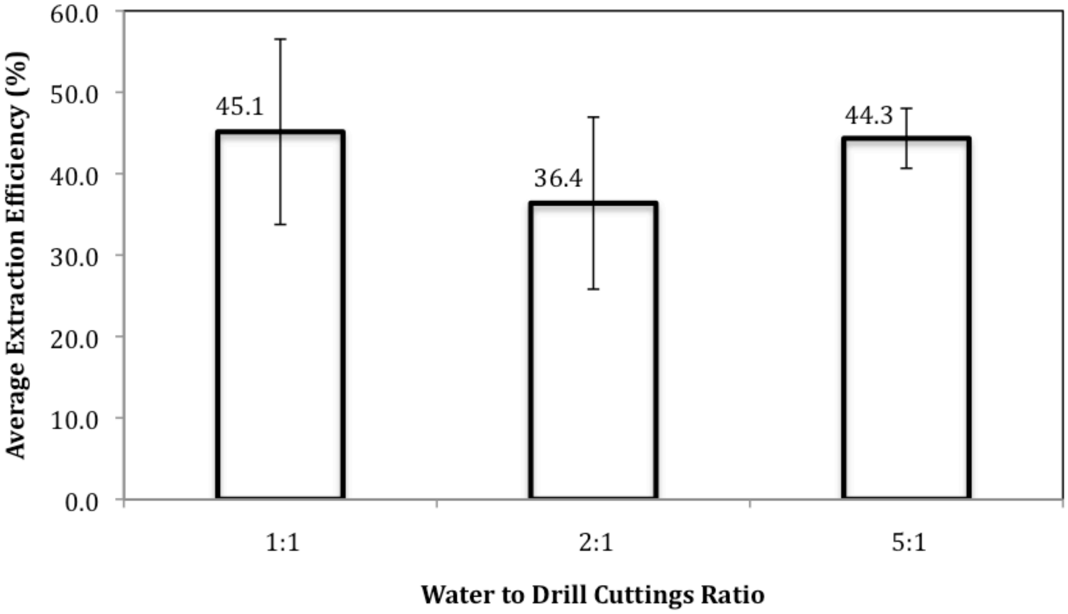


Figure 34: The hydrocarbon extraction efficiencies from 60mL of drill cuttings slurry at 14.5 MPa, 40°C, and 100rpm mixing with the helical mixer. The error bars represent the two-sided 95% confidence interval.

The mass of drill cuttings and/or the slurry volume affect the hydrocarbon extraction efficiency, as can be seen by comparing the extraction efficiencies of the 1:1, 2:1 and 5:1 slurries in Figure 33 (constant drill cuttings mass) to those in Figure 34 (constant slurry volume). In the 1:1 slurry, the average extraction efficiency dropped from 61.1% to 45.1% when the drill cuttings mass was increased from 25g to 38g, and the slurry volume was increased from 40 to 60mL. However, there was no significant difference between these average extraction efficiencies at the 95% confidence level, but this lack of statistical difference is likely a result of the low number of trials (i.e. 3). There is a significant difference at the 81% confidence level. An increase in the mass of drilling waste treated has lead to a decrease in extraction efficiency in other studies [34,37].

The extraction efficiency from the 2:1 slurry was similar in both the experiments with constant drill cuttings mass and constant slurry volume (35.4 versus 36.4%) because in each case, the drill cuttings and slurry volume were nearly identical (25 versus 23g, 65 versus 60mL). In this case, the 95% confidence intervals from both experiments (constant drill cuttings mass and constant slurry volume) overlap to a great extent.

The extraction efficiency from the 5:1 slurry decreased from 54.8% to 44.3% when the drill cuttings mass was reduced from 25 to 11g, and the slurry volume reduced from 140 to 60mL. The likely explanation is that the lower slurry volume meant that there was greater dead volume in the extraction vessel, and thus less contact between the CO_2 and the slurry. Once again, there was no significant difference between these average extraction efficiencies at the 95% confidence level, but this lack of statistical difference is likely a result of the low number of trials. There is a significant difference at the 84% confidence level.

Therefore, the drill cuttings mass and slurry volume likely both affect the extraction of D822 from drill cuttings using this particular SFE extraction vessel. Unfortunately, distinguishing between the effects of drill cuttings mass and slurry volume is impossible, and not one of the objectives of this research. However, the results do suggest that the extraction efficiencies are lower for slurries compared to plain drill cuttings, regardless of water content, drill cuttings mass or slurry volume.

4.7.3 Mass-based Extraction Results

In all SFE experiments, trap vials were used to collect the extracted D822 (hydrocarbons). The trap vials for the first 15 minute interval of selected experiments are shown in Figure 35. Figure 35 shows that the amount of D822 collected varied according to how much water was present in the slurry, with more D822 collected from drill cuttings with no water added (0:1) and less D822 collected from drill cuttings slurries.

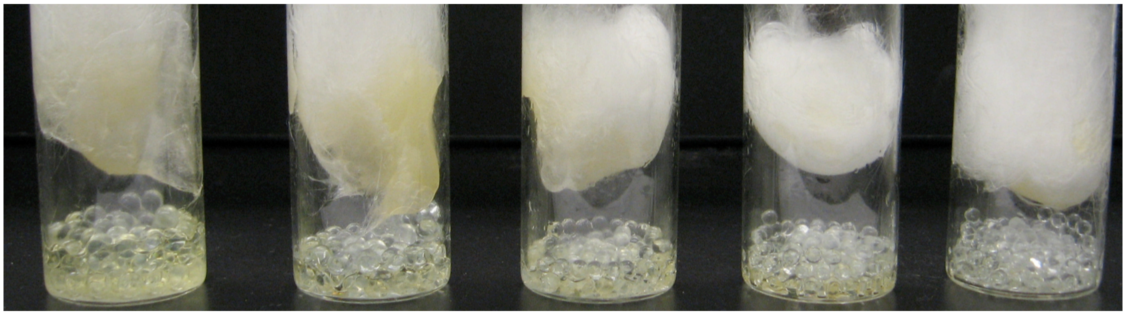


Figure 35: Trap vials containing D822 (yellow liquid) and water, extracted during the first 15 minute interval of SFE treatment of slurries with varying water content (from left to right: 0:1, 0.5:1, 1:1, 2:1 and 5:1 slurries).

When SFE was performed on slurries, water was visibly present in the trap vials. The average mass collected in the trap vials was 3.57g for the plain drill cuttings and 4.11g for the 1:1 slurry. If this data alone was used to judge the effectiveness of SFE treatment, one might conclude that SFE was more effective when a slurry was treated. However, Figure 33 shows that this conclusion would be incorrect. When Lopez Gomez concluded that the extraction of diesel from a 1:1 water to drill cuttings slurry was equally as effective as the extraction of diesel from plain drill cuttings, he did so based on the weight of the collected diesel in the trap vials [31], which did not account for any water which may have also been collected.

Liquid-liquid extractions on the trap vials from the constant slurry volume extractions were performed to resolve how much D822 and water was collected. Figure 36 shows the average cumulative mass of D822 collected during SFE treatments of the slurries, normalized for drill cuttings mass (because the mass of drill cuttings in the slurries varied). There are two important points to note from Figure 36. First, the mass of D822 collected from the 1:1 slurries is highest, which is reasonable since the hydrocarbon extraction efficiency was highest from those slurries. The mass collected was lowest from the 2:1 slurries, which had the lowest extraction efficiency. Second, most of the D822 was collected in the first 15 minutes of the extraction, independent of the slurry tested. After 15 minutes, the amount of D822 extracted diminishes greatly and the rate of extraction becomes relatively constant. This pattern of extraction is consistent with one that is diffusion limited [121], which is the case in the SFE treatment of drill cuttings and their slurries. The slight increase in slope in the final 15 minute interval (75 to 90 minutes) is due to the fact that the carryover vial's D822 was added on at the end.

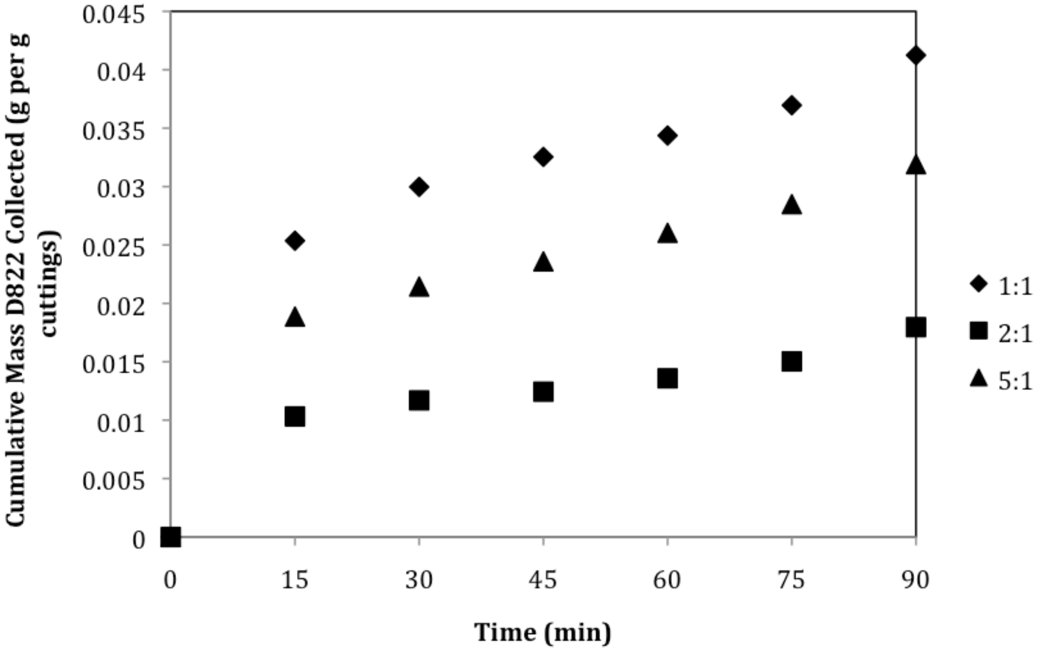


Figure 36: Cumulative mass of D822 collected per gram of drill cuttings over the course of SFE treatment (average of all 3 trials) for 60mL slurries with varying water to drill cuttings ratios

Figure 37 shows the cumulative water collected over the course of the extractions, normalized for drill cuttings mass. As expected, more water is collected per gram of drill cuttings as the water content in the slurry increases.

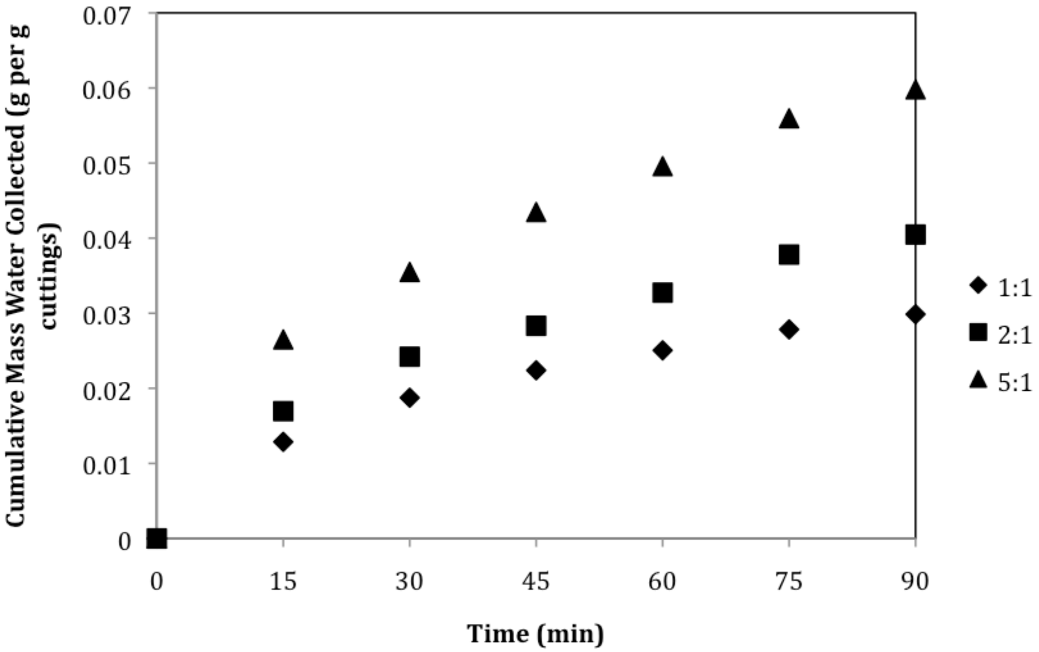


Figure 37: Cumulative mass of water collected per gram of drill cuttings over the course of SFE treatment (average of all 3 trials) for 60mL slurries with varying water to drill cuttings ratios

The solubility of water in supercritical CO_2 is about 0.002g/g at 14.5 MPa and 40°C, based on the data of King et al. [128] and later confirmed by Sabirzyanov et al. [129]. It should be noted that this value was calculated using the solubility calculator developed by Stiver and Rampley [140], and is based on the Chrastil modeling of the data set found by King et al. [128]. By multiplying this solubility by the mass of CO_2 used throughout an SFE experiment, the maximum amount of water that could be extracted due to solubilization was found, and is shown in Table 15. By comparing this mass with the actual mass of water extracted (which was determined by comparing the water content of the slurry before and after SFE treatment using Dean-Stark analysis), the mechanism of water extraction can be inferred. As seen in Table 15, the maximum mass of water that could be extracted by solubilization of the water in CO_2 is greater than the mass of water actually extracted. Therefore, the water that was extracted and collected with the D822 can be explained by solubilization. Another study also found that water was being extracted during the SFE treatment of wet soils, and the water extracted was attributed to the slight solubility of water in CO_2 [131]. However, this observation does not rule out water entrainment in the exiting CO_2 stream as another factor contributing to the water collected.

Table 15: Water extracted and maximum water extracted via solubility for the 60mL slurry SFE experiments

Slurry Type	Average Mass CO_2 Used (g)	Maximum Water Extracted via Solubility[a] (g)	Average Water Extracted[b] (g)
1:1	3395	6.79	2.13
2:1	3409	6.82	2.48
5:1	3361	6.72	2.58

[a] Estimate calculated by the product of the average mass of CO_2 (g) and the solubility of water in CO_2 (g/g), based on water solubility data found by King et al. [128] and confirmed by Sabirzyanov et al. [129]

[b] Based on the slurry water content before and after SFE treatment, as determined by Dean-Stark analysis

Water collection has important implications for the pilot-scale continuous SFE system to be developed, and the commercialization of this drill cuttings treatment technique. In particular, the water would likely have to be removed prior to the reuse of the collected base oil, and this would add an extra step in the process.

The average cumulative mass of D822 and water collected over the course of SFE treatment of the 1:1 slurries (60mL slurry volume) is shown in Figure 38. The amount of water collected is only slightly lower than the amount of D822 collected. Besides this important point, there is another important observation: Based on the average D822 content of the untreated drill cuttings (17.2% on a wet basis), the initial slurry, which contained 38g of drill cuttings, should contain about 6.5g of D822. From Figure 34, the average extraction efficiency from the 1:1 60mL slurry is 45.1%. Therefore, the expected mass of D822 collected should be about 45.1% of 6.5g, or about 2.9g. However, only an average of 1.61g was collected, as seen in Figure 38. Therefore, it can be concluded that the D822 collection system is not 100% efficient. In fact, for the 1:1 slurries, the trapping system was only about 55% efficient on average. Inefficient trapping can be attributed to the entrainment of base oil in the exiting gas stream [11]. Several authors note that solid phase cryogenic (cold) trapping, which was employed in this research, is inefficient due to the loss of volatiles and even semi-volatile compounds [86,93,118]. Based on this conclusion, the mass of D822 collected should not be used to assess the efficiency of SFE treatment. Instead, only the validated Dean-Stark and GC/FID analysis should be used. However, the mass of D822 collected over time during the extraction (Figure 36) can still be used to assess the relative rates of hydrocarbon extraction, and how they change as SFE treatment proceeds.

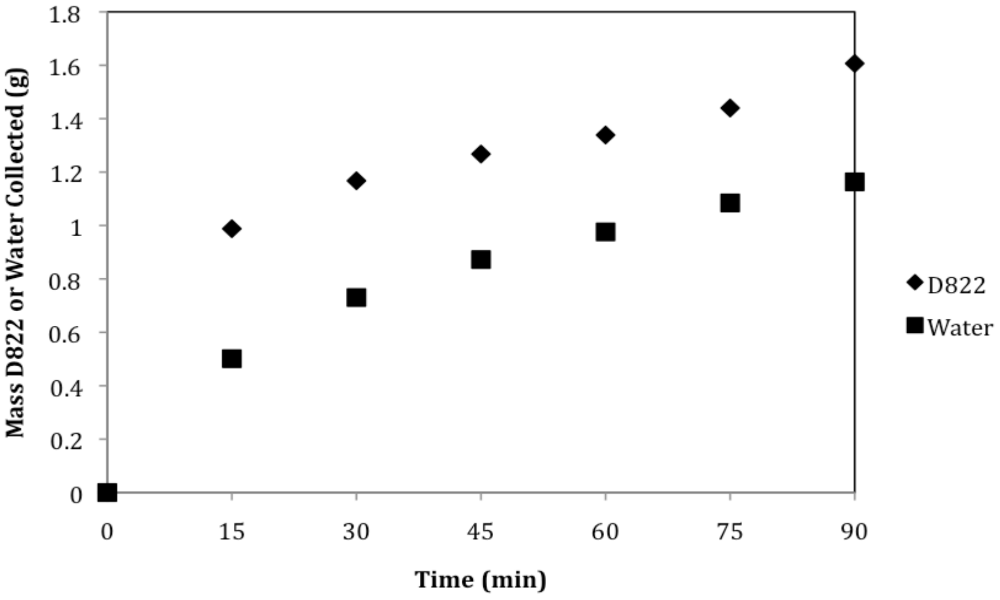


Figure 38: Average cumulative mass of D822 and water collected over the course of SFE treatment for 1:1 slurry containing approximately 38g of drill cuttings

4.8 Drill Cuttings Slurries After SFE Treatment

In addition to being free-flowing and “pumpable” before SFE treatment, the slurries must also be free-flowing after SFE treatment, so that, if a continuous

SFE system is used, the treated slurry can easily flow out of the continuous extraction column. All slurries, except for the 0.5:1 slurry, were free-flowing after SFE treatment. The 0.5:1 slurry was lumpy, and resembled a thick sludge that did not take the shape of the container it was placed in. This slurry was not free-flowing.

There are two reasons for the significant change in the 0.5:1 slurry characteristics after treatment. First, as noted previously, water was solubilized by the CO_2 and/or entrained in the flowing CO_2, causing the water content of the slurry to drop after SFE treatment. The lower water content of the slurry after SFE was confirmed by Dean-Stark analysis, which showed that an average of 52% of the water initially present in the 0.5:1 slurry was removed during SFE treatment. Second, after a significant amount of D822 is removed during SFE treatment, water may be absorbed by the clays (e.g. bentonite) that are present in the drill cuttings, causing the clays to swell [76,94,120,127]. Since the 0.5:1 slurry has less water than the other slurries, there is not enough free water present after SFE treatment to enable a free-flowing slurry.

All other SFE-treated slurries (i.e. 1:1, 2:1 and 5:1 slurries) had similar characteristics to the untreated slurries. However, Dean-Stark analysis and the presence of water in the trap vials both indicate that the water content of the treated slurries was somewhat lower. However, these slurries had enough free water present to be free-flowing. Like the untreated slurries, solids settling did occur rapidly, but only gentle stirring was required to suspend those solids. The large chunks of drill cuttings that were present in the untreated slurries were not as prevalent in the treated slurries. Instead, the solids were finer and not conglomerated.

Based on these findings, the 1:1 slurry was selected for further investigation. Along with the 0.5:1 and 5:1 slurry, the 1:1 slurry facilitated the greatest hydrocarbon extraction efficiency during SFE treatment. Unlike the 0.5:1 slurry, the 1:1 slurry was free-flowing both before and after SFE treatment and was more suitable for treatment in a continuous SFE column. Furthermore, a 1:1 slurry is lower in volume compared to a 5:1 slurry containing an equal mass of drill cuttings. Therefore, the size of a continuous SFE column would be smaller, and the capital cost lower, if a 1:1 slurry was to be treated, compared to a 5:1 slurry.

4.9 Efforts to Improve the Hydrocarbon Extraction Efficiency from 1:1 Slurries

Based on its flow characteristics and hydrocarbon extraction efficiency, the 1:1 slurry was selected for further investigation. Although it had the highest average extraction efficiency, only 61.1 and 45.1% of the D822 was removed from slurries containing 25g and 38g of drill cuttings, respectively. These correspond to 6.9 and 12.6% residual hydrocarbon content after SFE treatment on a dry mass basis, respectively. Both of these are well above 1%, the goal of SFE treatment that would meet most onshore and offshore regulations for safe disposal. Therefore, several experiments were conducted on 1:1 slurries to investigate different measures to improve the extraction efficiency. The results of these studies are presented in the following sections.

4.9.1 Extending CO_2 inlet to Bottom of Extraction Vessel

The CO_2 inlet, previously found several inches below the top of the extraction vessel, was extended to the bottom of the extraction vessel. Because the CO_2 outlet is at the top of the vessel, this scenario created an upward flow of CO_2 through the vessel, better simulating the countercurrent flow that will occur in the pilot-scale continuous SFE column. Introducing the CO_2 at the bottom of the vessel could lead to greater contact between the drill cuttings slurry and the CO_2, and could result in a more effective extraction. As mentioned previously, the helical impeller leaves no room to extend the CO_2 inlet to the bottom of the vessel. Therefore, the paddle impeller was used. The set-up, including the long inlet tube and paddle impeller, is shown in Figure 39.

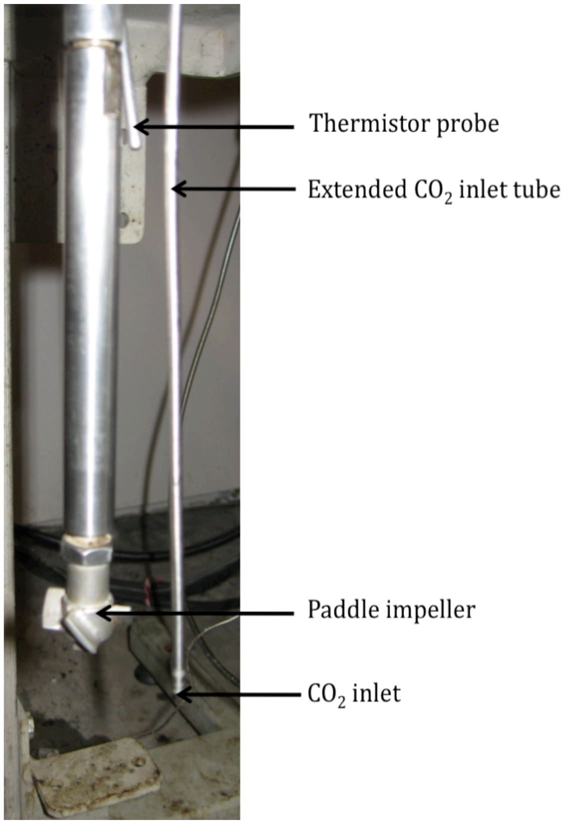


Figure 39: Modified SFE setup, including an extended CO_2 inlet tube and paddle impeller

The average extraction efficiency for the plain drill cuttings, and 1:1 slurries containing 25g and 38g of drill cuttings, are shown in Figure 40. Each was tested in duplicate. The results are compared with those from the previous experiments (with the CO_2 inlet near the top of the vessel, and using the helical impeller).

The results indicate that the extraction efficiency dropped with the modified set-up, although the change in extraction efficiency was not significant at the 95% confidence level, likely owing to the low number of samples (only two trials were conducted for the extended CO_2 inlet experiments because the preliminary results were not promising).

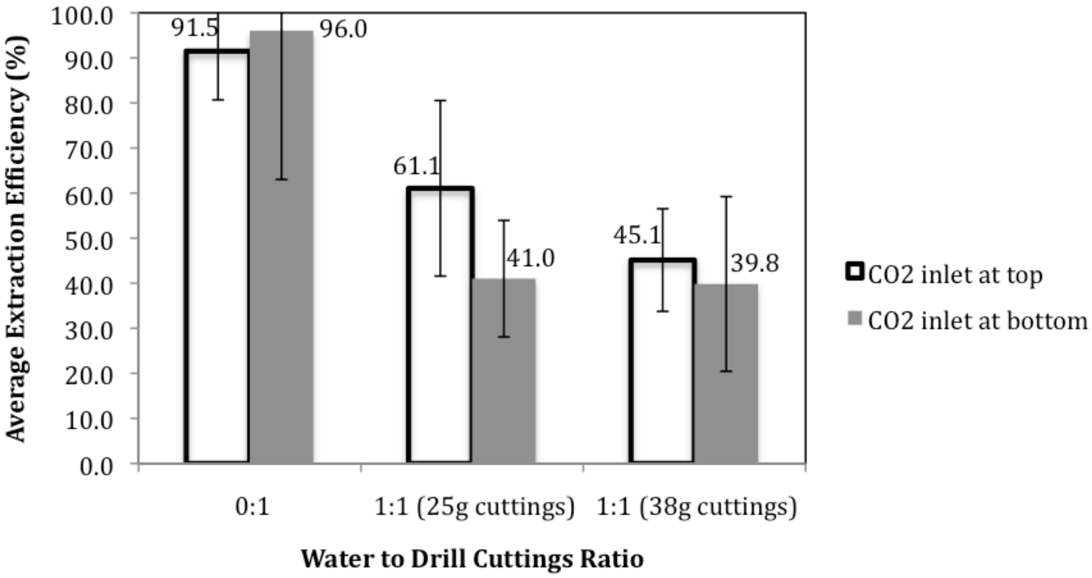


Figure 40: Results of SFE extraction of drill cuttings and 1:1 drill cuttings slurries when CO_2 was introduced at the bottom of the extraction vessel, and when the paddle impeller was used. The error bars represent the two-sided 95% confidence intervals.

Using the modified set-up, the extraction efficiency was only about 40% when 25g and 38g of cuttings were present in the slurry. The residual hydrocarbon content remained well above the 1% objective. The extraction efficiency rose slightly to 96% for plain drill cuttings. The less efficient mixing caused by the paddle impeller may have cancelled out any benefits of introducing the CO_2 at the bottom. With the helical impeller, the mixing action is such that the slurry gets lifted and tossed around, due to the upward motion of the spiral blades. However, the paddle impeller likely creates a vortex in the slurry, so there is less efficient contact between the slurry and the CO_2. In the SFE treatment of soil slurries, sufficient mixing capable of suspending agglomerated soil particles from the slurry in the CO_2 phase likely reduces the mass transfer barrier caused by water in the slurry [131]. This theory appears to apply in this research, as the helical impeller supplied upward motion to lift drill cuttings chunks out of the slurry phase and into the CO_2 phase, resulting in a thinner water barrier. However, the paddle impeller was not capable of achieving good mixing, and the mass transfer barrier posed by the water lead to lower extraction efficiencies, even with the CO_2 being introduced at the bottom of the extraction vessel.

4.9.2 Effect of Additives on Slurry Formation and SFE Treatment

An additive was used in the 1:1 drill cuttings slurries in an attempt to increase the hydrocarbon extraction efficiency from 1:1 slurries. The additive, thought to be environmentally benign, was added to the drill cuttings prior to water addition, in order to form free-flowing cuttings. A similar additive was used in previous research [33,34] to create more free-flowing drilling waste.

About 0.2g of additive for every 1g of drill cuttings seemed sufficient to produced free-flowing cuttings that flowed similar to sand. Next, water was added to form 1:1 slurries (based on the mass of additive-free drill cuttings). Two important differences between the slurries with and without the additive were noted: First, slurries made with the drill cuttings and additive mixture formed very easily. Without additive, one minute of intense wrist shaking was required to effectively mix the cuttings with the water. With additive, a uniform slurry formed after a couple seconds of shaking (much less energy input). Second, the drill cuttings in the slurries containing additive did not settle immediately. In fact, it took hours for a visible water phase to appear above the cuttings, in contrast to the additive-free slurries, where settling occurred nearly instantaneously. Figure 41 provides a photo of the slurries with and without additive taken after settling for about two minutes.

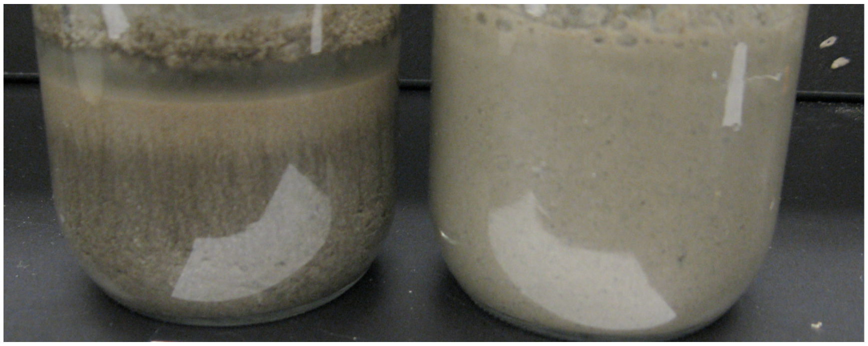


Figure 41: Untreated 1:1 slurries containing just drill cuttings (left), and drill cuttings previously mixed with additive (right), after about 2 minutes of settling

The reason for the more stable suspension when the additive is used is unclear, but could be related to the fact that large agglomerates in the drill cuttings are broken up because of the additive, and the finer particles are better suspended in the 1:1 slurry. The additive, when suspended in the water, may also form a "platform" from which the drill cuttings are supported.

A hypothesis was formulated that the additive would cause a greater hydrocarbon extraction efficiency from 1:1 slurries, due to the more dispersed nature of the cuttings within the slurry. To test this hypothesis, 1:1 slurries containing approximately 5g of additive and 25g of drill cuttings were treated with SFE in triplicate using both equipment set-ups: CO_2 inlet near the top of the vessel with the helical impeller, and CO_2 inlet at the bottom of the vessel with the paddle impeller. The results are shown in Figure 42. The additive did not lead to a significant difference in extraction efficiency when the CO_2 inlet was at the top or bottom of the extraction vessel, and the residual oil content remained well above the target of 1% on a dry mass basis. Therefore, although the additive helps in the production of the drill cuttings and water slurries, and decreases cuttings settling, it does not have a significant impact on extraction efficiency.

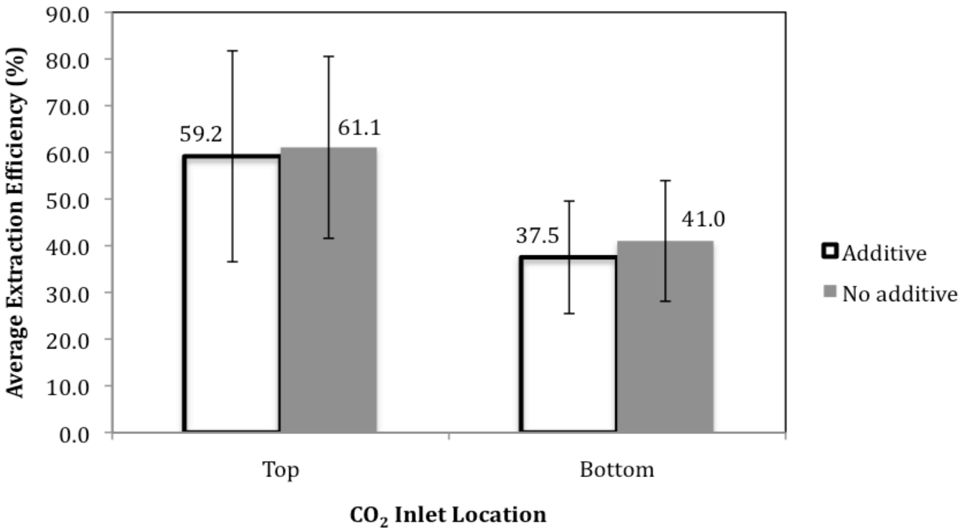


Figure 42: Effect of the use of additive on the hydrocarbon extraction efficiency from 1:1 slurries. The error bars show the two-sided 95% confidence intervals

4.9.3 Effect of CO_2 Introduction at Bottom of Extraction Vessel with Helical Impeller

Another attempt at increasing the hydrocarbon extraction efficiency from 1:1 slurries involved modification of the extraction vessel's interior. As mentioned, prior experimentation with introducing the CO_2 at the bottom of the vessel had to be done while using the paddle impeller, which is assumed to be less effective than the helical impeller. In order to use the helical impeller, a vessel sleeve, which holds the CO_2 inlet tube, was designed and inserted into the extraction vessel. A new helical impeller, with a smaller diameter, was produced to fit inside the vessel sleeve. With these modifications, the CO_2 was introduced at the bottom of the extraction vessel, while using a helical impeller, as shown in Figure 43.

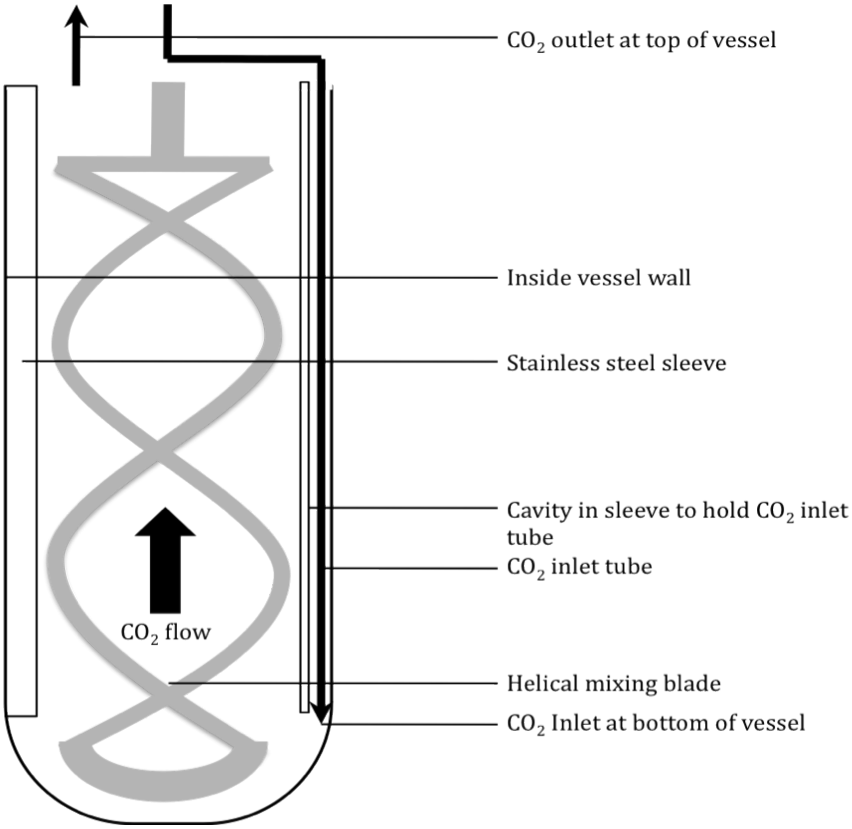


Figure 43: Cross-section view of the vessel modifications enabling CO_2 introduction at bottom of the extraction vessel and mixing with a helical impeller.

The average extraction efficiency, at the 95% confidence level, increased significantly from 61.1 +/- 19.5% with the CO_2 inlet near the top of the vessel, to 98.1 +/- 1.3% with the CO_2 inlet at the bottom of the vessel, both using a helical impeller. The small width of the latter confidence interval indicates that the extraction efficiencies from all three experiments with the modified vessel were consistently in the high 90% range. The mean residual hydrocarbon content, on a dry mass basis, was 0.34 +/- 0.22% when the modified vessel design was used, which meets the target of 1% at the 95% confidence level.

A single experiment was also performed on drill cuttings with no added water, and the vessel modifications lead to an extraction efficiency of 99.9% after a 45 minute flow period. This experiment was cut short because solids carryover plugged the vessel outlet, resulting in a significant reduction in CO_2 flow rate through the vessel (this problem is discussed further below). The corresponding residual hydrocarbon content was only 0.02%, and the treated solids had no hydrocarbon odour whatsoever, despite the shorter extraction.

The vessel modifications forced the CO_2 solvent to bubble through the slurry. In addition, the helical impeller allowed the slurry to be well mixed in the extraction vessel. Evidence of this effective mixing was seen when the vessel was opened after SFE treatment: when the helical impeller was used, there was treated slurry coating the entire inside of the vessel and the entire length of the impeller. When the paddle impeller was used, the slurry appeared to stay in the bottom of the vessel. Thus, the more effective mixing with the helical impeller decreases the thickness of the water barrier between the D822-coated drill cuttings and the supercritical CO_2 solvent. Although further testing is needed, the results suggest that the mass transfer barrier can be lowered with adequate CO_2-slurry contact, enabling effective removal of hydrocarbons from drill cuttings slurries using SFE.

There were two disadvantages to this modified vessel design. First, the treated slurries were less free-flowing, likely due to the absorption of water by the clays that occurred after the oil coating the particles was removed, or due to the increased solubilization and/or entrainment of water caused by the vessel modifications. Therefore, a slightly higher initial water content may be needed when operating the continuous SFE system. Second, the upward flow of CO_2 caused solids entrainment, which tended to plug the outlet of the extraction vessel. In all three experiments on 1:1 slurries, the plugging did not result in a significant reduction in CO_2 flow rate until the vessel was being depressurized after SFE treatment was complete. After these experiments, depressurization took significantly longer due to the hindered flow of CO_2 out of the vessel. However, as mentioned, nearly complete plugging of the outlet occurred midway through the flow period of the experiment on drill cuttings with no water added, and the run had to be aborted due to the significantly reduced CO_2 flow rate. However, these experiments were the first of their kind, and the operational difficulties experienced can likely be overcome.

4.10 Characteristics of Recovered Base Oil

The recovered base oil (D822) must have similar characteristics to the original base oil in order to be suitable for reuse. Figure 44 shows a chromatogram of D822 recovered during the SFE treatment of drill cuttings slurries, and a chromatogram of the original D822. The difference in height between the chromatograms is due to a difference in concentration in the injected samples. Visual inspection of the chromatograms indicates that the peaks between both chromatograms line up well, indicating that the recovered D822 has approximately the same chemical composition as the original D822.

The F2 to F3 ratio of the base oil gives an indication of the relative amounts of lighter (F2) versus heavier (F3) hydrocarbons in the D822. By comparing this ratio for residual D822 left in the treated cuttings versus the original D822, it should be possible to detect whether lighter hydrocarbons are preferentially extracted during SFE treatment, as indicated in some studies [35,36]. If this scenario were the case, then the recovered base oil would contain a higher amount of lighter hydrocarbons, which could affect the reuse of the recovered base oil.

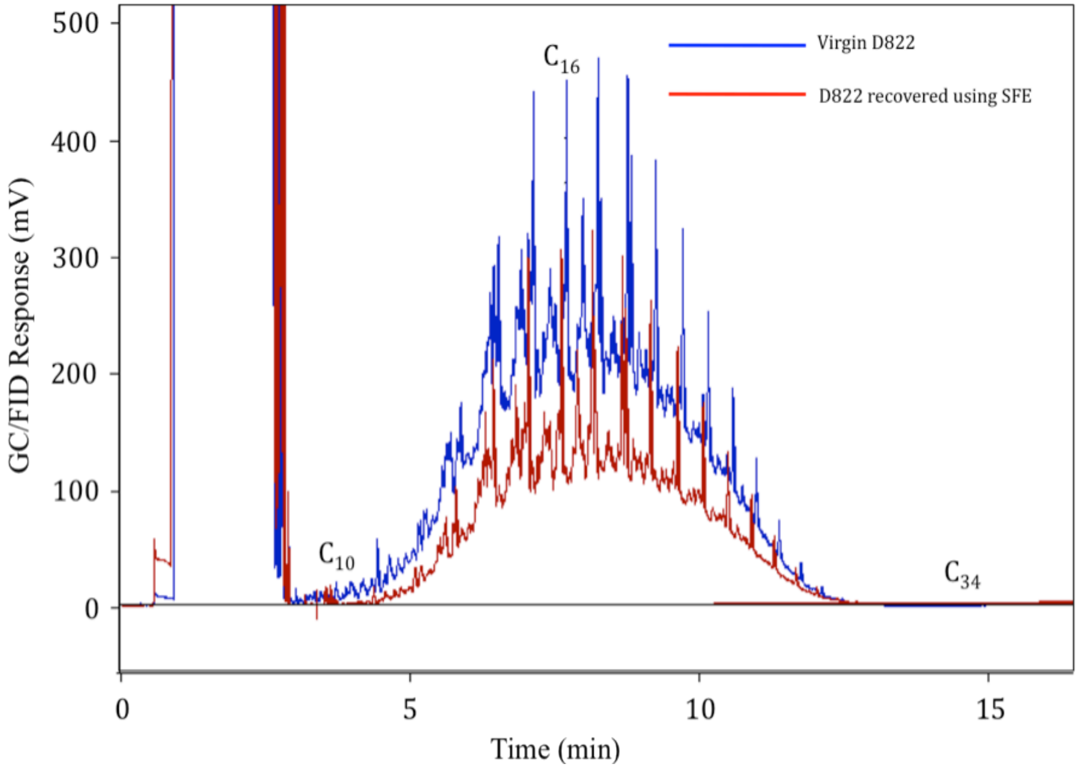


Figure 44: Chromatograms of D822 collected after SFE treatment (from trap vial) and virgin D822, showing that the composition is relatively unchanged

The original D822 contained an average F2 to F3 ratio of 0.642 +/- 0.017 at the 95% confidence level. The residual D822 in the cuttings after SFE treatment had an average F2 to F3 ratio of 0.641 +/- 0.011, indicating no statistical difference between the ratio in the original and residual D822. Therefore, SFE appears to extract all hydrocarbons in the D822 to the same extent. On the contrary, another study found that the recovered base oil from an SFE or near-critical fluid extraction process had a lower flash point, lower kinematic viscosity, and higher API gravity than original base oil [35,36], indicating the preferential extraction of lighter hydrocarbons.

The visual similarity of the chromatograms, and the identical F2 to F3 ratios of original and SFE-treated D822 indicates that the composition of the recovered base oil is very similar to the composition of original base oil, indicating that the reuse of the recovered base oil might be feasible. This hypothesis is consistent with several previous researchers [5,8,11,30-34,37]. Further testing should be done to compare properties such as viscosity, thermal stability, and lubricity prior to concluding, for certain, that the recovered base oil is suitable for reuse. It should be noted that the chromatogram in Figure 44 for D822 after SFE treatment was generated after water removal from the recovered D822. Therefore, in order to reuse the D822 or other base oil recovered after SFE treatment, an oil-water separation step might be required.

4.11 Sources of Error

Although the solubility and the slurry analysis (Dean-Stark and GC/FID) procedures were validated, other sources of error may have been present in this research. The following sections aim to quantify these.

4.11.1 Controlled Variables

The controlled variables (those not under investigation) during the solubility and apparent solubility experiments of this research program included the amount of D822 or cuttings in the vessel, mixing, and the CO_2 flow rate. Since the amount of D822 or cuttings, and the mixing were easy to control, there is no concern about these variables impacting the results. Although every effort was made to maintain a constant CO_2 flow rate, flow rate variations were inevitable because the flow rate was controlled manually, using the metering valve. In order to assess the effect of flow rate variations on the solubility measurements, a plot of measured solubility versus CO_2 flow rate was made for 15 measurements (including some preliminary measurements) at 40°C and 14.5 MPa, and is shown in Figure 45. There is no apparent correlation between the

CO_2 flow rate and measured solubility, indicating that the variations in CO_2 flow rate during the solubility and apparent solubility experiments likely had no effect on the results. Other researchers have made similar conclusions [5,8,29].

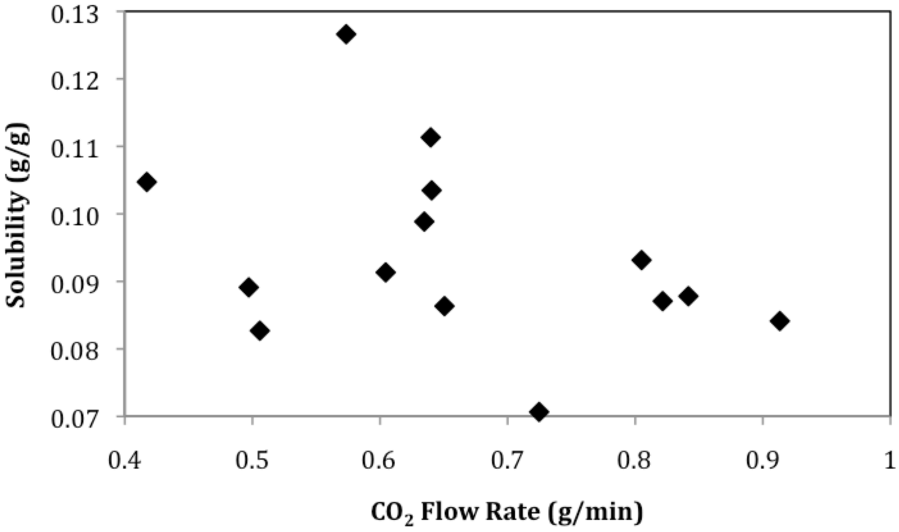


Figure 45: Plot of measured solubility at 14.5 MPa and 40°C versus CO_2 flow rate during the time interval in which the solubility measurement was made

The controlled variables during the SFE experiments included temperature, pressure, static and flow period times, mixing speed, and CO_2 flow rate. In some sets of experiments, the mixing was also controlled.

The hot water circulation through the heating jacket surrounding the extraction vessel controlled the temperature of the extraction. Because the circulating water temperature was controlled manually, the temperature inside the vessel was subject to some variation during an SFE experiment. Figure 46 shows the temperature profile during the course of a randomly selected SFE run. The temperature varied between about 39.5°C and 40.5°C for this particular run, and this observation was typical. The temperature only rose higher than this range during the first few minutes of the static period, where the temperature was near 45°C, before rapidly falling to near the setpoint of 40°C. This initial high temperature was observed in every SFE experiment, and was due to the heat produced when the CO_2 was first compressed to 14.5 MPa at the start of the static period. Since this excess heat quickly dissipated, and was present in all experiments, no appreciable error in the extraction efficiency results is expected.

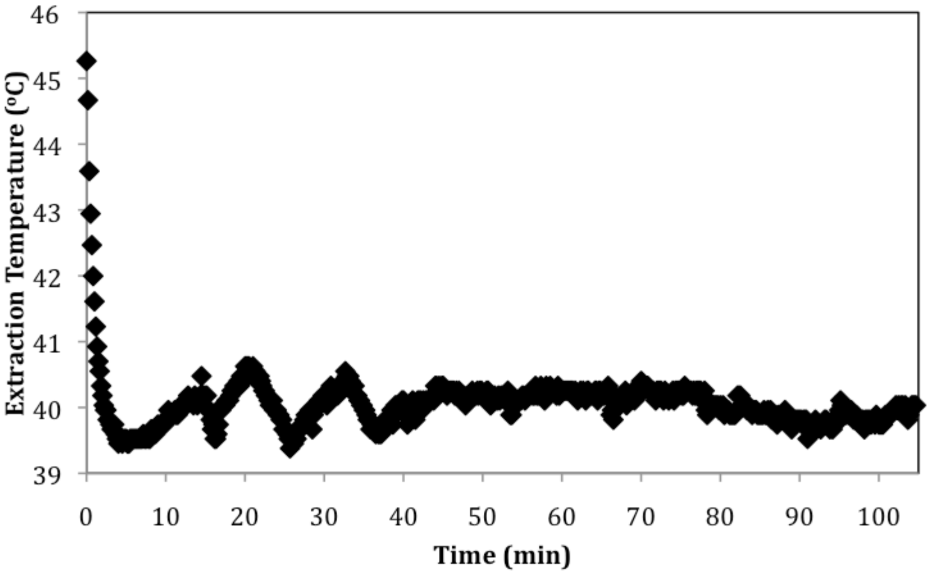


Figure 46: Typical temperature profile during SFE treatment. The first 15 minutes constitute the static period, and the final 90 minutes constitute the flow period.

The pressure was controlled by the pump controller, where a set-point of 14.5 MPa was maintained for all experiments. The pressure transducer was used to read the pressure inside the vessel and confirmed that the setpoint pressure (14.5 MPa) was indeed the pressure inside the vessel during the extraction. Figure 47 shows the pressure as measured by the pressure transducer and as measured by the pump controller for each pump. Figure 47 indicates that the pressure inside the vessel (pressure transducer) was maintained at just over 14.5 MPa for the entire extraction. This slightly higher reading is due to a slight error in the calibration of the pressure transducer, which is confirmed by the fact that, when exposed to the atmosphere, the pressure transducer reads between 0.4 and 0.8 MPa). At least one of the pumps (A or B) is maintained at 14.5 MPa throughout. The periodic rise and fall of pumps A and B is related to the refill, pressurize, and run cycle. When one pump is refilling and pressurizing, the other pump is maintaining the setpoint pressure. As indicated by the pressure transducer, the pressure inside the vessel was maintained at all points, and this trend was observed in all SFE experiments. Therefore, the pressure control was good and should not cause any errors in the extraction efficiency results.

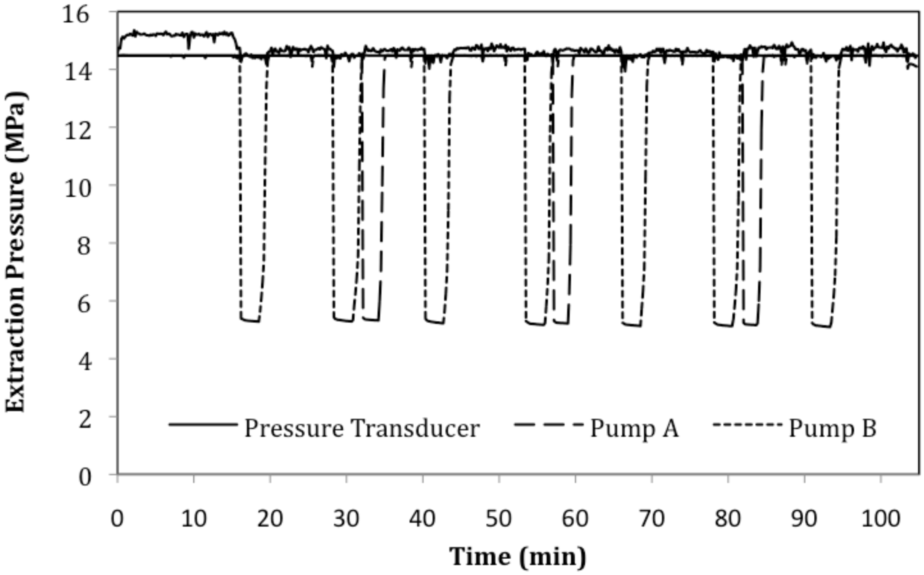


Figure 47: Typical pressure profile during SFE treatment. The first 15 minutes constitute the static period, and the final 90 minutes constitute the flow period.

The CO_2 flow rate was also maintained manually near 38g/min, or about 40mL/min at measured by the pump controller. Because of the manual control, the flow rate normally varied between 35 and 45mL/min. However, this random variation should not affect the results of the extraction because SFE is diffusion limited, and therefore minor flow variations should not affect the amount of D822 present in the exiting CO_2. Furthermore, these flow variations were present in all experiments, and so there should be no bias between individual experiments.

The mixing speed was controlled by a set point on the mixer controller. When set at 100rpm, the measured mixing speed normally fluctuated between about 95 and 105rpm in a random fashion for all SFE experiments, thus presenting no bias in the results.

All other controlled variables, such as static and flow period times, and mixer type were easily controlled, and should not present bias in the results.

4.11.2 Glasswear Blanks

The Dean-Stark extractions were carried out using a number of pieces of glassware, including flasks, graduated cylinders, filters, and others. In order to quantify the error in the Dean-Stark and GC/FID results that could have been introduced due to unclean glasswear or the method itself, duplicate Dean-Stark extractions followed by GC/FID analysis of the extracts were carried out without any analyte (drill cuttings or slurry). The exact procedure used in all analyses in this research was used, except that no drill cuttings or slurry was added to the Dean-Stark extraction flasks.

According to the results of these blank experiments, if 10g of drill cuttings (water-free) is subjected to Dean-Stark extraction, the glasswear and method would contribute a mass percentage of 0.0002% hydrocarbons to the results. The minimum hydrocarbon content found in any treated cuttings or cuttings slurry was 0.02%, which means that only 1% of those hydrocarbons were contributed by the method and glasswear. For untreated drill cuttings with a hydrocarbon content of 17.7%, only 0.001% of those hydrocarbons were contributed by the method and glasswear. Therefore, the glasswear and method do not introduce appreciable error into the hydrocarbon extraction efficiency measurements.

4.11.3 Daily Calibration Checks

As mentioned, the 5mg/L and 100mg/L n-alkane standards were injected in triplicate during each GC run in order to confirm that the GC/FID response was acceptable, and that the CCME criteria were being met. The AARD between the daily response factors and the response factor determined during GC/FID calibration was 6.1%. In addition, the average deviation was 0.8%, indicating that the deviation included approximately equal amounts of positive and negative deviation. These percentages were calculated using only the daily calibration checks that were within the CCME's criteria of 20% deviation for the low standard (5mg/L) and 15% deviation for the mid-point standard (100mg/L) [46]. For GC/FID analyses that did not meet this criteria, the analysis was repeated once the source of the error was identified and corrected.

4.11.4 Variability within SFE Experiments

As most SFE experiments were conducted in triplicate, and some in duplicate, the variability between SFE experiments conducted at the same conditions (temperature, pressure, drill cuttings mass, water content, mixer type, additive addition, etc.) was quantified using the relative standard deviation (RSD). The RSD ranged form 0.5 to 20% (the average was 9.4%) for the SFE experiments. This variation is likely due to random error, as all variables were controlled as much as possible (see Section 4.11.1). Heterogeneity in the drill cuttings and slurries is assumed to account for most of the observed variability.

4.11.5 Variability within Dean-Stark Analyses

Whenever possible, triplicate or duplicate Dean-Stark extractions were performed on the treated slurries, to estimate the residual hydrocarbon content after SFE treatment. The RSD within Dean-Stark tests ranged from 3.7 to 44% (the average was 21%), demonstrating that in some cases, there was significant variability between Dean-Stark tests performed on the same treated slurry. The most significant cause of this variability is heterogeneity in the treated slurry. As mentioned, the treated slurries contained rapidly-settling cuttings of variable size, and larger pieces of drill cuttings are likely to contain more hydrocarbons. However, this variability should not affect the final results presented in this thesis because each treated slurry was used almost in its entirety for the Dean-Stark analyses. Therefore, no matter whether a single, duplicate or triplicate Dean-Stark extraction was performed, the average hydrocarbon content calculated should be representative of the slurry as a whole.

4.11.6 Variability within GC/FID Injections

Each sample of extract from the Dean-Stark extractions was injected to the GC/FID in triplicate. The RSD between injections of the same sample ranged from 0.0 to 5.1% (the average was 2.0%), indicating very low variability between GC/FID injections of the same sample. This result, along with the results of the daily calibration checks, can be used to conclude that the GC/FID produced reliable and consistent results throughout this research program.

Chapter 5: Conclusions and Recommendations

5.1 Conclusions

This research program has allowed each of the seven objectives stated in Chapter 1 to be fulfilled. The following are conclusions regarding those objectives:

1. The solubility of D822 in supercritical CO_2 ranges from 0.002g/g at 50^oC and 10.3 MPa (the lowest CO_2 density tested: 0.43g/mL) to 0.105g/g at 35^oC and 17.2 MPa (the highest CO_2 density tested: 0.84g/mL). The conditions for further investigation were determined to be 40^oC and 14.5 MPa (CO_2 density of 0.77g/mL), where the solubility was 0.092g/g. Above this CO_2 density, no significant increase in solubility was found.
2. Both the Chrastil and modified Chrastil equations were used to model the solubility of D822 in supercritical CO_2. The Chrastil and modified Chrastil equations have AARDs of 15.8 and 9.9%, respectively, from the measured solubility values, indicating that the modified Chrastil model is the most suitable predictive model for the solubility of D822 in supercritical CO_2.
3. The apparent solubility of D822 from drill cuttings in supercritical CO_2 at 40^oC and 14.5 MPa is 0.067g/g. Because the apparent solubility is less than the solubility (0.092g/g), the SFE treatment of oily drill cuttings appears to be limited by the diffusion of the hydrocarbons out of the solid phase of the drill cuttings, a limitation that becomes greater as more hydrocarbons are extracted. The apparent solubility of D822 from a 1:1 water to drill cuttings slurry was much lower (less than 10^{-3}g/g), indicating a significant mass transfer barrier caused by the added water.

4. A minimum water to cuttings ratio of 1:1 before SFE treatment is required to obtain "free-flowing" and "pumpable" drill cuttings slurries both before and after SFE treatment. Intense agitation is required to mix the drill cuttings and the water, and the cuttings settle rapidly when agitation is stopped. The use of an additive reduces the agitation required to mix the drill cuttings with the water, and significantly reduces the rate the cuttings settling. However, the additive does not result in an increase in hydrocarbon extraction efficiency.

5. At 14.5 MPa and 40°C, SFE treatment resulted in average hydrocarbon extraction efficiencies ranging from over 90% in plain drill cuttings (no added water), to near 35% in 2:1 water to drill cuttings slurries. The highest extraction efficiencies from slurries occurred in the 0.5:1, 1:1 and 5:1 slurries containing 25g of cuttings, where between 55 and 63% of the hydrocarbons were removed.

6. The 1:1 slurry was selected for further investigation, because the extraction efficiency from 1:1 slurries was among the highest, and because the 1:1 slurry contained the lowest water content that resulted in a free-flowing and "pumpable" slurry both before and after SFE treatment.

7. The introduction of CO_2 at the bottom of the extraction vessel, in combination with the use of a helical impeller, resulted in the highest extraction efficiency from 1:1 slurries. Under these conditions, the additional diffusion barriers posed by the water in the slurry were overcome, and an average extraction efficiency of 98% was obtained, which corresponds to a residual hydrocarbon content in the treated slurry of less than 1% on a dry mass basis.

5.2 Recommendations

This research program has lead to the following recommendations:

1. Drill cuttings slurries containing a minimum water to drill cuttings ratio of 1:1 should be used as a starting point once testing of the pilot-scale continuous system begins. If the SFE treatment causes the treated slurry to plug up the extraction column, a higher initial water content should be used.
2. Conditions of 14.5 MPa and 40°C should be used as a starting point for testing on the pilot-scale continuous system. If other conditions of temperature and pressure are to be investigated, then the modified Chrastil equation, using the constants found in this study, should be used to estimate the solubility at the new conditions.
3. Research and testing should be conducted into the method for mixing the water and drill cuttings to form the initial slurry, as it was found that intense mixing is required. An additive could be used, but an analysis of the economics and technical feasibility of this additive should be conducted first. Drill cuttings slurries are produced on the industrial scale for the reinjection of cuttings, and this may be a good starting point for the research and testing to be conducted.
4. SFE treatment will produce a recovered base oil that may be reused. This base oil should be tested more rigorously for properties such as viscosity, thermal stability and lubricity, in order to make certain conclusions regarding the suitability of the extracted base oil for reuse.
5. The literature review conducted prior to this research project indicated that the hammermill (a type of thermal desorption treatment) is a drill cuttings treatment technique that will be in direct competition with SFE, because the hammermill can be used in offshore drilling

operations, and is the only treatment technique currently approved for use in offshore North Sea operations. Data collected from the pilot-scale continuous system will provide an estimate for the hydrocarbon extraction efficiency of SFE treatment on an industrial scale, and the associated capital and operating costs. The estimated extraction efficiency and costs for SFE treatment should be compared to those for hammermills.

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Appendices

Appendix A: Solubility and Apparent Solubility Measurement Procedure

The procedure used to measure the solubility of D822, and the apparent solubility of D822 from drill cuttings and drill cuttings slurried with water, is described below. Before the procedure is begun, ensure that all fitting on the SFE apparatus are sealed as well as possible (i.e. there are no significant leaks).

1. If the solubility of D822 is to be measured, use a graduated cylinder to measure 70mL of D822 into the extraction vessel. If the apparent solubility of D822 from drill cuttings is to be measured, use the analytical balance to measure approximately 100g of drill cuttings into the extraction vessel. If the apparent solubility of D822 from a 1:1 slurry is to be measured, add 100g of drill cuttings to a jar, and then add 100mL of water to the same jar. Shake vigorously for one minute, and add the slurry to the extraction vessel.
2. Turn on the cooling water refrigerator for the pumps and ensure the temperature is set to 7.5^{o}C. Thus, the pump flow data will be recorded at 7.5^{o}C and the set-point pressure of the pumps.
3. Fill the water baths with water. Set the outlet water bath (for the outlet metering valve) to 70^{o}C so that precipitated water and D822 do not solidify and plug the outlet.
4. Plug the outlet port of the extraction vessel lid with silane-treated glass wool, and place the Teflon cover over the outlet to prevent solids entrainment during the experiment. Place the Teflon o-ring on the extraction vessel. Make sure the helical mixer blade is attached.
5. Attach the extraction vessel to the lid/stand. Tighten the bolts with a wrench in a star pattern to ensure that the vessel is attached evenly to the

lid. Then tighten the bolts in a star pattern using a torque wrench in a series of three torques: 25, 35 and 42 ft-lbs.

6. Attach the mixer drive belt between the mixer motor and the MagneDrive®. If the solubility is to be measured, turn the mixer on to 20rpm. If the apparent solubility is to be measured, turn the mixer on to 100rpm.
7. Connect the hoses between the hot water circulator and the vessel. Set the water circulator to about 2^oC warmer than the desired temperature of the experiment (so 42^oC if the solubility measurement is to occur at 40^oC).
8. Start the Labview™ software to record the temperature, pressure, pump flow rates, etc. Save the data file appropriately.
9. Once the temperature inside the vessel reaches about 4^oC cooler then the desired temperature (so 36^oC for a 40^oC experiment), the CO_2 can be introduced into the vessel. To do this, open the CO_2 cylinder, refill the pumps, set the pumps to the desired extraction pressure, and allow them to run. Once both have reached pressure, the inlet valves to the vessel can be opened.
10. Monitor the pressure using the Labview™ software. After opening the vessel's inlet valves, the pressure should rise to the set-point pressure (in the case of the pressure transducer used in this research, the transducer read about 100psi over the actual pressure in the vessel). Once the vessel reaches the desired pressure, the 60 minute static soak period is commenced.
11. If there is a leak, which will be audible, then stop the pumps, depressurize the vessel by opening the outlet valves, and once depressurized unbolt the vessel and reattach the vessel (step 4). The Teflon o-ring may have to be replaced if the leak persists. For solubility

and apparent solubility measurements, a flow rate when the outlet valves are shut (i.e. leak rate) of well under 1mL/min at the pumps is desired, and indicates that there is very little CO_2 leaking from the SFE apparatus.

12. Allow a 60 minute static soak period. Ensure the temperature and pressure stay as near to the desired temperature and pressure as possible.
13. During the soak period, prepare one glass trap vial for each solubility or apparent solubility measurement to take place. If the solubility is to be measured, then normally six vials are needed. If an apparent solubility measurement is to take place, then prepare enough vials for taking measurements at five minute intervals for the first 90 minutes, and if required, enough vials to take measurements at 15 minute intervals after 90 minutes. For each case, also obtain one "dummy" vial that will be used at the start of the flow period to obtain a steady CO_2 flow rate. To prepare the vials, add enough glass wool to the vial so that the vial is "plugged" with glass wool, and label each vial appropriately. Record the weight of each vial.
14. Place the "dummy" vial on the SFE apparatus.
15. Attach the flowmeter to the outlet of the "dummy" vial. Ensure the flowmeter is set to totalizer mode, and that it is set to record the volume of CO_2.
16. Once the 60 minute static period is over, open the outlet ball valve. Slightly open the outlet metering valve so that the CO_2 flow rate is near 1-1.5mL/min as measured at the pumps, and is within the range of the flowmeter. If a slurry is being tested, a higher flow rate (10-15mL/min) will be required and the flowmeter cannot be used at this high flow rate. Once a suitable flow rate has been obtained, allow the flow to continue for approximately five minutes, to ensure a steady and consistent flow is occurring. Use the metering valve to make adjustments if necessary. If a solubility measurement is being taken, turn the mixer off at this time. If

an apparent solubility measurement is being taken, maintain mixing at 100rpm.

17. Once a steady CO_2 flow rate has been obtained, remove the “dummy” vial. Zero the totalizer on the flowmeter, and quickly attach the first trap vial to the SFE apparatus. Once the trap vial is in place, immediately start the stopwatch.
18. Allow a five minute flow period. Monitor the totalizer to ensure that the CO_2 flow rate remains in the range of the flowmeter.
19. After the five minute flow period, remove the trap vial. When the trap vial is removed, read the totalizer and record the volume (in standard cubic centrimetres) of CO_2 that was used during the five minute flow period. Zero the totalizer and reset the stopwatch. Add the second trap vial and restart the stopwatch.
20. For a solubility measurement, repeat steps 18 and 19 once more, so that a total of three solubility measurements are taken (one for each five minute flow period). Then allow a second 30 minute static soak period (with 20 rpm mixing) prior to repeating steps 18 and 19 three more times (for a total of six solubility measurements). For an apparent solubility measurement, repeat steps 18 and 19 for a total of 90 minutes, after which the same steps may be repeated, but with 15 minute flow period intervals.
21. After removal from the SFE apparatus, allow each trap vial to degas for 15 minutes. Record the weight of the vial plus the D822 that was collected. Use the difference in weight of the trap vial before and after the flow period interval to determine the mass of D822 that was collected during the flow period. In the case of measuring the apparent solubility of D822 from a drill cuttings slurry, add 20mL of toluene to each vial, and extract a portion of the toluene phase for GC analysis to determine the mass of D822 in the trap vial (because there is likely water extracted

from the slurry in the trap vial along with the D822, that would otherwise lead to an overestimate of the mass of D822 collected in the vial).

22. The solubility or apparent solubility is determined by dividing the mass (in grams) of D822 collected in the trap vial over a flow period interval by the mass of CO_2 (convert the standard volume obtained using the totalizer to mass) used over the course of the same flow period interval.
23. Once the solubility or apparent solubility measurements are complete, close the inlet valves and allow the vessel to depressurize through the outlet valves. Stop the mixer and water circulator, and unhook the hoses.
24. Once depressurized (according to Labview™), switch the valves to bypass, and allow CO_2 to flow through the tubing, but bypassing the vessel, for about 30 seconds to allow any precipitated solute to be purged from the tubing. After 30 seconds or so, stop the pumps, and close the CO_2 cylinder.
25. Unbolt the vessel, and remove it from the lid/stand. Dispose of the D822, drill cuttings or drill cuttings slurry appropriately.
26. Turn off the outlet hot water bath, pump cooling water refrigerator, and mixer controller. Drain both hot water baths partially using a siphon. Stop the Labview™ data collection. Clean the vessel and mixer with deionized water and toluene if necessary.
27. The flow rate data, as measured at the pumps and recorded in Labview™, can be numerically integrated using the trapezoid rule (see Appendix F) to determine the total volume (and mass) of CO_2 used during each flow period interval, to confirm the measurement made using the flowmeter. In the case of measuring the apparent solubility from the slurry, the pump flow data must be used to determine the mass of CO_2 during each time interval, because the higher flow rate (10-15mL/min) exceeds the capacity of the flowmeter.

Appendix B: SFE Procedure

The procedure described below is for conducting an SFE extraction for a drill cuttings slurry. Part 1 describes the procedure used to produce the drill cuttings slurry, and to determine the amount of drill cuttings that enter the extraction vessel for SFE treatment. This part can be modified slightly for drill cuttings with no added water. Part 2 describes the SFE treatment procedure itself.

Part 1: Drill Cuttings Slurry Preparation

1. Determine and record the mass of a jar (M_{jar}). Add the desired mass of drill cuttings to the jar, and record the mass of the jar + cuttings ($M_{jar+cuttings}$).
2. Measure out the desired volume of water in a graduated cylinder to be added to the drill cuttings to produce a slurry. Record the volume of water used (V_w). Pour the water into the jar containing the drilling waste.
3. Measure and record the weight of the lid of the jar (M_{lid}), and a spoonula (M_{spoon}) (use a beaker to hold the spoonula and weigh the spoonula and the beaker together).
4. Put the lid on the jar. Shake vigorously for 1 minute, using the stopwatch to time. Remove the lid and record the mass of the lid + wet residue ($M_{lid+wet\_residue}$). Allow the lid to dry overnight and following day record the mass of the lid + dry residue ($M_{lid+dry\_residue}$).
5. Rotate the jar with your hand so settled solids become suspended. Immediately pour the waste slurry into the extraction vessel, using the spoonula to get as much of the slurry into the vessel as possible. Record the mass of the spoonula + wet residue ($M_{spoon+wet\_residue}$) (use the same beaker to hold the spoonula). Set the spoonula and beaker aside, allow to dry overnight, and record the mass of the spoonula + dry residue ($M_{spoon+dry\_residue}$) the next day.

6. Record the mass of the jar + wet residue ($M_{jar+wet\_residue}$). Allow the jar to dry overnight, and the following day record the mass of the jar + dry residue ($M_{jar+dry\_residue}$). A mass balance can be used to estimate the mass of drill cuttings ($M_{cuttings}$) that was put into the extraction vessel, based on the mass of cuttings in the jar originally and the dry residual on the jar, lid and spoonula using Equation B1:

$$M_{cuttings} = \left(M_{jar+cuttings} - M_{jar+dry\_residue}\right) - \left(M_{spoon+dry\_residue} - M_{spoon}\right) - \left(M_{lid+dry\_residue} - M_{lid}\right)$$

Equation B1

7. If drill cuttings (no added water) are to be tested, then a similar procedure to the one described above can be used, except that no water is added. In that case, the lid is not required on the jar, so those terms can be left out of the mass balance. Also, since there is no water, the $M_{jar+dry\_residue}$ and $M_{spoon+dry\ residue}$ can be obtained immediately following transfer of the cuttings from the jar to the vessel.

Part 2: SFE Extraction Procedure

1. Turn on the cooling water refridgerator for the pumps and ensure the temperature is set to 7.5°C. Thus, the pump flow data will be recorded at 7.5°C and the set-point pressure of the pumps.
2. Fill the water baths with water. Set the outlet water bath (for the outlet metering valve) to 70°C so that precipitated water and oil do not solidify and plug the outlet.
3. Plug the outlet port of the extraction vessel lid with silane-treated glass wool, and place the Teflon cover over the outlet to prevent solids entrainment during the extraction. Place the Teflon o-ring on extraction vessel. Make sure the desired mixer blade is attached.

4. Attach the extraction vessel to the lid/stand. Tighten the bolts with a wrench in a star pattern to ensure that the vessel is attached evenly to the lid. Then tighten the bolts in a star pattern using a torque wrench in a series of three torques: 25, 35 and 42 ft-lbs.
5. Attach the mixer drive belt between the mixer motor and the MagneDrive®, and set the mixer controller to 100rpm.
6. Connect the hoses between the hot water circulator and the vessel. Set the water circulator to about 2°C warmer than the desired temperature of the extraction (so 42°C if the extraction temperature is 40°C).
7. Start the Labview software to record the temperature, pressure, pump flow rates, etc. Save the data file appropriately.
8. Once the temperature inside the vessel reaches about 4°C cooler then the desired extraction temperature (so 36°C for a 40°C experiment), the CO_2 can be introduced into the vessel. To do this, open the CO_2 cylinder, refill the pumps, set the pumps to the desired extraction pressure (2100psi for an experiment at 14.5 MPa), and allow them to run. Once both have reached pressure, the inlet valves to the vessel can be opened.
9. Monitor the pressure using the Labview™ software. After opening the vessel's inlet valves, the pressure should rise to the set-point pressure (in the case of the pressure transducer used in this research, the transducer read about 100psi over the actual pressure in the vessel). Once the vessel reaches the desired pressure, the 15 minute static soak period is commenced.
10. If there is a leak, which will be audible, then stop the pumps, depressurize the vessel by opening the outlet valves, and once depressurized unbolt the vessel and reattach the vessel (step 4). The Teflon o-ring may have to be replaced if the leak persists.

11. Use a stopwatch to time the 15 minute static soak period, starting from when the vessel reaches the desired pressure of the experiment.

12. During the static soak period, 7 trap vials (6 x 15 minute time intervals, plus one carryover vial) can be set up. Place some glass beads in the bottom, and plug the top with glass wool so that as much collected solute will be trapped as possible. Record the weight of each vial. Label each vial with the experiment and time interval, and place the first vial (0-15 minute interval) and carryover vial on the outlet of the SFE apparatus. Place an ice water bath around the vials to prevent volatilization of the collected solute.

13. Once the static soak period is complete, open the first outlet valve. Then slightly open the outlet metering valve to obtain a flow rate near 40mL/min as measured at the pump conditions of 7.5^{o}C and 2100psi (14.5 MPa). This flow rate corresponds to about 38g/min. Once the flow commences, start the stopwatch to mark the start of the 90 minute flow period.

14. Monitor the flow rate throughout the flow period, adjusting the outlet metering valve to maintain the desired flow near 40mL/min. Normally, the flow should be maintained between 35 and 45mL/min. The pumps will have to be refilled and run as necessary during the extraction to maintain a constant supply of CO_2 to the vessel.

15. At 15 minute intervals, change the main trap vial. Once the previous interval's vial has been removed, let the CO_2 degas for about 15 minutes before recording the weight of the trap vial, now containing the collected solute. The mass collected can be determined by the difference between the vial's weight before and after the solute is collected.

16. Once the 90 minute flow period is complete, close the inlet valves and allow the vessel to depressurize through the outlet valves. Stop the mixer and hot water circulator, and unhook the hoses.

17. Once depressurized (according to Labview™), switch the valves to bypass, and allow CO_2 to flow through the tubing, but bypassing the vessel, for about 30 seconds to allow any precipitated solute to be purged from the tubing. After 30 seconds or so, stop the pumps, and close the CO_2 cylinder.

18. Unbolt the vessel, and remove it from the lid/stand. Pour the treated slurry into a labeled jar for Dean-Stark analysis. Use a spoonula to recover any residual slurry in the vessel or left on the mixer blade.

19. Turn off the outlet hot water bath, pump cooling water refridgerator, and mixer controller. Drain both hot water baths partially using a siphon. Stop the Labview™ data collection. Clean the vessel and mixer with deionized water and toluene if necessary.

Appendix C: Hydrocarbon Content Analysis Procedure

The following procedure describes the steps used to determine the hydrocarbon content of untreated drill cuttings, SFE-treated solids or SFE-treated slurries. Part 1 describes the Dean-Stark extraction and Part 2 describes the GC/FID analysis, which together can be used to find the hydrocarbon, water and solids content of a given sample. Part 3 describes the data analysis, referring to the appropriate equations from Chapter 3.

Part 1: Dean-Stark Extraction Procedure

1. Measure and record the weight of 3 flat-bottomed 250mL extraction flasks (M_{flask}) (labeled 1, 2 and 3).
2. Add approximately 15g of slurry to each flask using an appropriate spoonula. Use a paper towel to wipe the 24/40 joint (inside and outside) free of water and drill cuttings. Weigh and record the mass of the flask + slurry after cleaning the joint ($M_{flask+slurry}$). For slurries with high water contents, only use about 10 or 11g of slurry so that the water does not exceed the trap's 10mL capacity. For untreated drilling waste, 10g of waste is sufficient to obtain a suitable hydrocarbon concentration for GC analysis.
3. In some cases, there might not be enough treated slurry to run 3 tests with 15g each. In this case, run one or two Dean-Stark tests. Use a minimum of 9 or 10g in each.
4. Determine the exact mass of slurry (or untreated drill cuttings or treated solids) (W) in each flask using the following Equation C1:

$$W = M_{flask+slurry} - M_{flask} \qquad \text{Equation C1}$$

5. Add 100mL of toluene (HPLC grade) to each of the three flasks.

6. Assemble the Dean-Stark apparatus on the heating mantle in the fume hood. Begin by attaching the Dean-Stark traps to the flasks. Clamp the trap / flask in place on the heating plates. Make sure the flask is sitting flat on the heating plate to ensure good heat transfer. Attach the condensers to the top of the traps, and hook up the hoses to the faucet and drain. Use the glassware clamps to clamp the joint between the Dean-Stark trap and the condenser.
7. Turn the water on so that the condensers fill with water, and there is a steady flow of cold water.
8. Plug the heating apparatus in, and turn the hot plates on. Record the time that the heat was turned on.
9. After several minutes, the toluene should boil, and liquid (water and toluene) should collect in the trap. The water will sink to the bottom of the trap, while the toluene will fill the remaining top volume in the trap, and reflux (overflow) back into the flask below.
10. Allow the Dean-Stark test to run for 5 hours (from the time you recorded in step 6 above). While running, check periodically to ensure the toluene is boiling, and liquid is being collected in the trap. If not, ensure that there is good contact between the heating plate and the flask, or adjust the heat.
11. Before the end of the 5 hour extraction, ensure that all water from the sample has been collected in the trap (the dense phase). This will normally happen on its own if good contact between the flask and heating plate has been obtained. All of the water has been collected when the condensate running back into the flask (reflux) is homogeneous and free of water droplets (i.e. only toluene is refluxing – if water is still present in the flask, water drops will be prevalent in a distinct droplet-phase in the tubing between the flask and trap).

12. At the 5 hour mark, turn off the heating plates and unplug the heating apparatus. Allow the assembly to cool for at least 15 minutes before proceeding.
13. At the completion of the Dean-Stark extraction, squirt a small amount of toluene into the top of the condenser, so that it flows down to the bottom and runs into the flask. This is to knock off any water droplets that have condensed in the base of the condenser and top of the Dean-Stark trap, but are stuck on the walls (i.e. water that has been removed from the sample in the flask, but has not been collected in the trap).
14. Record the final volume of water in the Dean-Stark Trap (V_w) for each of the three set-ups. Use the bottom of the meniscus to obtain the reading. In the event that the water level is above the 10mL capacity of the trap, pour the contents of the trap into a 25mL graduated cylinder, allow the phases to separate, and read the water volume there.
15. Turn off the water, and disassemble the condensers.
16. Set up the retort stand containing the clamp (for the sodium sulphate column – see below) and the ring clamp. Close the valve of the separatory funnel and place it in the ring clamp.
17. For the first flask, remove the Dean-Stark trap from the flask, being careful not to lose any of the liquid in the trap. Pour the contents of the trap into the separatory funnel, and wait a few seconds for the phases to re-separate. Drain the water into a waste flask, being sure to keep as much of the toluene (top phase) from escaping with the water as possible. Leave the waste flask in the fume hood to evaporate.
18. Rinse the Dean-Stark trap with methanol and leave it in the fume hood to dry.
19. Once the water has been removed, drain the remaining toluene from the separatory funnel back into the 250mL extraction flask. Rinse the separatory funnel with toluene, and place it back on the ring clamp with the valve open to permit drying.

20. Set up the vacuum filtration device. Connect the tube from the vacuum line to the flask. Place the funnel filter on the vacuum flask, and turn on the vacuum. Pour the contents of the extraction flask into the funnel and filter the entire sample. Use a few inches of PTFE tape to seal the connection between the funnel filter and the vacuum flask. Adjust the vacuum strength so that filtration happens at a reasonable rate (a good rate is when it takes about 3-5 minutes for the entire sample to be filtered). If the vacuum is too strong, significant toluene may be sucked into the vacuum tube. Try to avoid this.
21. Using the graduated cylinder, measure out 50mL of toluene. Pour this into the 250mL extraction flask and shake gently. Allow most of the solids to re-settle. Pour this toluene through the filter as well. This is to rinse out any residual toluene containing extracted hydrocarbons from the extraction flask.
22. Using the graduated cylinder, measure out 30mL of toluene. Once all of the liquid has been filtered, pour this directly through the filter. This is to recover any extracted hydrocarbons stuck in the solid filter cake.
23. Once filtration is complete, turn off the vacuum, and detach the tube. Invert the dirty filter funnel on top of a beaker, and squirt toluene into the bottom (now on top) section of the filter funnel. Connect the tube to the air hose, and turn the air on slightly. Use the compressed air to force the toluene backwards through the funnel filter to remove the filter cake that has formed (this is the backwash step). The toluene will be forced backwards through the filter by the air pressure to wash away the filter cake. Repeat this backwash once more. Use toluene to rinse the funnel filter so that little solids remain.
24. Pour the contents of the vacuum flask (which should now contain all extracted hydrocarbos from the slurry sample) into a graduated cylinder. Measure the record the volume as the “final toluene volume” (V_f). This number will be used with the GC results to calculate the concentration of

the hydrocarbos in the slurry, as the entire amount of extracted hydrocarbons should be contained in this volume of toluene. In total, about 180mL of toluene was used in the extraction (100 initially, 50 from rinsing the flask, and 30 from rinsing through the filter). However, typically 165-175mL will remain at the end (some is lost to evaporation, or to residual in the glassware).

25. Use a small amount of glass wool to plug the bottom of the glass column, and use the clamp to attach it to the retort stand. Measure about 8-9g of sodium sulphate (10-60 mesh) into a weighing dish, and pour it into the column. Place a clean flask (clean with methanol and dry first, if needed) under the column.
26. Pour approximately 50mL of the toluene solution from the opaque graduated cylinder through the column containing the sodium sulphate. This is to remove any residual water from the sample that could damage the GC column.
27. Fling the sodium sulphate from the column into the garbage can. Remove the glass wool plug. Rinse the column with toluene, and then run a stream of air (from the air tap) through the column to remove any leftover sodium sulphate.
28. Obtain the syringe, needle and syringe filter. Use the large half of the syringe filter to cut out a ring of filter paper. Screw the other half of the syringe filter on to secure the filter in place.
29. Use the long needle to suck toluene solution (from the flask below the sodium sulphate column) into the syringe until it is full. Reject this first sample into the waste container.
30. Using the long needle, suck a syringe-full (3mL) of toluene solution. Remove the needle and replace it with the syringe filter. Slowly filter (to avoid breaking through the filter paper) the sample into a labelled amber vial.

31. Repeat step 29 two more times, so that approximately 9mL of solution is in the amber vial.
32. Rinse the syringe and needle with toluene (by sucking up and rejecting a syringe-full of clean toluene). Remove and discard the used filter paper from the syringe filter holder, and rinse both halves with toluene.
33. Store the amber vials in the refrigerator for later GC analysis.
34. Repeat steps 17 to 33 for each of the remaining extraction flasks.

NOTE: The above Dean-Stark procedure can be followed exactly for untreated drilling waste, or treated solids (no water added to make a slurry).

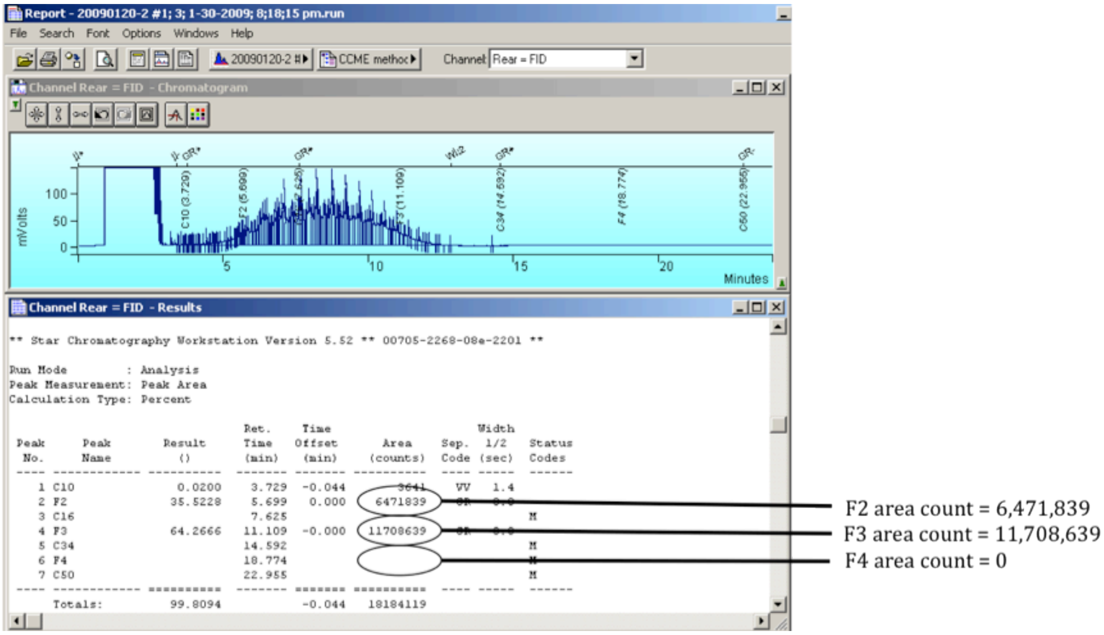
Part 2: GC/FID Analysis

1. Obtain the desired amber vials from the refrigerator, along with the 5 and 100mg/L n-alkane (C_{10},C_{16},C_{34}) standard solutions.
2. Label 2mL GC vials with the experiment number and Dean-Stark number corresponding to the samples to be tested.
3. Pipette a sample from the amber vial into the corresponding GC vial. Also pipette a sample of 5 and 100ppm alkane standards into two GC vials. Finally, fill one GC vial with pure toluene (HPLC grade) for the toluene blank.
4. Place all vials in the autosampler of the GC. Activate the F2 to F4 analysis method.
5. Enter the sample list into the GC software. This list dictates the order of the GC injections. Start with 3 toluene blanks (put the toluene blank vial in slot #1 on the autosampler). Triplicate injections of each sample, as well as the two n-alkane standards, should be done. After the samples, and before the alkane injections, be sure to activate the calibration method for individual alkanes (the calibration method has the same oven temperature profile, injector temperature and detector temperature, and all other settings; however, the calibration method is set-up to calculate

the area count of individual n-alkanes, rather then groups of alkanes (e.g. F2 and F3) as in the F2 to F4 analysis method). Between each sample vial (i.e. every 3 sample injections), run a toluene blank. At the end, run 2 toluene blanks. The last row of the sample list should activate the "CCME Standby" method. Store the data files in an appropriately labeled folder.

Note: it is best to run the Alkane standards at the end of the GC run, so that all preceding injections to the GC are validated.

6. After the GC has completed all injections, open the chromatogram from the first injection. If the baseline is low enough that the entire Distillate 822 peak has been counted in the area count, then no re-integration is necessary.
7. Open the report file for the chromatogram, and record the F2, F3 and F4 area counts for that sample. A sample report file is shown in Figure C1.



```
** Star Chromatography Workstation Version 5.52 ** 00705-2268-08e-2201 **

Run Mode         : Analysis
Peak Measurement: Peak Area
Calculation Type: Percent

                                  Ret.    Time                    Width
 Peak     Peak         Result     Time   Offset      Area    Sep.  1/2   Status
  No.     Name           ()       (min)   (min)    (counts)  Code (sec)  Codes
 ---- ------------ ----------  ------- ------- ----------  ---- -----  ------
    1 C10              0.0200    3.729  -0.044       3641    VV   1.4
    2 F2              35.5228    5.699   0.000    6471839
    3 C16                        7.625                                  M
    4 F3              64.2666   11.109  -0.000   11708639
    5 C34                       14.592                                  M
    6 F4                        18.774                                  M
    7 C50                       22.955                                  M
 ---- ------------ ==========  ------- ======= ==========  ---- -----  ------
      Totals:         99.8094           -0.044   18184119
```

F2 area count = 6,471,839
F3 area count = 11,708,639
F4 area count = 0

Figure C1: Sample report file from Varian's *Star Chromatography Workstation* (*Version 5.5*) showing the area count of the F2, F3 and F4 hydrocarbon fractions. Note that the n-alkanes are also marked on the report, but their area counts are included in the F2, F3 and F4 fractions.

8. Sometimes, particularly with low concentration samples, the baseline will rise dramatically and so a significant portion of the Distillate 822 peak will not be counted in the area count. In this case, use the “forced peak” function (right click near the bottom of the screen to find it) to find the total area count from the beginning to end of the Distillate 822 peak. Click “reintegrate now” to recalculate the area count, and look at the new baseline to ensure it includes the entire peak. If necessary, readjust slightly the start and endpoints of the forced peak so that the area count is representative of the peak. In this case, the total area count will be summed together, instead of individual F2 and F3 area counts. This is ok, since it is the total concentration that is of most concern. Record this lumped area count, and the fact that a forced peak was used to obtain it.
9. Repeat steps 6 to 8 for all samples and standards that were injected.
10. Record the F2, F3 and F4 area counts for all toluene blanks, except for the very first and second toluene blanks. These first ones should be omitted because it flushes out any residual junk from the column, and is usually not representative of the actual toluene baseline.
11. Average the F2, F3 and F4 area counts from the toluene blanks (except the first two injection), and subtract this average from each of the sample injections. If forced peaks were used, subtract the sum of the averages of the F2, F3 and F4 toluene blank area counts from the lumped (F2+F3+F4) area count obtained from the forced peak. Note: typically, F4 area count will be zero for D822.
12. If the area count is higher than the verified calibration range (i.e. higher than the area count determined from the 50000ppm Distillate 822 standard), a 10x dilution may have to be performed, and the diluted sample re-injected.

Part 3: Data Analysis for Dean-Stark and GC/FID Results

The concentration of oil in the slurry on a wet and dry basis can be obtained from the Dean-Stark test and subsequent GC/FID analysis. The oil concentration on a dry basis should be used to assess the SFE extraction efficiency, to ensure that comparisons between samples of different water contents are valid.

The raw data that must be known for the calculations is summarized in Table C1:

Table C1: Required data for oil-water-solids determination

Description	Symbol	Units	Source	Equations[a]
Average GC/FID response factor for n-alkanes	RF_{avg}	$(mg/kg)^{-1}$	GC/FID calibration	4 (take average)
F2 area count (corrected)	$A_{C10\text{-}C16}$	None	GC/FID analysis	N/A
F3 area count (corrected)	$A_{C16\text{-}C34}$	None	GC/FID analysis	N/A
F4 area count (corrected)	$A_{C34\text{-}C50}$	None	GC/FID analysis	N/A
Mass of slurry (or cuttings or solids) for Dean-Stark analysis	W	g	Dean-Stark analysis	B1
Final toluene volume	V_f	mL	Dean-Stark analysis	N/A
Water volume in Dean-Stark trap	V_w	mL	Dean-Stark analysis	N/A
Hydrocarbon fraction of untreated drill cuttings, dry mass basis	$F_{h,dry,untreated}$	None	Dean-Stark analysis of untreated cuttings	N/A

[a] Equation number, found in Chapter 3

The calculations then proceed as follows, with reference to the equations provided in Chapter 3:

1. Calculate the concentration of F2, F3 and F4 hydrocarbons (C_{F2}, C_{F3}, C_{F4}) in the slurry samples, using Equations 10 to 12.
2. Calculate the total hydrocarbon concentration (C_{total}) using Equation 8, followed by the fraction of hydrocarbons on a wet mass basis ($F_{h,wet}$) using Equation 9.
3. Calculate the mass fraction of water in the slurry (F_w) using Equation 13.
4. Calculate the mass fraction of solids in the slurry (F_s) using Equation 14.
5. Calculate the mass fraction of hydrocarbons in the treated slurry on a dry mass basis ($F_{h,dry}$) using Equation 15.
6. Calculate the extraction efficiency (η) using Equation 16.

Appendix D: Determination of Oil and Water Collected

Both water and oil are collected in the trap vials when SFE is performed on a slurry. A liquid-liquid extraction can be performed on the vials to determine the amount of oil and water collected during each 15 minute time interval. The procedure is as follows:

1. Add 30mL (exact) of toluene (HPLC grade) to each vial being tested.
2. Shake the vials vigorously. After, it is a good idea to let them sit for some time to allow all oil to dissolve in the toluene phase. Letting them sit overnight is ideal.
3. If not all oil can dissolve in 30mL of toluene, or you suspect that the concentration will be too high for the GC (this nearly always happens for the 0-15 minute vial, when much of the oil is recovered), rinse the entire contents of the vial with toluene into a graduated cylinder or volumetric flask, and top the volume up to 100mL.
4. Obtain the long needle, syringe filter housing, and glass syringe.
5. Using the large half of the syringe filter housing, cut out a circle of filter paper, and place it in the syringe filter.
6. Fill the small half of the syringe filter housing with sodium sulphate (10-60 Mesh) and screw the two ends together such that the sodium sulphate remains in the filter housing.
7. Using the syringe with the long needle, suck up a syringe-full of toluene from near the middle of the vial (avoid the bottom where the water is). Replace the long needle with the filter assembly, and filter the toluene into an appropriately labeled GC vial. Note: sample is filtered through the sodium sulphate to remove trace water, and through the filter paper to remove particulate.
8. Analyze the samples on the GC (Appendix B, Part 2). The mass of oil collected in the vial (m_{D822}) can be found using Equation 17.

Appendix E: Sample LabView™ Output

Table E1 shows a sample of the data collected during an SFE experiment by Labview™. As can be seen, the data was read every 10 seconds or so. The sample shown is just a small section (just over 1 minute) of the data collected for an entire SFE run.

Table E1: Sample Labview™ data collection

Scan#	Time (s)	Pressure (psi)[a]	Temperature (°C)	Pump A Flow Rate (mL/min)	Pump B Flow Rate (mL/min)	Pump A Pressure (psi)[b]	Pump B Pressure (psi)[b]
:	:	:	:	:	:	:	:
:	:	:	:	:	:	:	:
178	1790.7	2150	39.74	0.639	35.892	2100	2100
179	1800.3	2135	39.74	0.642	39.485	2100	2100
180	1811.1	2117	39.67	0.657	44.637	2100	2100
181	1820.7	2130	39.74	0.636	41.901	2100	2100
182	1830.3	2114	39.81	0.646	46.628	2100	2100
183	1841.1	2153	40.11	0.612	36.071	2100	2100
184	1860.3	2174	40.33	1.133	30.078	2100	2100
:	:	:	:	:	:	:	:
:	:	:	:	:	:	:	:

[a] As measured inside the vessel by the pressure transducer. The reading was consistently high due to a calibration offset (at atmospheric pressure, it consistently read 50-100psi).

[b] As measured at the pumps by the pump controller.

Appendix F: Analysis of CO_2 Flow Data

In some instances, it was necessary to find the total mass of CO_2 that was used during the course of an SFE experiment. These instances included confirmation of the flowmeter data during the solubility and apparent solubility experiments, determining the total mass of water that could have been solubilized over the course of an SFE run, and for quality assurance reasons (to ensure that the CO_2 flow rate was relatively consistent from run to run). The trapezoid rule was used to integrate the CO_2 flow rate, as measured at the pumps, over time, in order to determine the total volume of CO_2. The volume was converted to mass by using the known CO_2 density. Labview™ was used to collect time and flow rate data over the course of each run (See Appendix E for sample Labview output). Because Labview™ collected the time in seconds, and the flow rate data in mL/min (see Table E1), the time was converted to minutes prior to numerical integration. The trapezoid rule equation is shown in Equation F1:

$$V_{CO_2} = \sum_0^{t_f} \left(\frac{Q_1 + Q_2}{2} \Delta t \right) \qquad \text{Equation F1}$$

where V_{CO2} is the total CO_2 volume used up to time t_f, t_f is the total time (min) (=90 minutes for an SFE run, =5 minutes for solubility experiments), Q_1 is the CO_2 flow rate at beginning of time interval (mL/min), Q_2 is the CO_2 flow rate at end of time interval (mL/min) and Δt is the length of time interval (normally about 10 seconds)

Note: At times when both pumps were running, only one pump was actively feeding CO_2 to the extraction vessel. The flow rate on the other pump was just to maintain pressure due to small leaks. For example, in Table E1, Pump B is clearly feeding CO_2 to the vessel, so Q_1 and Q_2 would be taken from Pump B during that section.

The total mass of CO_2 was found using Equation F2:

$$m_{CO_2} = V_{CO_2} \rho_{CO_2} \qquad \text{Equation F2}$$

where m_{CO2} is the total CO_2 mass used up to time t_f and ρ_{CO_2} *is the* CO_2 density at pump conditions (= 0.963g/mL at 7.5^{o}C, 14.5 MPa).