University of Alberta

The Use of Supercritical Fluid Extraction for the Treatment of Oil Contaminated Drilling Waste

by

Jairo Javier López Gómez ©

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Master of Science

in

Environmental Engineering

Department of Civil and Environmental Engineering

Edmonton, Alberta

Spring 2004

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Your file Votre référence
ISBN: 978-0-494-22422-9
Our file Notre référence
ISBN: 978-0-494-22422-9

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Jan. 30/2004

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Faculty of Graduate Studies and Research

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Jan 30/2004

Date

ABSTRACT

Supercritical fluid extraction (SFE) with CO_2 is a promising new technique to treat drilling waste. In this research, two types of drilling waste were investigated: centrifuge underflow cuttings and invert cuttings. The extraction conditions studied were from 8.96 MPa to 15.2 MPa for pressure and from 40°C to 60°C for temperature.

Within the conditions tested, the suggested operating conditions were 14.5 MPa and 40°C. Under these conditions, the treated cuttings appeared dry, powder-like, and light in color. The high extraction efficiencies indicated that the SFE process was able to reduce the oil content from 19.4% to approximately 0.3%, which is below regulatory guidelines.

Good mixing by a ribbon blender led to high extraction efficiencies. The use of high water contents (1:1 drilling waste:water ratio) and drying agents did not affect the extraction efficiency.

The results are helpful to determine the loading ratio of cuttings in SC CO_2 at larger scales.

ACKNOWLEDGMENTS

First, I would like to especially thank Dr. Selma E. Guigard for giving me the opportunity to develop this work. Her great supervision, dedication and commitment to this work made this research more productive and agreeable during the time. In addition, I would like to thank the technical staff (Nick, Garry, Bob, Dale, Debra and Maria) in the Department of Environmental Engineering at the University of Alberta for their invaluable help during my thesis work. Without their help, the lab work would not have been as successful. I would also like to recognize the priceless support of Bernhard, Vaishalie and Luo in my activities in the lab.

In addition, I would like to thank Dr. Suzanne Kresta in the Department of Chemical Engineering at the University of Alberta for her valuable advice related to the mixing process in my work.

As well, I would like to thank the technical support of Paul Sicotte, Francisco Fernández and Ari Laurell of Unique Oilfield Technologies Services UNOTEC, Calgary. Without their belief and support in this project, this research would not have been carried out.

Additionally, I would like to thank Dr. Ian D. Buchanan and Dr. Feral Temelli for agreeing to be on the examining committee for my defense.

Also, I would like to thank my parents Jairo José and Amelia for their unconditional love and support during my studies at the University of Alberta.

Finally, I would like to express my gratitude for all those people -professors and friends- that helped in some way during my work. It is not possible to mention all of then because it would be extensive, but I would like to especially distinguish the ones that

have read and given me continuous criticism and suggestions that helped to improve this work. THANK YOU VERY MUCH!

DEDICATION

To God, my parents Jairo José and Amelia, and relatives with all my effort and dedication.

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ABREBIATIONS

CCME	The Canadian Council of Ministers of the Environment
CSTR	Continuous Stirred tank reactor
D N L	Data Norwest Labs
FID	Flame Ionization Detector
GC	Gas Chromatography
HC	Hydrocarbon
Injs	Injections
LWD	Landspraying while Drilling
MPa	Mega Pascal
N-alk	Normal alkane
PHC	Petroleum Hydrocarbon
RFavg	Response factor – average
RPM	Revolutions per minute
RSD	Relative Standard Deviation
SC CO_2	Supercritical Carbon Dioxide
SFE	Supercritical Fluid Extraction
UNOTEC	Unique Oilfield Technology Services
η	Efficiency

CHAPTER 1 INTRODUCTION

During the process of drilling for oil, significant quantities of drilling waste are generated. In some cases, depending on the type of drilling mud used to aid in the drilling process, this waste may be contaminated with oil and therefore it must be treated before disposal. Treatments may include on-site and off-site disposal technologies but these technologies may be limited for oil-contaminated drilling waste. For example, drilling waste containing oil may not be suitable for biological treatment since biological treatment requires a long period of time and it is influenced by the season (i.e. winter months) since colder temperatures affect their performance. Landfilling of oil-contaminated drilling waste is also an option but with this technology, the constituents of concern are not normally destroyed. Incineration may also be used to dispose of oil-contaminated drilling waste but this process is costly.

Supercritical fluid extraction (SFE) with CO_2 is a technology currently being investigated for the treatment of drilling waste. Its use places new importance on the management of contaminated drilling waste since it is a technique that leaves the drilling waste clean and undamaged in a relatively short period of time. This process, which is not dangerous to human health, has been in use for many years with great success. It is used, for instance, in the extraction of vegetable oils, in the production of hop extracts, in the extraction of spices, in the removal of nicotine from tobacco leaves, and in the decaffeination of tea and coffee.

Supercritical fluid extraction has not been commonly used to treat wastes on a commercial scale for environmental applications thus far, but as new technologies are emerging, there are new possible applications, as this method increases the purity of extracted substances, enables the solvent to be reused without further treatment, and thus enhances environmental protection.

The basic principle behind SFE is that when the feed material comes in contact with a supercritical fluid, the soluble substances partition into the supercritical fluid. Supercritical fluid extraction makes use of the solvency of a supercritical fluid such as carbon dioxide (CO_2) to extract a specific substance. In this research, diesel oil will be the soluble substance and drilling waste, the feed material. The supercritical carbon dioxide is mixed with the drilling waste in an extraction vessel. The diesel oil then dissolves into the supercritical fluid and the solubilized oil can then be removed.

This new technology can be implemented to remediate drilling waste that has been contaminated with oil during drilling operations. This technology extracts the diesel oil from the solid leaving the solid material clean and undamaged. The oil is recovered and the solid material may be safely disposed.

Previous investigations by Odusanya (2003) and Saintpere and Morillon-Jeanmaire (2000) have studied the use of SFE for the treatment of drilling waste. Both Odusanya (2003) and Saintpere and Morillon-Jeanmaire (2000) found that SFE was a promising new technology to treat drilling waste. In Odusanya's preliminary study, the results of supercritical fluid extraction experiments using carbon dioxide as the solvent suggested that SFE had the potential to extract oil from drilling waste. Optimum conditions were identified as 12.4 MPa and 60°C, using a small amount of drill cuttings. In the study of Saintpere and Morillon-Jeanmaire (2000), the results of extractions using supercritical carbon dioxide as a solvent suggested that the SFE process worked efficiently for diverse oil-contaminated drill cuttings at 35°C and 10 MPa.

1.1 Objectives

The main objective of this work was therefore to further investigate the extraction of oil from oil-contaminated drilling waste using SFE. In particular, the objectives were to determine:

1. the optimum pressure, temperature and mixing conditions to achieve the maximum extraction of oil from drill cuttings inside a 300 mL extraction vessel;
2. the appropriate flow of CO_2 for the maximum mass of drill cuttings placed in the vessel;
3. the effect of the nature of contaminated solids on Supercritical Fluid Extraction with CO_2 and;
4. the effect of water content on Supercritical Fluid Extraction with CO_2.

The following sections will present the results of this work. Chapter 2 will provide an overview of pertinent literature. Chapter 3 will present the materials and methods used in this study. Chapter 4 will present the results and discussion of these results. Chapter 5 will finally present the conclusions and recommendations.

CHAPTER 2 LITERATURE REVIEW

2.1 General Overview

Canada is the third-largest producer of natural gas and the thirteenth largest producer of crude oil in the world (CAPP 2003a; PCF 2003), with most of the production centered in the Western Canada Sedimentary Basin. Covering 1,502,193,103,994 square meters, this basin contains one of the world's richest deposits of oil and natural gas (CAPP 2003a). The Western Canada Sedimentary Basin extends across parts of all four western provinces and includes portions of the Northwest and Yukon Territories (CAPP 2003a). Alberta, in which 75% of the production occurs, produces 70% of Canada's crude oil and 80% of its natural gas (CAPP 2003a).

Federal and provincial governments regulate this petroleum production in slightly different ways depending on where the operations take place (PCF 2003). The respective provincial utility boards regulate the petroleum production that takes place within provincial boundaries (PCF 2003). For these provincial boards, the environment and safety are important concerns (PCF 2003).

During petroleum production, extremely large volumes of drilling waste (which includes drill cuttings and spent drilling muds) are created by the oil- and gas-well drilling process (Bybee 2002).

This drilling fluid or "drilling mud" "is pumped down through drill pipes where it blows out through nozzles in the drill bit. The mud has several functions in the drilling process. The mud clears the hole by carrying the formation cuttings back up the hole to the surface. The mud also lubricates the drill pipe and cools the drill bit. The weight of the mud in the column prevents formation fluids from entering the wellbore, preventing a 'blowout'" (Militronics 2003).

Drilling muds can be fresh water-based, salt water-based, oil-based, or synthetic-oil-based. The use of certain types of drilling muds while drilling depends on the conditions found (Williams 2001).

Usually fresh water-based mud is used at the beginning of the drilling process. However, when the well gets deeper and reaches the limits of the water-based mud in terms of lubricity and wellbore stabilization, the mud is then substituted with an oil-based mud (Schlumberger 2003).

Normally, the drill cuttings from water-based muds are much less damaging to the environment and are normally discharged to the sea or to land. Water-based drilling mud systems are not always as effective as oil- or synthetic-based fluids, especially for solving the problems associated with lubricity (Schlumberger 2003).

2.2 Drilling waste generation

Essentially, drilling waste is a mixture of clays, chemicals, and water generated by the drilling process. Commonly, drilling muds are neither dry solids nor pure liquids but are usually somewhere in between (Richards 2002). Drilling muds are pumped down the drill pipe to lubricate the drill bit, to flush out the cuttings, and to strengthen the sides of the hole.

The upstream oil and gas industry produces an enormous quantity of drilling waste which is made up of a large quantity of drilling fluids (S.E.M. 1999). The majority of the wells that are drilled to take out oil or gas make use of drilling fluid to control the wellbore during the drilling process (S.E.M. 1999). According to Saskatchewan's

Drilling Waste Management Guidelines, “the drilling fluids turn out to be polluted with formation material and the effect is a big volume of liquid and solid waste generated that must be disposed of. In some cases, the drilling fluid can be reused or recycled, but much of the time it is disposed of on the lease site or close to agricultural ground (stubble fields and cultivated domain)” (S.E.M. 1999).

Variables that can have an effect on the composition and amount of drilling mud used are hole size, penetration rate, drilling fluid type, formation reactivity, and solids removal efficiency (Richards 2002).

Emissions from solids control equipment vary in particle size from a small number of microns to more than a few inches (Richards 2002). Various quantities of fluids are found in these drilled solids, and as a result their collected form can be stackable piles or free-flowing liquids (Richards 2002). Typically, upper hole segments will generally contain “drier” drilling wastes than lower hole sections (Richards 2002). If at all possible, even if they are not useful at the moment, drilling wastes must be separated into a solid phase and a liquid phase, thereby allowing active technologies to transport them safely to a disposal location (Richards 2002).

Depending on the situation found during the period of drilling, there are many additives that can be utilized in drilling fluid systems; however, the greater part of the fluids systems are composed of a mixture of water and a small number of additives (S.E.M. 1999). Specific systems, for instance, those involving salt-based and hydrocarbon-based fluids, are being used more and more to control wellbores (S.E.M. 1999).

Several drilling wastes are regulated as high-risk materials under "*The Dangerous Goods Transportation Act* (i.e., drilling waste with a pH less than 2.0 or greater than 12.5)" (AEUB 1996). Drilling fluids have to be disposed of in an environmentally acceptable way if they cannot be used again or recycled (AEUB 1996). For this reason, the following sections will present the treatment and disposal options for drilling waste.

It should be noted that drilling waste can be generated both onshore and offshore. In general, onshore and offshore treatments have made use of a variety of methods to deal with drilling wastes (Bybee 2002). Offshore wells may use synthetic-based muds (SBMs), while the majority of onshore wells are drilled with water-based muds (WBMs) or oil-based muds (OBMs) (Bybee 2002). For offshore platforms, nearly all WBMs, cuttings, and synthetic-based cuttings are released into the ocean. Any OBMs and oil-based cuttings from offshore drilling must be transported onshore for disposal or injected underground at the well site. The majority of onshore drilling wastes are disposed of at the site of the well that generated them (Bybee 2002). Some onshore drilling wastes are brought to off-site commercial disposal facilities (Bybee 2002).

Some examples of offshore disposal options for drilling waste include partial discharge, underground injection, or transport back to shore for disposal. Several methods are available for the onshore treatment of drilling waste. Treatment technologies for both onshore and offshore-generated drilling waste will be reviewed in the following sections.

2.3 Onshore Treatment and Disposal of Drilling Waste

Drilling mixtures are made of water, drilling muds, additives, and additional materials (AEUB 1996). Some of these drilling materials end up as waste materials in a sump (AEUB 1996). The waste in the sump should be sampled, treated, and disposed of (AEUB 1996).

Alberta regulations define the main disposal options for drilling wastes as follows: *on-site disposal, off-site disposal, land treatment disposal, and alternate disposal methods* (AEUB 1996).

A mixture of disposal methods can be brought into play at some locations. Each of the disposal options involves exact sampling, testing, and gathering of other types of information, all of which are described in detail in the *Summary of Loading Criteria for Disposal Methods*: *Guide 50* (AEUB 1996).

This guide reviews the main points related to testing requirements, information requirements, and different loading criteria intended to assure environmentally safe disposal of drilling waste (MacLachlan 1999).

Guide 50 was put forward by three regulatory agencies -- the EUB; the AEP; and Public Lands, Alberta Agriculture, Food and Rural Development ("AAFRD") -- in combination with the industry, as a combined set of draft guidelines for drilling waste disposal (MacLachlan 1999). On private land, the EUB controls drilling waste disposal through its eight area offices (MacLachlan 1999). If the land at issue is municipal, or a "White Area," the district office of Public Lands controls the drilling waste disposal (MacLachlan 1999). Inside a forested "Green Area," the controller is the local office of the Land and Forest Service of Alberta Environmental Protection (MacLachlan 1999).

In summary, EUB *Guide 50* provides regulations for management of the sampling, analysis, technical requirements, disposal criteria, and documentation relating to drilling waste management. Guide 50 specifically deals with on-shore generated waste although the technologies provided in the following sections may be viable for offshore-generated drilling waste that has been sent to shore for treatment and/or disposal.

2.3.1 Onshore Treatment Options

2.3.1.1 Mechanical separation and centrifuge washing

When dealing with drill cuttings, solid-liquid partitioning is used to remove the solids from the liquid (Cripps 1998). Several techniques such as coagulation and centrifugation, sedimentation and filtration are available to perform this solid-liquid partitioning (Cripps 1998).

The first important stage when treating oily cuttings is a "solid-control system" (Cripps 1998). In order to develop this first stage, high efficiency shale shakers are commonly brought into play to remove most of the solids before mechanical abrasion wears the particles down in size (Cripps 1998). In addition, de-sanders and de-silters are also frequently employed to remove large amounts of the solids (Cripps 1998).

In order to preserve acceptable properties of fluids, centrifuges must be brought into play to remove the fine particles that the shale shakers are not capable of separating (Cripps 1998).

Solids and any associated liquid wastes discarded from the shale shakers, de-sanders, de-silters, mud cleaners and centrifuges can then be treated by washing using either spray washing or immersion washing methods (Cripps 1998), as described in the next section. "*Spray washing* involves sluicing cuttings from all or part of the solids control equipment on a vibrating screen unit" (Cripps 1998). *"Immersion washing* involves sluicing cuttings from the solids-control system to an agitated tank containing diesel or aqueous-based wash fluid" (Cripps 1998).

2.3.1.2 Distillation and evaporation

In order to separate the constituents of liquid mixtures, distillation and evaporation can be employed (Cripps 1998). The methodology of these two separation techniques consists of heating the liquid and extracting its components as they evaporate at different temperatures (Cripps 1998). Two processes of this type exist that can be implemented:

- "Thermo-mechanical conversion and cracking: drill cuttings are subjected to a distillation/cracking process, with water and oil being boiled off" (Cripps 1998).
- "Thermal stripping: operates on much the same principle by boiling off oil and water. The process does not, however, crack the oil due to the lower temperatures used, and the oil can thus be reused" (Cripps 1998).

The solid material released by these processes can be used again in several practical applications rather than being disposed of at a landfill. These methods (Thermo-mechanical conversion and cracking and Thermal stripping) are the current standard procedures (Cripps 1998).

Troubles associated with distillation and evaporation include the presence of heavy metals and chloride salts. In order to cope with this problem, chloride stripping is one of several available options that can be used (Cripps 1998).

2.3.1.3 Biological treatment

Examples of biological processes for the treatment of drilling waste and drilling produced water include aerated lagoons, anaerobic digestion, stabilization ponds and composting (Cripps 1998). Biological treatment technologies rely on microorganisms to breakdown the waste into non toxic end products (Cripps 1998). The most important benefit of biological treatment methods is that they are not harmful to the environment and they have little damaging impact (Cripps 1998).

2.3.2 Onshore Disposal Options

2.3.2.1 On-site Disposal Options

Usually, on-site disposal involves the use of the subsoil for the dumping of drilling waste (AEUB 1996). Generally, this disposal option involves the use of stripped well sites and sump locations (AEUB 1996).

When an oil or gas operator needs to dispose of drilling waste within the borders of the well site, "the surface lease or right-of-entry agreement generally addresses the requisite landowner approval. For on-site disposal, subsoil is used for disposal because the well site and sump are generally stripped of topsoil" (MacLachlan 1999).

Commonly, draining liquids from the drilling pit and putting the residuals solids in the ground or spreading them over the lease site are the most frequent on-site practices (Bybee 2002). As well, reinjection of slurried drill cuttings into underground formations is also an on-site disposal option (Bybee 2002). Wastes can be introduced from the beginning to the end of the drilled well annulus or transported to a dedicated injection well at the same site (Bybee 2002).

2.3.2.1.1 Mix-Bury-Cover

According to *Guide 50,* mixing drilling waste with subsoil stabilizes drilling waste taken from an excavated pit (AEUB 1996). Waste testing determines the ratio of mixing required, and then "the solid waste and soil mixture are buried on the wellsite and covered with at least one meter of clean subsoil, after which the original topsoil is replaced" (AEUB 1996). *Guide 50* also states that groundwater should be protected by dividing the waste and soil mixture from the water table with at least one meter of impermeable soil (AEUB 1996).

2.3.2.1.2 Landspreading

Landspreading is a disposal option that consists of spreading drilling waste on-site over an "assured" land area, as determined by waste testing, and incorporating it into the subsoil (AEUB 1996). This disposal option, which is not utilized for wastes resulting from the utilization of hydrocarbon-based mud systems, is based on a calculated loading rate (AEUB 1996). The typical methods for landspreading are the following: (1) ripping the subsoil, (2) spreading it and incorporating the waste on-site, or compacting the waste on-site, drying, and then incorporating it (AEUB 1996).

2.3.2.2 Off-site Disposal Options

Off-site disposal takes place outside the well site borders, and it requires property-owner approval (MacLachlan 1999). For off-site methods, "the topsoil is employed for the disposal of drilling waste; the receiving land may be cultivated, vegetated, or simply a non-stripped portion of a wellsite or drilling waste storage area" (MacLachlan 1999).

Off-site disposal is typically more expensive than on-site disposal (Bybee 2002). In regions of high oil and gas production, a number of landfills are selected for oil and gas waste disposal (Bybee 2002). In other regions, operators transport drilling wastes to public or industrial landfills if the wastes meet the requirements of landfilling (Bybee 2002).

2.3.2.2.1 Landspraying

Landspraying is a disposal option that involves dispersing the slurried waste off-site on top of cultivated ground or "grassland" at very low application rates; it may or may not be combined with the topsoil (MacLachlan 1999). In order to guarantee that the concentration of waste remains within environmentally safe or regulatory limits, a proper land area should be chosen during waste testing (MacLachlan 1999). Landspraying methods include: (1) applying the waste on cultivated ground and (2) incorporating it through cultivation, and applying the waste on cultivable ground, with the waste not being incorporated (AEUB 1996).

2.3.2.2.2 Pump-off (clear liquid only)

Clear drilling waste liquids may be pumped off-site onto cultivated ground. (MacLachlan 1999). Pumping drilling waste through hoses or irrigation equipment such as guns, sprinklers, gated pipes, or perforated hoses is the most common Pump-Off method (AEUB 1996). Clear liquids are not usually incorporated into the subsoil (AEUB 1996).

2.3.2.2.3 Landspraying while Drilling (LWD)

Landspraying While Drilling (LWD) is a method by which drilling wastes are sprayed at very low application rates. This method is acceptable only for permitted mud systems (MacLachlan 1999). The land spray area is determined based on a maximum application rate (less than 40 m^3 of drilling waste per hectare) (AEUB 1996; MacLachlan 1999). This method does not allow for the disposal of wastes containing hydrocarbons (MacLachlan 1999).

2.3.2.2.4 Land Treatment Disposal option

The Land Treatment Disposal method is used for hydrocarbon-based drilling wastes and wastes with a high salt content. This method is an environmentally acceptable drilling waste disposal option (AEUB 1996). It can occur either on-site or off-site (MacLachlan 1999). The Land Treatment Disposal Method should be used when hydrocarbon-based mud systems have been employed, and it requires frequent application of nutrients to permit microorganisms to break down the hydrocarbons in the soil in an optimal way (AEUB 1996). *Guide 50* requires that the hydrocarbon content should be reduced to less than 0.1 or 0.5 % for land treatment (AEUB 1996).

2.4 Offshore Treatment and Disposal of Drilling Waste

2.4.1 Offshore Treatment Option

2.4.1.1 Treat offshore, discharge to sea

The number of *Treat offshore, discharge to sea* options is considerable. Diverse combinations using different techniques in the individual stages of a generic system can be used (ERM 2000) (see **Figure 2-1**).

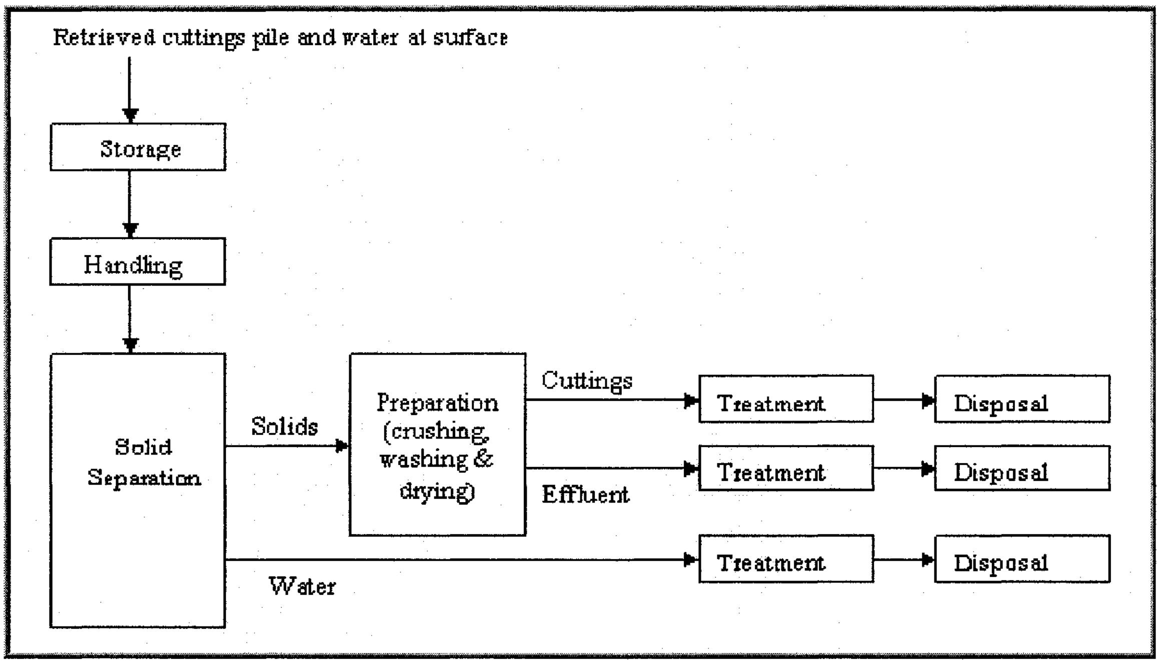


Figure 2-1. A Generic Discharge to Sea System. Adapted from (ERM 2000)

The steps of this treatment option are described below:

- <u>Solids Separation</u>: Solid separation includes removing the solids from freely available liquids (different from those that are adhered by adhesive, capillary or adsorptive forces) (ERM 2000). These techniques incorporate shale shakers (vibrating sieves) and centrifuges (ERM 2000).

- Solids Treatment: Since there is no offshore technique for consistently cleaning cuttings to less than 1% residual oil content, solid treatment is at the present the most significant type of any *discharge to sea option.* However, a number of related techniques that may be able to attain this level of performance are either under investigation or currently operating *onshore* (ERM 2000). These techniques consist of the following:

  a. *Grinding*: The drill cuttings are frictionally ground in a closed chamber. The grinding process reaches temperatures of 250- 270°C, which are high enough to evaporate both oil and water, resulting in a dry, oil-free powder (ERM 2000).

  b. *Indirect thermal desorption*: Radiation and convection are used to heat the pre-dried cuttings, which are not located close to the combustion gases. By keeping an oxygen deficit on the cutting solids side, a safe thermal desorption process is maintained (ERM 2000). The dust taken from desorbed hydrocarbon vapor is again passed into the combustion zone (ERM 2000).

  c. *Direct Thermal Desorption:* This process diverges from the indirect thermal desorption system (ERM 2000). In this case, the cuttings are heated through direct contact with combustion gases (ERM 2000).

  d. *Microemulsion:* Through the use of a conventional centrifuge, drill cuttings are pre-treated by passing them through a centrifuge to decrease the oil content to approximately 7-10% by weight (ERM 2000). An aqueous solution of a microemulsion-forming surfactant is then used to wash the contaminated cuttings at room temperature and pressure (ERM 2000).

The oil, in the form of an oil-in-water emulsion, is pumped from the well, and a centrifuge then separates this microemulsion from the oil-free cuttings (ERM 2000). An aqueous wash containing the recovered solids contaminated with traces of microemulsion are taken out (ERM 2000). In order to recover the surfactant and oil, the microemulsion is subsequently sent to a phase-separation unit (ERM 2000).

e. *Supercritical fluid extraction:* Cripps (1998) identifies SFE as a method for offshore treatment of drilling waste: SFE will be described in more detail later in the chapter.

- *Water Treatment:* For the clean up of produced water in particular, systems for water treatment are regularly employed offshore (ERM 2000). Produced water must be treated to reduce hydrocarbons content in order to meet regulatory limits to be released to the sea (ERM 2000).

  There are two stages for water treatment: a gravity separation process first separates the oil and water. Following this, mechanical skimmers remove the floating layer of oil and polishings. Oily water from the separation process is then further processed to decrease its hydrocarbon content ('polishing') before discharge (ERM 2000).

- *Discharge of Cleaned Solids and Water to Sea:* The temporary behavior of the sediments in suspension is determined by different modes of dispersion when a suspension is released into an ambient water body, for example, a cuttings discharge. (ERM 2000). These modes of dispersion, as well as the boundaries between them, are not clear-cut or mutually exclusive (ERM 2000). "Any model of cuttings dispersion for marine discharge must therefore consider the potential for a density flow to form, which enables a substantial proportion and often the bulk of the discharge to be rapidly transferred to the seabed. Nonetheless, a degree of mixing occurs at the point of discharge, where a fraction (5-100%) of the descending density flow becomes dispersed into the surface waters" (ERM 2000).

2.4.2 Offshore Disposal options

2.4.2.1 Reinjection

Reinjection is the process by which recovered materials are disposed of by reinjection into an appropriate well or formation. In general, fresh cuttings are returned back to the platform where they were produced (local reinjection) (ERM 2000). This process includes "pumping fluids and seawater-diluted cuttings that have been ground into small particle sizes into an underground formation" (CAPP 2003b).

As the Canadian Association of Petroleum Producers' (CAPP) East Coast Committee states, "cuttings can be injected through the annulus of a well being drilled or into a dedicated or dual use disposal well (a well that will later be completed for production)." According to CAPP (2003), injection is a complex procedure that requires specialized equipment. The design of injection systems is complicated, and requires cautious monitoring, and detailed emergency plans (CAPP 2003b).

2.4.2.2 Transport to Shore

According to Environmental Resources Management Limited, within the transport to shore category there are various options (ERM 2000):

- transference of all recovered materials to shore for onshore treatment and disposal / reuse of solids and liquids; water treatment and disposal offshore;
- transference to shore of all solids for onshore treatment and disposal / reuse, and
- treatment and disposal of water and larger solids offshore, with transference to shore of fines for onshore.

2.4.3 Surface discharge

This technology is applicable to wastes and water-based wastes and can be performed either onshore or offshore (AEUB 1996).

This alternative option is used for the direct disposal of treated or untreated aqueous wastes into the environment; for instance, on top of the soil or into surface waters (AEUB 1996).

2.5 Alternative Treatment and Disposal Options

Alternative Disposal Methods are for the most part used for drilling wastes that cannot be disposed of using the methods described previously (AEUB 1996). The proper regulatory office must be informed as soon as possible and provide authorization before waste disposal if one of these alternative disposal methods are being contemplated (AEUB 1996). As well, "new mud formulations or additives may also require consideration by the approving agency before being eligible for treatment by these methods" (AEUB 1996).

The Alternative Disposal Methods are discussed in the following sections:

2.5.1 Composting

Composting, which may be a suitable treatment technology for certain waste streams that are contaminated with (lighter) petroleum hydrocarbons, can be implemented on dry land (onshore) (AEUB 1996). Composting may be appropriate for contaminated soil, drilling mud, tank bottom sludge, and other "granular" solids and sludge (AEUB 1996).

Composting, a process by which the hydrocarbons are broken down into shorter-chain hydrocarbons that may volatilize, is one type of biodegradation process (AEUB 1996). Normally the hydrocarbon-contaminated material is combined with fertilizer and moisture (AEUB 1996). "The mixture may be covered in order to maintain the high temperatures and thus accelerate the biodegrading process. The final material composted may be able to be used as fertilizer or as a soil amendment" (AEUB 1996).

2.5.2 Incineration

This option, which can be applied to a variety of wastes including paper, wood, kitchen wastes, hydrocarbons and hydrocarbon containing wastes, can be carried out either onshore or offshore (AEUB 1996).

This alternative disposal method may be used to reduce the quantity of waste, and to convert unwanted organic constituents such as oil and solvents into non toxic ash, water vapor, and carbon dioxide (AEUB 1996). This technique is also used to destroy (burn) infectious/pathogenic agents such as medical waste (AEUB 1996).

Furthermore, treating retrieved oily drill cuttings by incineration is an economical disposal option (Cripps 1998). High temperature purpose-built plants are required for this procedure. This method is utilized for the disposal of organic wastes that are highly toxic, highly flammable, and/or resistant to biological processes (Cripps 1998). This method, which cannot be used for liquid wastes, usually produces a solid debris or ash that is finally disposed of at a landfill (Cripps 1998).

2.5.3 Solidification and stabilization

If space/equipment allows, solidification and stabilization can be used either onshore or offshore. These methods are also practical for aqueous wastes having free water that can be separated by gravity or pressure (AEUB 1996).

Solidification and stabilization make use of similar principles and have equivalent results, but the goal is different as is explained in the following sections.

Solidification

The goal of solidification is to make a hard soil where there is too much water (AEUB 1996). The solidification process "chemically binds the water or liquid so that it cannot be readily separated from the waste by gravity or pressure. Solidification is achieved by adding hydrophilic polymers, sawdust, soil, cement or other water absorbent materials to water-based liquid wastes to bind the water and thus solidify the waste. *Solidification renders the waste as solid waste, binding the water and hence "trapping" the contaminant. The contaminants do not change in chemical from as is the case in stabilization*" (AEUB 1996).

Stabilization

Stabilization makes use of a chemical process to cause a reaction of the contaminant of concern (typically metals), changing them from a more soluble form to a less soluble form. An example of stabilization is the "the reaction of a silica material with lead carbonate (higher lead solubility) to form lead silicate (lower lead solubility)" (AEUB 1996).

Stabilization can be performed in batch or continuous mode (AEUB 1996). Stabilization can be applied either in-situ or ex-situ. "In an ex-situ system, the waste to be treated is placed in a hopper and then into a processing unit that mixes the waste with cement or a comparable pozzolan (for example, fly ash)" (AEUB 1996). The waste material is transformed from a wet sludge to a stable powder by means of silica-based cement like reactions (AEUB 1996). Water may have to be supplemented to finish the cement-like reaction if the initial waste was dry (AEUB 1996).

2.5.4 Burial pits

This alternative option is located onshore and is only pertinent to non-hazardous solid wastes. The use of such pits should be in general restricted to those locations where there is no danger to either the surface water or groundwater. However, using onsite burial pits is tolerable for some kinds of non-hazardous wastes (AEUB 1996).

2.5.5 Injection

This technology, which is appropriate to oil and water-based liquid wastes, can be applied either onshore or offshore (AEUB 1996).

Basically, injection involves pumping liquids under pressure into an injection well (AEUB 1996). "Aqueous wastes such as produced water are injected into wells that terminate in the oil-bearing zone (injection wells or waterflood wells) or in non-oil-bearing zones (disposal wells)"(AEUB 1996).

If it is possible that the wastes may block the well or the receiving formation or react with the well construction materials or subsurface soils, they may be percolated to eliminate solids, high concentrations of oil, or other contaminants before injection to avoid these problems (AEUB 1996).

2.5.6 Landfilling

This technology is appropriate for wastes with high solids content (typically, no free liquids) (AEUB 1996).

Landfills, which are engineered areas for the burial of wastes, are sometimes constructed particularly for the disposal of certain types of wastes (AEUB 1996). Normally, landfills are designed with compacted soil bottoms or liners to limit the potential for contaminants to migrate from the landfill. Landfills are typically constructed with a leachate collection system and/or a leak detection/collection system to further minimize and control the migration of contaminants from the landfill (AEUB 1996).

2.6 Supercritical Fluid Extraction

Supercritical fluid extraction (SFE) is the most technologically refined extraction system in the world. SFE requires taking gases, usually CO_2, and compressing them into a dense fluid. This fluid is then passed through a pressurized vessel containing the material to be extracted. From there, the supercritical mixture is pumped into a separation vessel where the extract is separated from the gas and the gas is recovered for reprocessing. CO_2's solvent properties can be manipulated and adjusted by changing the pressure and temperature. Under supercritical conditions, CO_2 has properties intermediate between those of a liquid and gas, with densities close to those of liquids and viscosities and diffusivities close to those of gases. The solvent power of a supercritical fluid changes with density, which in turn can be modified by changing the pressure and temperature (Cripps 1998). The high diffusivity provides rapid mass transfer and yields a faster rate of extraction from porous matrices compared to conventional solvent extraction.

As Cripps states, the utilization of supercritical extraction techniques to eliminate and recover oil from cuttings was first proposed in 1981 by Eppig *et al.* (1984) in US-patent 4,434,028 (Cripps 1998). The process was carried out using fluids such as CO_2, propane or Freon to remove oil and to completely (99 %) recover the fluid (Cripps 1998).

The method and apparatus are mainly appropriate for eliminating oil from oil-contaminated drill cuttings. As is stated in the patent, "the solids to be treated are transferred into a pressure vessel wherein they are contacted with an extractant, which is normally a gas but is under conditions of pressure and temperature to provide the extractant in a fluidic solvent state for the constituents to be removed, whereby the constituents are transferred to the extractant. This invention relates to the removal of one or more organic constituents from particulate, inorganic-rich mineral solids and more particularly to process and apparatus for removing oil from oil-contaminated cuttings resulting from oil well drilling" (Eppig *et al.* 1984).

Three supercritical solvents were studied and all were able to extract oil from the drill cuttings. CO_2, which does not result in pollution or environmental problems was, for the most part, effective in this task (Eppig *et al.* 1984).

The method and apparatus involved in this technique allowed the cuttings to be disposed of without creating undesirable pollution problems when the oil was removed from drill cuttings (Eppig *et al.* 1984).

The patent presented a choice of solvents, working conditions, and ways of handling the solids to be treated and the products of the extraction (Eppig *et al.* 1984). The conditions for the extraction ranged from 30 to 70°C and 3.45 MPa to 20.68 MPa (Eppig *et al.* 1984). Carbon dioxide was the most effective in this decontamination (Eppig *et al.* 1984). The invention makes possible the removal of oil from drill cuttings to a level that they can be safely disposed of (Eppig *et al.* 1984).

Other studies have also investigated SFE to treat contaminated drill cuttings. Eldrich (1996) indicates that supercritical fluid extraction reduces the oil-based mud contamination of drill cuttings to a level that would allow for offshore disposal using HFC 134a (Freon) and propane as the extraction solvents. The samples of oil-based mud contamination of drill cuttings were taken from North Sea OBM drilling operations (Eldridge 1996).

The design of the proposed processing scheme takes advantage of the solvents' low critical pressures and temperatures. Both solvents' vapor pressures allow the feed to be pressurized with a centrifugal pump, thus significantly reducing the equipment's cost and complexity (Eldridge 1996). However, the use of SC Freon and propane introduces environmental concerns because propane is very flammable and SF Freon deteriorates the ozone layer (Odusanya 2003).

Saintpere and Morillon-Jeanmaire (2000) state that SFE using carbon dioxide is a technology that works efficiently for diverse OBM drill cuttings. SFE was able to decrease the final residual oil content from 6 to 13% to around 0.5% or less (0.2g of oil by 100g per dry cuttings) (Saintpere and Morillon-Jeanmaire 2000). The tests were performed using 200g cuttings per batch, a temperature of 35 to 45°C, and pressure of 6 to 12 MPa. The suggested operating conditions were 35°C and 10 MPa. The major effect on the extraction efficiency was the pressure; increasing pressure from the critical point resulted in a noticeable increase in extraction efficiency up to the suggested pressure of 10 MPa. The effect of temperature, however, was minimal. Increasing the temperature did not improve the extraction efficiency, and as a result, 35°C was suggested (Saintpere and Morillon-Jeanmaire 2000). No major differences in the optimized extraction conditions could be identified, regardless of the type of cuttings and OBM. It seemed as though 10 MPa and 35°C provided very efficient extraction for a large range of OBM cutting types (Saintpere and Morillon-Jeanmaire 2000). One of the advantages of this process was that there was no alteration in the oil composition and therefore it could be reutilized (Saintpere and Morillon-Jeanmaire 2000). According to Saintpere and Morillon-Jeanmaire (2000), agitation was not necessary, although this variable was not closely considered (Saintpere and Morillon-Jeanmaire 2000).

In addition, Odusanya (2003) states that SFE using carbon dioxide as the solvent had the potential to extract oil from drilling waste. Optimum conditions were identified as 12.4 MPa and 60°C, using a small amount of drill cuttings. This study is the starting point of the current thesis research.

2.7 Limitations, Advantages and Environmental Concerns of Current Practices

As it is explained in the Environmental Management Plan (EXXON 1999), the limitations and advantages of the currently used disposal options are described in the following sections.

2.7.1 Composting

Advantages

Composting, which does not have any need for specialized equipment or large amounts of power and energy, can be carried out by just employing a simple mixing equipment or manual labor (EXXON 1999). As a result, even in isolated locations, composting may be able to treat hydrocarbon-contaminated wastes (EXXON 1999).

Limitations

Due to the requirement of mixing, composting may be limited if large volumes of waste must be treated or if space is limited (EXXON 1999).

In addition, since composting is a biodegradation process, it requires a fairly long time for highly contaminated soils to be treated and reach low levels of contamination (EXXON 1999).

Finally, composting is not practical for non-granular wastes such as oily scrap metal or oily wastewater and it is also not practical for heavy hydrocarbons such as polynuclear aromatic hydrocarbons (EXXON 1999). Composting does not work well on non-hydrocarbons such as metals and inorganic salts (EXXON 1999).

2.7.2 Incineration

Advantages

Incinerators do not require much room to operate (EXXON 1999). Nearly all of the room is utilized to control the ash generated by the incineration process and to store the waste before incineration (EXXON 1999). Frequently, when using incinerators, most of the labor required is to transport the waste into the incinerator and to remove the ash from the incinerator (EXXON 1999).

Limitations

A proper fuel supply is required for incineration (EXXON 1999). Furthermore, water may perhaps be required to cool the incinerator parts or to cool the ash or off gases depending on the design and working temperatures (EXXON 1999). As a result, a cooling water system and therefore a water supply are required (EXXON 1999).

Normally, for waste streams that have fairly high concentrations of the constituents of concern, incineration is a viable option since the entire waste stream needs to be heated to the incineration temperature (EXXON 1999).

Naturally, when most of the waste will not burn or has a low heat content (oily wastewater, for example), incineration is not chosen (EXXON 1999). As well, some constituents may be converted into unwanted by-products (e.g., dioxins and furans from certain plastics, metal oxides from certain metal containing wastes, acid gases from waste or combustion air, etc.)" (EXXON 1999).

In addition, the conditions of combustion can change the chemical state of salts and metals. (EXXON 1999). Furthermore, particulates may possibly be released in the air stream (EXXON 1999).

As a final point, in general, temperatures in the incinerator will be between 760°C and 982°C (EXXON 1999), necessitating large energy inputs to achieve these high temperatures.

2.7.3 Landspreading and Landspraying

Advantages

Landspreading can be performed with low capital costs (EXXON 1999). Only some landspreading systems require more sophisticated “disking equipment” and systems to supply water and nutrients (EXXON 1999).

Limitations

Land treatment often needs a large area of land depending on the amount of waste (EXXON 1999). Control systems may be needed and therefore must be provided if water is to be added or if the process is situated in a rainy area (EXXON 1999).

Usually, when treating metals, inorganic salts or very heavy hydrocarbons such as polynuclear aromatic hydrocarbons, biological processes, such as land application, are not successful (EXXON 1999). The existence of a quantity of constituents such as metals, salts, or halogenated compounds may possibly obstruct biodegradation and therefore be toxic to the microorganisms (EXXON 1999). As well, the bioremediation process can be influenced by a high, low, or rapidly fluctuating temperature (EXXON 1999).

Furthermore, volatilization could be high and could result in odors if light hydrocarbons are brought in the process (EXXON 1999). Odorous emissions could also be produced by the existence of sulfur-bearing compounds in the waste (EXXON 1999).

Finally, before using a land treatment technology, it must be determined whether the waste can be left in place after treatment or whether the treated waste will be excavated and transported to another location (EXXON 1999).

2.7.4 Solidification and stabilization

Advantages

The success of solidification or stabilization is only dependant on waste-specific factors and reagent specific factors (EXXON 1999). In general, testing representative samples of the waste in a laboratory using different processes and formulations are needed (EXXON 1999).

Limitations

Normally, in order to confirm that the desired solidification/stabilization treatment has been attained and kept under the conditions of disposal, a test of the treated material is desirable (EXXON 1999).

In the solidification/stabilization processes, a number of waste streams may have contaminants that inhibit the process (EXXON 1999). For instance, the creation of a stable matrix may be obstructed by the existence of high concentrations of hydrocarbons, salts or particular metals (EXXON 1999).

General rules for efficient stabilization specify that the "salts must be less than 4 percent of the waste by weight, whereas the oil content must be below 25 percent by weight" (EXXON 1999). It is essential to check the efficacy of the stabilization process in order to decide whether adjustments have to be made when the stabilization technology is applied to wastes with high salt or oil content (EXXON 1999).

Furthermore, as a consequence of the large amount of reagents required, solidification/stabilization is normally not performed on aqueous waste streams that have low solids content (EXXON 1999).

Finally, often salts (e.g., NaCl) are not stabilized and therefore will leach from the treated material (EXXON 1999).

2.7.5 Burial Pits

Environmental Concerns

The utilization of burial pits is a common practice in several places (EXXON 1999). Areas to avoid are those with nearby surface water, shallow groundwater, or locations where 1) the waste may inadvertently be unearthed, or 2) where contaminants in the waste have the potential to migrate out of the waste into surface or groundwater or significant gas emissions may escape to the atmosphere (EXXON 1999).

Usually, if there is infiltration of rainwater into the waste, the wastes should not be disposed of in a way that would permit them to react with, or produce leachate containing components of concern (EXXON 1999).

2.7.6 Injection

Limitations

In order to limit propagated fractures, injection must be performed in a subsurface region to ensure the formation of a fluid and to ensure the presence of geological barriers (EXXON 1999).

In addition, the wastes have to be pumpable and be free enough of solids or other unwanted components (EXXON 1999).

As a final point, in the injection procedure, fracturing of the formation rock may be produced by the increased injection well pressure (EXXON 1999). As well, "injection into a limited formation could lead to over-pressuring, necessitating augmented mud weight for new wells drilled into the equivalent enclosed formation" (EXXON 1999).

2.7.7 Landfilling

Environmental concerns

Landfills can be designed to deal with a broad diversity of waste streams (EXXON 1999). "A key concern is to take steps to reduce the likelihood that waste constituents will react with each other or with the landfill's construction materials in a manner that results in the waste and/or leachates from degrading the liners or leachates/leak detection systems" (EXXON 1999).

Since the constituents of concern are not destroyed, landfills must be designed to ensure the long-term compatibility of all of the wastes placed in the landfill and to ensure compatibility of these wastes with the landfill construction materials (EXXON 1999).

2.7.8 Surface discharge

Advantages/Limitations

Wastewater must be discharged in an adequate way that decreases the risk for erosion (EXXON 1999).

In addition, in order to protect the surface watercourses or drainage ways, including dry or flowing creeks, drilling wastes should not be directly released into them (EXXON 1999).

As a final point, an advantage of surface discharge is that they may not have components of concern higher than the permissible concentrations designed for the receiving land or water (EXXON 1999).

2.7.9 Supercritical Fluid Extraction

Advantages

Principally, the advantage of using supercritical fluids for extraction is that they are inexpensive. SCFs, in particular CO_2, are generally cheap, simple to use and environmentally friendly. Disposal expenses are much less and in industrial processes, the fluids can be easily recycled (Mansoori 2003).

SCFs have solvating powers similar to those of liquid organic solvents; however, with higher diffusivities, lower viscosities, and lower surface tensions (Mansoori 2003). Also, in order to make the separation of analytes from solvent faster and easier, the solvating power is adjusted by simply varying the pressure or temperature (Mansoori 2003)

A supercritical solvent such as CO_2 is available in large quantities at high purity and at low cost. Supercritical solvents are typically more environmentally friendly than organic solvents. For these reasons, supercritical CO_2 is the reagent commonly used as the supercritical solvent. In addition, in order to have more selective separation power, the polarity can be altered by adding modifiers to the SCF (such as methanol to CO_2) (Mansoori 2003).

In industrial processes related to food or pharmaceuticals, there is no need to be concerned about solvent residuals since "typical" organic solvents are not used (Mansoori 2003).

In conclusion, one of the main advantages of SFE is its versatility. SFE can remove constituents from a given material, leaving no solvent residue (for example, when using CO_2, the CO_2 evaporates completely when it is depressurized).

Limitations

One limitation of SFE at present is its high capital cost and the fact that it is still not widely used.

CHAPTER 3 MATERIALS AND METHODS

The materials and methods used to evaluate the extraction of diesel oil from drilling waste using supercritical fluid extraction are summarized in the following sections.

3.1 Materials

This section summarizes the materials used for the present research. The following will be discussed.

- Drill cuttings
- Aged diesel oil
- Sand
- Chemicals
- Extraction vessel
- SFE system

3.1.1 Drill Cuttings

Centrifuge underflow oil-based cuttings

Unique Oilfield Technology Services (UNOTEC), (Calgary, Alberta), supplied the centrifuge underflow. These cuttings were generated from the drilling operations at an active drilling site in Alberta, Canada. Centrifuge underflow cuttings (see **Figures 3-1** and **3-2**) are generated from the centrifuges that are used to separate very fine cuttings and barite from oil-based cuttings.

Once the cuttings arrived at the University of Alberta, they were stored in a refrigerator at 4°C until use. The cuttings had an oil content of approximately 19% and a water content of less of than 1%. The cuttings were chunky, dark chocolate fudge-like in color and texture, and sticky. The cuttings had a characteristic diesel odor.

Figure 3-1. **Centrifuge Underflow**

Figure 3-2. **The centrifuge underflow cutting used**

Invert Drill Cuttings

Unique Oilfield Technology Services (UNOTEC) (Calgary, Alberta), also supplied invert drill cuttings. Once the invert drill cuttings were received, they were also stored in the refrigerator at 4°C until use. The invert was an oil/water system with water containing calcium chloride. The properties of the invert drill cuttings are provided in **Table 3-1**.

These cuttings had an oil content of approximately 11% and a water content of approximately 7%. The cuttings also looked chunky, chocolate fudge-like in texture, but lighter in color than the centrifuge underflow. The cuttings were also sticky and had a characteristic diesel odor (see **Figure 3-3**).

Table 3-1. Invert Cuttings Characteristics (Norwest Lab Report)

Analysis		Units	Result	Detection Limit
Aggregate Organic Constituents				
Oil	Dean Stark, dry wt.	%	11.2	0.05
Oil	Dean Stark, wet wt.	%	10.4	0.05
Water		%	6.8	0.1
Solids		%	82.7	0.1
Salinity				
pH	Saturated Paste	pH	11.0	-
Electrical Conductivity	Saturated Paste	dS/m at 25C	39.0	0.01
SAR	Saturated Paste		3.0	-
% Saturation	Saturated Paste	%	32	-
Calcium	Saturated Paste	meq/L	487	0.01
Calcium	Saturated Paste	Mg/kg	3110	-
Magnesium	Saturated Paste	meq/L	<2	0.02
Magnesium	Saturated Paste	Mg/kg	<6	-
Sodium	Saturated Paste	meq/L	46.7	0.04
Sodium	Saturated Paste	Mg/kg	343	-
Potassium	Saturated Paste	meq/L	19	0.03
Potassium	Saturated Paste	Mg/kg	240	-
Chloride	Saturated Paste	meq/L	51.0	0.03
Chloride	Saturated Paste	Mg/kg	577	-
Sulphate-S	Saturated Paste	Mg/kg	<30	-
Sulphate-S	Saturated Paste	meq/L	<6	0.0
TGR	Saturated Paste	T/ac	<0.1	-

Figure 3-3. **The invert drill cutting used**

3.1.2 Aged Diesel Oil

The oil present in the oil-based drill cuttings was diesel oil. It was therefore necessary to use diesel oil to calibrate the gas chromatograph/flame ionization detector (GC/FID). Commercially available diesel oil was purchased at a gas station and then "aged". Aging involved placing approximately 100 mL in a beaker and placing the beaker in a fume hood at room temperature for a period of two weeks. Aging the diesel oil allowed hydrocarbons with a carbon number lower than C_{10} to volatilize, simulating the loss of light end hydrocarbons that occurs in the drilling process.

3.1.3 Sand

Sand was obtained from the Geotechnical Group in the Department of Civil and Environmental Engineering at the University of Alberta. It was used as a matrix to prepare spiked samples necessary for the validation of the GC/FID method used in this work (CCME 2001).

3.1.4 Chemicals

Toluene (GC grade, Fisher Scientific, Nepean, Ontario) was used as the extraction solvent for Soxhlet extraction. Toluene was also used to prepare the diesel oil standards and as the solvent trap in the supercritical fluid extraction system (see **Section 3.1.7** on the SFE apparatus).

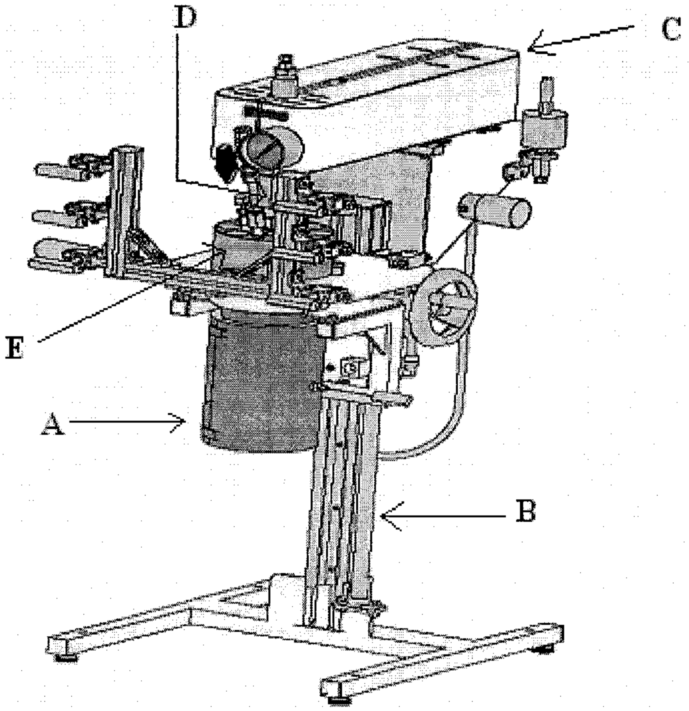
Hexane and acetone (GC grade, Fisher Scientific, Nepean, Ontario) were used as dispersing agents during the Soxhlet extraction. Decane (C_{10}, 99% purity, Acros Organics, New Jersey), hexadecane (C_{16}, 99% purity, Acros Organics, New Jersey), and tetratriacontane (C_{34}, 99% purity, Acros Organics, New Jersey) were used to determine GC retention times and to verify adequate response of the GC/FID.

Sodium sulfate purchased from Chemical Stores, Department of Chemistry, University of Alberta was used as a drying agent prior to Soxhlet extraction.

Liquid carbon dioxide (supercritical grade, Praxair, Edmonton, Alberta) was used as the solvent in the SFE process.

3.1.5 Extraction Vessel

The extraction vessel used to perform this investigation was a 300 mL, 316 stainless steel bolted closure reactor supplied by Autoclave Engineers (Pittsburgh, Pennsylvania) (see **Figure 3-4**). The lid was machined from the same material as the vessel. The cover of the unit remained fixed in a short bench top stand to permit the vessel to be opened without disassembling any process connections. The body is easily removed and drops away from the cover. This reactor had a heating jacket so that it could be heated by introducing a hot fluid inside the jacket. In this work, hot water was circulated through the heating jacket to provide heating to the vessel.



Legend

A. 300 mL vessel equipped with heating jacket	C. Motor for the MagneDrive®
B. Bench top stand	D. MagneDrive® mixer
	E. Lid for the 300 mL vessel

Figure 3-4. Extraction vessel. Adapted from (Autoclave Engineers 2003)

The stainless steel bolted closure reactor had a maximum allowable working pressure (MAWP) of 37.9 MPa @ 343° C.

The vessel is equipped with a 3300 rpm rated MagneDrive® MAG075-01 Series mixer (see **Figure 3-5**) with 0.79 N•m of static torque, and carbon/graphite bearings (Autoclave Engineers 2003). The MagneDrive® is driven by a 1/2 HP (0.37 kW) general-purpose DC motor with a 90V armature (120V unit) with an electronic speed adjustment. An attached safe magnetic sensor senses the speed of the MagneDrive® mixer (Autoclave Engineers 2003).

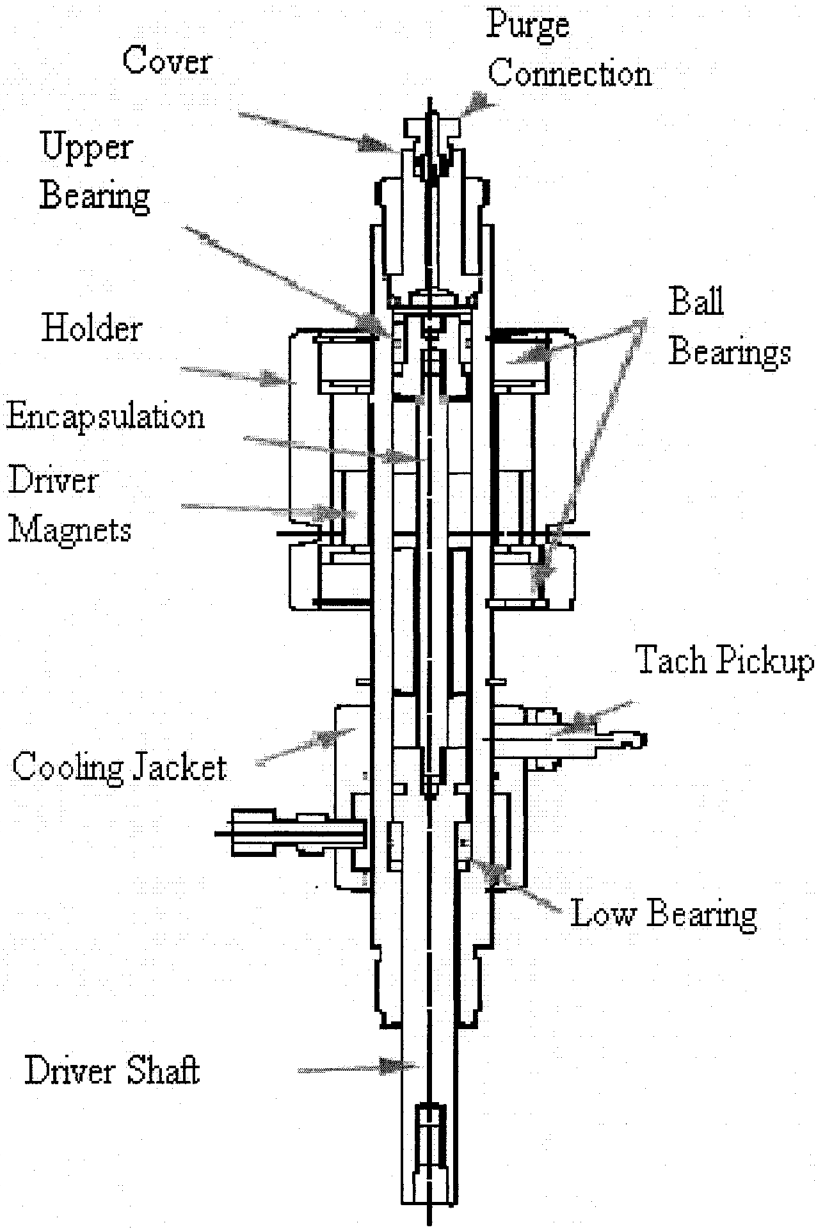


Figure 3-5. **MagneDrive®. Adapted from (Autoclave Engineers 2003)**

Although the vessel lid was equipped with many openings, only three 1/8"OD openings were used in this investigation (See **Figure 3-6**).

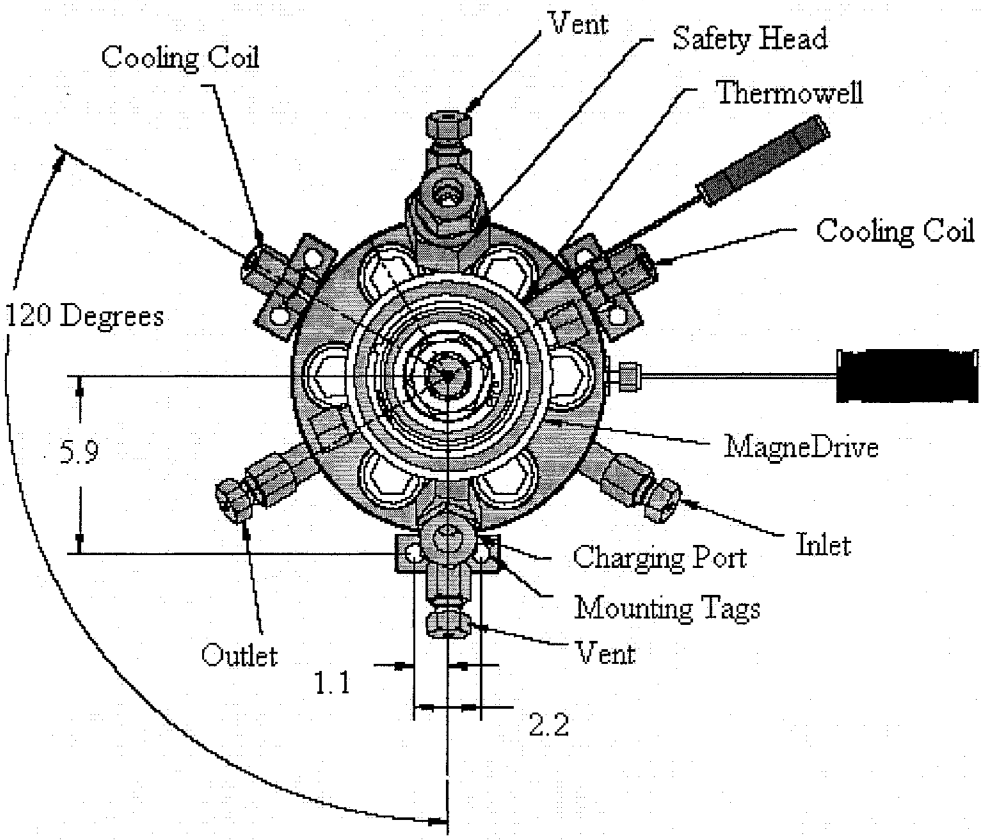


Figure 3-6. **Extraction vessel lid (Top view). All dimensions are given in centimeters (cm). Adapted from (Autoclave Engineers 2003)**

The openings are illustrated in **Figure 3-6** and consist of one for the inlet, one for the outlet, and one for depressurization (depicted as "vent" in **Figure 3-6**). The remaining openings were closed. For the inlet and outlet, 1/16" stainless steel tubing with a 0.05 mm inside diameter (ID) was connected with male connectors.

In addition, a thermistor probe introduced in a 1/8"-stainless steel thermowell was installed within the extraction vessel lid. The thermistor probe sensed the temperature inside the extraction vessel. Both pressure (pump pressure and pressure transducer) and temperature data were monitored using the Lab View 5.1 (National Instruments) program. The dimensions of the vessel can be seen in **Figure 3-7**.

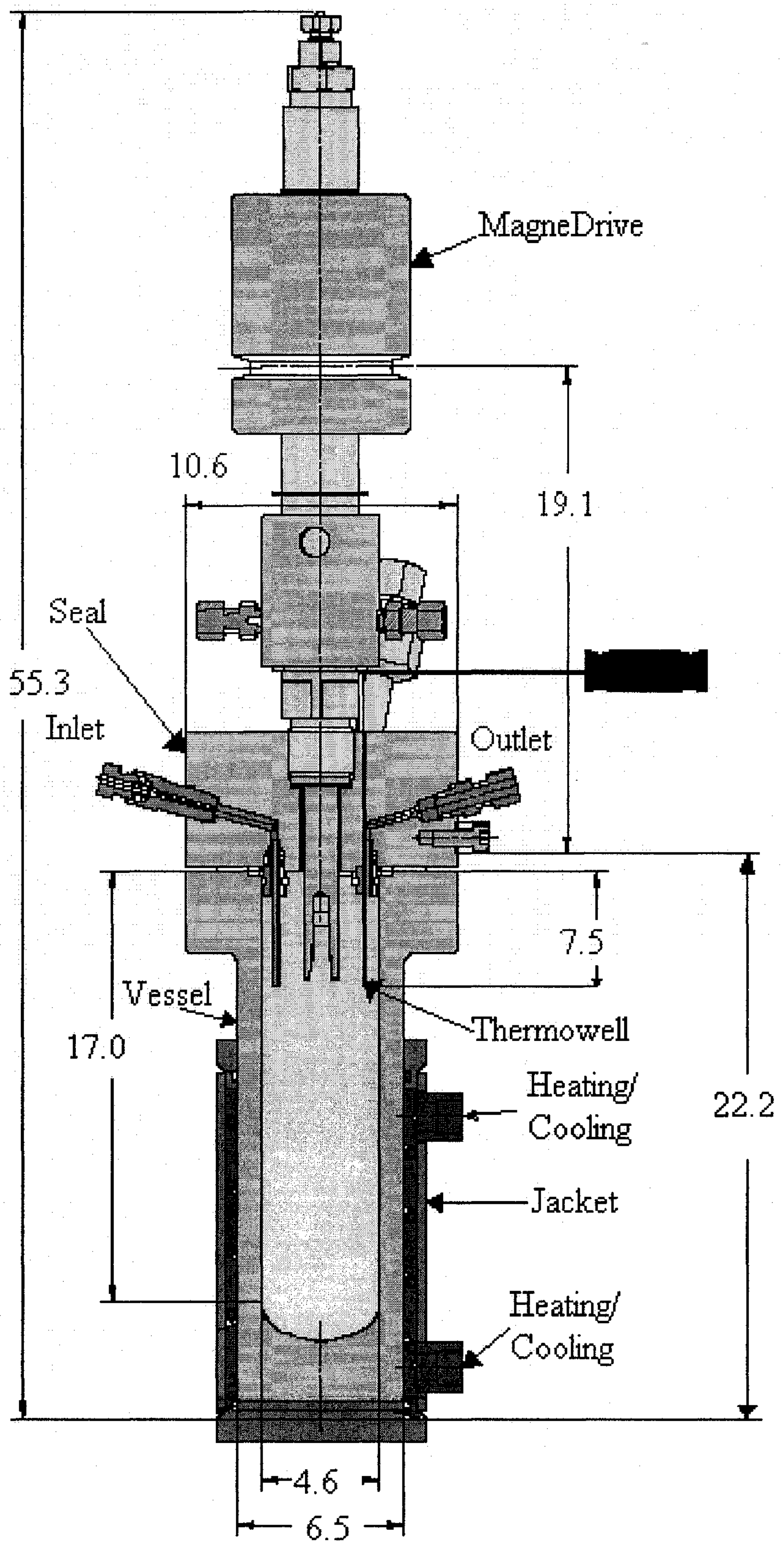


Figure 3-7. **Extraction vessel. All dimensions are given in centimeters (cm). Addapted from (Autoclave Engineers 2003)**

When using the vessel, the directions given by Autoclave Engineers were followed. The body was installed and removed from the cover using an Allen Torque wrench applying an increasing tightening sequence of torques from 25 ft-lb$_f$ to 42 ft-lb$_f$.

3.1.6 Impeller (Ribbon Blender)

The impeller used in this work is shown in **Figure 3-8**. The design was modified from a Lab Korean design (Kuweol-3dong, Namdongku, Incheon, Korea). The impeller used in the present study was made of 316 stainless steel and had two sets of helical blades. The impeller was manufactured by PRECIMAX (Edmonton, Alberta) and was designed to be easily mounted to the drive shaft of the MagneDrive®.

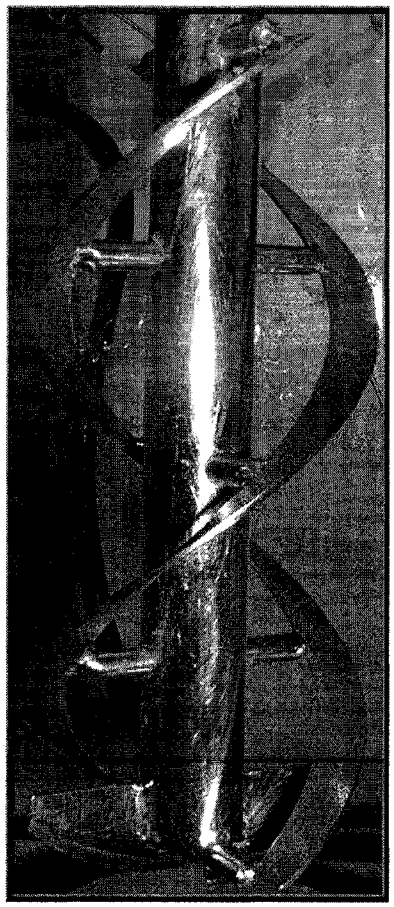
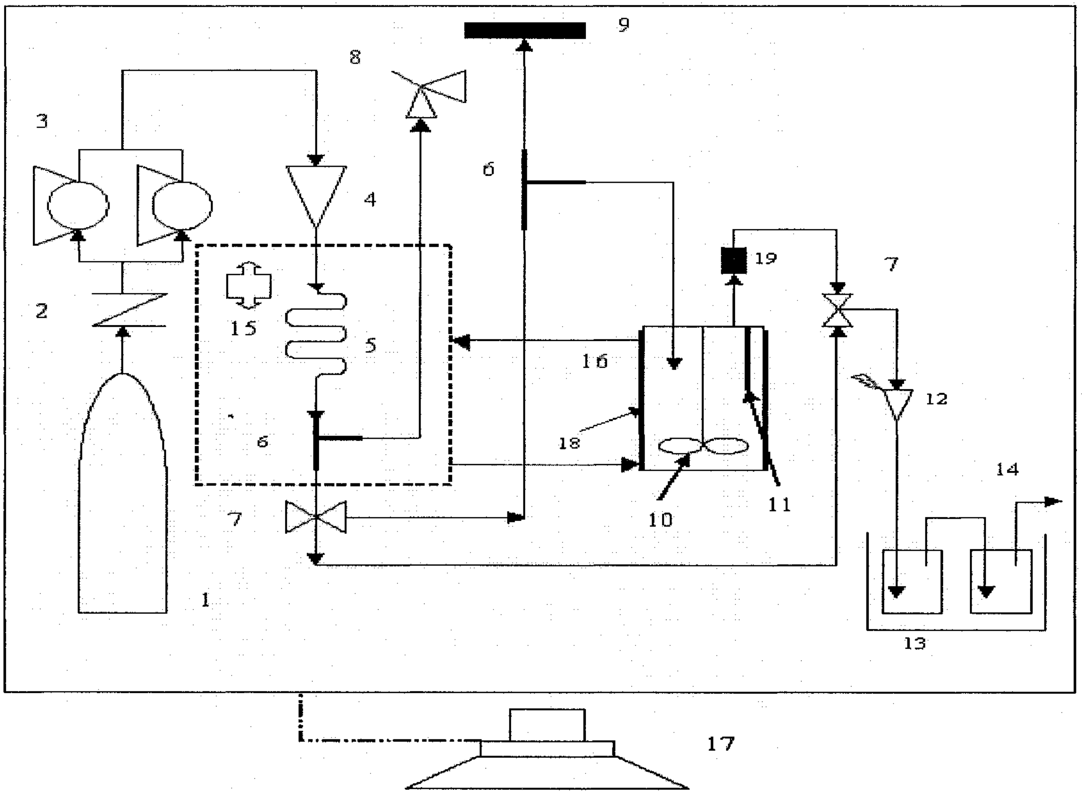


Figure 3-8. Impeller (Ribbon Blender)

3.1.7 SFE system

The diagram of the SFE system is shown in **Figure 3-9**. In order to perform the SFE extractions, liquid CO_2 was taken from a pressurized cylinder at 5.80 MPa. The liquid carbon dioxide was passed through a 0.5-micron filter using 1/16" tubing with a 0.5 mm ID and then compressed with an ISCO 500D continuous flow syringe pump.



Legend

1. Carbon Dioxide Cylinder
2. Filter
3. Syringe Pumps
4. Check Valve
5. Heating Coil
6. Tee
7. 3-Way Valve
8. Pressure Relieve Valve
9. Pressure Transducer
10. Impeller (Ribbon Blender)
11. Thermistor Probe
12. Heated Metering Valve
13. Trap Vials (in an ice bath)
14. Carbon Dioxide vent to Fume Hood
15. Heated Circulating Water Bath
16. Extraction Vessel
17. Data Acquisition
18. Heating Jacket
19. Filter

Figure 3-9. SFE System

The pump heads were cooled to 7.5°C using cold water from a refrigerated circulating water bath. CO_2 was supplied to the pumps from a cylinder of pressurized CO_2 (5.8 MPa). The pumps pressurized the CO_2 to the required pressure and delivered it to the vessel through a check valve. The check valve ensured that the CO_2 would not flow back to the pumps and potentially carry with it any material that could damage the pumps.

The tubing containing the CO_2 was submerged in a temperature-controlled water bath. The long tubing was twisted, giving it a spiral-like shape (heating coil) to enable the CO_2 to reach the same temperature as the water bath.

At the end of the heating coil, a first tee split the flow to a pressure relief valve set at 17.24 MPa. This pressure relief valve acted as a safety mechanism to ensure that the pressure would not exceed the pressure limit of SFE apparatus and avoided any high-pressure that might destroy the system.

Following this pre-heating coil, the CO_2 passed through a first three-way valve that allowed the CO_2 to flow either directly to the vessel or through a bypass line that allowed flow to bypass the extraction vessel. The bypass line flowed to a second three-way valve located downstream of the outlet of the vessel.

A second tee was located on the line that led to the extraction vessel. This tee conducted the CO_2 to a pressure transducer, so that the pressure in the system and in the vessel could be monitored.

After the extraction vessel, the SC CO_2 with the extracted solutes (oil in this case) flowed from the vessel through the outlet and through a 0.5-micron filter to retain any fine particulate entrained by the flow. At this point, the oil-containing SC CO_2 passed through a second three-way valve, which joined the outlet from the vessel to the bypass line coming from the first three-way valve. This second three-way valve took either the SC CO_2-oil mixture from the vessel or the clean flow of SC CO_2 from the bypass line to the heated metering valve. The SC CO_2 was depressurized through this metering valve and then passed through two glass vials.

The first glass vial contained glass beads to "trap" the extracted oil while the second vial contained toluene to trap any oil carried over from the first trap. The exhaust CO_2 was vented to the fume hood. The flow of CO_2 measured by the pumps, the pressure from the pumps, the pressure from the pressure transducer were also monitored using Lab View 5.1.

Finally, a ribbon blender was used as a mixer. The speed of the mixer was controlled with an electronic control device supplied by Autoclave Engineers (Pittsburgh, Pennsylvania).

3.2 Methodology

The following section describes the methodology used for the SC CO_2 extractions of drilling waste and for the petroleum hydrocarbon analysis.

3.2.1 SFE Extractions

The SFE extractions were performed at 40°C and 60°C, with the pressure varying from 8.96 MPa to 15.2 MPa. The extraction period comprised of 15 minutes of static extraction (no flow of SC CO_2) and 90 minutes of dynamic extraction (continuous constant flow of SC CO_2).

The procedure for the SFE experiments was as follows:

- Approximately 100g of homogenized drill cuttings were placed in a clean vessel.
- The vessel outlet was plugged with glass wool to prevent entrainment of particulates and potential clogging of the downstream lines and valves by entrained particles. The vessel body was bolted firmly to the lid using bolts whose threads were lubricated with Jet-Lube MP-50 Moly-Paste. A torque wrench was used to tighten the bolts and an increasing tightening sequence of torques from 25, 35, 40 to 42 ft-lb_f was applied. This tightening sequence of torques prevented leaks during the extraction.
- A water bath was filled with water at a specific temperature and the tubing was attached to the heating jacket of the vessel.
- The Lab view program was started to monitor the pressure, temperature, and SC CO_2 flow rate.
- The vessel was heated to the desired temperature. The impeller was turned on intermittently during the heating to allow the vessel to reach the desired temperature quickly.
- Once the desired temperature was reached, the vessel was pressurized.
- Once the desired pressure and temperature were reached, the total flow of CO_2 through the system was checked. The total flow should be less than 1 mL/min, indicating no leaks in the system.
- Once the conditions of pressure, temperature, and no flow were reached, the impeller was started. At this stage, the static phase of the extraction begins.
- Static extraction was conducted for 15 minutes.

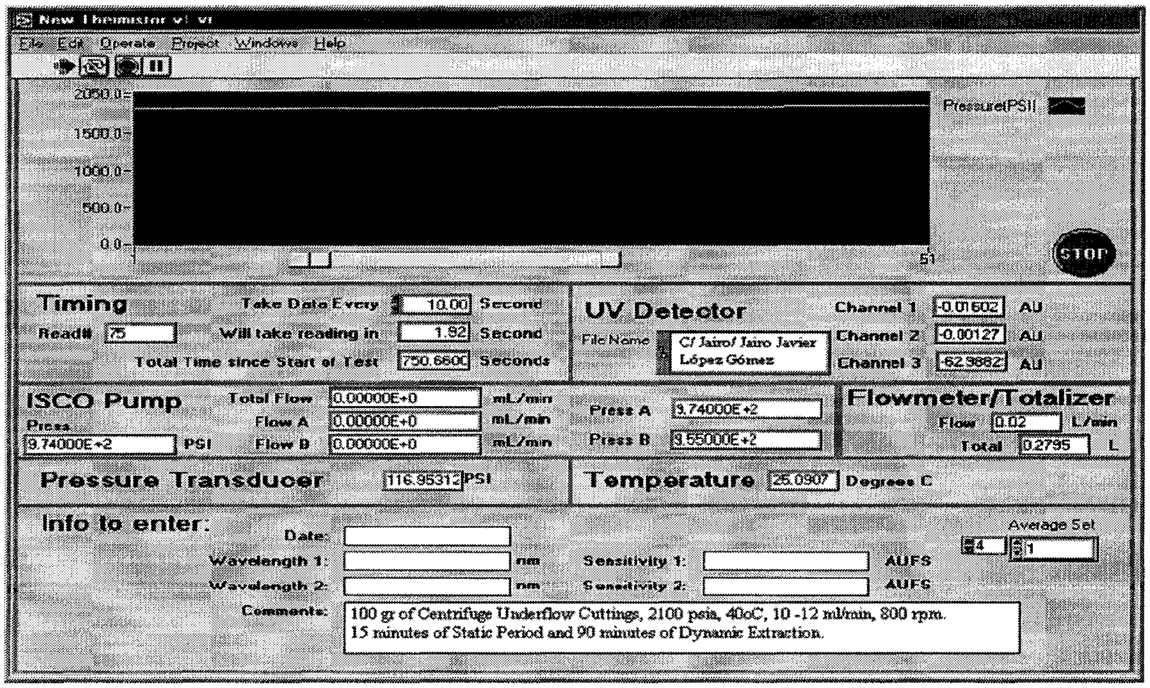
- During the static period, the metering valve was pre-heated using a variable autotransformer tape heater (heating tape) to prevent freezing and plugging by depressurizing CO_2. The glass vials that acted as traps were also prepared. The first trap was filled with glass beads and was weighed prior to being used for oil collection. The second trap contained clean toluene to collect any remaining oil that was not captured in the first trap. Both traps were placed in an ice bath.
- Once the static period was finished, the second three-way valve was opened, allowing the SC CO_2 to flow out of the vessel. The metering valve was adjusted to achieve the desired SC CO_2 flow rate. This marked the beginning of the dynamic phase. The dynamic phase lasted for 90 min.
- The extracted oil was collected in the traps, with the glass bead trap being changed every 10 minutes. The trap was weighed immediately after being changed; allowing time for weight to stabilize.
- Once the dynamic period was finished, the first and second three-way valves were closed, the mixer was stopped, and the vent was opened to begin depressurization.
- The depressurized vessel was opened and the treated drill cuttings were collected for analysis.
- Before and after extraction the drill cuttings were analyzed for petroleum hydrocarbon content (C_{10}–C_{34}) using the method outlined in CCME (2001) (see **Section 3.2.2**).
- The extraction efficiency was calculated.

Lab View Software

Lab View software was used to monitor the SFE extractions. A sample screen of the Lab View software is provided in **Figure 3-10**. It can be used for data control, data analysis and data presentation; however, in this investigation, it was only used for monitoring and data acquisition. Data acquisition was done every 10 seconds and saved to an Excel file. Each column of the resulting Excel file represents one of the parameters monitored during the experiment. Comments can also be introduced and will appear in the Excel file.

The data collected and their respective units are:

- Time since start of test (s)
- Pump Flow (mL/min)
- Transducer pressure (psi)
- Vessel Temperature (°C)
- Pump A flow (mL/min)
- Pump B flow (mL/min)
- Pump A pressure (psi)
- Pump B pressure (psi)



Take Data Every 10.00 Second
Read# 75
Will take reading in 1.92 Second
Total Time since Start of Test 750.6600 Seconds

File Name C:/ Jairo/ Jairo Javier López Gómez

Channel 1 -0.01602 AU
Channel 2 -0.00127 AU
Channel 3 -62.9882 AU

Press 9.74000E+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 9.74000E+2
Press B 9.55000E+2

Flow 0.02 L/min
Total 0.2795 L

Pressure Transducer 116.95312 PSI

Temperature 25.0907 Degrees C

Date:
Wavelength 1: nm
Wavelength 2: nm
Sensitivity 1: AUFS
Sensitivity 2: AUFS
Average Set 4 1

Comments: 100 gr of Centrifuge Underflow Cuttings, 2100 psia, 40oC, 10 -12 ml/min, 800 rpm.
15 minutes of Static Period and 90 minutes of Dynamic Extraction.

Figure 3-10. Sample screen from Lab View Software

3.2.2 Petroleum hydrocarbon analysis

The oil content of the raw and treated drill cuttings was determined using Soxhlet extraction and gas chromatography (GC/FID) analysis as outlined in the *Reference Method for the Canada-Wide Standard for Petroleum Hydrocarbons in Soil - Tier 1 Method (CCME 2001).*

According to the Canada-Wide Standard for Petroleum Hydrocarbons, four fractions are determined analytically to decide whether a site meets an acceptable criterion for various land uses (CCME 2001). The four fractions are: F1 F2, F3 and F4, and these fractions correspond to the following carbon numbers: F1 (nC_6 to nC_{10}), F2 (nC_{10} to nC_{16}), F3 (nC_{16} to nC_{34}), and F4 (nC_{34} to nC_{50}) (CCME 2001).

According to the CCME guidelines (CCME 2001), this Canada-Wide Standard for Petroleum Hydrocarbons is not appropriate to quantify individual hydrocarbon; however, it is appropriate to determine petroleum hydrocarbon content for soil and sediment (CCME 2001). This Canada-Wide Standard for Petroleum Hydrocarbons is not suitable for all PHC/soil combinations, but it is believed to be valid for almost all of the contaminated sites at which refined products have been discharged (CCME 2001). Furthermore, this method is also appropriate to several sites where crude oil operations have led to contamination (CCME 2001).

The fraction F1 (nC_6 to nC_{10}) was not considered in this investigation because the hydrocarbons present in this fraction are easily volatilized. Hydrocarbons of F1 fraction will therefore be lost during drilling process and will not appear as part of the PHCs present in drilling waste. The hydrocarbons in the aged diesel oil ranged from C_{10} to C_{34}

approximately. For this reason, the PHC analysis was performed to include fractions F2 to F4 only.

3.2.3 Gas Chromatography (GC) method used in this research

The gas chromatograph was a computer controlled Varian CP-3800 (Walnut Creek, California, U.S.A) with a CP-model auto-injector and a flame ionization detector (FID). This gas chromatograph makes use of Star Chromatography Workstation Version 5 software to program the functioning and sequencing of the gas chromatograph.

This GC had a capacity for ten 2-mL auto-sampler vials and three 5-mL solvent vials. Toluene was used in the solvent vials to clean the syringe. For each injection, six pre-flushes and six post-flushes were performed. The 5 mL solvent vials with toluene were changed at the beginning of each run of the GC to avoid any contamination of the syringe. In addition, pure solvent injections were done in between sample injections to clean the column and to reduce the false positives produced by remaining traces of contaminants inside the column from previous sample injections.

Standards with known concentrations were injected in between batches to verify the response of the gas chromatograph.

The following GC conditions were used in this investigation:

Carrier gas (Hydrogen) flow rate:	10 mL/min
Makeup gas (Hydrogen) flow rate:	30 mL/min
Injector temperature:	310°C
Injection Volume:	2 μL
Injector mode:	Split/splitless
Split/Splitless program:	
Initial:	Split state ON, with split ratio of 50
At 0.01 min:	Split state OFF
At 1.00 min:	Split state ON, with split ratio of 50
Column temperature program:	
Initial temperature:	40°C, hold for 2 minutes

Program: 40°C to 340 °C, at 15°C/minutes
Final temperature: 340°C, hold for 5 minutes
FID Detector temperature: 340°C
Airflow rate: 300 mL/min
H_2 flow rate: 20 mL/min

3.2.4 GC calibration requirements

The GC calibration requirements directly followed the CCME guidelines (CCME 2001). The CCME guidelines are summarized as follows (CCME 2001):

- The gas chromatograph should be equipped with a flame ionization detector and 100% poly (dimethylsiloxane) low bleed chromatography column, having 15 m minimum length, and 0.53 mm maximum diameter for analysis of the C_{10} to C_{50} hydrocarbons (CCME 2001). Having these devices installed, the chromatography system must separate the nC_{10} peak from the solvent peak.
- A mixture of approximately equal amounts of nC_{10}, nC_{16}, and nC_{34} normal hydrocarbons is used as the main calibration standard for the C_{10} to C50 hydrocarbons.
- nC_{50} response factor must be within 30% of the average of nC_{10}, nC_{16}, and nC_{34} response factors for instrument performance criteria for C_{10} to C_{50}. As well, the nC_{10}, nC_{16}, and nC_{34} response factors have to be within 10% of each other.

3.2.4.1 GC calibration procedure

The GC calibration procedure also directly followed the CCME guidelines, which are as follows (CCME 2001):

- With approximately equal weights of nC_{10}, nC_{16} and nC_{34} hydrocarbons dissolved in toluene, the calibration and retention time marking for the C_{10} to C_{50} hydrocarbons was performed.
- In order to have the retention time and response factor standard for the C_{10} to C_{50} hydrocarbons, a solution of nC_{50} in toluene was used.
- After running a blank (toluene) before analysis began, a minimum of a 3-point calibration curve using the nC_{10}, nC_{16}, and nC_{34} hydrocarbons was run for the C_{10} to C_{50} hydrocarbons.
- According to CCME guidelines, the highest standard had to provide a higher peak height than the highest peak height in the samples to be run, and dilution of the samples had to be performed when the peak height of the largest sample peak was higher than the peak height of the highest calibration standard.
- The linearity of the detector response was established using diesel oil and with the single compound (i.e. nC_{10}, nC_{16}, nC_{34} and nC_{50}) calibration standards. Linearity of the detector response had to be within 15% in each of the calibrated carbon ranges (i.e. F2, F3, and F4) for products (diesel oil in this case) and within 10% for single compounds.
- In order to confirm stability of the calibration curve, a daily check of the lowest calibration standard and the midpoint calibration standard had to be run. However, in this research, this confirmation of the stability of the calibration curve was performed by analyzing diesel oil standards when samples were analyzed. If the result obtained from this standard deviated by more than 20%

from the calibration curve or if the midpoint calibration standard deviated by more than 15% from the calibration curve, the calibration curve had to be rerun.

In this research, aged diesel oil was used to perform the calibration procedure. The standards were prepared at 100, 200, 500, 1,000, 2,500, and 5,000 ppm by dissolving the appropriate amount of aged diesel oil in toluene using a volumetric flask.

This procedure was carried out on an analytical balance (Model AX 205 delta range, Mettler Toledo, Columbus, Ohio). These concentrations corresponded to the working range of the GC. All of the standards were stored at $4^{\circ}C$ in the refrigerator until GC analysis was carried out.

Calculation of average response factor (RFavg): – According to CCME (2001), for all of the hydrocarbon standards (nC_{10}, nC_{16} and nC_{34}), a response factor (RF) had to be calculated and the average of all these response factors had to be taken.

Each individual RF was calculated as:

$$RF = \frac{A_{n-alk}}{C_{n-alk}}$$ **Equation 3-1**

where

A_{n-alk} = the area under the individual n-alkane peak, and

C_{n-alk} =the concentration of the individual n-alkane standard.

The average response factor is calculated as:

The RF_{avg} was calculated as:

$$RF_{avg} = \frac{Sum\,of\ individual\ RF\ values}{Number\,of\ RF\ values\ \ used}$$ **Equation 3-2**

Calculation of the amount of petroleum hydrocarbons in a sample: According to the CCME guidelines, the average response factor (RF) had to be utilized to estimate concentration of the hydrocarbons in each of the ranges C_{10} to C_{16}, C_{16} to C_{34} and C_{34} to C_{50}.

The fraction F2 was calculated as:

$$C_{10} - C_{16}\ Hydrocarbons\,(mg/kg) = \frac{A_{C10-C16} * Vol * F}{RF_{avg} * Wd} \qquad \textbf{Equation 3-3}$$

The fraction F3 was calculated as:

$$C_{16} - C_{34}\ Hydrocarbons\ (mg/kg) = \frac{A_{C16-C34} * Vol * F}{RF_{avg} * Wd} \qquad \textbf{Equation 3-4}$$

The fraction F4 was calculated as:

$$C_{34} - C_{50}\ Hydrocarbons\ (mg/kg) = \frac{A_{C34-C50} * Vol * F}{RF_{avg} * Wd} \qquad \textbf{Equation 3-5}$$

where

$A_{C10-C16}$ = the integration of all area counts from the apex of the C_{10} peak to the apex of the nC_{16} peak

$A_{C16-C34}$ = the integration of all area counts from the apex of the C_{16} peak to the apex of the nC_{34} peak

$A_{C34-C50}$ = the integration of all area counts from the apex of the C_{34} peak to the apex of the nC_{50} peak

Vol = Final volume of the sample extract (mL)

F = dilution factor applied to bring the samples and standards into the appropriate peak height range.

RF_{avg} = Average response factor calculated according to **Equation 3-2**.

W_d = Dry weight of sample taken (g)

Equation 3-3 to **3-5** required a value for the dry weight of the sample. This value was calculated using the following equations:

$$\% \, Moisture = \frac{Sb(g) - Sa(g)}{Sb(g)}$$ **Equation 3-7**

where

S_b = weight of sample before drying, in grams.

S_a = weight of sample after drying, in grams.

and

$$Wd\,(g) = Wt * (1 - \frac{\% \, Moisture}{100})$$ **Equation 3-7**

where

W_d = dry weight of sample, in grams.

W_t = weight of the sample taken from bottle, in grams.

3.2.5 CCME procedure

For each sample, three subsamples were taken to minimize the variability in the results. This procedure was performed on raw and treated centrifuge underflow and invert cuttings.

Samples of drilling waste prior to and following SFE extractions were analyzed for PHC content using the procedure outlined by CCME (2001). For SFE extracted drilling waste, three subsamples were prepared for analysis. According to CCME (2001), the fractions F2, F3, and F4, extractable hydrocarbons in the range C_{10} to C_{50}, are generally determined by extracting the hydrocarbons from an approximate amount of 5g dry weight sample with 50:50 (V:V) hexane:acetone using a Soxhlet extraction apparatus (see **Figure 3-11**). Subsequently, the extracts are analyzed using a gas chromatograph/flame ionization detector (GC/FID) (CCME 2001).

The following paragraphs provide a more detailed description of the method.

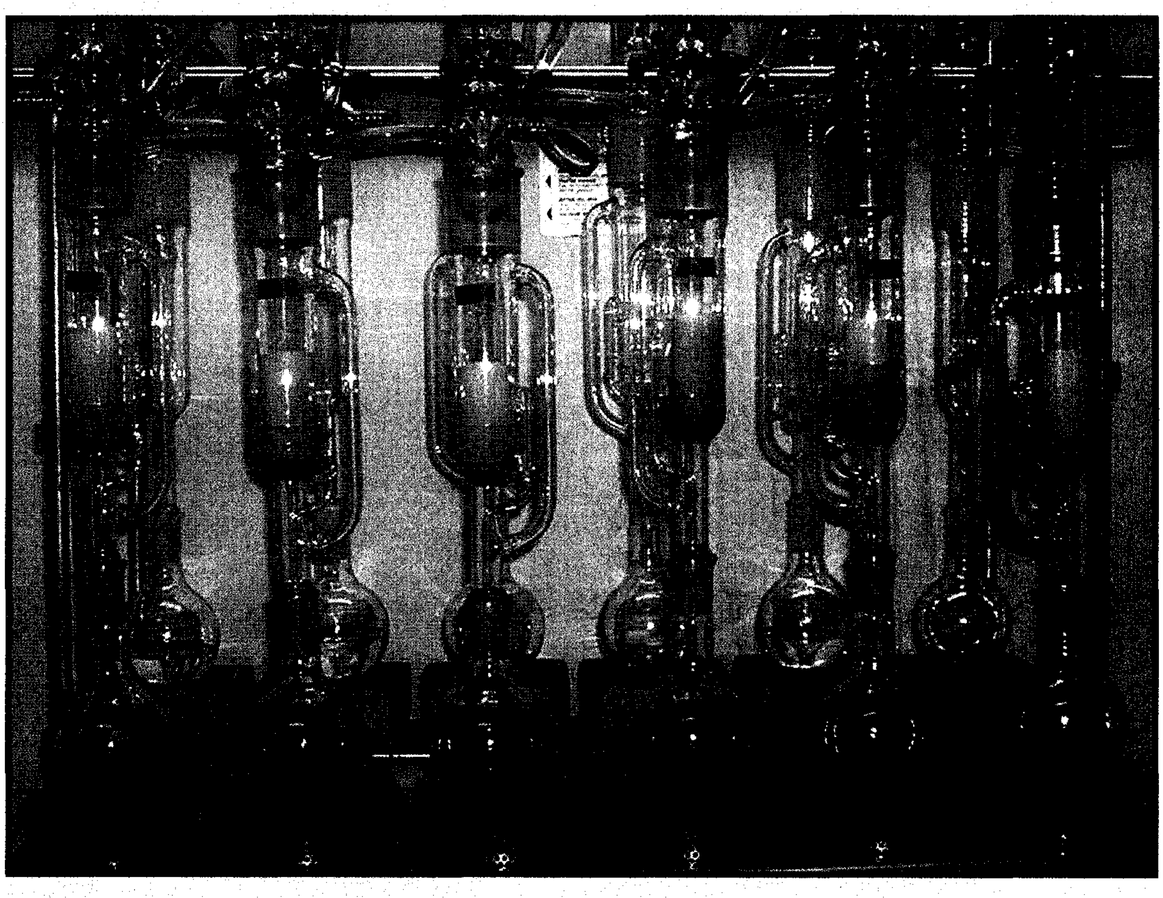


Figure 3-11. Soxhlet extraction apparatus

Steps for CCME procedure

The method for preparing samples for GC/FID analysis is as follows (CCME 2001):

- Take an approximate sample size of 5g (dry weight) and accurately weigh into a tared Soxhlet extraction thimble. Place the thimble into the Soxhlet extraction apparatus.

- Add 50:50 (V:V) n-hexanes:acetone solution at a minimum 20:1 (V:W) solvent:dry soil ratio. Then let the extraction proceed for 16 to 24 hours with the Soxhlet extraction apparatus operating at 4 to 6 cycles per hour.
- After Soxhlet extraction, recover the solvent and pass through 8g to 9g of dried sodium sulphate in a column. Rinse the sodium sulphate with approximately 10 mL of hexane.
- Add 1 to 2 mL of toluene to the recovered solvent and then place it in an evaporating vessel (Rotovap) to bring the volume down to 1 to 2 mL. The evaporation conditions should avoid the loss of the nC_{10} hydrocarbon by maintaining the desired temperature (80°C) in the Rotovap.

The following are important factors that must be considered when performing this method:

- Since the evaporation leaves the final sample hot, bringing the temperature of the remaining sample (extract) to room temperature by cooling with cold water is extremely important. The final extract must be at room temperature so that errors are not introduced when measuring the exact final volume.
- With a small gas tight syringe, measure the final volume of the extract. Do not measure the final volume if the remaining volume is still hot in the flask.

According to CCME (2001), the remaining extract is dried using sodium sulphate and can be treated either in situ or by column chromatography with silica gel to remove polar material (CCME 2001). However, in this investigation, silica gel treatment was not performed.

After the Soxhlet extraction process is performed, the sample is then analyzed by GC/FID for F2 (C_{10} to C_{16}), F3 (C_{16} to C_{34}) and F4 (C_{34} to C_{50}) fractions.

For the main calibration, the average response factor for nC_{10}, nC_{16}, and nC_{34} hydrocarbons is utilized (CCME 2001). The GC response factor of the nC_{50} must be within 30% of the average response factor of the nC_{10}, nC_{16} and nC_{34} hydrocarbons (CCME 2001).

3.2.6 Water content experiments

Since the invert cutting had 7% water content, the effect of water content on supercritical extraction with CO_2 was explored. Various experiments were carried out using different water contents. As well, drying agents were added to the cuttings to investigate water contents higher than 7%.

1. Experiment 1: extraction of 100g of invert cuttings with 7% water content (no water or drying agents added).
2. Experiment 2: extraction of 100g of invert cuttings with 15% water content (by adding water).
3. Experiment 3: extraction of 100g of invert cuttings with 7% water content and 70g of calcium sulfate added as a drying agent
4. Experiment 4: extraction of 100g of invert cuttings with 15% water content and 140g of calcium sulfate added as a drying agent
5. Experiment 5: extraction of 100g of invert cuttings with 15% water content and 26g of silica gel added as a drying agent
6. Experiment 6: extraction of 50g of invert cuttings with 50g of water added.

3.2.7 Solubility experiments

In order to make it possible to determine the most favorable loading ratio of raw cuttings to SC CO_2 for a larger scale system, the diesel oil's solubility in SC CO_2 was investigated. The diesel solubility was calculated using two methods.

First, the diesel oil solubility was determined by placing 20g of pure diesel oil in the 300 mL extraction vessel with a low flow rate (1.5 mL/min approximately) to ensure equal results during the sampling. The oil was collected in toluene, and respective conversions were made to determine the solubility in SC CO_2.

The parameters for the solubility experiment were 40°C, 14.5 MPa (suggested operating conditions), but as was previously stated, with a low flow rate.

The second method of determining collected oil solubility was using the data from the drill cuttings extraction experiments. The results were calculated by tracing a tangent line during the first 30 minutes (zone governed by solubility) on the curves of cumulative collected oil mass vs. cumulative mass of CO_2.

3.2.8 Quality control

A number of parameters and components were checked on a regular basis to ensure proper functioning and appropriate response of the GC. GC components includes glass inserts, injector septum and injector syringe. GC parameters included column pressure, flow of the different gases (carrier gas and make up gas), injector temperature, injector mode (split/splitless program), column temperature program and FID detector temperature. Periodic inspections using standards with known concentrations were tested to check the instrument's response. Once the percent of drift was above 15%, the glass insert, the septum, and the syringe were cleaned to restore the appropriate instrument response. If even after changing these components the instrument continued to show a percent of drift above 15%, the column was "baked" to ensure that the column was clean. This procedure ensured that the percent of drift was always below 15% when the samples were analyzed and that the GC response was consistent during analysis.

CHAPTER 4 RESULTS AND DISCUSSION

The following chapter presents a description of the extraction experiments carried out and the results obtained. For the experiments conducted, the following will be presented and discussed:

- **Summary of the extractions performed**
- **Different data obtained for the SFE experiments**
- **Visual Observations**
- **Petroleum Hydrocarbon Analysis**
- **Extraction efficiencies**
- **Solubility results**
- **Chromatograms of the oil collected in traps**
- **Quality assurance**

4.1 Summary of the extractions performed

Experiments were performed initially by placing 50g of cuttings inside the vessel, with a pressure setting of 12.4 MPa, a temperature of 60°C, and a mixing speed of 120 rpm. Experiments consisted of a 15-minute static phase and a 30-minute dynamic extraction. After the experiment, the treated cutting was visually observed and the conditions of mass of cuttings and mixing speed were changed until the cuttings looked dry, lighter in color, fine powder-like and had free flowing characteristics.

After this first set of experiments, the number of static and dynamic periods was increased to two and the mixing speed was increased to 550 rpm to see whether the quality of the treated cuttings was better. Because the treated cuttings did not exhibit appropriate characteristics, it was decided that the static and dynamic phases should be increased to three and the revolutions of the impeller to 800 rpm since the treated cuttings still had wet particles at the bottom and dryer particles on the top after the end of the extraction.

When the experiments were completed using three static and dynamic cycles, the drill cuttings looked drier than before and the revolutions were sufficient to lift the entire amount of drilling cuttings from the bottom. However, the appearance of the cuttings was still dark and sticky.

It was then decided to increase the pressure to 13.8 MPa, and the treated cuttings improved even more in appearance. At this point, it was decided to increase the pressure to 14.5 MPa at a constant temperature of 60°C to see whether the quality of the cuttings would improve.

The resulting treated cuttings looked extremely good and powder-like. After performing some experiments using these conditions, it was decided to explore higher pressures at the same temperature to see whether the quality of the cuttings would increase, but it showed no improvement. At this time, since good results were now being achieved, the intermediate static phases between dynamic phases were eliminated to see whether the quality of the treated cuttings would change. The result was that no difference was observed, so the static extractions were removed.

At this point, the effect of low temperature was tested to see whether the quality of the treated cuttings would change. Experiments maintaining the same pressure of 14.5 MPa but reducing the temperature from 60°C to 40°C showed that reducing the temperature at a constant pressure (14.5 MPa) did not affect the quality of the treated cuttings. The result was that same pressure at different temperatures did not lead to any considerable differences; the pressure was governing the process.

The effect of flow rates was also investigated at 14.5 MPa and 40°C. Lower and higher flow rates (5 mL/min and 20 mL/min respectively) were tested, and the most favorable flow rate was identified to be 10 to 12 mL/min. The results and trends presented above will be discussed in greater detail in the following sections.

4.2 Data obtained for the SFE experiments

The following sections discuss the data obtained for the SFE experiments. A sample Excel data file obtained during an experiment is presented in **Appendix A1**.

4.2.1 Pressure Data

Data from the ISCO syringe pumps and pressure transducer were taken from the Lab View program every ten seconds. The data from the ISCO syringe pumps A and B indicated the pressure at which the pumps were pressurized and therefore the pressure at which the pumps were delivering the pressurized liquid CO_2. The temperature of pressurized liquid CO_2 delivered by the pumps was 7.5°C. The data from the pressure transducer indicated the pressure of the pressurized CO_2 at the desired temperature (40°C or 60°C depending on the experimental conditions). The pressure data from the pressure transducer was taken immediately upstream of the extraction vessel and therefore indicated the pressure inside the extraction vessel.

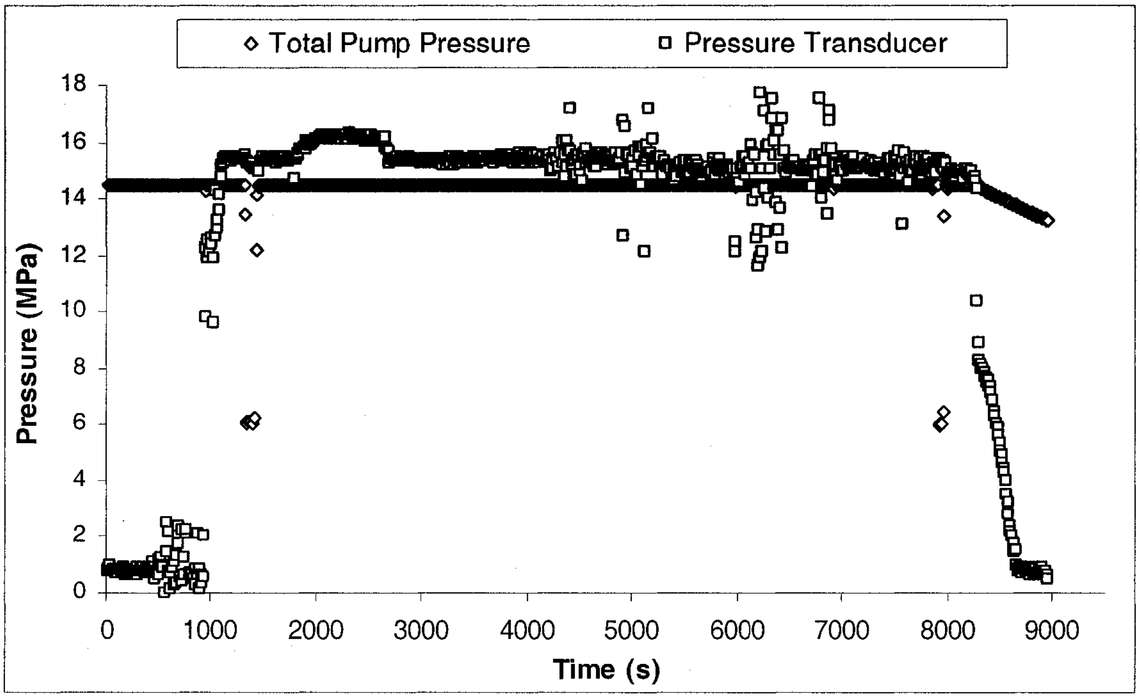


Figure 4-1. **Pressure data for an experiment conducted at 14.5 MPa and 40°C**

Figure 4-1 shows representative pressure data for a typical experiment performed in this investigation. The pressure transducer had different offsets for the same set pressure for pumps A and B. The pressure transducer readings indicated that for both pumps set at 14.5 MPa, the readings for pump A were 15.10 MPa and for pump B 15.35 MPa.

Pumps A and B were run simultaneously for each SFE experiment but independently from each other to ensure a constant supply of pressurized liquid CO_2.

In **Figure 4-1,** from 0 to 1000s, it can be seen that prior to the extraction experiment, the total pump pressure was at the desired pressure (14.5 MPa), while the pressure transducer reading showed a pressure of around 0.83 MPa in the line prior to the extraction.

After this period, with Pump B running first, it was seen that as a result of pressurizing the extraction vessel for approximately 60s, the pressure in the lines reached

15.35 MPa. Seconds later, a drop in the pump pressure indicated that pump B was depressurized and completely refilled again to ensure that there was enough CO_2 for a complete extraction experiment. At the same time, pump A was also depressurized and refilled.

From 1500 to 2500s, a slight increase in the pressure from 15.4 MPa to 16.2 MPa was noticed. This increase was due to the fact that, during this time, the temperature of the SC CO_2 increased from 40°C to 44°C. This produced an expansion inside the vessel and therefore a slight increase in pressure. This effect was seen in all extractions and was produced by the heating system as it was trying to stabilize the temperature inside the vessel. After this period, the system again reached the desired temperature and therefore the pressure returned to 15.4 MPa.

After pressurization and stabilization, both the total pump pressure and the pressure transducer were stable during the static and dynamic extraction periods. Some isolated points of high or low pressure were seen during the dynamic period (4000 to 7000s). These high and low pressures were produced by momentary instabilities in the pressure transducer.

At 8000s, the pumps were depressurized and refilled to complete the experiment. This refilling was necessary in almost all experiments in order to have sufficient CO_2 to complete the extraction.

Finally, from 8500 to 9000s, it can be seen from the pressure transducer reading that the system was depressurized while the pumps remained at pressure. At the end of the experiment, the system was depressurized but the pumps were left at pressure, ready for another experiment.

4.2.2 Flow Data

The flow rate data for a typical experiment are shown in **Figure 4-2.** These flow rate data were collected from the ISCO syringe pumps and were monitored using the Lab View program. **Figure 4-2** shows the range of flow rates for an extraction at 14.5 MPa and 40°C. All the flows at different times of the experiment (refilling, pressurization and normal periods like static and dynamic) can be seen.

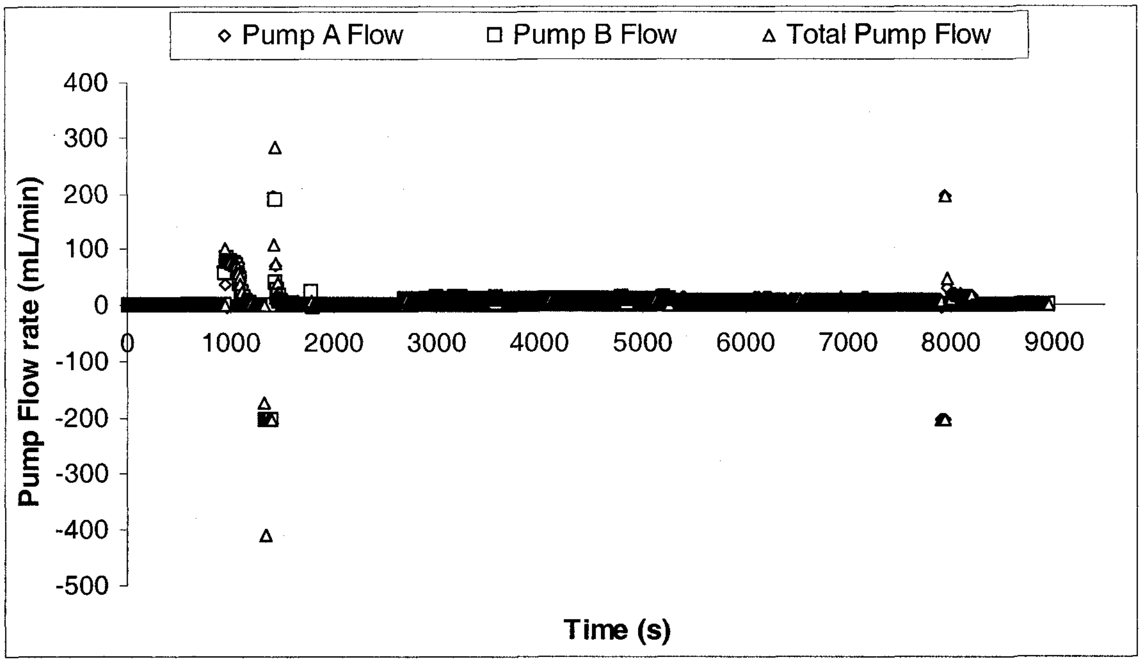


Figure 4-2. **Full-scale flow rate data for an experiment conducted at 14.5 MPa, 40°C and 10 mL/min**

Figure 4-3 presents the same flow rate data but on a reduced scale to better show the fluctuations in the flow rate.

The data from ISCO syringe pumps A and B indicated the flow rate at which each pump was delivering the pressurized liquid CO_2. The total pump flow is indicated by the sum of the flows coming from both pumps; A and B.

The flow rate data were taken from the pump controllers and therefore indicated the flow rate delivered by the pumps to the extraction vessel. Since the pumps operated in constant pressure mode, this total flow rate was controlled during the static period by two three-way valves (on/off valves) located before and after the extraction vessel. During the dynamic periods, the total flow was controlled by the heated metering valve located after the second three-way valve (prior to cold traps).

Figure 4-2 shows that the maximum flow rate for each pump when refilling was approximately -200 mL/min: When delivering, the maximum flow rate was +200 mL/min. These two values matched with the set flow rates on the pump controllers. Values of -400 mL/min and +400 mL/min for **Total Pump Flow** on **Figure 4-2** indicate that both pumps A and B were running or refilling at the same time.

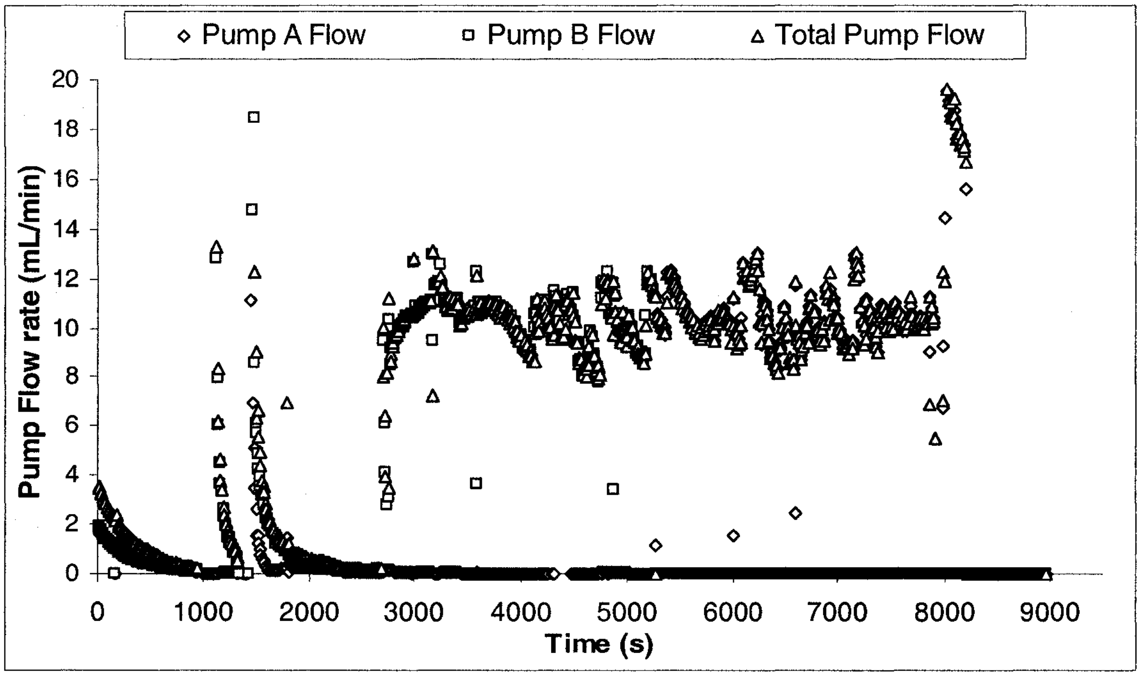


Figure 4-3. Pump flow data (on a reduced scale) for an experiment conducted at 14.5 MPa, 40°C and 10 mL/min

Figure 4-3 shows that during the dynamic period (from 3000s to 8000s), pump B was initially running (from 3000s to 5000s) until it was empty, and the pump A started running (from 5000s to 8000s) and continued until the end of the experiment.

Finally, in **Figure 4-3**, it can be seen that the most favorable flow rate, as was mentioned before, was around 10 to 12 mL/min during the dynamic period. **Figure 4-3** also indicates an instability in the total pump flow during the dynamic phase (4000 to 8000s) caused by the nature of the process. The fluctuations in the flow were believed to be caused by fine particles that momentarily clogged the vessel outlet, as well as depressurized CO_2 that sometimes created ice and freezing.

4.2.3 Temperature Data

The temperature data for a typical experiment are shown in **Figure 4-4**. The temperature was monitored using a thermistor probe inserted into the extraction vessel. The temperature of the extraction vessel was controlled by an external circulating heated water bath that was connected to the heating jacket of the vessel. The temperature controller of the water bath was able to stabilize the temperature to $\pm 0.5^{\circ}C$ of the desired temperature inside the extraction vessel during the experiments. The temperature in the water bath was also monitored by a mercury thermometer placed directly in the water bath.

Since the water bath temperature was almost the same as the one sensed in the extraction vessel, direct checking and corrections to the water bath were performed to maintain the desired temperature in the vessel. These checks and corrections were performed by monitoring the temperature of the water bath using a mercury thermometer (located in the water bath) and by changing the setting of the temperature controller for the circulating heated water bath.

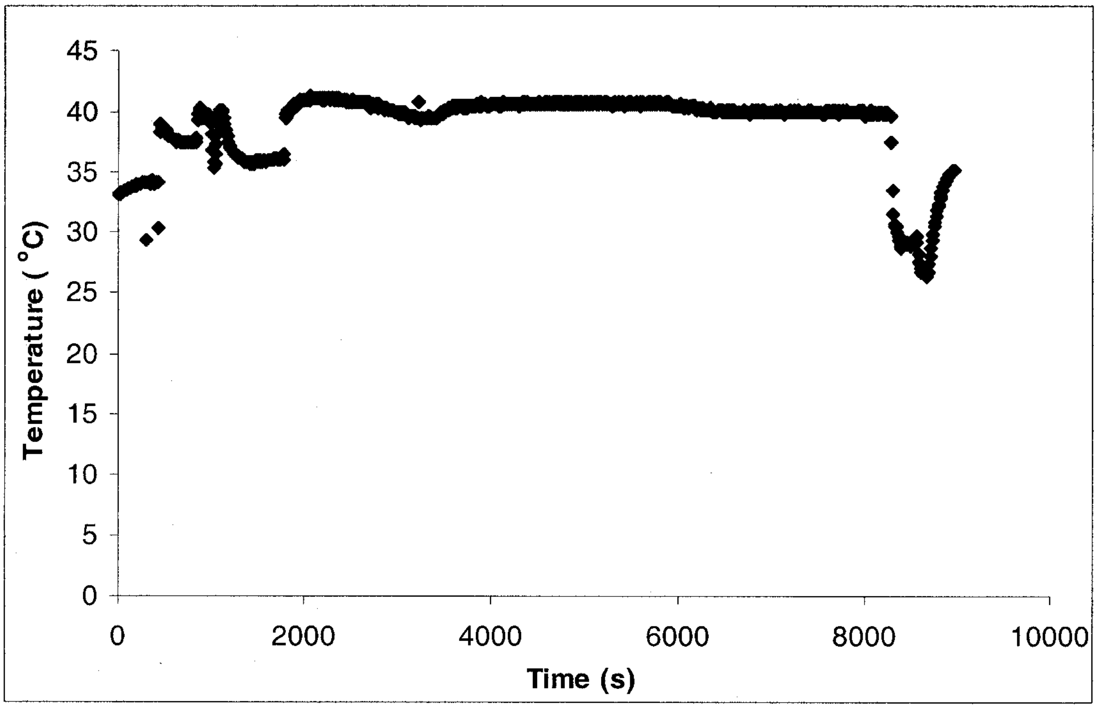


Figure 4-4. **Temperature data for an experiment conducted at 14.5 MPa, 40°C and 10 mL/min**

As seen in **Figure 4-4,** the temperature of the extraction vessel increased progressively and stabilized at 40°C ± 0.5°C. As soon as the pressurized CO_2 was introduced to the heated vessel that was maintained at 40°C (2000s to 2500s), the temperature increased to approximately 43°C and then came back to the desired temperature of 40°C. During this period, the temperature of the water bath remained stable at 40°C, indicating that only the temperature of the vessel increased as the vessel was pressurized with CO_2.

4.3 Visual Observations

The following section presents visual observations of the cuttings before and after supercritical fluid extraction with CO_2, visual observations of the cuttings inside the vessel and visual observations of the oil collected in traps.

4.3.1 Observations of the Cuttings Before and After SFE

Before and after SFE, visual observations of the cuttings were made to provide an indication of the extraction efficiency of the process. **Figures 4-5** and **4-6** provide visual observations of the centrifuge underflow and invert cuttings, respectively, before and after the SFE.

Centrifuge Underflow Cuttings

The centrifuge underflow cuttings before SFE shown in **Figure 4-5** looked extremely sticky, viscous, fudge-like in texture and dark in color, with an intense diesel oil smell. Once the extractions were performed at the suggested operating conditions (14.5 MPa and 40°C) the cuttings looked dry, lighter in color, and fine powder-like. The cuttings also had free flowing characteristics.

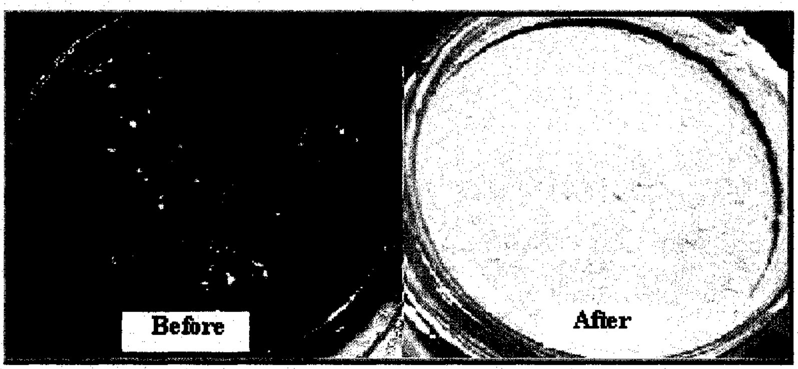


Figure 4-5. Centrifuge underflow cuttings before and after SFE

Invert Cuttings

The invert cuttings before SFE, shown in **Figure 4-6**, also looked extremely sticky, viscous, fudge-like in texture, dark in color (lighter than the centrifuge underflow cutting), and also had an intense diesel oil smell. Once the extractions were performed at the suggested operating conditions (14.5 MPa and 40°C), the cuttings looked lighter in color and dry. The texture of the treated invert cuttings after SFE was not as powder-like as compared with the centrifuge underflow after SFE. For this reason, some visual observations for each type of cutting in the extraction vessel after SFE are presented in the following section.

Figure 4-6. **Invert cuttings before and after SFE**

4.3.2 Observations of Cuttings in the Extraction Vessel

Once the SFE was performed for both centrifuge underflow and invert cuttings, direct visual observations of the cuttings in place in the extraction vessel after SFE were performed. These observations would provide some indication of how easy it is to remove the treated cuttings from the extraction vessel. These observations would also help determine the capability of removing the cuttings after SFE from an extraction vessel if extractions were conducted on a larger scale (pilot or commercial).

Figures 4-7 and **4-8** show the two types of drill cuttings inside the vessel after SFE.

Centrifuge Underflow Cuttings

The centrifuge underflow cuttings shown in **Figure 4-7** reveal how the cuttings appeared when the vessel was opened after the SFE.

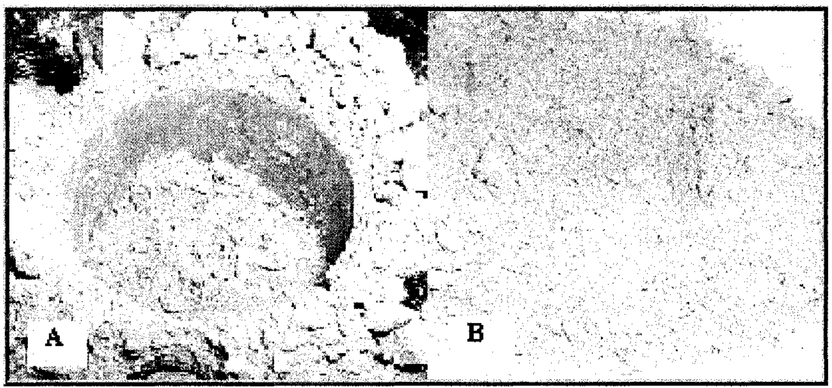


Figure 4-7. Centrifuge Underflow after extraction inside extraction vessel (A) and spread on a paper (B)

As can be seen in **Figure 4-7**, the appearance of the cuttings in the vessel was good. The cuttings appeared as fine powder, easy to remove from the vessel. The cuttings were not caked onto the vessel walls and impeller **(Photo A in Figure 4-7)**. By simply inverting the extraction vessel, the treated cuttings could be removed without any mechanical action such as scratching the walls of the vessel with a spatula. Once removed from the vessel, the cuttings remained as very fine particles **(Photo B in Figure 4-7)**.

In summary, handling and removing the treated centrifuge underflow cuttings from the extraction vessel after SFE did not represent any difficulty. The results indicate that at a larger scale, it would be easy to deal with these treated cuttings. However, precautions must be taken since there is a lot of dust (fine particles) released when handling the treated cuttings due to their fine powder-like characteristic.

Invert Cuttings

The sequence of photos shown in **Figure 4-8** illustrates the process used to remove the invert cuttings from the extraction vessel.

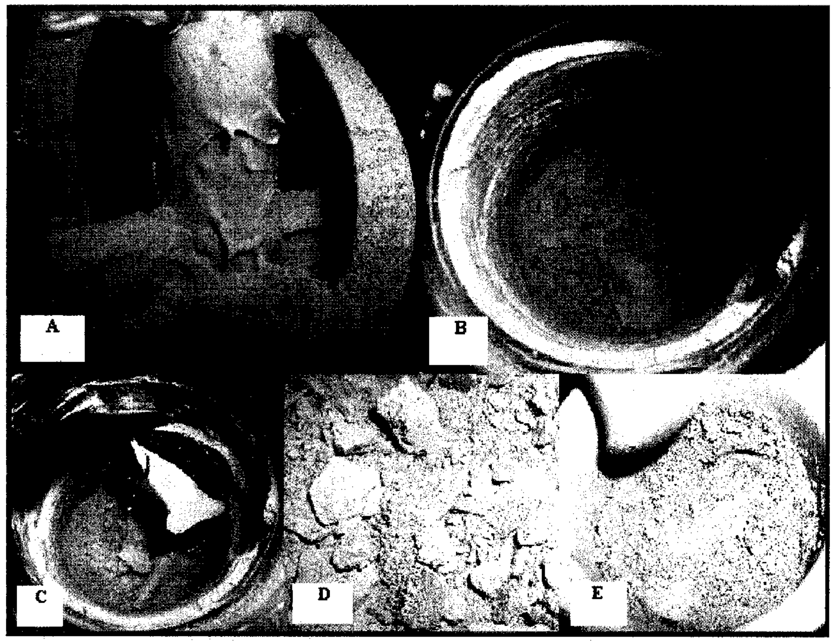


Figure 4-8. Steps taken to remove the treated invert cuttings from the vessel. A (treated invert cuttings adhered to the impeller), B (treated invert cuttings adhered to the vessel walls), C (removing the treated invert cuttings adhered to the vessel walls), D (treated invert cuttings without maceration), and E (treated invert cuttings after maceration)

It was found that the treated invert cuttings had a texture of dry flakes or dry chunks (**Photo D in Figure 4-8**) that adhered to the internal surfaces (impeller and internal vessel walls) at the end of the extraction process **(Photo A and B in Figure 4-8).** Mechanical action such as scratching the walls of the vessel with a spatula (**Photo C in Figure 4-8**) was necessary to remove the treated invert cuttings from the vessel. In addition, macerating the dry chunks was also necessary to convert the dry flakes into fine powder (**Photo E in Figure 4-8**).

In summary, manipulating and taking out the treated invert cuttings from the extraction vessel after SFE was difficult since the cuttings adhered to the internal surfaces. This phenomenon of caking (adherence) to all surfaces (vessel walls and impeller surface) may be due to the hydration of the clay since invert cuttings has a higher moister content (approximately 7%) than the centrifuge underflow cuttings.

Hydration of the clay occurs when dry bentonite (a principal kind of hygroscopic material used in drilling mud) is mixed with water (Schlumberger 2003). According to the observations above, hydration of the clay may enhance its adherence characteristics to metal surfaces.

4.3.3 Observations of the Oil Collected in the Traps

The oil extracted from both the centrifuge underflow and invert cuttings were collected in traps containing glass beads (**Figure 4-9**).

Figure 4-9. Oil collected in glass bead traps

The oil extracted from the centrifuge underflow cuttings and invert cuttings had the same characteristics as diesel oil (a yellowish color and characteristic diesel-like smell). It also had the same color as the weathered diesel oil used to prepare the calibration standards. Moreover, the color and smell of the oil collected during the experiments evidently did not change when the centrifuge underflow cuttings and invert cuttings were extracted. Finally, the color and smell of the oil extracted from centrifuge underflow cuttings and invert cuttings did not change as a function of time through the dynamic extraction process.

4.4 Petroleum Hydrocarbon Analysis

The petroleum hydrocarbon content of centrifuge underflow and invert cuttings was determined prior to and after SFE using the CCME method (CCME 2001). The CCME method uses Soxhlet extraction and GC/FID to determine F2, F3, and F4 fractions separately. The total petroleum hydrocarbon content is the sum of the F2, F3, and F4 fractions. With the CCME method, the quantity of oil present in the cuttings prior to treatment (i.e. the raw cuttings) as well as the quantity of oil remaining in the cuttings after treatment by SFE at different conditions could be determined. The different extraction efficiencies for each condition investigated could then be calculated.

Additionally, the composition of the oil collected from the traps was evaluated using gas chromatography/flame ionization detection (GC/FID). Making use of GC/FID detection, qualitative comparisons between the oil extracted, the oil in raw cuttings, the oil in treated cuttings, and commercial diesel oil were performed.

4.4.1 Alkane Retention Times

The retention time marking for the C_{10} to C_{50} hydrocarbons was performed using standards prepared by mixing approximately equal amounts of nC_{10}, nC_{16}, and nC_{34} hydrocarbons in toluene (as a solvent).

A sample chromatogram of a 5,000-ppm standard containing a mixture of decane (C_{10}), hexadecane (C_{16}), and pentacontane (C_{50}) is shown in **Figure 4-11**. Due to the fact that C_{34} has a low solubility in toluene, a single 5,000-ppm standard containing just tetratriacontane (C_{34}) had to be prepared separately, and is shown in **Figure 4-12**. The retention times of these alkanes was determined from these chromatograms and are presented in **Table 4-1.** A solution of nC_{50} in toluene was used as a retention time standard and a response factor standard for the C_{10} to C_{50} hydrocarbons.

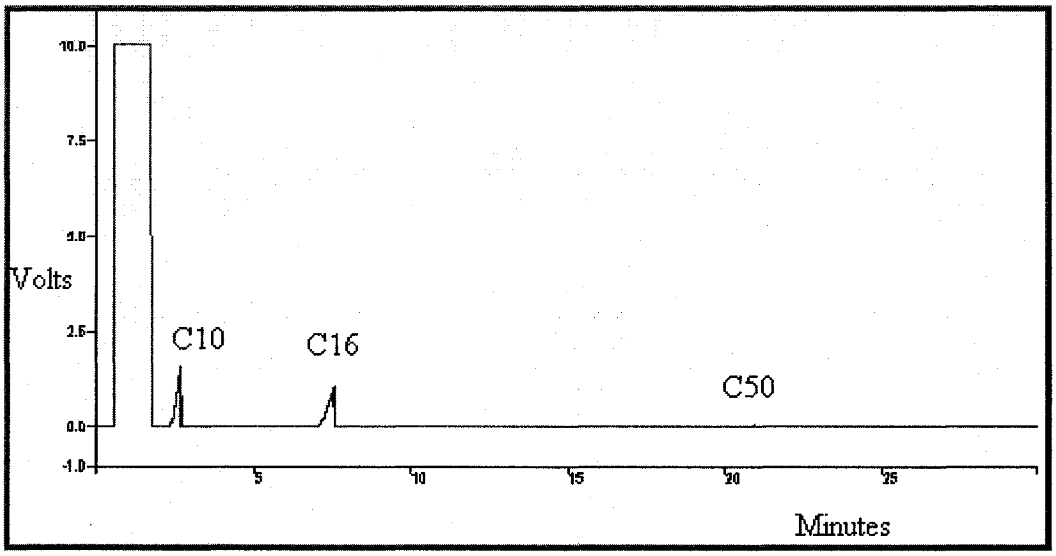


Figure 4-10. C_{10}, C_{16}, C_{50} retention time chromatogram

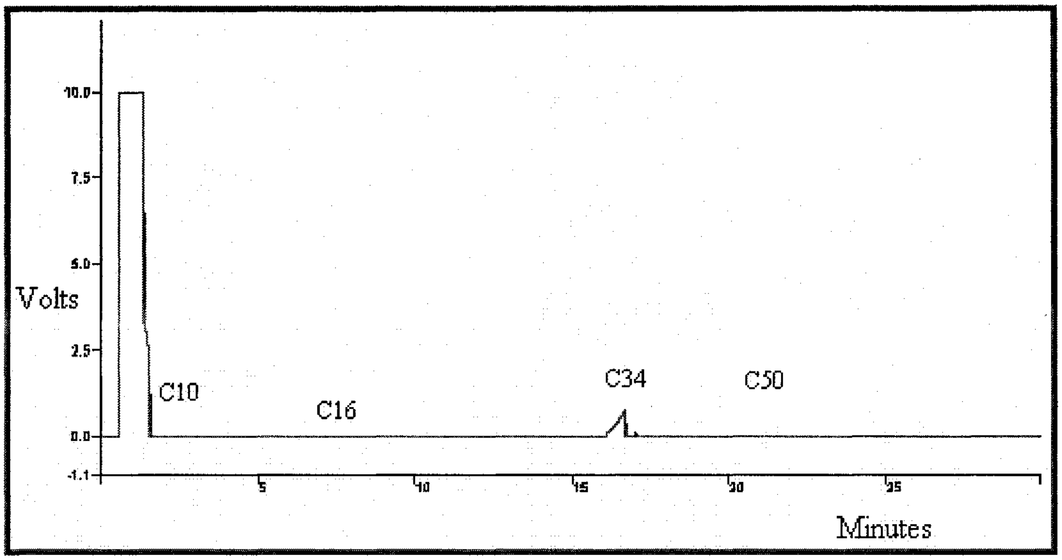


Figure 4-11. C_{34} **retention time chromatogram**

As an example of the characteristic hump of the diesel having the peaks belonging to each alkane, a 5,000-ppm diesel oil standard chromatogram is presented in **Figure 4-12.**

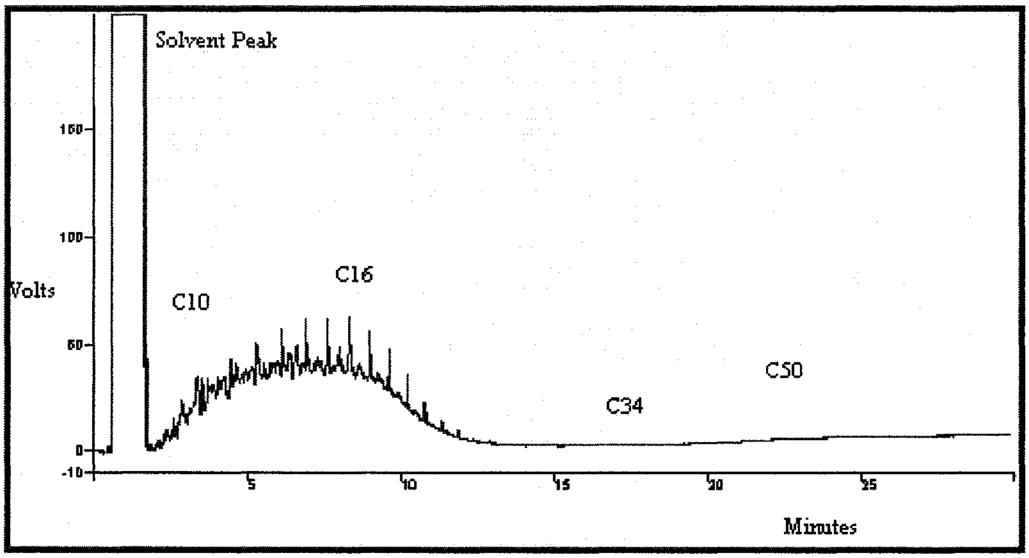


Figure 4-12. 5,000 ppm Diesel Oil Standard

The retention times shown in **Table 4-1** are related to F2, F3, and F4 fractions as follows:

- The F2 fraction is determined using all area counts between retention times 2.320 min to 7.081 min.

- The F3 fraction is determined using all area counts between retention times 7.081 min to 16.489 min.
- The F4 fraction is determined using all area counts between retention times 16.489 min to 20.908 min.

Table 4-1. Retention times for the different alkanes

Peak	Retention Time (minutes)
Toluene (solvent)	0.999
C_{10}	2.320
C_{16}	7.081
C_{34}	16.489
C_{50}	20.908

As a result of the retention times presented in **Table 4-1**, the GC/FID program had a length of 27 minutes in total, and the retention time window was from 2.320 to 20.908 minutes.

4.4.2 GC/FID Calibration

During this investigation, two GC/FID calibrations were performed due to an impasse with the GC (broken column). The first calibration was performed at the beginning of the work and is valid for all experiments carried out prior to June 25, 2003. The second calibration was performed after a modification to the GC column and is valid for all experiments carried out after June 25, 2003.

The GC/FID calibration was based on the integration of the area under the peaks between the retention time markers as described in **Section 4.4.1**.

The first GC/FID calibration for C_{10} to C_{50} hydrocarbons was done by running a 3-point calibration curve using mixtures of nC_{10}, nC_{16} and nC_{34} hydrocarbons at different concentrations (see **Figure 4-13**), as well a solvent blank (toluene) before analysis.

A second GC/FID calibration for C_{10} to C_{50} hydrocarbons was also done by running a 5-point calibration curve using mixtures of nC_{10}, nC_{16}, and nC_{34} hydrocarbons at different concentrations following the same procedure (see **Figure 4-14**).

As specified by CCME (2001), the instrument performance criterion for C_{10} to C_{50} was achieved for both GC/FID calibrations. The nC_{50} response factor was within 30% of the average of nC_{10}, nC_{16}, and nC_{34} response factors. The nC_{10}, nC_{16}, and nC_{34} response factors were within 10% of each other (See **Table 4-2**).

In order to perform the peak area integration for the different fractions of hydrocarbons, a function available in the Star Chromatography software called "Group Peaks (GR)" was used. This feature allowed for the splitting of the area and therefore the summing up of the areas corresponding to different fractions of hydrocarbons. This GR feature available in this software allowed all peaks to be reported as a single area peak and summed up by fractions (F2, F3 and F4) (see **Appendix B1** for a representative report).

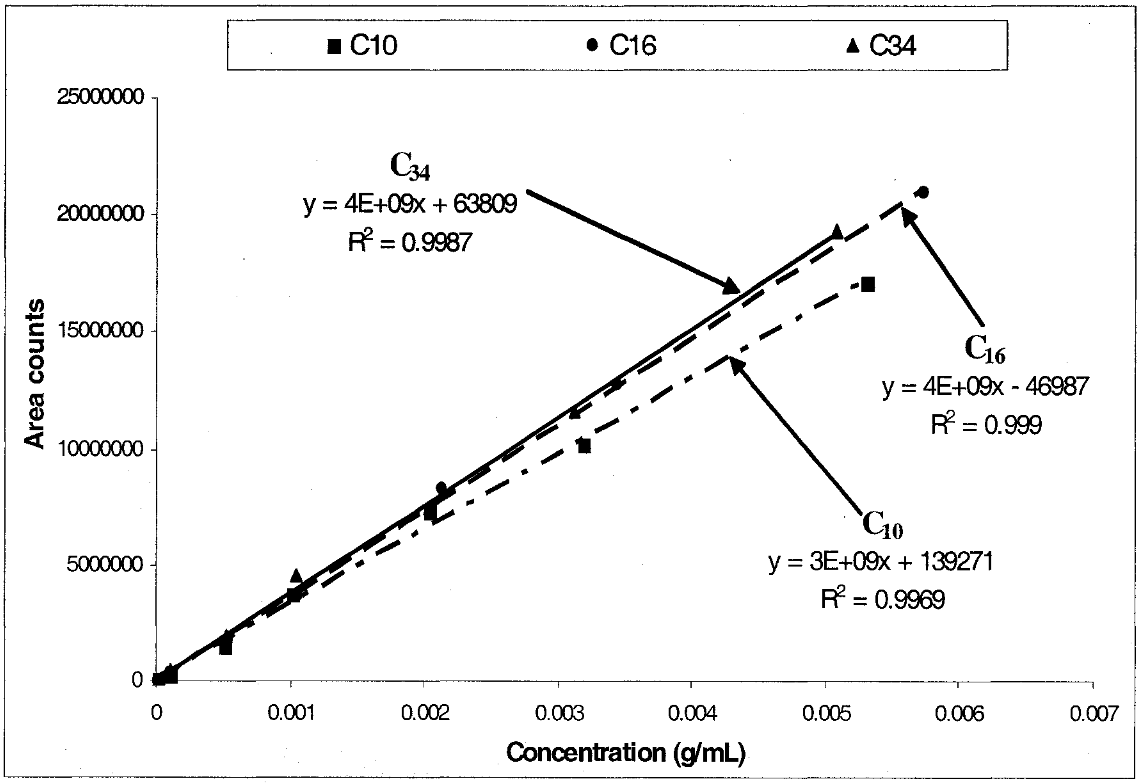


Figure 4-13. Alkane Calibration Curve # 1 valid for all experiments carried out prior to June 25, 2003

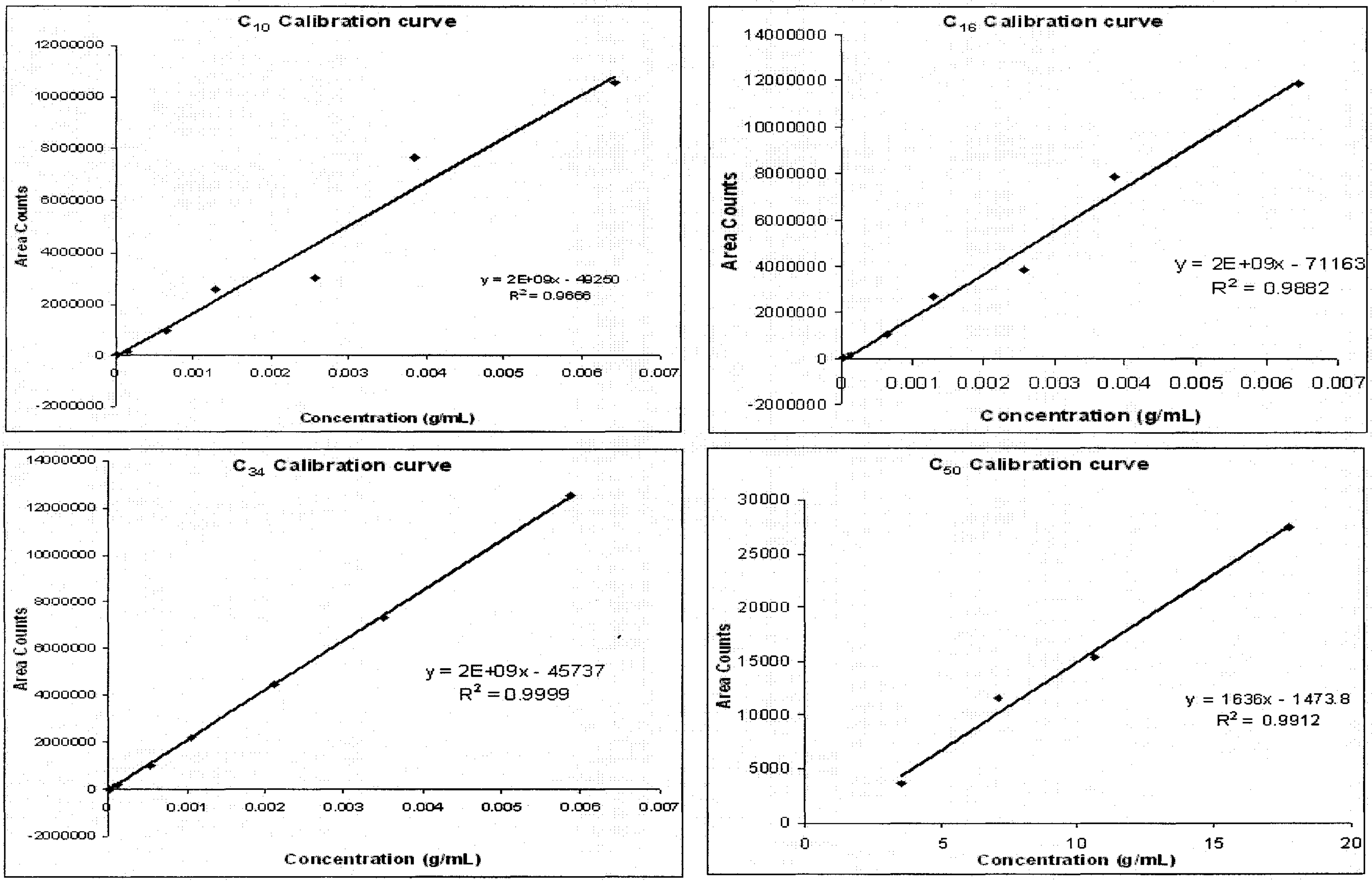


Figure 4-14. Alkane Calibration Curve # 2 valid for all experiments carried out after June 25, 2003

Table 4-2. **Response factor check for GC/FID Calibration**

Alkane	Response factor Calibration #1	Response factor Calibration #2	% Error		
			Calibration # 1	Calibration # 2	CCME Criteria
C_{10}	3,403,906,175.68	1,659,832,155.49	4.51	2.89	**<10%**
C_{16}	3,492,329,419.58	1,663,422,236.06	2.03	2.68	**<10%**
C_{34}	3,798,342,853.47	1,804,557,987.60	6.55	-5.28	**<10%**
Average	**3,448,117,797.63**	**1,709,270,793.05**	-	-	-
Standard Deviation	**206,979,541.89**	**82,540,652.13**	-	-	-
% RSD	**6.00**	**4.83**	-	-	<10%

In addition, the linearity of the detector response was established by using diesel oil (since it was the main contaminant present in the raw cuttings), and by using single alkane calibration standards. According to CCME (2001), the linearity of the detector response was established using diesel oil and single compound (i.e. nC_{10}, nC_{16}, nC_{34} and nC_{50}) calibration standards. Linearity of the detector response had to be within 15% for each of the calibrated carbon ranges (i.e. F2, F3, and F4) for products (diesel oil in this case) and within 10% for single compounds. In this work, linearity was determined by a linear regression of the calibration curves for the individual alkanes and for the F2 and F3 fractions of diesel oil. If the R^2 values of this linear regression were greater than 0.9 for the compounds and 0.85 for the F2 and F3 fractions of diesel oil, the criteria was said to be met. The R^2 values achieved in this work are presented in **Tables 4-3** and **4-4**.

Linearity was within 15% in each of the calibrated fractions for diesel oil (F2 and F3) and within 10% for the individual alkane. Fraction F4 was not considered since diesel oil does not have hydrocarbons in the range of the F4 fraction (see **Tables 4-3, Table 4-4**, **Figures 4-15**, **Figure 4-16** and **Appendix B2**).

Table 4-3. Single compound CCME Criteria

Alkanes	Linear Correlation R^2		CCME Criteria
	Calibration #1	Calibration #2	
C_{10}	0.9969	0.9666	**>0.90**
C_{16}	0.9990	0.9882	**>0.90**
C_{34}	0.9987	0.9999	**>0.90**

Table 4-4. Diesel Oil CCME Criteria

Hydrocarbon Fraction	Linear Correlation R^2		CCME Criteria
	Calibration #1	Calibration #2	
F2	0.9997	0.9950	**>0.85**
F3	0.9832	0.9947	**>0.85**
F4	-	-	**>0.85**
Hump	0.9977	0.9981	**>0.85**

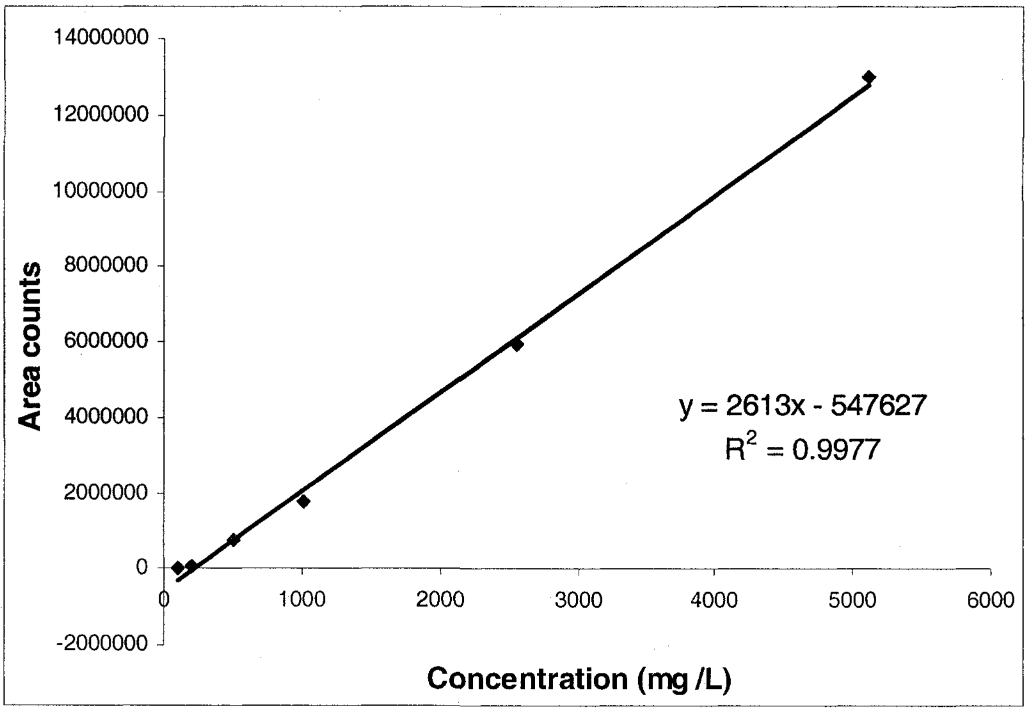


Figure 4-15. Diesel oil calibration (F2 + F3) #1 valid for all experiments carried out prior to June 25, 2003

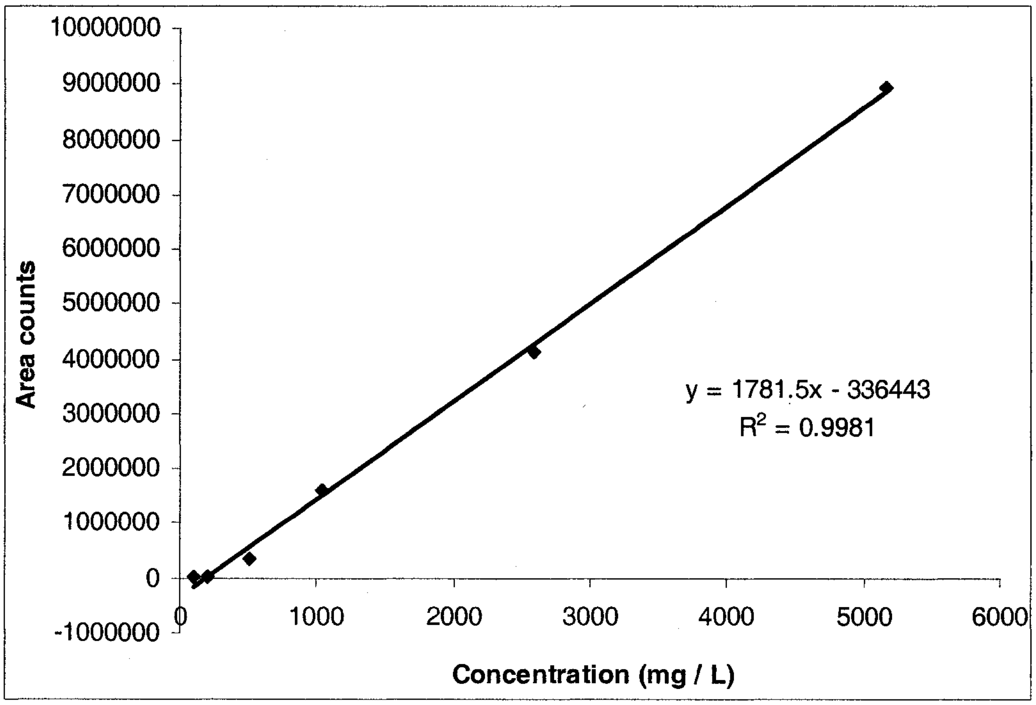


Figure 4-16. **Diesel oil calibration (F2 + F3) #2 valid for all experiments carried out after June 25, 2003**

4.5 Extraction Efficiencies

The extraction efficiencies are calculated using the oil or PHC content in the cuttings prior to extraction and following extraction. The petroleum hydrocarbon contents then allowed the extraction efficiency to be calculated according to the following equation:

$$Extraction\ efficiency\ (\%) = \frac{PHC_{Raw} - PHC_{Treated}}{PHC_{Raw}} * 100\% \quad \textbf{Equation 4-1}$$

where PHC_{Raw} is the petroleum hydrocarbon content in the raw sample and $PHC_{Treated}$ is the petroleum hydrocarbon content in the treated sample.

The petroleum hydrocarbon content determined by the CCME analysis was found to be 19.4% for the raw centrifuge underflow cuttings and 14.8% for the raw invert cuttings. The value of 19.4% for the centrifuge underflow cuttings was similar to that reported by Odusanya (2003), who worked with similar centrifuge underflow cuttings. In addition, Saintpere and Morillon-Jeanmaire (2000) reported ranges between 6 and 13%, values closer to those for the invert cuttings analyzed in this investigation.

The extraction efficiencies were calculated using the PHC or oil contents reported above for the raw cuttings and using those determined for the treated cuttings. Extraction efficiencies are reported for pressure conditions ranging from 8.96 MPa to 15.2 MPa, temperature conditions ranging from 40°C to 60°C, flow conditions ranging from 5 mL/min to 20 mL/min, and mixing conditions of 800 rpm.

Extraction efficiencies for the various conditions are presented in **Table 4-5** and **Figure 4-17**. The high extraction efficiencies shown both in **Table 4-5** and **Figure 4-17** indicate that the SFE process was able to reduce the oil content in the centrifuge underflow cuttings from 19.4% to approximately 0.3%. According to CCME (2001), the regulatory guidelines for PHCs in soil state that the cuttings should have less or equal to 0.5% of PHCs to be considered below regulatory guidelines.

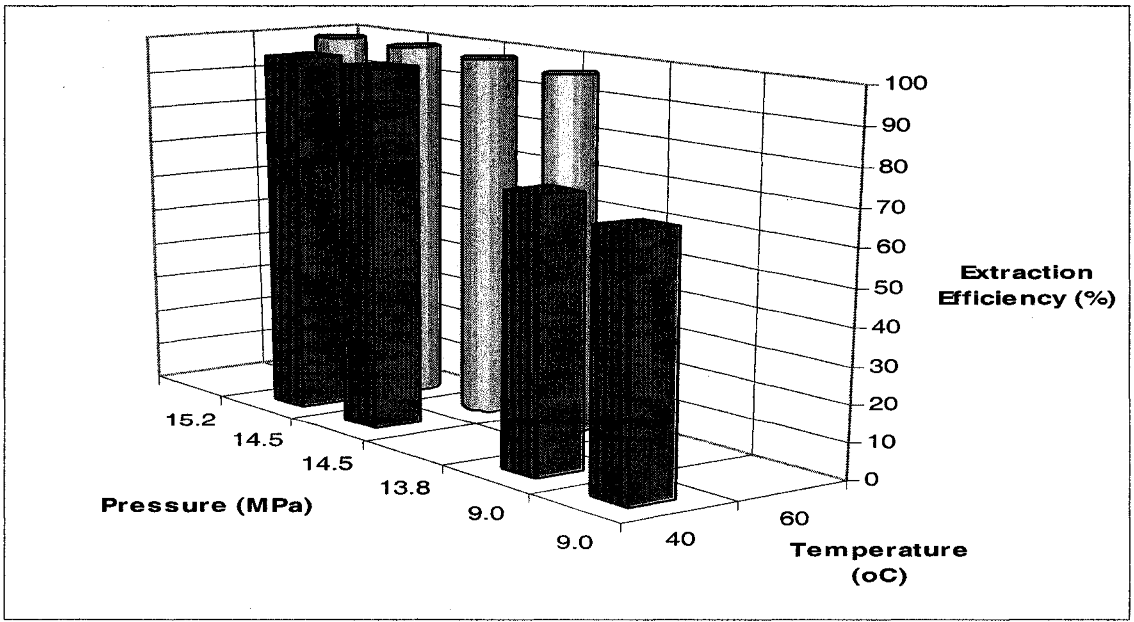


Figure 4-17. **Extraction efficiency vs. Temperature and Pressure at a flow rate of 10-12 mL/min**

In this work, within the range of conditions tested, the suggested operating conditions would be 14.5 MPa and 40°C, flow rates of 10 to 12 mL/min and 800 rpm, with an initial 15-minute static phase followed by 90 minutes of dynamic extraction. These suggested operating conditions yielded the highest extraction efficiencies and were valid for both kinds of cuttings (centrifuge underflow and invert cuttings). Under these conditions, the treated cuttings appeared dry, powder-like, and light in color. The oil extracted from the cuttings was collected in traps with glass beads throughout the experiment, and was the same color as diesel oil. The extracted oil was analyzed using Gas Chromatography/flame ionization detection (GC/FID). The results of this analysis are presented in **Section 4-7**.

It should be noted that the extraction efficiencies are calculated using the PHC of cuttings after SFE resulting from two subsamples. Each subsample is injected three times and therefore the PHC content is the average of the six values. This quantity of subsamples from each experiment was taken to reduce any variability in the results and hence lower the standard deviation of the results.

Table 4-5. Results of SFE extractions at different conditions

Mass of cuttings added to the vessel (g)	Pump Pressure (MPa)	Temp. (°C)	Ave. flow rate (mL/ min)	Mass of collected oil (g)	Efficiency according to mass of collected oil (%)	CCME Analysis Ave. F2 (mg / kg)	Ave. F3 (mg / kg)	Ave. F4 (mg / kg)	Ave. CCME (% total Hc)	Std. Dev.	RSD (%)	# Sub samples	# Injs	Extraction Efficiency η (%)
Centrifuge underflow cuttings														
103.0	12.4	60	10.5	14.0	84.9									
100.0	12.4	60	8.5	10.7	66.3	Testing period								
100.0	12.4	60	11.0	14.7	91.5									
100.0	13.8	60	11.5	21.9	136.0	-	-	-	0.5		-	DNL		96.8
100.0	13.8	60	11.0	22.7	141.0	-	-	-	0.7		-	DNL		95.6
101.0	13.8	60	11.5	18.7	116.0	-	-	-	-		-	-	-	-
100.0	13.8	60	11.7	18.9	118.0	1,750.0	4,330.0	-	0.6	0.24	39.2	2	6	97.0
100.0	14.5	60	10.7	20.1	126.0	646.0	1,620.0	-	0.2	0.08	36.2	2	6	98.6
100.0	14.5	60	10.5	21.8	136.0	1,080.0	2,350.0	-	0.3	0.03	8.8	2	6	97.8
101.0	15.2	60	10.5	18.7	116.0		-	-	-		-	-	-	-
102.0	15.2	60	11.0	20.5	126.0	490.0	1,380.0	-	0.2	0.07	37.7	3	9	98.8
101.0	14.5	60	5.0	16.4	102.0	8,190.0	7,230.0	-	1.5	0.34	21.9	2	6	90.5
100.0	14.5	60	5.0	13.1	81.0	4,850.0	6,500.0	-	1.1	0.23	20.2	2	6	93.0
100.0	14.5	40	10.5	17.5	110.0	2,155.0	2,110.0	-	0.4	0.08	18.7	2	6	98.0
101.0	14.5	40	10.5	22.2	137.0	1,980.0	2,070.0	-	0.4	0.04	9.6	2	6	98.0
100.0	8.96	40	10.5	15.6	97.5	29,800.0	30,400.0	-	6.0	0.11	1.8	2	6	69.0
100.0	8.96	40	10.5	18.2	114.0	20,500.0	23,700.0	-	4.4	0.37	8.3	2	6	77.0
100.0	14.5	40	20.0	16.7	104.0									
100.0	14.5	40	20.0	13.2	68.8	Data evaluated qualitatively and according to the amount of collected oil								
100.0	14.5	40	20.0	16.0	83.0									
Invert cuttings														
101.0	14.5	40	12.5	11.1	74.7	1,980.0	1,920.0	1,340.0	0.5	0.48	78.2	3	9	96.5
101.0	14.5	40	13.0	10.4	69.9	834.0	2,390.0	806.0	0.4	0.32	90.9	3	9	97.3

Extraction efficiencies (η) were based on 19.4% oil in raw centrifuge underflow cuttings and 14.8% in raw invert cuttings.

For **Sections 4.5.1**, **4.5,2** and **4.53**, the following **Table 4-6** presents the complete data for the **Figures 4-18**, **4-19** and **4-20**.

Table 4-6. Complete data from different authors

Pressure (MPa)	Temperature (°C)	SC CO_2 density (g/mL)	Extraction Efficiency (%)
This work			
13.8	60	0.550	96.8
14.5	60	0.583	98.8
15.2	60	0.610	98.8
14.5	60	0.583	98.2
14.5	40	0.771	97.9
14.5	40	0.771	97.8
9.0	40	0.475	68.6
9.0	40	0.475	76.9
Odusanya (2003)			
8.3	35	0.574	33.0
10.3	35	0.723	66.0
10.3	50	0.420	47.0
12.4	50	0.607	84.0
12.4	60	0.464	90.0
13.8	50	0.665	84.0
13.8	60	0.551	85.0
17.2	40	0.810	83.0
17.2	50	0.744	87.0
17.2	60	0.669	88.0
Saintpere and Morillon-Jeanmaire (2000)			
9.0	45	0.337	30.8
10.0	45	0.498	92.3
11.0	45	0.603	93.8
12.0	45	0.662	94.2
8.0	35	0.419	68.5
9.0	35	0.662	92.3
10.0	35	0.712	94.2
11.0	35	0.743	95.4
12.0	35	0.767	95.4
9.0	40	0.485	69.2
10.0	40	0.628	92.3
11.0	40	0.683	96.5
12.0	40	0.717	95.4

4.5.1 Effect of Temperature

Theoretically, at a constant pressure, the temperature influences the volatility of the compound to be extracted (in this case oil). Increasing the extraction temperature at a constant pressure will therefore increase the volatility of the oil, and hence lead to an increase in the extraction efficiency. However, increasing the temperature at a constant pressure might have a drawback with respect to the extraction efficiency since, as the temperature increases, the density of the CO_2 decreases. Many authors have stated that liquid-like densities (i.e. high densities) favour extraction (Odusanya 2003).

As it can be seen, the temperature effect on extraction efficiencies is not straightforward as it depends on a balance between the effects of increased oil volatility and decreased SC CO_2 density (Odusanya 2003).

In this investigation, the temperature did not considerably influence the extraction efficiency. The temperature did not seem to affect the extractions performed above 40°C. Increasing the temperature from 40 °C to 60°C did not considerably improve the extraction efficiency of the process. The extraction efficiency at 40°C was on average 98.2% while the extraction efficiency at 60°C was 98%. Extractions at both temperatures yielded petroleum hydrocarbon contents that were below regulatory guidelines ($\leq$0.5%). The effect of temperatures higher than 60°C was not investigated.

Based on the above discussion, 40°C was suggested as the best extraction temperature within the conditions tested. Extractions at 40°C yielded good extraction efficiencies and, if this technology is to be applied on a large scale, a temperature of 40°C is technologically and economically achievable.

Figure 4-18 shows the effect of temperature as found by various researchers for drill cuttings, as well as the results obtained in this work.

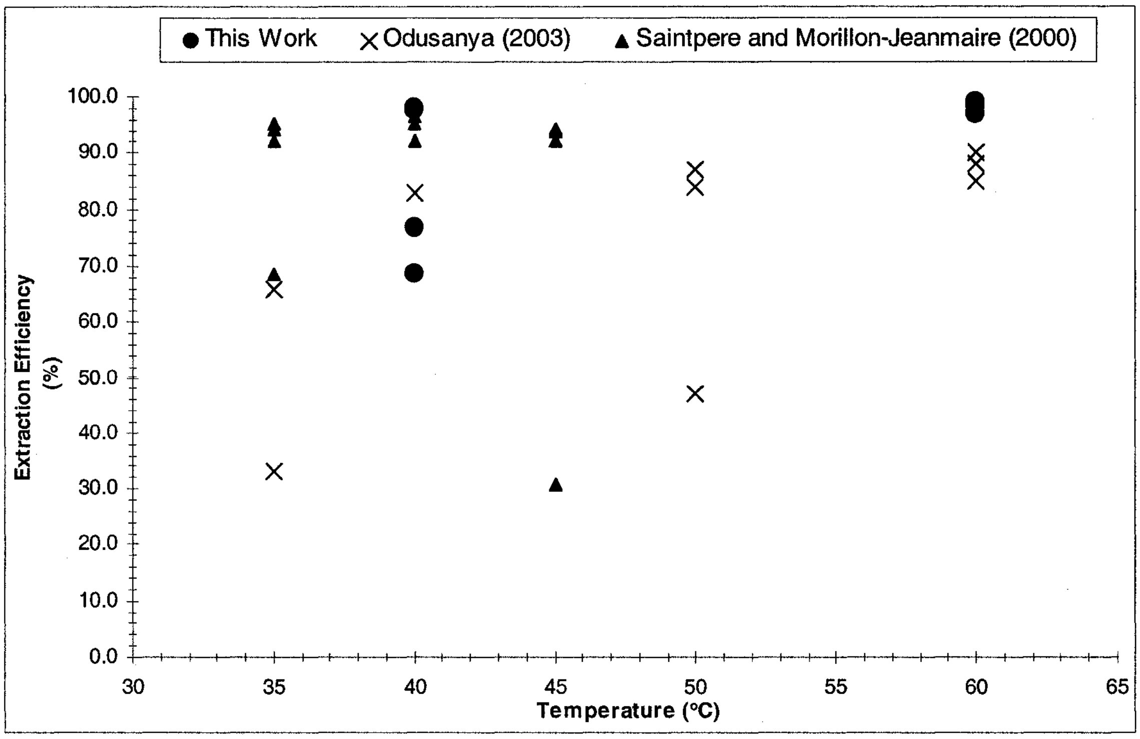


Figure 4-18. Extraction efficiency vs. Temperature

4.5.2 Effect of Pressure

Figure 4-19 shows the effect of pressure found by different researchers, including the results from this investigation. From this investigation and from the work of Odusanya (2003) and Saintpere and Morillon-Jeanmaire (2000), it can be affirmed that increasing the pressure increases the extraction efficiency up to a certain point.

The type of drill cuttings or the type of oil and additives present in the drill cuttings might influence the specific pressure at which the extraction efficiency no longer increases.

Odusanya (2003) worked with a different type of centrifuge underflow cuttings (larger cuttings) having approximately 17% of PHC content while Saintpere and

Morillon-Jeanmaire (2000) worked with shaker table cuttings having a PHC content ranging from approximately 6% to 13%. The best pressure was found to be 12.4 MPa for Odusanya (2003) and 10 MPa for Saintpere and Morillon-Jeanmaire (2000). These findings support that the drill cuttings nature may affect the pressure at which extraction efficiency no longer improve.

Raising the pressure from 8.96 MPa to 14.5 MPa improved the extraction efficiency from 70% to 80%, but past this point, the efficiency did not improve any further. Given this fact, the suggested operating pressure was determined to be 14.5 MPa, a pressure at which SFE was able to reduce the oil content to less than that defined by the regulatory guidelines (≤0.5%) (AEUB 1996).

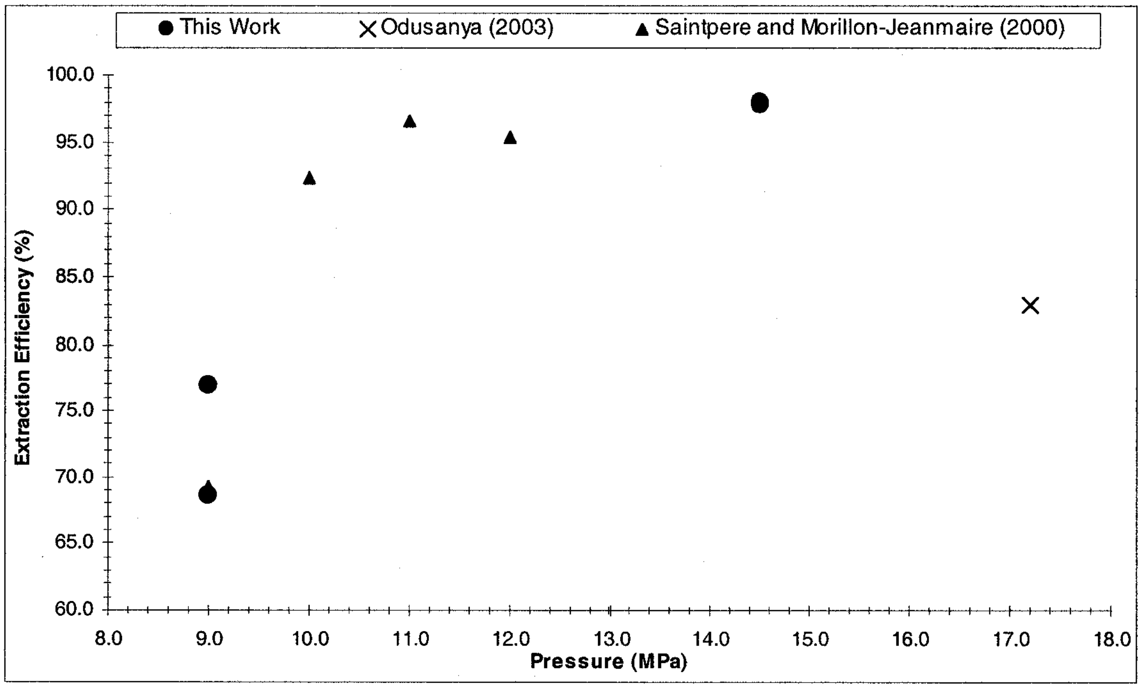


Figure 4-19. Extraction efficiency vs. Pressure at 40°C

4.5.3 Effect of Density

Figure 4-20 shows the effect of density on the SFE of drill cuttings as found by various researchers, as well as the results obtained in this work.

The effect of pressure on the SFE of a contaminant at a constant temperature is generally related to a density change (Huang 1995; Odusanya 2003). Increasing the pressure of the system at constant temperature increases the density of the SC CO_2, and as a result, it is expected that higher extraction efficiencies will be obtained since the SC CO_2 has more liquid-like solvating powers (Huang 1995; Saintpere and Morillon-Jeanmaire 2000; Odusanya 2003). This statement was corroborated in this investigation when an increase in the pressure (from 8.96 to 14.5 MPa) at a constant temperature (40°C) increased the extraction efficiency from 70% to 98%. The corresponding densities were 0.475 g /mL at 8.96 MPa and 40°C, and 0.771 g /mL at 14.5 MPa and 40°C.

In addition, increasing the density (from 0.583 g/mL to 0.771 g/mL) at a constant pressure (14.5 MPa) by decreasing the temperature (from 60°C to 40°C) did not affect extraction efficiency: the extraction efficiency in both cases was 98%. These results show that, beyond a certain density (0.583 g/mL in this work) the extraction efficiency no longer increases, therefore increasing the densities (i.e. more liquid-like densities) does not further increase the extraction efficiencies.

This trend was also observed in the results of Odusanya (2003) and Saintpere and Morillon-Jeanmaire (200). The results of Odusanya (2003) suggested that increasing the SC CO_2 beyond 0.55 g/mL does not seem to improve the extraction efficiencies. The results of Saintpere and Morillon-Jeanmaire (2000) suggested that the SC CO_2 density beyond 0.498 g/mL does not seem to improve the extraction efficiencies.

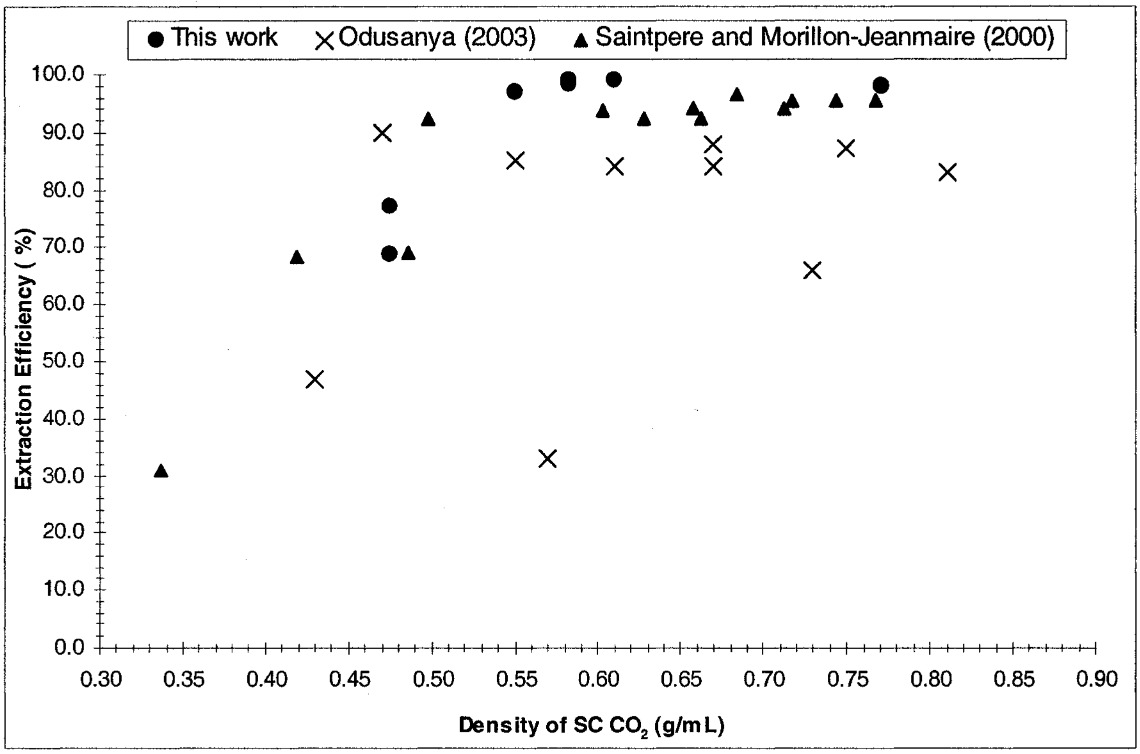


Figure 4-20. **Extraction Efficiency vs. Density of SC CO_2**

4.5.4 Effect of Flow Rates

In this section, the effect of flow rate on extraction efficiency is analyzed. Flow rates of 5mL/min, 10-12mL/min, and 20mL/min were investigated. Representative data illustrating the effect of the flow rates are presented in **Figures 4-21**, **4-22**, **4-23** and **4-24,** and are discussed in the following paragraphs. It should be noted that the effect of flow rate was studied for the centrifuge underflow cuttings at extraction conditions of 40°C and 14.5 MPa.

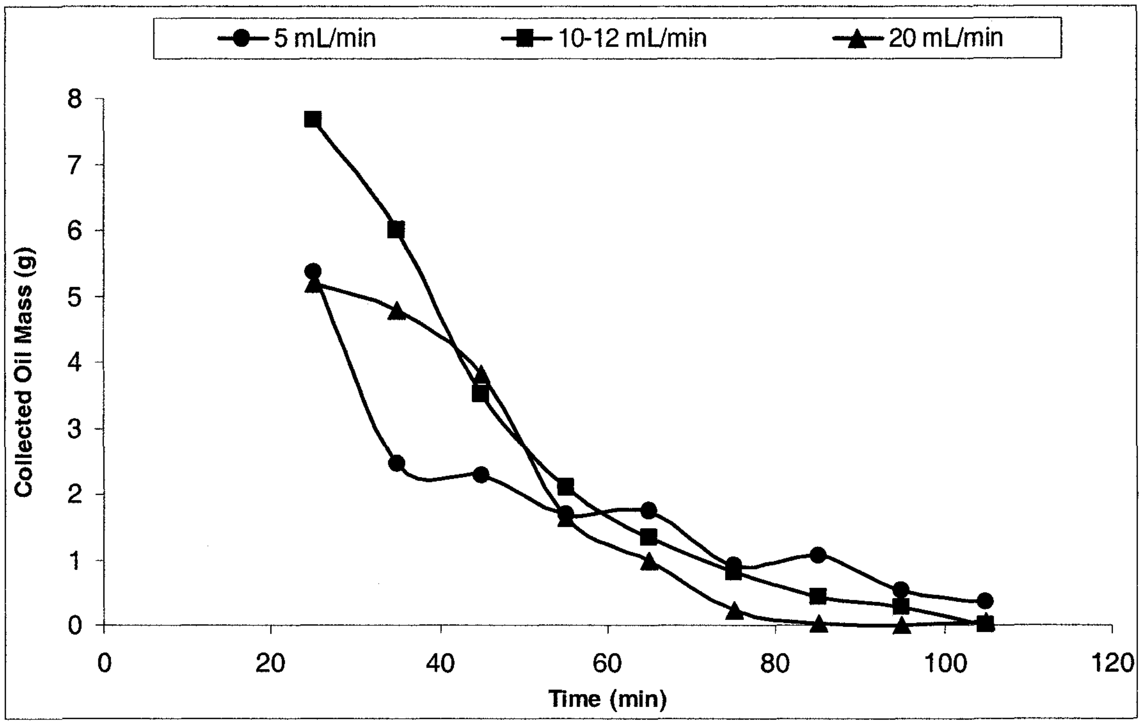


Figure 4-21. Collected oil mass vs. Time at different flow rates (5 mL/min, 10-12 mL/min and 20 mL/min)

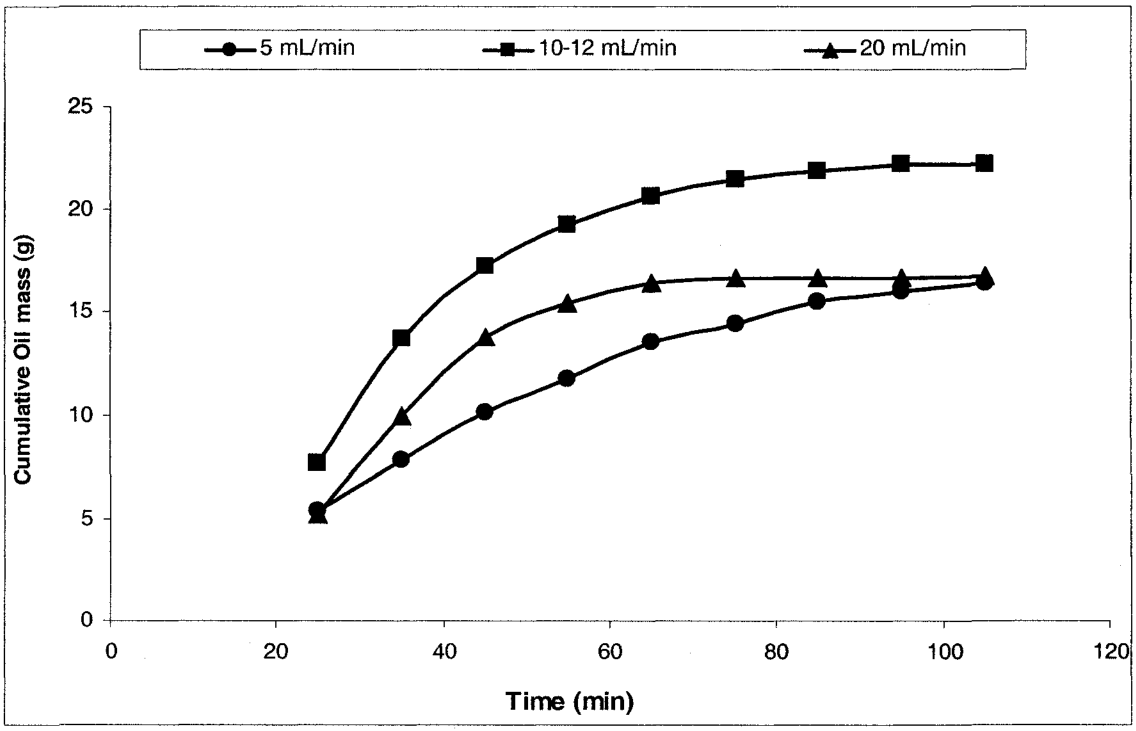


Figure 4-22. Cumulative oil mass collected vs. Time at different flow rates (5 mL/min, 10-12 mL/min and 20 mL/min)

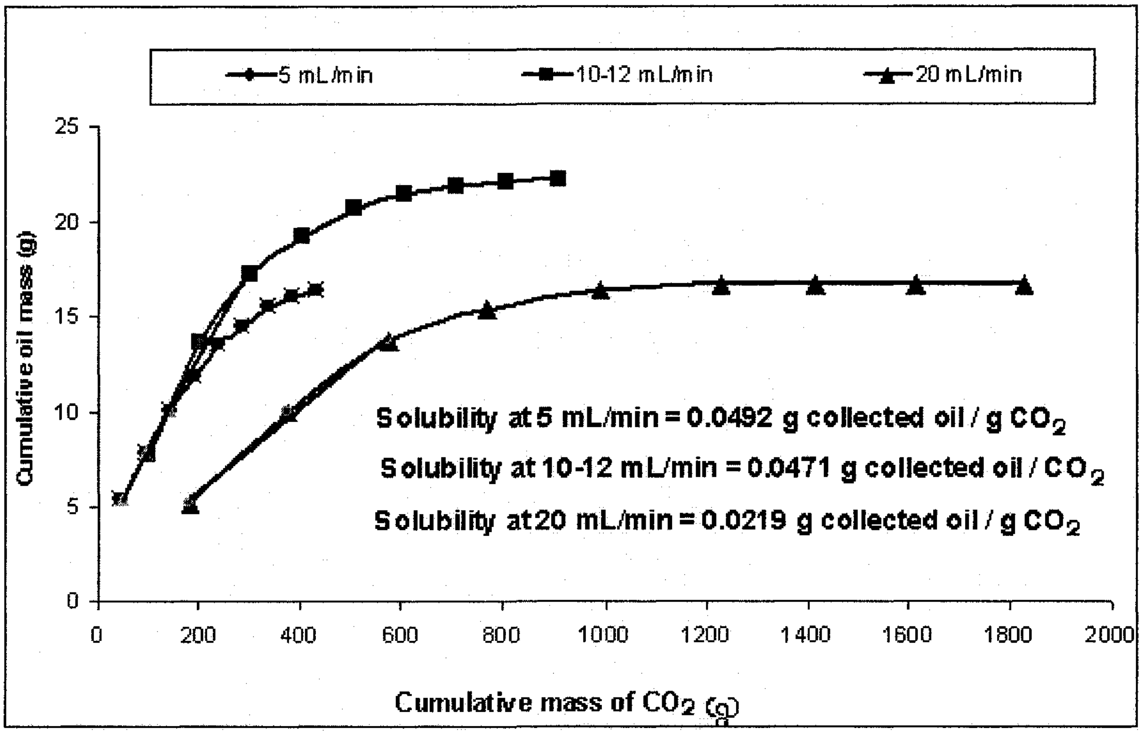


Figure 4-23. Cumulative oil mass at different flow rates (5 mL/min, 10-12 mL/min and 20 mL/min) vs. Cumulative mass of CO_2

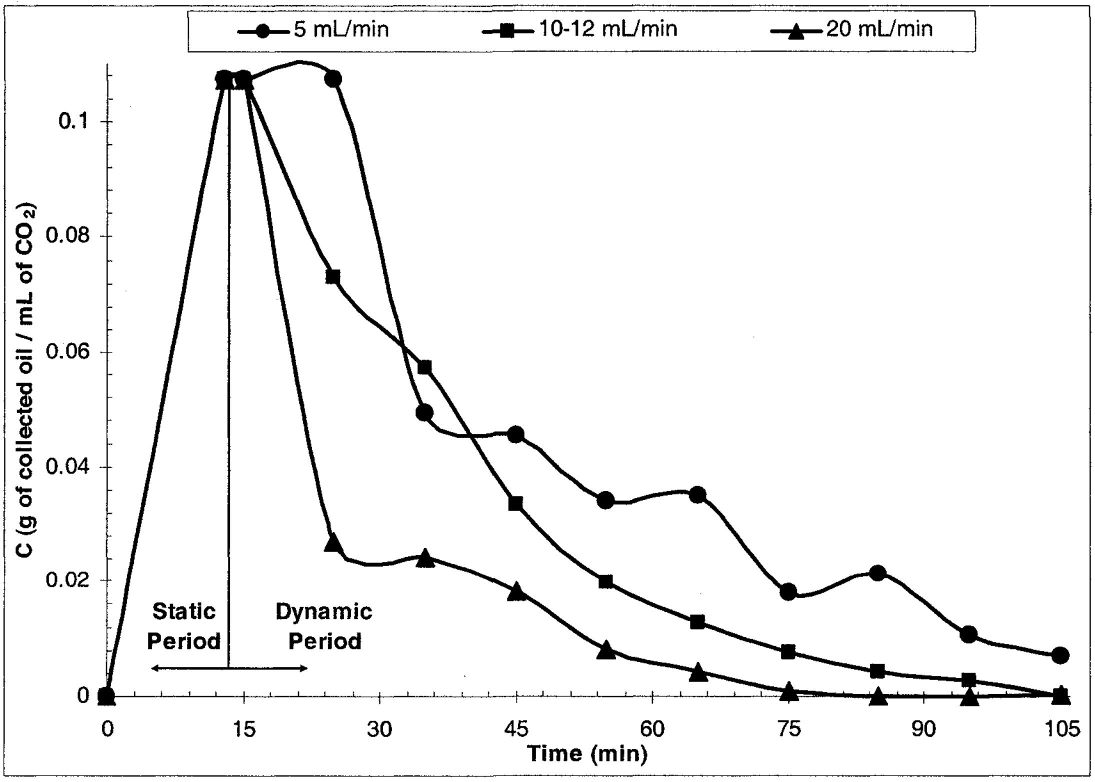


Figure 4-24. Concentration of oil in supercritical phase vs. time

Extractions at 5 mL/min

Figure 4-21 shows the amount of oil collected over the length of the experiment. Looking at the 5 mL/min data, for the extractions performed at a low flow rate, minor amounts of oil were collected at the beginning of the process, but as the extractions proceeded, similar amounts of oil were collected at 5 mL/min as were collected at higher flow rates.

As can be seen in **Figure 4-21**, lower amounts were extracted at the beginning of the process since it was clearly seen that with a low flow rate, the expected amount of diesel oil to be extracted from the centrifuge underflow cuttings would have needed more time to be taken out.

As well, similar quantities of diesel oil were collected later on in the process because during extractions performed at lower flow rates, their supercritical phase was kept more concentrated than the supercritical phase in extractions performed at higher flow rates (see **Figure 4-24**).

Another point noticed was that in experiments performed at low flow rates, there were fluctuations in the desorption of the oil when a smooth decay in the desorption was expected. According to Al-Jabari (2002), these fluctuations are explained by the reversible adsorption/desorption process that occurs when extractions are performed using low flow rates (Al-Jabari 2002). This reversible adsorption/desorption process was not evident at the beginning of the process in view of the fact that the concentration in the supercritical phase was still high. However, as the diesel oil was removed from the vessel, this reversible adsorption/desorption process became more noticeable.

The main drawback of extractions at low flow rates is that, as a result of extending the extraction time, less oil might be collected since the re-adsorption of the oil into the cuttings may affect the desorption process, making the estimated time for removal of all of the oil uncertain.

Extractions at 20 mL/min

In order to have lower extraction times, a higher flow rate (20 mL/ min) was tested (see **Figures 4-21**, **4-22**, **4-23**, and **4-24**).

In this investigation it was found that this high flow rate led to lower extraction efficiencies. The reason for this according to Al-Jabari (2002), might have been due to the "rate of purging of solute out of the SFE vessel (fluid displacement) with respect to the rate of its desorption into the SF and that, when the fluid displacement rate is faster than solute desorption rate, the concentration in the SF is considered to be constant or zero in some cases" (Al-Jabari 2002). This observation was made in this investigation, and as a consequence, more CO_2 was used to extract less oil in the same amount of time.

To sum up, according to Al-Jabari (2002), when higher flow rates are used, "the rate of refreshment of SF is much faster than the rate of the solute release from the solid surface and the external mass transfer resistance is negligible; internal diffusion in the solid controls the whole SF process. The solute concentration in the bulk of the SF is usually taken to be negligible (zero) since the SF phase is considered to be displaced with fresh SF at a rate that is faster than the rate of solute transfer from solids into the SF phase" (Al-Jabari 2002).

Extractions at 10-12 mL/min

Extractions conducted at 10 to 12 mL/min yielded high extraction efficiencies, extracting almost all of the oil from the drilling waste and avoiding the disadvantages mentioned previously.

According to Al-Jabari (2002), when the rate of refreshment of SF is similar to the rate of the solute release from the solid surface and is not slow enough to produce a reversible adsorption/desorption process, the internal diffusion in the solid does not control the whole SF process (Al-Jabari 2002).

It should be noted that in the first moments of the dynamic extraction, having the suggested flow rate (10-12 mL/min) is crucial in the SFE process. Almost all the oil that has been solubilized during the static phase is now in the supercritical phase and can be removed with the SC CO_2 flow, in this case 10-12 mL/min. Having a low flow rate (5 mL/min) at the beginning of the dynamic extraction can lead to reversible adsorption/desorption processes later in the dynamic extraction as it is indicated in the fluctuations in the SFE performed at 5mL/min (lower flow rates) (See **Figure 4-21**).

4.5.5 Effect of mixing

The effect of mixing had a great impact on extraction efficiency. Using a ribbon blender as a mixer allowed the process to handle greater quantities of drill cuttings without decreasing the efficiency of the process. A 100g of cuttings loading to the vessel was able to be easily handled. The mixer was able to properly mix all cuttings placed inside the vessel.

The effect of mixing facilitates the extraction since the dynamics of the system (mixing) influence in a direct way the mass transfer by producing more mass transfer area for the SFE processes and by reducing the internal diffusion process.

Mixing results in a “breaking up” of the cuttings and thus the oil that is inside the cuttings is exposed more rapidly to the bulk of the SC CO_2 phase. By decreasing the internal diffusion process through the cuttings, the oil that is in the interstices of the drill cuttings comes in contact with the bulk of the SC CO_2 phase more rapidly; therefore making the extraction more effective and faster. The solubilization process between the oil and the SC CO_2 is not delayed by the internal diffusion process through the drill cuttings.

This effective mixing of the oil present in the drill cuttings and the bulk of the SC CO_2 phase in the extraction vessel results in more effective mass transfer. A better understanding of the effect of mixing at larger scale may be achieved by determining the Reynolds number and Froude number of the system since these numbers are dependent on the size of the system, the speed of mixing, and physical quantities such as the viscosity and density of the supercritical mixture inside the vessel (including cuttings properties). Since larger quantities of cuttings will be placed in larger scale systems, the effect of mixing may become predominant and may impede the effect of the pressure and temperature. For this reason, experiments using larger scale systems would have to be tuned for “optimal” operational conditions since the dynamics of the system and physical quantities involved should be evaluated at the same time.

It should be noted that care must be taken to avoid the release and entrainment of fine particles; and the potential of clogging in downstream lines (see **Photos A, B** and **C** in **Figure 4-25**).

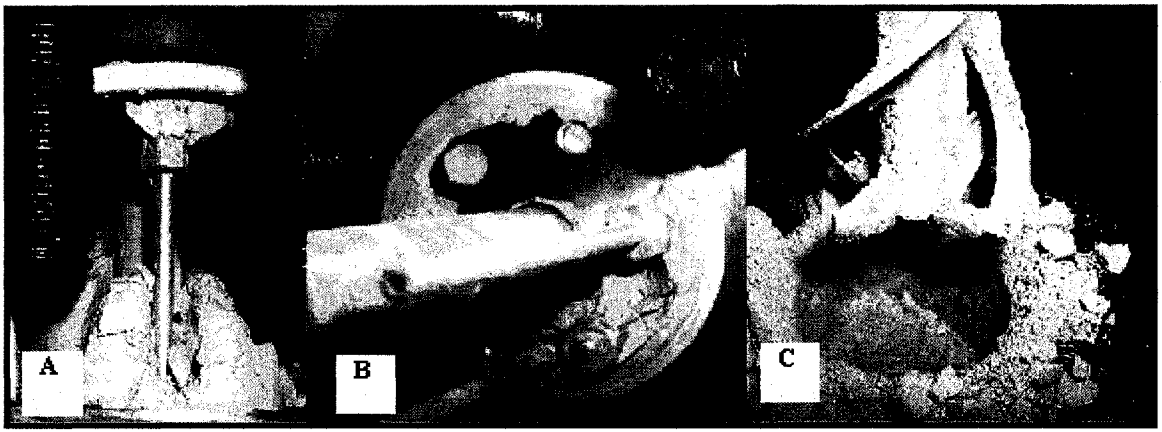


Figure 4-25. Mixing effect. A (Inlet line totally submerged in the drill cuttings), B (vessel outlet clogged) and C (treated cuttings inside the vessel)

A good system of filters with higher capacities will be necessary to avoid clogging. Having multiple outlets at different places might also provide a solution if this problem is not solved by having a good system of filters. The multiple outlet lines could be operated at different times if one of them becomes clogged.

4.5.6 Effect of Drill Cutting Mass

With the introduction of controlled mixing, experiments were conducted to determine if even greater quantities of cuttings could be placed inside the vessel. Experiments were conducted with a loading of 200 g and 285 g of raw cuttings. Visual observations during and after these experiments showed that, despite these higher loadings, the mixing was still good. However, in the two experiments, the flow rate was restricted at the beginning of the experiment and increased gradually throughout the experiment as oil was removed. In addition, large amounts of oil were removed in the beginning of these experiments despite the flow restriction. For example, in the experiment with 200 g of cuttings, even though the flow rate was set to 10 mL/min, the flow rate at the beginning of the experiment was 2.5 mL/min and gradually increased to 8.5 mL/min. In the experiment with 285 g of cuttings, again with a set flow rate of 10 mL/min, the flow rate started at 1.2 mL/min and gradually increased to 5.85 mL/min.

This restriction of the flow rate at the beginning of the experiment might be due to a combination of two things. First, it is believed that, during the extraction of oil from drilling waste, the drill cuttings experience an "expansion" as the SC CO_2 penetrates the drill cuttings and dissolves into the oil. The solubilization of SC CO_2 into the oil present inside the drill cuttings causes an increase in the total volume and therefore causes an "expansion" of the drill cuttings. It should be noted that this "expansion" would be greater at the beginning of the experiment than at the end of the experiment since more oil is present at the beginning of the experiment. It would be expected that this "expansion" effect would diminish as oil is removed since there is less oil for the SC CO_2 to dissolve into.

The second effect that may be causing the flow restriction at the beginning of these experiments is the "compaction" of the "expanded" drill cuttings resulting from the pressure of flowing SC CO_2 and from the continuous lifting action of the impeller set at 800 rpm. Since the impeller was designed to transport the mass of cuttings toward the top of the vessel (where the inlet and outlets are localized) the majority of the "expanded" drill cuttings remained at the top of the vessel during the extraction, potentially blocking the outlet line.

As the experiment progressed, however, the flow increased slowly, indicating that there was less and less flow restriction. It is possible that, as oil was being removed from the system, this "expansion" and "compaction" effect may have changed. It is possible that, as the oil was being removed from the drill cuttings, the consistency of the drill cuttings became powder-like (loss of cohesiveness, lower density and lower adherence to the internal surfaces) and the amount of expansion produced by SC CO_2 dissolution into the oil decreased. Both of these factors resulted in SC CO_2 flowing more easily through the drill cuttings, and therefore, resulted in a gradual increase of the flow rate.

Visual observations and masses of the oil collected during these two experiments seem to support the explanation of an "expansion" and "compaction" effect that led to flow restriction. Visual observations indicated that the oil collected at the beginning of the experiment (when flow was restricted) was different than that collected towards the end of the experiment (when flow was restored to the set value). **Figure 4-26** presents photos of the oil collected at the beginning of the extraction (first three vials from the left of **Figure 4-26**) and at the end of the extraction (last three vials). **Figure 4-26** shows that, at the beginning of the experiment, the oil was much darker than the oil obtained at the end of the experiment. The oil collected at the end of the experiment resembled the oil collected during other extraction experiments with lower cutting loadings and no flow restriction.

It is believed that the oil obtained at the beginning of the experiment is "squeezed" or physically removed from the drill cuttings and therefore carries with it additives and potentially some very fine particles. Both of these lead to a darker colored oil. At the end of the experiment, however, the oil collected has been solubilized by the SC CO_2 and is therefore pure, lighter colored oil with no additives or particulate matter.

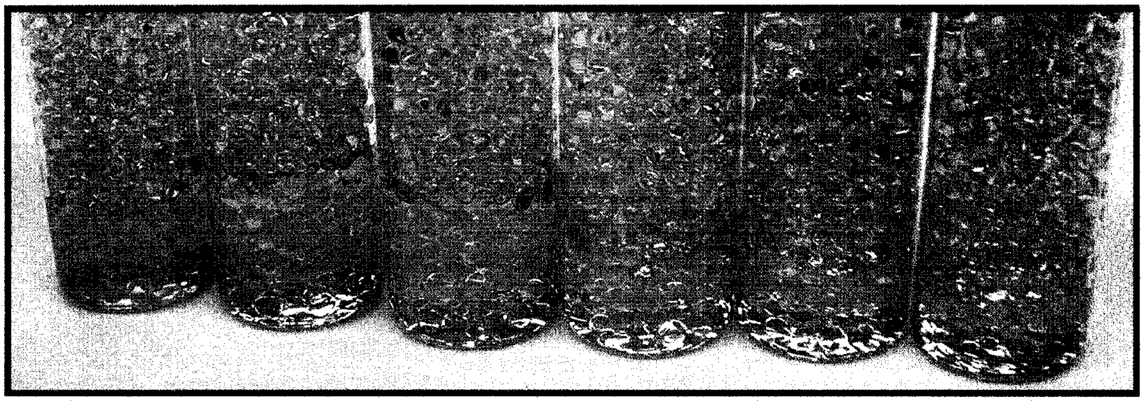


Figure 4-26. Coloration of the collected oil

The mass of oil collected during the experiment using 285g of raw drill cuttings was compared to the mass of oil collected during an experiment at the same conditions of pressure, temperature and flow but with a smaller mass of raw cuttings (100g). The results of this comparison are presented in **Figure 4-27**. **Figure 4-27** shows that the experiment with 285g of raw cuttings yielded greater ratios of extracted oil (i.e. mass of oil per g of SC CO_2) at the beginning of the experiment despite the restricted flow rate. This greater amount of oil supports the argument that the oil was physically removed from the vessel rather than being solubilized by the SC CO_2. If the oil was indeed solubilized, one would expect that the amount of oil collected at the beginning of the experiment would be less that that collected in the experiment at the same conditions but with a higher flow rate. This was however not the case – more oil was extracted despite the flow restriction.

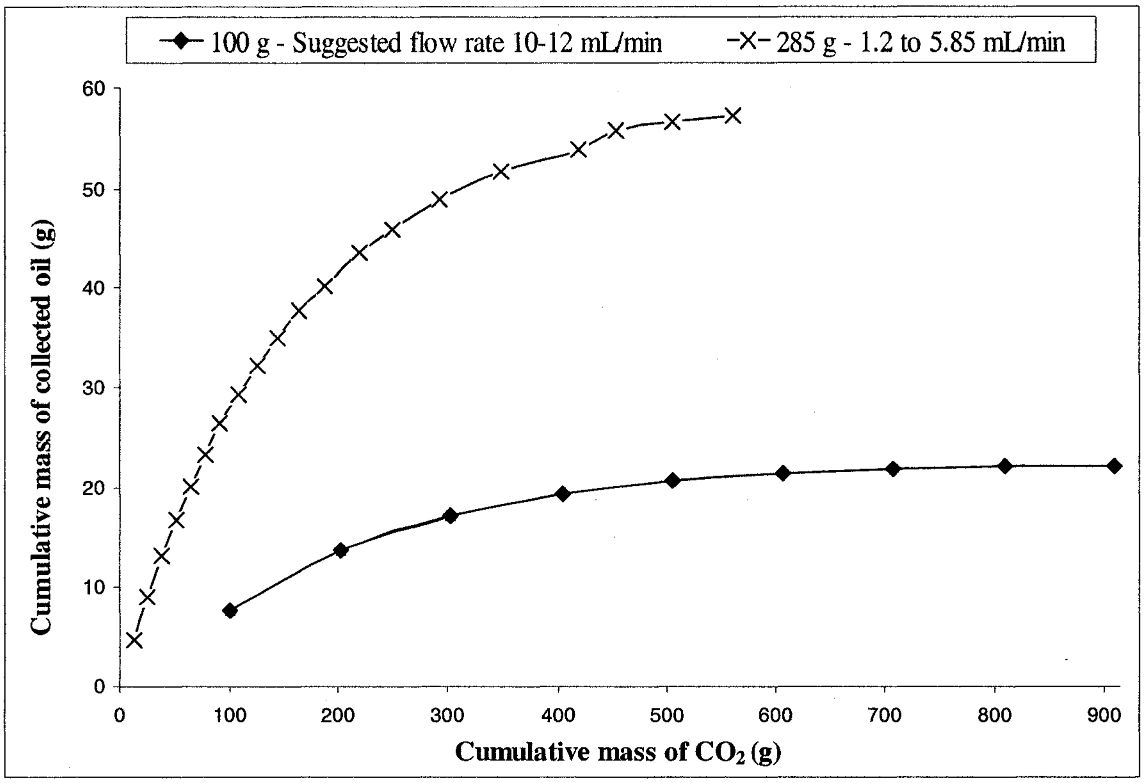


Figure 4-27. Cumulative mass of oil collected vs. cumulative mass of CO_2 for experiments performed using 100 g and 285 g of drill cuttings

The results of these experiments indicate that there is a maximum amount of cuttings that can be placed in the extraction vessel to ensure that no flow restriction occurs. The results seem to indicate that the maximum mass of cuttings that may be placed in the vessel is somewhere between 150g and 200g. It should be noted that this mass may depend of the amount of oil originally present in the raw cuttings.

4.5.7 The Effect of Water Content

Several experiments were performed at the best operating conditions (14.5 MPa, 40°C and 10-12 mL/min) to investigate the effect of water content.

In experiment 1, the mass of oil extracted was approximately 10.7g (of a possible 14.8g). The appearance of the cuttings in the vessel was good (a fine powder similar to regular (non-invert) cuttings), however, some of the treated cuttings were caked onto the vessel walls and impeller (see **Figure 4-28**). The appearance of the cuttings in terms of oil content was excellent. The extracted oil had the characteristic diesel oil color.

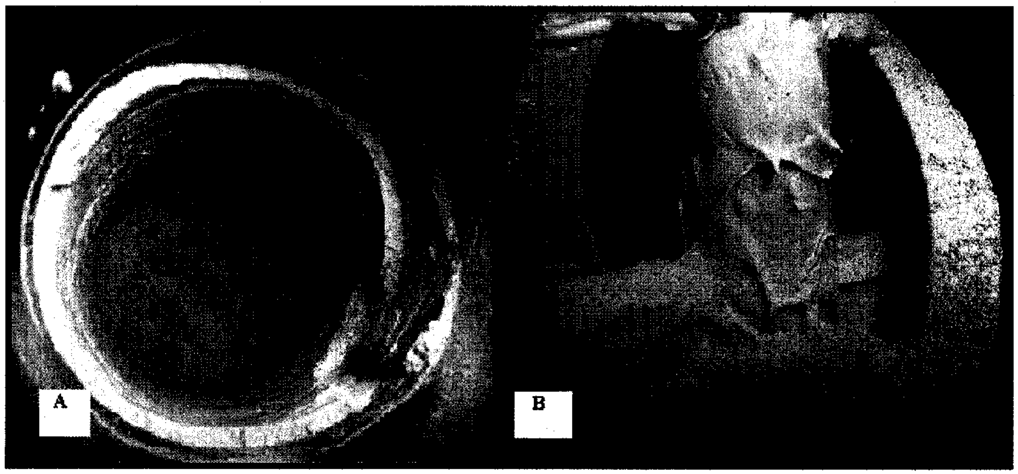


Figure 4-28. Appearance of Treated Invert Cuttings 7% water content. A (treated cuttings adhered to the vessel walls), and B (treated cuttings adhered to the impeller surface)

In experiment 2, the mass of oil extracted was approximately 6g (of a possible 14.8g). The appearance of the cuttings in vessel was not good: the treated cuttings looked sticky and wet. The appearance of the cuttings in terms of oil content was not good since the cuttings seemed to contain a lot of oil even after the extraction. It seemed that, for extractions using invert cuttings with 15% water content without any drying agent, the water had a negative effect. The result was a low amount of collected oil, caking of cuttings to the vessel wall and impeller, and problems with maintaining a good flow of CO_2 through the vessel (the outlets were clogged easily and a high flow could not be maintained) (see Photos **A** and **B** in **Figure 4-29** and **Figure 4-30**). It was noted that the flow during this experiment was low, and this low flow rate may have been the reason for the low amount of oil extracted. The extracted oil had the characteristic diesel oil color.

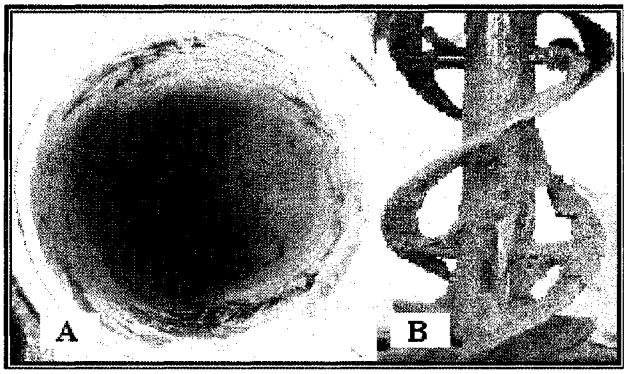


Figure 4-29. **Treated invert cuttings with 15% water content in the vessel and impeller. A (treated cuttings adhered to the vessel walls), and B (treated cuttings adhered to the impeller surface)**

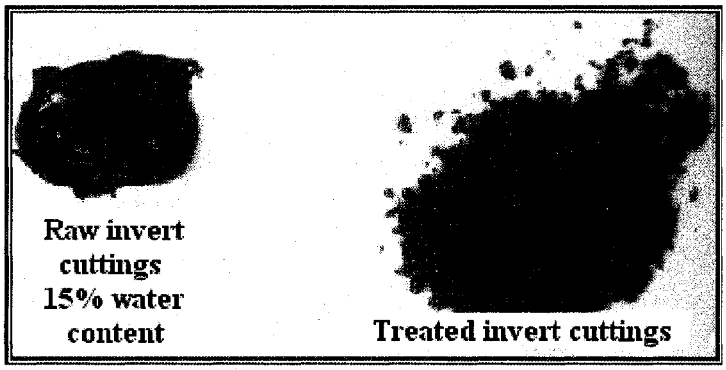


Figure 4-30. **Raw and treated invert cuttings with 15% water**

In experiment 3, the mass of oil extracted using this invert cuttings was approximately 10.7g (of a possible 14.8g), the same amount as without the drying agent. The appearance of the cuttings in the vessel was good (a fine powder similar to regular (non-invert) cuttings). Removing the cuttings from the vessel was easy: they were not caked onto the vessel walls and impeller (see **Figure 4-31**). The appearance of the cuttings in terms of oil content was excellent. The extracted oil did not have the characteristic diesel color. The oil was light in color as compared to diesel oil and was clear (see **Figure 4-32**).

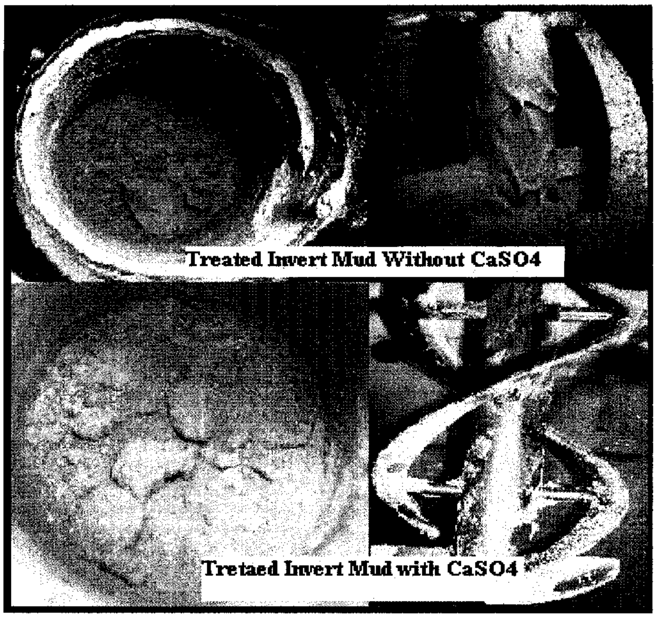


Figure 4-31. **Treated Invert Cuttings with and without $CaSO_4$**

Figure 4-32. **Collected oil from invert cuttings plus $CaSO_4$ in a glass trap**

In experiment 4, the mass of oil extracted was approximately 6.5g (of a possible 14.8g). The appearance of the cuttings in the vessel was good (a fine powder). The appearance of cuttings in terms of oil content was not good. The treated cuttings were not caked onto the walls of the vessel. The extracted oil did not have the characteristic diesel color. The extracted oil was light in color as compared to diesel oil and was clear. The results for experiment 4 were the same as those for experiment 3, but much less oil was collected.

In experiment 5, the mass of oil extracted was approximately 7g (of a possible 14.8g). The appearance of the cuttings in vessel was not as good (similar in appearance to the cuttings in experiment 4). The treated cuttings were a fine powder, but some cuttings were caked onto the vessel walls and impeller. The appearance of cuttings in terms of oil content was not good. The extracted oil was "cloudy": it seemed that either the cuttings or silica gel was entrained (see **Figure 4-33**).

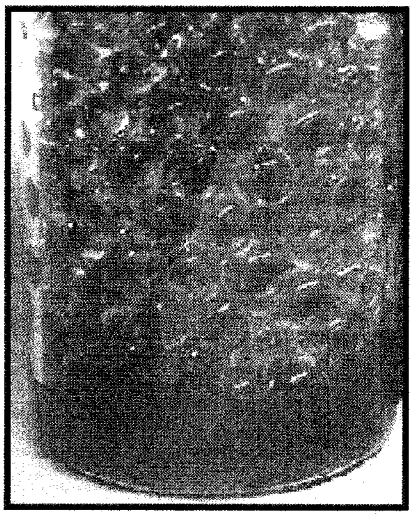


Figure 4-33. Cloudy oil collected using silica gel

In experiment 6, the mass of oil extracted was approximately 5g (of a possible 5.3g). The appearance of the cuttings in the vessel was good: the extracted cuttings formed a slurry that was easily removed from the vessel. There was no caking onto the vessel walls or on the impeller. The oil extracted in the first vial looked clear and had the characteristic diesel color. The oil in the remaining vials was "cloudy", indicating some entrainment of the cuttings' particles (see **Figure 4-34**).

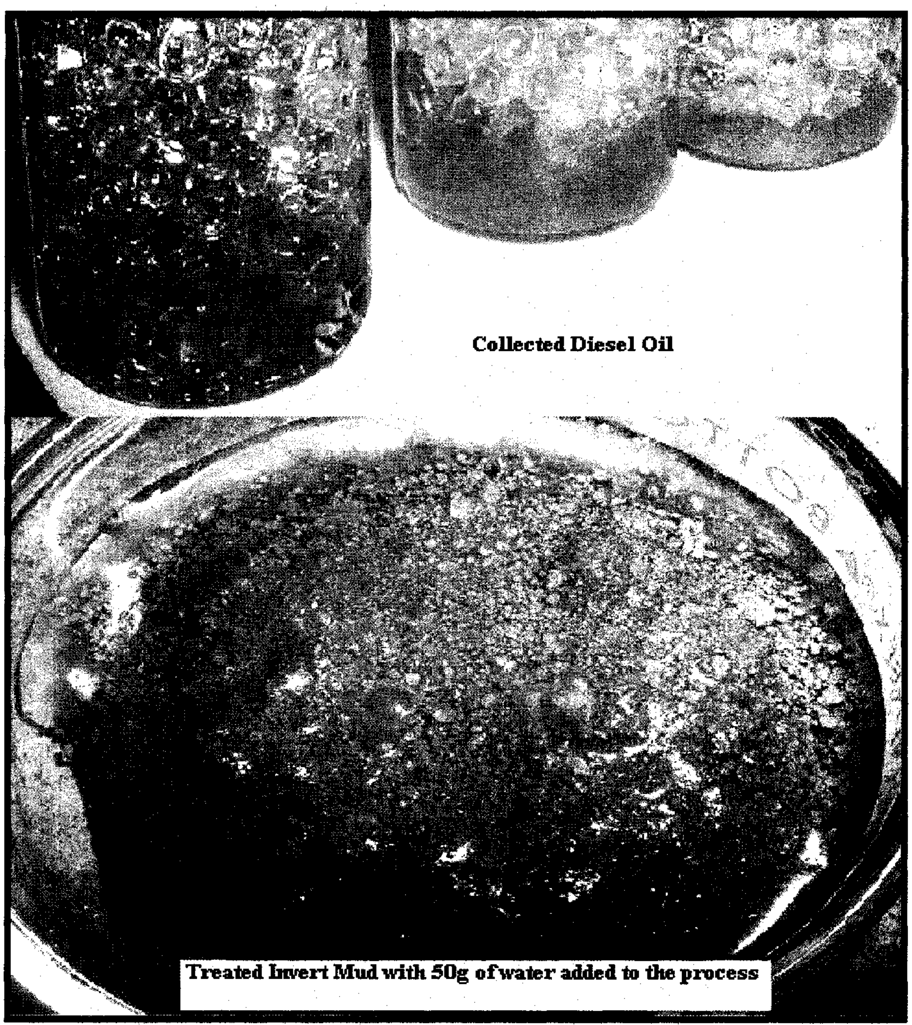


Figure 4-34. **Treated Invert Cuttings with 50g of water added to the process**

The results of all of six experiments suggest that both calcium sulfate and silica gel worked well as drying agents with invert mud cuttings at low initial moisture contents, yielding extracted cuttings that were easy to handle and low in oil content. The slurry of 1:1 mass ratio of cuttings:water worked well both in terms of extracting the diesel oil and handling the cuttings.

Furthermore, it should be noted that the experiments performed below 7% water content and above 20% water content led to good extraction efficiencies while experiments having water contents between 7% and 20% did not lead to good extractions efficiencies. Some authors have stated that having up to 10% water in contaminated soils improved extraction efficiencies of organic compounds but that water contents above 10% caused a decrease in the extraction efficiency (Laitinen et. al 1994; Reindl 1994; Fortin and Stiver 2001). It is believed that water acts as a polar modifier and positively influences the extraction (Reindl 1994). In addition, some authors have found that water contents of 50%, 100% and 200% enhances the extraction process and the extraction proceeds in the same way as for a dry soil (Akgerman 1996; Fortin and Stiver 2001).

It is believed in this investigation that the reason for this is that when the water content is approximately below 7% the water may not be a "barrier" for the solubilization process between SC CO_2 and the oil present in the drill cuttings, therefore the extraction proceeds normally.

When the water content is approximately between 7% and 20%, it represents a "barrier" for the solubilization process between SC CO_2 and the oil present in the drill cuttings. The amount of water present in the drill cuttings may be covering the oil that adhered on the clay, therefore impeding the contact of the SC CO_2 with the oil present in the drill cuttings. Because of that, the extraction of oil from drill cuttings may have decreased. It is believed that water content ranging from approximately 7% to 20% may not be able to take off the oil from the clay and therefore represents an obstacle or "barrier" for the extraction of oil from drill cuttings. This may be happening since water contents between 7% and 20% may not be able to break the emulsion formed by the oil and water. Since the emulsion is not broken with this amount of water, the water may act as a "resistant polar layer" between the oil adhered on the clay and the supercritical CO_2 phase.

When the water content is approximately above 20% the large amount of water present in the drill cuttings may be able to displace the oil from the clay and expose it more directly to the SC CO_2 because the emulsion formed by the oil and water is broken by the large amount of water added to the process. This phenomenon produces a similar effect as the one obtained when the water content is approximately below 7%; in terms of extraction efficiency.

4.5.8 Standard Deviation in the Results

In general, the relative standard deviation in the results was produced by the internal nature of the GC, SFE extractions, cuttings sampling, and by any misstep that occurred during the analysis (Soxhlet extraction). A sample chromatogram with results is presented in **Appendix B1.** As well, in **Appendix B7** and **B8**, sample calculations are provided for determining the extraction efficiencies for centrifuge underflow cuttings and invert cuttings.

Table 4-5 presents the relative standard deviations found in the results. The relative standard deviations (% RSD) ranged from 1.83 to 39.2% for the extractions of centrifuge underflow cuttings, and 78.2 to 90.9% for the extractions of invert cuttings. Two to three subsamples were used and three injections in the GC for each subsample were made.

It is believed that the standard deviations are the result of several factors, most importantly the sample heterogeneity, and the GC analysis. In addition, it is important to note that the experiments with centrifuge underflow cuttings yielded lower standard deviations than experiments with invert cuttings.

The low standard deviation found for experiments with centrifuge underflow cuttings is most likely due to the excellent mixing introduced in this investigation that minimized the heterogeneity of the samples. Most of the deviation seen in the experiments with the centrifuge underflow cuttings might have been introduced for the most part by the GC analysis with some variability introduced by subsampling.

On the other hand, for the invert cuttings, the water content, the high boiling point resulting from the additives and the amount of salt present, might have contributed to the high RSD. Since the reduction of the final extract to less than 2 mL was performed in a Rotovap operated at approximately 80°C, the water content present in samples and the high boiling point additives impeded sample concentration. As a result, more variability was seen in the three subsamples from the same batch.

Ideally, three subsamples should have been analyzed for each extraction and three GC injections should have been carried out for each subsample. However, doing so would have required a great deal of time and would have incurred high costs for chemicals and gases.

Preliminary testing indicated that increasing the number of subsamples taken from one batch was found not to reduce the variability in the results.

For extractions performed under the same conditions, low standard deviation values were found between them. The extractions performed at the same conditions were representative and did not vary from each other. For instance, the results obtained for the extractions at 40°C and 14.5 MPa for the centrifuge underflow cuttings showed that the results for one extraction, which ranged from 0.35 to 0.51% (average of 0.43% ± 0.08% oil content) and the second extraction, which ranged from 0.32 to 0.44% (average of

0.40% ± 0.04% oil content), were the same. There was an overlap region between 0.32 to 0.51% of possible values, indicating that they were not different from each other. After this procedure was carried out for all the extractions, it was found that the results of the extractions under the same conditions were representative and not different.

The suggested operating conditions were established and were corroborated with qualitative visual observations. The fact that there was no difference in the final oil content when using different settings allowed for the suggested operating conditions to be determined: the lowest pressure, temperature, and most favorable flow rate (40°C, 14.5 MPa, and 10-12 mL/min).

Above all, it was believed that the low standard deviation of the results in this investigation resulted from the fact that the effect of mixing was improved. The mixing generated more homogeneous treated cuttings, reducing the variability of the results in the experiments.

4.6 Solubility Results

Using the first method mentioned in **Section 3.27**, some experiments were performed, and the most representative experiment is illustrated in **Table 4-7.** The pure diesel oil's solubility in SC CO_2 was around 0.10g of pure diesel oil /g CO_2. Three injections using GC/FID were performed on each vial collected during the experiments to ensure consistent results (See **Appendix B6** for solubility calculation).

Table 4-7. **Solubility Experiment**

Vial Number #	Time for each vial (min)	Average Flow of CO_2 per vial (mL/ min)	Concentration (g diesel / g toluene)	Mass of diesel per vial (g)	Average mass of CO_2 per vial (g)	Solubility (g diesel /g CO_2)	Average solubility (g diesel /g CO_2)	Final average solubility (g diesel /g CO_2)
1	5	1.9	0.05	0.8	9.0	0.09	0.09	0.10
	5	1.9	0.05	0.8	9.0	0.09		
	5	1.9	0.05	0.8	9.0	0.09		
2	5	2.0	0.06	1.0	9.4	0.10	0.11	
	5	2.0	0.05	0.9	9.4	0.10		
	5	2.0	0.06	1.1	9.4	0.12		
3	5	1.3	0.03	0.5	6.1	0.09	0.10	
	5	1.3	0.04	0.7	6.1	0.12		
	5	1.3	0.03	0.6	6.1	0.09		
4	5	1.2	0.04	0.7	5.7	0.12	0.12	
	5	1.2	0.04	0.7	5.7	0.12		
	5	1.2	0.04	0.7	5.7	0.13		
5	5	1.5	0.04	0.8	7.3	0.10	0.10	
	5	1.5	0.04	0.8	7.3	0.10		
	5	1.5	0.04	0.8	7.3	0.10		

The second method of determining diesel oil solubility was using the data from the drill cuttings extraction experiments. There were many experiments of this kind, and a sample of how solubility was calculated is illustrated in **Figure 4-35** (see **Appendix B3 and B4** for the sample experiment data for this dynamic solubility experiment).

The data for oil solubility was approximately 0.047g of oil /g CO_2 at a flow rate of 10-12 mL/min.

The difference in solubility results calculated using the two methods may be attributed to the diesel oil used in the solubility determinations. The diesel oil used in the first solubility determination was commercially available diesel oil while the diesel oil used in the second method was diesel oil containing additives required for drilling process. It may be possible that these additives resulted in a solubility that was lower. In addition, the second method was also affected by the presence of drill cuttings. These cuttings may have also affected how much oil could dissolve in the SCF and thus the solubility measured is an apparent solubility rather than the actual solubility.

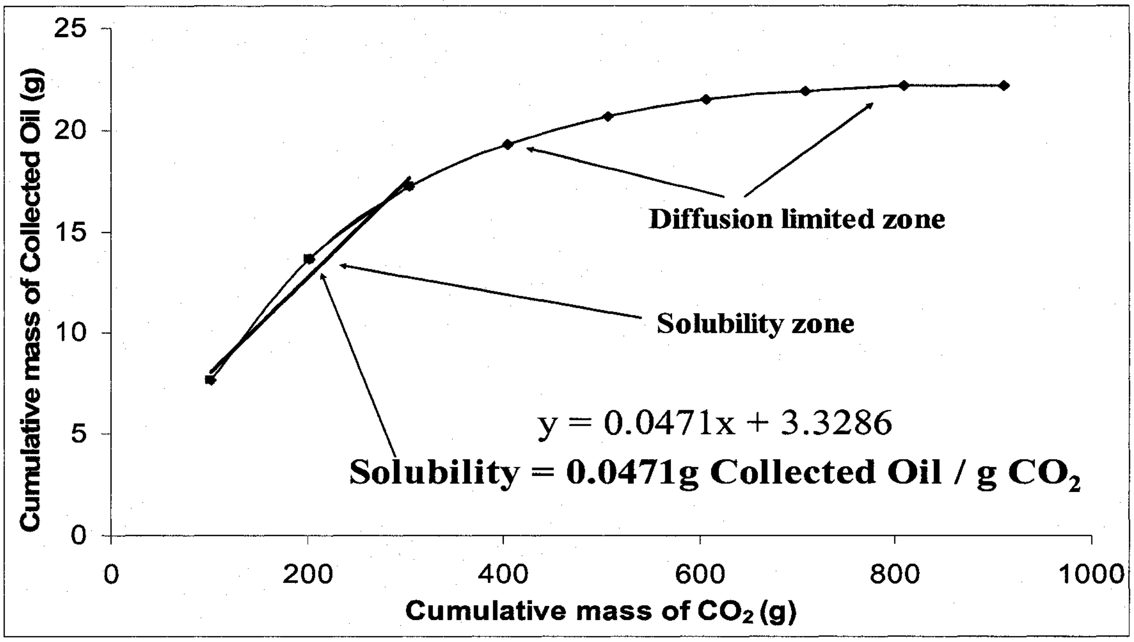


Figure 4-35. **Dynamic solubility experiment for an experiment conducted at 14.5 MPa and 40°C**

4.7 Chromatograms of the oil collected in traps

Figures 4-36 and **4-37** present the chromatograms for pure standard diesel oil, the SFE-extracted oil, the raw cuttings oil and the oil extracted via Soxhlet extraction for both the centrifuge underflow cuttings and invert mud cuttings, respectively.

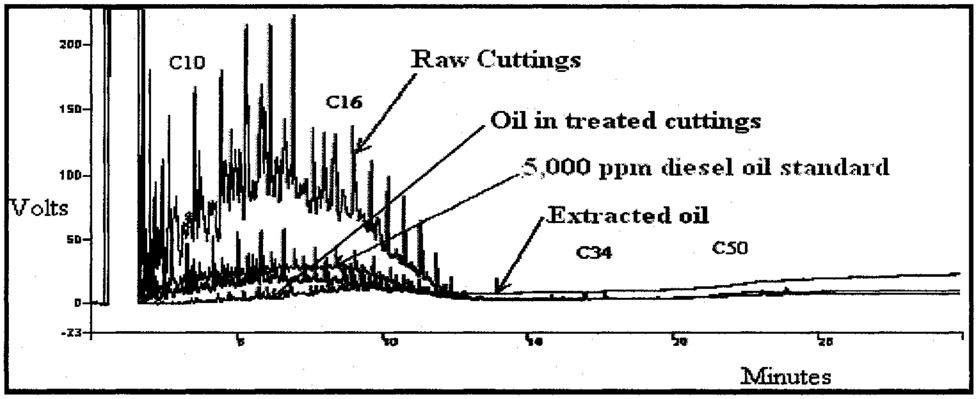


Figure 4-36. **Chromatograms of pure diesel oil, SFE-extracted oil, raw cuttings oil and oil extracted oil via Soxhlet extraction found in centrifuge underflow cuttings**

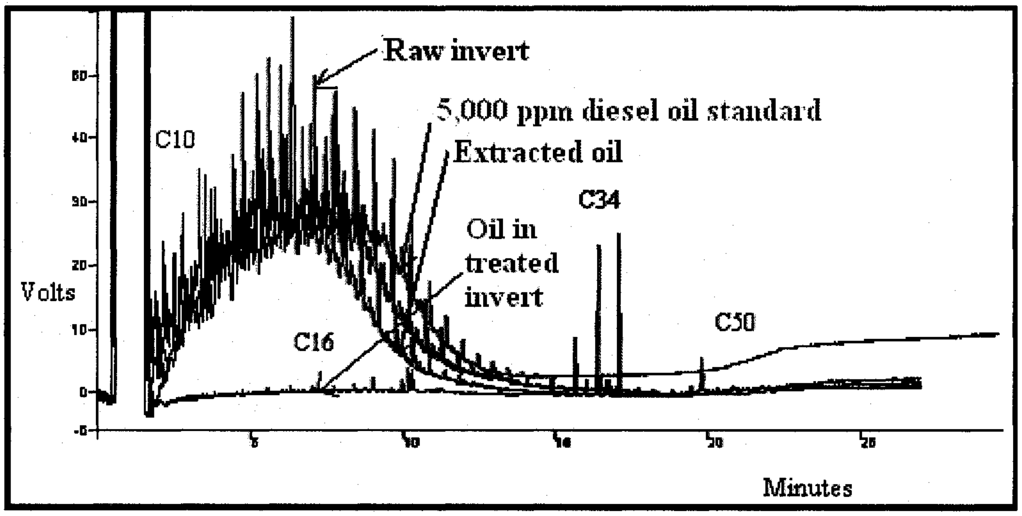


Figure 4-37. Chromatograms of pure diesel oil, SFE-extracted oil, raw cuttings oil and oil extracted oil via Soxhlet extraction found in invert mud cuttings

Figure 4-36 shows that when treating centrifuge underflow cuttings, the characteristics of the oil did not change. The chromatogram of the diesel oil standard revealed that what was being extracted was similar in carbon number range as commercially available diesel oil. Some small peaks around C_{34} came out in the raw and treated cuttings chromatograms, indicating that the centrifuge underflow may have had extremely low concentrations of hydrocarbons around C_{34}. These small peaks that were occasionally observed were below the detection limit of the gas chromatograph and therefore were not measured.

It was also noted that small peaks at higher retention times sometimes appeared in the raw and treated cuttings but did not appear in the extracted oil. This result indicates that extracting higher end hydrocarbons was more difficult than extracting lighter end hydrocarbons. Despite this fact, the concentrations of PHCs were below the regulation limits, and therefore the SFE process was demonstrated to be successful in treating centrifuge underflow.

Figure 4-37 shows the same type of chromatograms for the invert cuttings. The quality of the extracted oil obtained when treating invert cuttings was similar to that from the centrifuge underflow, but with a distinct characteristic. The oil from the raw and treated invert cuttings presented appreciable quantities of hydrocarbons around C_{34}, and a few large peaks were noticed around the area of C_{34}. This result indicated that the oil present in the invert mud cuttings experienced significant weathering during drilling. In addition, additives may have contributed to these peaks in the chromatograms of raw and treated cuttings.

In addition, it was noted that, when invert cuttings was treated, a few large peaks that always appeared in the raw and treated cuttings did not appear in the extracted oil. This result indicates again that certain higher end hydrocarbons in invert mud cuttings were not extracted. For these peaks, the gas chromatogram did show representative concentrations for these compounds and therefore they were included in the PHC content. In spite of this, the concentrations were below the regulation limits, and therefore the SFE process was demonstrated to be successful in treating invert cuttings.

In both the centrifuge underflow cuttings oil and invert mud cuttings oil chromatograms, the humps of oil present in the treated cuttings were not as large as the humps observed in their respective raw cuttings. This fact indicated lower concentrations in the treated cuttings.

Moreover, according to all the chromatograms, the SFE process did not change the nature and composition of the oil. The oil in the cuttings had the same composition before and after the SFE, showing no fractioning of hydrocarbons during the SFE process. This result indicates that the extracted oil can potentially be reused in drilling operations.

Furthermore, the chromatogram of the oil extracted from the centrifuge underflow cuttings and invert cuttings showed the same pattern as the aged diesel oil used to prepare the standards. The composition of the extracted oil from the centrifuge underflow cuttings and invert cuttings during the extractions was the same as diesel oil. No compositional change in the extracted oil was obvious in the chromatograms. This implies that all the hydrocarbons in the oil came out at the same time.

Finally, **Figure 4-38** shows the chromatograms of the extracted oil from invert cuttings when it was treated with drying agents and had higher water content. The chromatograms also showed that the nature and characteristics of the oil remained the same before and after SFE extraction, and therefore it can be potentially reused.

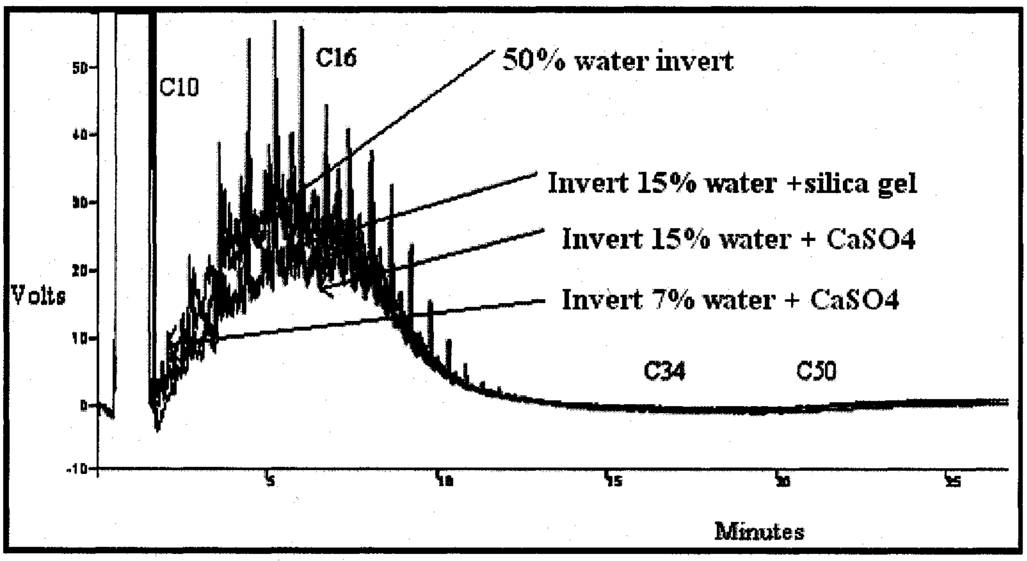


Figure 4-38. **Extracted oil from invert cuttings with drying agents**

4.8 Quality assurance

In this research, quality control measures were performed regularly by injecting pure standards of diesel oil to test the response of the GC.

The acceptable percentage of drift from the theoretical concentration was ±15%, and when the calculated value was far from this acceptable range, correcting actions such as cleaning the autosampler injection syringe, changing the glass insert (liner), changing the gas cylinder with low pressure, and injector septa were performed. On occasions when the percentage of drift was far from the acceptable range even though all these correcting actions were performed, baking the column was an effective alternative that returned the response of the GC to within the acceptable drift range.

Comparisons were made by sending samples to Norwest Labs to ensure that the results obtained in house were correct. In **Table 4-5,** the data from Norwest Labs are presented, as well as the data obtained internally for the same samples. It should be noted that Norwest labs reports values of C_{10} to C_{40} while the in house analysis reports values from C_{10} to C_{50}. These two results are essentially the same since the oil in the drill cuttings contains essentially no hydrocarbons in the range of C_{40} to C_{50}. For instance, the value for centrifuge underflow raw cuttings presented by Norwest Labs was 183,380 mg HC/ kg of dry cuttings, and the one obtained internally was 194,227 mg HC / kg of dry cuttings.

However, the data obtained internally for the raw invert cuttings had a variation in comparison with the value reported by Norwest Labs. Since raw invert cuttings was found to have quantities of heavy hydrocarbons in the area from C_{34} to $C_{50,}$ the data reported by Norwest Labs (11.2%) was lower than that obtained internally (14.8%)

because its analysis went from C_{10} to C_{40} whereas the analysis performed internally went from C_{10} to C_{50}.

Finally, the method detection limit (MDL) was not performed in this work because low concentration spiked samples were difficult to prepare.

CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

Chapter five presents the conclusions and recommendations related to this research.

5.1 CONCLUSIONS

- This investigation provided evidence that SFE using SC CO_2 as a solvent was effective at treating drilling waste contaminated with diesel oil.
- This research used an appropriate SFE system to conduct the investigation and therefore obtain reliable results.

In particular, the following conclusions can be drawn from this work:

- Within the conditions tested, the suggested operating conditions were found to be 14.5 MPa, 40°C, 10 to 12 mL/min, and 800 rpm, with an initial 15 minutes static period followed by 90 minutes of dynamic extraction. These suggested operating conditions were valid for both kinds of drill cuttings (centrifuge underflow and invert cuttings). Under these conditions, the treated cuttings appeared dry and light in color.
- Having only one static period of 15 minutes at the beginning of the process and 90 minutes of dynamic extraction, the SFE system was able to decontaminate the studied drilling wastes to below regulatory guidelines (0.5% oil content).
- The oil extracted from the cuttings had the same color as commercial diesel oil.
- According to gas chromatography, the composition of the oil extracted remained the same with no alteration after the extraction. The extracted oil can be potentially reused in the drilling process.

- The composition of the extracted oil throughout the process was the same. No change in the hydrocarbons was seen in the chromatograms. All the hydrocarbons of the oil came out at the same time. Fractioning of the hydrocarbons during the experiments was not seen.
- The solubility of pure diesel oil in SC CO_2 at 40°C and 14.5 MPa was close to 0.10g pure diesel oil /g CO_2.
- The solubility of the oil present in drilling waste in SC CO_2 at 40°C and 14.5 MPa ranged between 0.021 and 0.047g collected oil / g CO_2
- For the range of temperatures studied in this work, the temperature did not seem to have an important effect on the extraction efficiency.
- For the range of pressures studied in this work, the pressure of the system had an important impact on the extraction efficiency, although pressures beyond 14.5 MPa did not have any effect on the extraction efficiency.
- Mixing was an important factor in the efficiency of the process, generating treated cuttings that were homogeneous thus reducing the variability of the results in the experiments.
- Using a ribbon blender as a mixer, the SFE process was able to treat higher quantities of drill cuttings placed in a vessel.
- The flow rate effect had a noticeable impact on the extraction efficiency. For the range of flow rates studied in this work, the suggested flow rate was 10-12 mL / min.
- Water content had an impact on extraction efficiency.

- Water contents between 7% and 20% affected the extraction efficiency, however high water contents (>20%) or low water content (<7%) did not have an effect.
- Drying agents improved the quality of the treated cuttings and therefore the discharge of the treated invert cuttings from the vessel.

5.2 RECOMMENDATIONS

- Having multiples outlets in the vessel is recommended since this SFE outlet system was inefficient when operated with high quantities of drilling cuttings. Outlets located in different positions and operated at different times might improve the capacity of the process as a whole because the SFE process in this investigation was limited at higher loadings. Eliminating the clogging problem could make the SFE process a successful alternative for large-scale operations.

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Appendix A

Appendix A1 Sample experiment data

Date: 5/16/2003

Comments: 101.1896g, 2100 psi, 40°C, 10 mL/min, 800-rpm long single cycle.
Static started at 1790 seconds. Dynamic started at 2690 seconds and stopped at 8090 seconds.
Change to pump A at 5260 seconds.
In the last minutes, refilling pumps was necessary. The flow was the same even though it was shown higher flow for the last vials on the screen.

Time (s)	Pump Pressure (psi)			Pressure Transducer Reading (psi)	Pump Flow rate (mL/min)			Vessel Temperature (°C)
	Pump A	Pump B	Total Pressure		Pump A	Pump B	Total Flow rate	
Lab View program initiated having pumps pressurized and full with CO_2. Both pumps running at the same time but independently								
10.10	2,100.00	2,100.00	2,100.00	123.22	1.63	1.95	3.58	33.18
20.92	2,100.00	2,100.00	2,100.00	115.20	1.59	1.84	3.44	33.24
30.48	2,100.00	2,100.00	2,100.00	123.47	1.56	1.78	3.34	33.30
40.09	2,100.00	2,100.00	2,100.00	145.05	1.54	1.70	3.22	33.36
50.91	2,100.00	2,100.00	2,100.00	107.58	1.49	1.62	3.12	33.36
60.52	2,100.00	2,100.00	2,100.00	112.75	1.47	1.55	3.04	33.48
70.08	2,100.00	2,100.00	2,100.00	117.22	1.42	1.49	2.96	33.54
80.90	2,100.00	2,100.00	2,100.00	112.13	1.41	1.41	2.83	33.60
90.51	2,100.00	2,100.00	2,100.00	120.00	1.39	1.36	2.74	33.60
100.07	2,100.00	2,100.00	2,100.00	100.97	1.35	1.30	2.65	33.67
110.89	2,100.00	2,100.00	2,100.00	101.16	1.32	1.26	2.58	33.73
120.50	2,100.00	2,100.00	2,100.00	117.44	1.28	1.20	2.51	33.73
130.11	2,100.00	2,100.00	2,100.00	125.23	1.28	1.16	2.42	33.73
140.88	2,100.00	2,100.00	2,100.00	107.08	1.26	1.11	2.36	33.91
150.49	2,100.00	2,100.00	2,100.00	108.84	1.21	1.06	2.30	33.85
160.10	2,100.00	2,100.00	2,100.00	131.46	1.19	1.02	2.22	33.91
170.87	2,100.00	2,100.00	2,100.00	120.54	-0.02	-0.03	2.16	33.91
180.48	2,100.00	2,100.00	2,100.00	93.87	1.18	0.99	2.36	33.91
190.09	2,100.00	2,100.00	2,100.00	112.27	1.10	0.91	2.03	33.91
200.86	2,100.00	2,100.00	2,100.00	102.35	1.08	0.87	1.96	33.98
210.47	2,100.00	2,100.00	2,100.00	105.60	1.05	0.84	1.92	33.98
220.08	2,100.00	2,100.00	2,100.00	110.05	1.02	0.81	1.84	34.04
230.90	2,100.00	2,100.00	2,100.00	117.77	1.01	0.77	1.79	34.10
240.46	2,100.00	2,100.00	2,100.00	109.48	0.96	0.76	1.73	34.04
250.07	2,100.00	2,100.00	2,100.00	112.66	0.95	0.73	1.70	34.16
260.89	2,100.00	2,100.00	2,100.00	119.03	0.93	0.70	1.64	34.16
270.45	2,100.00	2,100.00	2,100.00	111.36	0.90	0.68	1.60	34.22
280.06	2,100.00	2,100.00	2,100.00	104.85	0.89	0.65	1.54	34.29
290.88	2,100.00	2,100.00	2,100.00	131.48	0.86	0.63	1.50	34.22
300.49	2,100.00	2,100.00	2,100.00	92.93	0.85	0.61	1.45	34.29
310.05	2,100.00	2,100.00	2,100.00	112.25	0.83	0.59	1.42	29.47
320.87	2,100.00	2,100.00	2,100.00	109.35	0.79	0.58	1.38	34.29
330.48	2,100.00	2,100.00	2,100.00	111.90	0.77	0.56	1.34	34.29
340.04	2,100.00	2,100.00	2,100.00	119.30	0.74	0.54	1.32	34.29
350.86	2,100.00	2,100.00	2,100.00	112.47	0.73	0.53	1.26	34.04

360.47	2,100.00	2,100.00	2,100.00	133.49	0.71	0.51	1.24	34.16
370.03	2,100.00	2,100.00	2,100.00	97.73	0.70	0.50	1.19	34.41
380.85	2,100.00	2,100.00	2,100.00	108.43	0.69	0.48	1.17	34.29
390.46	2,100.00	2,100.00	2,100.00	110.79	0.66	0.48	1.12	34.10
400.07	2,100.00	2,100.00	2,100.00	131.51	0.63	0.47	1.11	34.16
410.84	2,100.00	2,100.00	2,100.00	115.17	0.62	0.46	1.08	34.29
420.45	2,100.00	2,100.00	2,100.00	117.99	0.59	0.44	1.06	30.31
430.06	2,100.00	2,100.00	2,100.00	133.54	0.59	0.44	1.04	34.22
440.83	2,100.00	2,100.00	2,100.00	162.08	0.57	0.42	0.98	38.32
450.44	2,100.00	2,100.00	2,100.00	113.98	0.55	0.41	0.98	39.09
460.05	2,100.00	2,100.00	2,100.00	129.38	0.53	0.40	0.97	39.02
470.82	2,100.00	2,100.00	2,100.00	71.92	0.54	0.40	0.94	38.88
480.43	2,100.00	2,100.00	2,100.00	110.11	0.53	0.38	0.90	38.74
490.04	2,100.00	2,100.00	2,100.00	97.43	0.51	0.38	0.89	38.60
500.86	2,100.00	2,100.00	2,100.00	168.28	0.50	0.36	0.86	38.46
510.42	2,100.00	2,100.00	2,100.00	91.96	0.47	0.35	0.84	38.46
520.03	2,100.00	2,100.00	2,100.00	160.43	0.46	0.36	0.82	38.32
530.85	2,100.00	2,100.00	2,100.00	179.06	0.46	0.33	0.78	38.25
540.41	2,100.00	2,100.00	2,100.00	139.09	0.43	0.32	0.76	38.11
550.02	2,100.00	2,100.00	2,100.00	134.52	0.41	0.31	0.74	38.11
560.84	2,100.00	2,100.00	2,100.00	(0.34)	0.40	0.30	0.70	38.04
570.45	2,100.00	2,100.00	2,100.00	208.86	0.39	0.29	0.68	37.83
580.01	2,100.00	2,100.00	2,100.00	363.22	0.38	0.28	0.66	37.90
590.83	2,100.00	2,100.00	2,100.00	315.03	0.37	0.28	0.65	37.76
600.44	2,100.00	2,100.00	2,100.00	114.08	0.35	0.23	0.62	37.76
610.00	2,100.00	2,100.00	2,100.00	20.96	0.33	0.24	0.58	37.76
620.82	2,100.00	2,100.00	2,100.00	102.04	0.33	0.24	0.57	37.55
630.43	2,100.00	2,100.00	2,100.00	132.20	0.30	0.24	0.56	37.76
640.04	2,100.00	2,100.00	2,100.00	133.97	0.31	0.23	0.55	37.69
650.81	2,100.00	2,100.00	2,100.00	36.74	0.31	0.23	0.52	37.69
660.42	2,100.00	2,100.00	2,100.00	159.90	0.28	0.22	0.49	37.55
670.03	2,100.00	2,100.00	2,100.00	195.88	0.27	0.21	0.49	37.55
680.80	2,100.00	2,100.00	2,100.00	53.48	0.23	0.21	0.48	37.49
690.41	2,100.00	2,100.00	2,100.00	255.75	0.24	0.21	0.44	37.49
700.02	2,100.00	2,100.00	2,100.00	343.59	0.25	0.20	0.44	37.55
710.79	2,100.00	2,100.00	2,100.00	78.22	0.24	0.19	0.43	37.55
720.40	2,100.00	2,100.00	2,100.00	324.76	0.23	0.19	0.42	37.49
730.01	2,100.00	2,100.00	2,100.00	64.35	0.23	0.19	0.41	37.55
740.78	2,100.00	2,100.00	2,100.00	179.63	0.24	0.19	0.49	37.55
750.39	2,100.00	2,100.00	2,100.00	87.41	0.20	0.17	0.36	37.49
760.00	2,100.00	2,100.00	2,100.00	302.34	0.20	0.17	0.37	37.49
770.82	2,100.00	2,100.00	2,100.00	321.06	0.19	0.17	0.37	37.55
780.38	2,100.00	2,100.00	2,100.00	(201.18)	0.18	0.17	0.35	37.49
791.20	2,100.00	2,100.00	2,100.00	(153.38)	0.17	0.17	0.34	37.55
800.81	2,100.00	2,100.00	2,100.00	98.19	0.17	0.16	0.33	37.55
810.37	2,100.00	2,100.00	2,100.00	90.72	0.16	0.16	0.32	37.55
821.19	2,100.00	2,100.00	2,100.00	83.29	0.15	0.16	0.31	37.62
830.80	2,100.00	2,100.00	2,100.00	96.18	0.15	0.15	0.30	37.49
840.41	2,100.00	2,100.00	2,100.00	72.48	0.15	0.15	0.30	37.90
851.18	2,100.00	2,100.00	2,100.00	120.22	0.14	0.15	0.29	39.38

860.79	2,100.00	2,100.00	2,100.00	41.38	0.14	0.15	0.29	39.89
870.40	2,100.00	2,100.00	2,100.00	86.98	0.13	0.15	0.29	40.11
881.17	2,100.00	2,100.00	2,100.00	303.91	0.13	0.15	0.27	40.33
890.78	2,100.00	2,100.00	2,100.00	121.39	0.13	0.15	0.27	40.11
900.39	2,100.00	2,100.00	2,100.00	19.75	0.12	0.15	0.27	39.74
910.00	2,100.00	2,100.00	2,100.00	51.50	0.12	0.15	0.27	39.52
920.77	2,100.00	2,100.00	2,100.00	95.63	0.11	0.15	0.26	39.45
930.38	2,100.00	2,100.00	2,100.00	290.49	0.11	0.15	0.26	39.96
941.14	2,083.00	2,028.00	2,100.00	77.83	0.11	0.15	0.26	39.81

Pressurized flow opened to the vessel

950.76	2,091.00	2,045.00	2,073.00	1,419.32	36.75	57.80	99.49	39.74
960.37	2,100.00	2,091.00	2,100.00	1,780.20	-1.34	83.86	79.75	39.81
971.19	2,100.00	2,100.00	2,100.00	1,725.22	-0.16	78.22	79.16	39.74
980.75	2,100.00	2,100.00	2,100.00	1,814.72	-0.10	77.48	78.08	39.60
990.36	2,100.00	2,100.00	2,100.00	1,752.66	0.01	76.60	76.71	39.16
1001.18	2,100.00	2,100.00	2,100.00	1,828.05	0.00	75.95	76.04	38.18
1010.74	2,100.00	2,100.00	2,100.00	1,802.75	0.00	75.46	75.53	36.94
1020.35	2,100.00	2,100.00	2,100.00	1,727.83	0.00	75.10	75.19	35.88
1031.17	2,100.00	2,100.00	2,100.00	1,395.18	-0.07	75.00	75.03	35.30
1040.78	2,100.00	2,100.00	2,100.00	2,076.15	-0.02	73.95	74.06	35.69
1050.34	2,100.00	2,100.00	2,100.00	1,837.40	0.00	72.56	72.80	36.48
1061.16	2,100.00	2,100.00	2,100.00	1,879.42	-0.01	69.44	70.41	37.42
1070.77	2,100.00	2,100.00	2,100.00	1,915.55	0.00	65.62	65.92	38.25
1080.33	2,100.00	2,100.00	2,100.00	1,972.97	0.00	58.09	58.61	39.02
1091.15	2,100.00	2,100.00	2,100.00	2,049.87	0.00	47.00	49.26	39.81
1100.76	2,100.00	2,100.00	2,100.00	2,141.67	0.00	35.98	36.81	40.18
1110.37	2,100.00	2,100.00	2,100.00	2,203.21	0.00	23.00	24.44	40.25
1121.14	2,100.00	2,100.00	2,100.00	2,218.07	0.00	12.84	13.31	40.03
1130.75	2,100.00	2,100.00	2,100.00	2,235.34	0.00	7.96	8.37	39.52
1140.36	2,100.00	2,100.00	2,100.00	2,243.20	0.01	5.99	6.16	39.02
1151.12	2,100.00	2,100.00	2,100.00	2,243.73	0.09	4.45	4.66	38.60
1160.74	2,100.00	2,100.00	2,100.00	2,249.30	0.10	3.62	3.77	38.18
1170.35	2,100.00	2,100.00	2,100.00	2,233.81	0.09	3.29	3.40	37.97
1181.11	2,100.00	2,100.00	2,100.00	2,234.91	0.05	2.64	2.72	37.55
1190.73	2,100.00	2,100.00	2,100.00	2,245.00	0.04	2.36	2.41	37.49
1200.34	2,100.00	2,100.00	2,100.00	2,225.29	0.06	2.02	2.10	37.21
1211.10	2,100.00	2,100.00	2,100.00	2,240.33	0.05	1.96	2.03	37.08
1220.72	2,100.00	2,100.00	2,100.00	2,240.49	0.05	1.71	1.79	36.94
1230.33	2,100.00	2,100.00	2,100.00	2,238.11	0.04	1.54	1.58	36.81
1241.15	2,100.00	2,100.00	2,100.00	2,241.43	0.05	1.46	1.51	36.61
1250.70	2,100.00	2,100.00	2,100.00	2,246.89	0.04	1.23	1.29	36.54
1260.32	2,100.00	2,100.00	2,100.00	2,245.37	0.04	1.14	1.21	36.54
1271.14	2,100.00	2,100.00	2,100.00	2,249.50	0.05	1.02	1.08	36.34
1280.69	2,100.00	2,100.00	2,100.00	2,241.04	0.04	0.89	0.93	36.41
1290.31	2,100.00	2,100.00	2,100.00	2,247.41	0.04	0.88	0.92	36.28
1301.13	2,100.00	2,100.00	2,100.00	2,243.76	0.04	0.87	0.92	36.21
1310.74	2,100.00	2,100.00	2,100.00	2,247.45	0.03	0.66	0.70	36.28
1320.30	2,100.00	2,100.00	2,100.00	2,250.47	0.00	0.53	0.53	36.15
1331.12	1,501.00	2,100.00	1,954.00	2,238.68	203.90	0.00	175.35	36.08

Refilling pumps A and B with more CO_2 and stopping flow to the vessel

1340.73	875.00	846.00	879.00	2,229.58	204.08	204.08	408.20	36.08
1350.28	869.00	842.00	869.00	2,214.51	204.17	204.09	408.12	35.95
1361.11	879.00	853.00	879.00	2,216.76	0.00	204.11	204.05	36.02
1370.72	879.00	854.00	879.00	2,217.63	0.00	204.11	204.06	35.82
1380.33	879.00	855.00	879.00	2,202.63	0.00	204.10	203.67	35.82
1391.09	879.00	855.00	879.00	2,204.15	0.00	204.04	204.08	35.82
1400.71	878.00	855.00	878.00	2,210.54	0.00	204.00	203.79	35.88
1410.32	877.00	855.00	877.00	2,197.63	0.00	204.08	204.07	35.82

Re-depressurization of pumps A and B but having no flow to the vessel

1421.08	999.00	863.00	901.00	2,187.89	195.83	0.00	109.19	35.75
1430.70	1,852.00	1,420.00	1,765.00	2,180.16	71.26	189.85	283.10	35.75
1440.31	2,066.00	1,947.00	2,048.00	2,185.61	24.70	41.83	74.95	35.82
1451.07	2,100.00	2,100.00	2,094.00	2,171.56	11.14	27.16	41.11	35.75
1460.69	2,100.00	2,100.00	2,100.00	2,178.37	6.96	14.77	22.90	35.88

Pressurized flow is let again to go to the vessel

1470.30	2,100.00	2,100.00	2,100.00	2,228.75	5.10	18.42	24.29	35.82
1481.06	2,100.00	2,100.00	2,100.00	2,229.64	3.50	8.59	12.25	36.08
1490.67	2,100.00	2,100.00	2,100.00	2,241.65	2.64	6.13	9.04	35.95
1500.29	2,100.00	2,100.00	2,100.00	2,228.16	1.51	5.75	6.32	35.95
1511.11	2,100.00	2,100.00	2,100.00	2,229.67	1.51	4.88	6.66	36.02
1520.66	2,100.00	2,100.00	2,100.00	2,229.64	1.24	4.28	5.59	36.08
1530.28	2,100.00	2,100.00	2,100.00	2,233.86	1.01	3.90	4.93	35.95
1541.10	2,100.00	2,100.00	2,100.00	2,231.02	0.78	3.52	4.42	35.95
1550.65	2,100.00	2,100.00	2,100.00	2,236.86	0.65	3.14	3.78	35.95
1560.26	2,100.00	2,100.00	2,100.00	2,230.42	0.54	3.03	3.57	36.08
1571.09	2,100.00	2,100.00	2,100.00	2,224.47	0.43	2.75	3.30	36.02
1580.70	2,100.00	2,100.00	2,100.00	2,238.34	0.35	2.49	2.86	35.95
1590.25	2,100.00	2,100.00	2,100.00	2,226.17	0.29	2.28	2.62	35.95
1601.07	2,100.00	2,100.00	2,100.00	2,234.53	0.18	2.23	2.39	36.02
1610.69	2,100.00	2,100.00	2,100.00	2,241.75	0.21	2.01	2.26	36.02
1620.24	2,100.00	2,100.00	2,100.00	2,218.15	0.19	1.99	2.18	36.08
1630.08	2,100.00	2,100.00	2,100.00	2,238.57	0.17	1.90	2.09	36.02
1640.84	2,100.00	2,100.00	2,100.00	2,232.79	0.16	1.67	1.87	36.02
1650.45	2,100.00	2,100.00	2,100.00	2,230.84	0.15	1.63	1.79	36.02
1660.06	2,100.00	2,100.00	2,100.00	2,221.73	0.15	1.61	1.76	36.02
1670.88	2,100.00	2,100.00	2,100.00	2,220.59	0.15	1.30	1.33	36.15
1680.44	2,100.00	2,100.00	2,100.00	2,239.79	0.16	1.36	1.64	36.08
1690.05	2,100.00	2,100.00	2,100.00	2,232.28	0.16	1.32	1.51	36.15
1700.93	2,100.00	2,100.00	2,100.00	2,240.74	0.17	1.28	1.45	36.15
1710.54	2,100.00	2,100.00	2,100.00	2,228.53	0.17	1.34	1.56	36.08
1720.15	2,100.00	2,100.00	2,100.00	2,225.07	0.19	1.17	1.37	36.08
1730.97	2,100.00	2,100.00	2,100.00	2,239.26	0.20	1.09	1.30	36.08
1740.53	2,100.00	2,100.00	2,100.00	2,223.11	0.21	1.05	1.19	36.15
1750.14	2,100.00	2,100.00	2,100.00	2,232.77	0.22	1.05	1.28	36.15
1760.96	2,100.00	2,100.00	2,100.00	2,237.23	0.23	0.95	1.17	36.21
1770.52	2,100.00	2,100.00	2,100.00	2,239.07	0.24	0.96	1.17	36.08
1780.13	2,100.00	2,100.00	2,100.00	2,235.40	0.24	0.97	1.18	36.08

Pressurized vessel, temperature ready and impeller turned on (static period started).

1790.95	2,100.00	2,049.00	2,100.00	2,133.21	1.43	22.31	6.92	36.54
1800.56	2,100.00	2,100.00	2,100.00	2,240.38	0.08	-2.47	-1.96	39.60

1810.12	2,100.00	2,100.00	2,100.00	2,231.09	0.42	0.75	1.21	39.81
1820.94	2,100.00	2,100.00	2,100.00	2,243.76	0.29	0.60	0.86	39.89
1830.55	2,100.00	2,100.00	2,100.00	2,258.23	0.31	0.60	0.88	40.11
1840.11	2,100.00	2,100.00	2,100.00	2,270.02	0.31	0.57	0.88	40.11
1850.93	2,100.00	2,100.00	2,100.00	2,281.90	0.30	0.57	0.89	40.25
1860.54	2,100.00	2,100.00	2,100.00	2,283.74	0.30	0.56	0.88	40.40
1870.15	2,100.00	2,100.00	2,100.00	2,286.69	0.32	0.53	0.86	40.40
1880.92	2,100.00	2,100.00	2,100.00	2,293.95	0.32	0.52	0.85	40.40
1890.53	2,100.00	2,100.00	2,100.00	2,283.85	0.32	0.49	0.82	40.63
1900.20	2,100.00	2,100.00	2,100.00	2,288.99	0.33	0.47	0.80	40.70
1911.02	2,100.00	2,100.00	2,100.00	2,325.06	0.32	0.45	0.77	40.70
1920.63	2,100.00	2,100.00	2,100.00	2,324.34	0.32	0.43	0.75	40.78
1930.24	2,100.00	2,100.00	2,100.00	2,304.55	0.32	0.42	0.73	40.70
1941.01	2,100.00	2,100.00	2,100.00	2,307.48	0.32	0.40	0.72	40.85
1950.62	2,100.00	2,100.00	2,100.00	2,316.36	0.31	0.39	0.68	40.85
1960.23	2,100.00	2,100.00	2,100.00	2,312.46	0.31	0.37	0.68	41.08
1971.00	2,100.00	2,100.00	2,100.00	2,329.34	0.31	0.35	0.66	41.00
1980.61	2,100.00	2,100.00	2,100.00	2,330.68	0.30	0.35	0.64	41.08
1990.22	2,100.00	2,100.00	2,100.00	2,327.55	0.29	0.32	0.63	41.08
2000.99	2,100.00	2,100.00	2,100.00	2,334.39	0.25	0.31	0.55	41.08
2010.60	2,100.00	2,100.00	2,100.00	2,335.99	0.29	0.30	0.66	41.08
2020.21	2,100.00	2,100.00	2,100.00	2,335.50	0.28	0.29	0.59	41.08
2031.03	2,100.00	2,100.00	2,100.00	2,345.19	0.27	0.28	0.56	41.23
2040.59	2,100.00	2,100.00	2,100.00	2,344.32	0.22	0.28	0.49	41.08
2050.31	2,100.00	2,100.00	2,100.00	2,352.16	0.26	0.27	0.52	41.30
2061.08	2,100.00	2,100.00	2,100.00	2,342.15	0.27	0.22	0.50	41.08
2070.69	2,100.00	2,100.00	2,100.00	2,343.85	0.21	0.25	0.45	41.23
2080.30	2,100.00	2,100.00	2,100.00	2,346.46	0.25	0.25	0.50	41.15
2091.12	2,100.00	2,100.00	2,100.00	2,349.70	0.25	0.25	0.50	41.15
2100.68	2,100.00	2,100.00	2,100.00	2,343.21	0.25	0.25	0.50	41.15
2110.29	2,100.00	2,100.00	2,100.00	2,332.50	0.25	0.25	0.50	41.23
2121.11	2,100.00	2,100.00	2,100.00	2,351.92	0.25	0.25	0.51	41.15
2130.67	2,100.00	2,100.00	2,100.00	2,354.03	0.25	0.25	0.50	41.15
2140.28	2,100.00	2,100.00	2,100.00	2,345.27	0.25	0.24	0.49	41.23
2151.10	2,100.00	2,100.00	2,100.00	2,354.19	0.25	0.24	0.49	41.23
2160.71	2,100.00	2,100.00	2,100.00	2,339.90	0.25	0.23	0.47	41.15
2170.27	2,100.00	2,100.00	2,100.00	2,349.55	0.24	0.22	0.47	41.23
2181.09	2,100.00	2,100.00	2,100.00	2,355.53	0.23	0.21	0.44	41.15
2190.70	2,100.00	2,100.00	2,100.00	2,345.92	0.22	0.20	0.42	41.08
2200.26	2,100.00	2,100.00	2,100.00	2,347.78	0.21	0.19	0.40	41.08
2211.08	2,100.00	2,100.00	2,100.00	2,342.71	0.20	0.19	0.39	41.15
2220.69	2,100.00	2,100.00	2,100.00	2,360.04	0.19	0.17	0.37	41.08
2230.30	2,100.00	2,100.00	2,100.00	2,338.32	0.18	0.16	0.35	41.15
2241.07	2,100.00	2,100.00	2,100.00	2,359.45	0.18	0.15	0.33	41.15
2250.68	2,100.00	2,100.00	2,100.00	2,340.72	0.16	0.15	0.31	41.15
2260.29	2,100.00	2,100.00	2,100.00	2,357.07	0.15	0.15	0.30	41.23
2271.06	2,100.00	2,100.00	2,100.00	2,354.79	0.15	0.14	0.29	41.15
2280.67	2,100.00	2,100.00	2,100.00	2,340.45	0.14	0.14	0.28	41.08
2290.28	2,100.00	2,100.00	2,100.00	2,352.82	0.13	0.14	0.27	41.15
2301.05	2,100.00	2,100.00	2,100.00	2,334.64	0.12	0.13	0.26	41.15

2310.66	2,100.00	2,100.00	2,100.00	2,352.26	0.12	0.13	0.25	41.08
2320.27	2,100.00	2,100.00	2,100.00	2,361.96	0.11	0.13	0.24	41.15
2331.03	2,100.00	2,100.00	2,100.00	2,354.15	0.11	0.13	0.23	41.15
2340.65	2,100.00	2,100.00	2,100.00	2,352.22	0.11	0.13	0.24	41.08
2350.26	2,100.00	2,100.00	2,100.00	2,349.17	0.11	0.14	0.25	41.15
2361.08	2,100.00	2,100.00	2,100.00	2,341.93	0.11	0.13	0.24	41.00
2370.64	2,100.00	2,100.00	2,100.00	2,348.60	0.11	0.13	0.25	41.15
2380.25	2,100.00	2,100.00	2,100.00	2,341.45	0.11	0.13	0.24	41.00
2391.07	2,100.00	2,100.00	2,100.00	2,339.25	0.11	0.13	0.24	41.00
2400.62	2,100.00	2,100.00	2,100.00	2,340.29	0.12	0.13	0.25	41.08
2410.24	2,100.00	2,100.00	2,100.00	2,352.19	0.12	0.13	0.24	41.08
2421.06	2,100.00	2,100.00	2,100.00	2,340.47	0.12	0.12	0.23	41.00
2430.67	2,100.00	2,100.00	2,100.00	2,349.33	0.12	0.12	0.24	41.08
2440.23	2,100.00	2,100.00	2,100.00	2,343.25	0.11	0.11	0.22	41.00
2451.05	2,100.00	2,100.00	2,100.00	2,347.25	0.12	0.12	0.24	40.93
2460.66	2,100.00	2,100.00	2,100.00	2,331.14	0.11	0.11	0.22	40.93
2470.22	2,100.00	2,100.00	2,100.00	2,348.28	0.11	0.11	0.21	40.93
2481.04	2,100.00	2,100.00	2,100.00	2,338.07	0.10	0.11	0.21	40.85
2490.65	2,100.00	2,100.00	2,100.00	2,337.30	0.10	0.16	0.20	40.85
2500.26	2,100.00	2,100.00	2,100.00	2,337.10	0.10	0.09	0.19	40.93
2511.03	2,100.00	2,100.00	2,100.00	2,340.45	0.09	0.10	0.19	41.00
2520.64	2,100.00	2,100.00	2,100.00	2,350.18	0.09	0.10	0.18	40.93
2530.25	2,100.00	2,100.00	2,100.00	2,357.30	0.08	0.09	0.17	40.85
2541.01	2,100.00	2,100.00	2,100.00	2,331.31	0.07	0.09	0.17	40.85
2550.63	2,100.00	2,100.00	2,100.00	2,329.73	0.07	0.09	0.16	40.85
2560.24	2,100.00	2,100.00	2,100.00	2,337.67	0.07	0.09	0.15	40.78
2571.00	2,100.00	2,100.00	2,100.00	2,351.48	0.07	0.10	0.17	40.85
2580.62	2,100.00	2,100.00	2,100.00	2,336.28	0.07	0.11	0.17	40.85
2590.23	2,100.00	2,100.00	2,100.00	2,343.40	0.07	0.11	0.19	40.93
2600.99	2,100.00	2,100.00	2,100.00	2,328.33	0.08	0.12	0.20	40.78
2610.61	2,100.00	2,100.00	2,100.00	2,336.63	0.09	0.13	0.22	40.93
2620.33	2,100.00	2,100.00	2,100.00	2,340.85	0.09	0.13	0.22	40.78
2631.09	2,100.00	2,100.00	2,100.00	2,339.15	0.10	0.13	0.23	40.85
2640.70	2,100.00	2,100.00	2,100.00	2,345.11	0.10	0.14	0.23	40.78
2650.32	2,100.00	2,100.00	2,100.00	2,346.87	0.11	0.14	0.25	40.93
2661.14	2,100.00	2,100.00	2,100.00	2,295.21	0.10	0.15	0.26	40.70
2670.69	2,100.00	2,100.00	2,100.00	2,288.60	0.11	0.15	0.25	40.78
2680.31	2,100.00	2,100.00	2,100.00	2,289.86	0.11	0.15	0.26	40.78
2691.13	2,100.00	2,100.00	2,100.00	2,279.55	0.12	0.15	0.27	40.70

Static period ends, and dynamic extraction starts having a flow of 10 mL/min approximately.
Pump B starts

2700.68	2,100.00	2,086.00	2,100.00	2,210.80	0.11	9.60	8.02	40.40
2710.29	2,100.00	2,100.00	2,100.00	2,236.07	0.12	9.53	10.06	40.48
2721.12	2,100.00	2,100.00	2,100.00	2,236.42	0.13	6.08	6.43	40.48
2730.73	2,100.00	2,100.00	2,100.00	2,230.96	0.13	4.10	3.90	40.63
2740.28	2,100.00	2,086.00	2,100.00	2,221.88	0.13	2.78	8.20	40.55
2751.10	2,100.00	2,100.00	2,100.00	2,227.49	0.13	10.38	11.19	40.55
2760.72	2,100.00	2,100.00	2,100.00	2,240.10	0.13	3.11	3.46	40.63
2770.27	2,100.00	2,100.00	2,100.00	2,224.16	0.13	9.16	8.98	40.55
2781.09	2,100.00	2,100.00	2,100.00	2,226.09	0.12	8.48	8.67	40.55
2790.71	2,100.00	2,100.00	2,100.00	2,224.57	0.12	9.23	9.30	40.63

2800.26	2,100.00	2,100.00	2,100.00	2,230.71	0.12	9.35	9.46	40.40
2811.08	2,100.00	2,100.00	2,100.00	2,225.49	0.11	9.53	9.63	40.48
2820.70	2,100.00	2,100.00	2,100.00	2,229.35	0.11	9.59	9.70	40.48
2830.31	2,100.00	2,100.00	2,100.00	2,238.05	0.12	9.63	9.73	40.40
2841.07	2,100.00	2,100.00	2,100.00	2,224.70	0.11	9.83	9.89	40.33
2850.68	2,100.00	2,100.00	2,100.00	2,232.64	0.10	10.00	10.09	40.33
2860.30	2,100.00	2,100.00	2,100.00	2,223.91	0.10	10.15	10.24	40.25
2871.06	2,100.00	2,100.00	2,100.00	2,229.84	0.09	9.99	10.12	40.33
2880.78	2,100.00	2,100.00	2,100.00	2,241.59	0.09	10.06	10.13	40.33
2890.40	2,100.00	2,100.00	2,100.00	2,221.70	0.08	10.18	10.23	40.25
2901.16	2,100.00	2,100.00	2,100.00	2,232.77	0.07	10.18	10.26	40.25
2910.77	2,100.00	2,100.00	2,100.00	2,226.80	0.06	10.36	10.38	40.18
2920.38	2,100.00	2,100.00	2,100.00	2,232.33	0.06	10.49	10.57	40.25
2930.00	2,100.00	2,100.00	2,100.00	2,227.69	0.06	10.47	10.52	40.18
2940.76	2,100.00	2,100.00	2,100.00	2,228.95	0.05	10.44	10.50	40.18
2950.37	2,100.00	2,100.00	2,100.00	2,221.51	0.05	10.48	10.51	40.11
2961.14	2,100.00	2,100.00	2,100.00	2,226.14	0.04	10.51	10.56	40.03
2970.75	2,100.00	2,100.00	2,100.00	2,227.12	0.04	10.55	10.56	40.03
2980.36	2,100.00	2,100.00	2,100.00	2,224.13	0.04	10.50	10.54	40.03
2991.18	2,100.00	2,100.00	2,100.00	2,219.97	0.04	10.52	10.55	40.03
3000.74	2,100.00	2,100.00	2,100.00	2,219.34	0.04	12.68	12.79	39.96
3010.35	2,100.00	2,100.00	2,100.00	2,228.39	0.04	10.92	10.63	39.89
3021.17	2,100.00	2,100.00	2,100.00	2,235.98	0.05	10.64	10.67	39.89
3030.73	2,100.00	2,100.00	2,100.00	2,216.41	0.05	10.68	10.71	39.96
3040.34	2,100.00	2,100.00	2,100.00	2,226.96	0.06	10.73	10.79	39.96
3051.16	2,100.00	2,100.00	2,100.00	2,224.37	0.06	10.84	10.88	39.89
3060.77	2,100.00	2,100.00	2,100.00	2,219.58	0.06	10.86	10.90	39.89
3070.33	2,100.00	2,100.00	2,100.00	2,215.17	0.06	10.91	10.97	39.96
3081.15	2,100.00	2,100.00	2,100.00	2,230.22	0.06	10.94	10.99	39.81
3090.76	2,100.00	2,100.00	2,100.00	2,225.87	0.07	10.94	11.02	39.74
3100.32	2,100.00	2,100.00	2,100.00	2,228.99	0.07	11.01	11.07	39.81
3111.14	2,100.00	2,100.00	2,100.00	2,229.54	0.07	11.02	11.11	39.67
3120.75	2,100.00	2,100.00	2,100.00	2,219.65	0.07	11.01	11.10	39.60
3130.37	2,100.00	2,100.00	2,100.00	2,214.77	0.06	10.99	11.05	39.67
3141.13	2,100.00	2,100.00	2,100.00	2,223.37	0.06	10.98	11.06	39.74
3150.74	2,100.00	2,100.00	2,100.00	2,231.88	0.06	11.02	11.08	39.74
3160.35	2,100.00	2,100.00	2,100.00	2,223.35	0.05	11.09	11.15	39.74
3171.12	2,100.00	2,083.00	2,100.00	2,210.27	0.06	9.46	7.28	39.74
3180.73	2,100.00	2,100.00	2,100.00	2,232.82	0.04	13.01	13.09	39.60
3190.34	2,100.00	2,100.00	2,100.00	2,236.68	0.04	11.77	11.83	39.60
3201.11	2,100.00	2,100.00	2,100.00	2,208.84	0.04	11.80	11.83	39.60
3210.72	2,100.00	2,100.00	2,100.00	2,231.38	0.03	11.84	11.86	40.85
3220.33	2,100.00	2,100.00	2,100.00	2,235.53	0.03	11.89	11.92	39.52
3231.10	2,100.00	2,100.00	2,100.00	2,231.92	0.03	11.84	11.89	39.52
3240.71	2,100.00	2,090.00	2,100.00	2,204.14	0.05	12.55	11.60	39.38
3250.32	2,100.00	2,100.00	2,100.00	2,232.00	0.04	11.86	12.16	39.52
3261.14	2,100.00	2,100.00	2,100.00	2,223.78	0.04	11.69	11.73	39.52
3270.70	2,100.00	2,100.00	2,100.00	2,247.10	0.05	11.63	11.69	39.52
3280.31	2,100.00	2,100.00	2,100.00	2,210.05	0.05	11.02	11.12	39.60
3291.13	2,100.00	2,100.00	2,100.00	2,240.23	0.05	10.84	10.90	39.52

3300.80	2,100.00	2,100.00	2,100.00	2,206.67	0.05	11.09	11.09	39.60
3310.41	2,100.00	2,100.00	2,100.00	2,220.48	0.06	10.94	11.12	39.45
3320.02	2,100.00	2,100.00	2,100.00	2,229.57	0.06	10.76	10.74	39.45
3330.79	2,100.00	2,100.00	2,100.00	2,230.44	0.06	11.13	11.17	39.67
3340.40	2,100.00	2,100.00	2,100.00	2,248.45	0.06	11.15	11.26	39.60
3350.01	2,100.00	2,100.00	2,100.00	2,217.03	0.07	10.78	10.85	39.52
3360.83	2,100.00	2,100.00	2,100.00	2,229.17	0.06	11.06	11.09	39.60
3370.39	2,100.00	2,100.00	2,100.00	2,236.30	0.06	11.18	11.23	39.60
3380.00	2,100.00	2,100.00	2,100.00	2,216.24	0.06	10.84	10.94	39.60
3390.82	2,100.00	2,100.00	2,100.00	2,230.06	0.05	10.98	11.02	39.52
3400.38	2,100.00	2,100.00	2,100.00	2,233.33	0.05	11.18	11.21	39.60
3411.20	2,100.00	2,100.00	2,100.00	2,234.31	0.05	10.83	10.94	39.52
3420.81	2,100.00	2,100.00	2,100.00	2,229.71	0.04	10.19	10.35	39.60
3430.37	2,100.00	2,100.00	2,100.00	2,232.88	0.04	10.17	10.09	39.74
3441.19	2,100.00	2,100.00	2,100.00	2,227.15	0.04	10.12	10.16	39.81
3450.80	2,100.00	2,100.00	2,100.00	2,234.28	0.03	10.48	10.52	40.03
3460.41	2,100.00	2,100.00	2,100.00	2,231.46	0.03	10.45	10.41	39.96
3471.18	2,100.00	2,100.00	2,100.00	2,231.06	0.03	10.45	10.50	39.96
3480.79	2,100.00	2,100.00	2,100.00	2,216.59	0.02	10.74	10.76	39.89
3490.40	2,100.00	2,100.00	2,100.00	2,247.22	0.03	10.44	10.48	40.18
3501.17	2,100.00	2,100.00	2,100.00	2,230.47	0.02	10.73	10.80	40.11
3510.78	2,100.00	2,100.00	2,100.00	2,228.06	0.02	10.62	10.57	40.25
3520.39	2,100.00	2,100.00	2,100.00	2,216.95	0.02	10.63	10.76	40.25
3530.00	2,100.00	2,100.00	2,100.00	2,218.04	0.02	10.68	10.61	40.25
3540.77	2,100.00	2,100.00	2,100.00	2,235.41	0.02	10.54	10.59	40.25
3550.38	2,100.00	2,100.00	2,100.00	2,246.25	0.02	10.81	10.76	40.40
3561.20	2,100.00	2,100.00	2,100.00	2,227.38	0.01	10.55	10.60	40.33
3570.76	2,100.00	2,100.00	2,100.00	2,237.23	0.01	10.88	10.87	40.40
3580.37	2,100.00	2,085.00	2,100.00	2,230.72	0.08	3.60	10.59	40.40
3591.19	2,100.00	2,100.00	2,100.00	2,241.74	0.00	12.28	12.09	40.48
3600.75	2,100.00	2,100.00	2,100.00	2,226.62	0.03	10.84	10.98	40.40
3610.36	2,100.00	2,100.00	2,100.00	2,228.39	0.02	11.03	10.99	40.48
3621.18	2,100.00	2,100.00	2,100.00	2,249.91	0.01	10.68	10.69	40.40
3630.79	2,100.00	2,100.00	2,100.00	2,241.74	0.01	11.03	11.01	40.55
3640.35	2,100.00	2,100.00	2,100.00	2,243.54	0.01	10.65	10.71	40.55
3651.17	2,100.00	2,100.00	2,100.00	2,238.50	0.02	11.00	11.00	40.55
3660.78	2,100.00	2,100.00	2,100.00	2,233.77	0.02	10.76	10.82	40.48
3670.34	2,100.00	2,100.00	2,100.00	2,221.11	0.01	10.91	10.86	40.48
3681.16	2,100.00	2,100.00	2,100.00	2,247.39	0.02	10.80	10.89	40.40
3690.77	2,100.00	2,100.00	2,100.00	2,219.12	0.00	10.81	10.78	40.48
3700.33	2,100.00	2,100.00	2,100.00	2,231.07	0.01	11.07	11.12	40.40
3711.15	2,100.00	2,100.00	2,100.00	2,240.96	0.01	10.73	10.72	40.55
3720.76	2,100.00	2,100.00	2,100.00	2,245.43	0.00	11.04	11.01	40.40
3730.37	2,100.00	2,100.00	2,100.00	2,233.45	0.00	10.72	10.81	40.48
3741.14	2,100.00	2,100.00	2,100.00	2,232.30	0.00	10.90	10.85	40.40
3750.75	2,100.00	2,100.00	2,100.00	2,221.85	0.00	11.01	11.05	40.55
3760.36	2,100.00	2,100.00	2,100.00	2,252.56	0.00	10.67	10.66	40.55
3771.13	2,100.00	2,100.00	2,100.00	2,253.85	0.00	11.02	10.99	40.55
3780.74	2,100.00	2,100.00	2,100.00	2,239.80	0.00	10.70	10.77	40.48
3790.35	2,100.00	2,100.00	2,100.00	2,241.69	0.00	10.66	10.59	40.55

3801.12	2,100.00	2,100.00	2,100.00	2,230.66	0.00	10.86	10.84	40.55
3810.73	2,100.00	2,100.00	2,100.00	2,234.59	0.00	10.45	10.46	40.55
3820.34	2,100.00	2,100.00	2,100.00	2,229.62	0.00	10.72	10.67	40.48
3831.16	2,100.00	2,100.00	2,100.00	2,240.24	0.00	10.80	10.86	40.63
3840.72	2,100.00	2,100.00	2,100.00	2,229.42	0.00	10.41	10.42	40.63
3850.33	2,100.00	2,100.00	2,100.00	2,237.31	0.00	10.72	10.67	40.63
3861.15	2,100.00	2,100.00	2,100.00	2,259.24	0.00	10.62	10.67	40.55
3870.71	2,100.00	2,100.00	2,100.00	2,214.35	0.00	10.36	10.31	40.55
3880.32	2,100.00	2,100.00	2,100.00	2,235.06	0.00	10.67	10.62	40.78
3891.14	2,100.00	2,100.00	2,100.00	2,230.20	-0.03	10.42	10.48	40.48
3900.75	2,100.00	2,100.00	2,100.00	2,240.35	-0.03	10.24	10.19	40.63
3910.31	2,100.00	2,100.00	2,100.00	2,229.61	-0.02	10.51	10.44	40.63
3921.13	2,100.00	2,100.00	2,100.00	2,260.87	-0.01	10.23	10.31	40.63
3930.74	2,100.00	2,100.00	2,100.00	2,222.83	-0.01	10.10	10.07	40.63
3940.30	2,100.00	2,100.00	2,100.00	2,249.69	0.00	10.30	10.30	40.55
3951.12	2,100.00	2,100.00	2,100.00	2,223.00	0.00	9.77	9.87	40.48
3960.73	2,100.00	2,100.00	2,100.00	2,234.02	0.00	9.64	9.62	40.55
3970.29	2,100.00	2,100.00	2,100.00	2,244.29	0.00	9.89	9.90	40.55
3981.11	2,100.00	2,100.00	2,100.00	2,213.41	0.00	9.56	9.62	40.63
3990.72	2,100.00	2,100.00	2,100.00	2,256.02	0.00	9.47	9.46	40.63
4000.33	2,100.00	2,100.00	2,100.00	2,230.47	0.00	9.69	9.70	40.63
4011.10	2,100.00	2,100.00	2,100.00	2,235.00	0.00	9.29	9.38	40.63
4020.71	2,100.00	2,100.00	2,100.00	2,243.07	0.00	9.29	9.24	40.63
4030.32	2,100.00	2,100.00	2,100.00	2,222.08	0.00	9.49	9.49	40.63
4041.08	2,100.00	2,100.00	2,100.00	2,262.60	0.00	9.11	9.18	40.63
4050.70	2,100.00	2,100.00	2,100.00	2,255.00	0.00	9.12	9.09	40.70
4060.31	2,100.00	2,100.00	2,100.00	2,220.07	0.00	9.36	9.35	40.70
4071.18	2,100.00	2,100.00	2,100.00	2,229.45	0.00	8.94	9.01	40.55
4080.80	2,100.00	2,100.00	2,100.00	2,218.29	0.00	8.93	8.89	40.70
4090.41	2,100.00	2,100.00	2,100.00	2,232.45	0.00	9.15	9.13	40.55
4100.02	2,100.00	2,100.00	2,100.00	2,254.92	0.00	8.78	8.88	40.63
4110.79	2,100.00	2,100.00	2,100.00	2,220.29	0.00	8.69	8.64	40.78
4120.40	2,100.00	2,100.00	2,100.00	2,217.38	0.00	10.07	9.82	40.63
4130.01	2,100.00	2,090.00	2,100.00	2,232.50	-0.30	10.58	8.63	40.70
4140.77	2,100.00	2,100.00	2,100.00	2,238.09	0.03	11.08	11.23	40.63
4150.39	2,100.00	2,100.00	2,100.00	2,240.35	0.00	10.54	10.52	40.63
4160.00	2,100.00	2,100.00	2,100.00	2,239.91	0.00	10.14	10.28	40.70
4170.76	2,100.00	2,100.00	2,100.00	2,214.51	0.00	9.87	9.85	40.63
4180.38	2,100.00	2,100.00	2,100.00	2,234.56	0.00	10.96	10.77	40.63
4191.20	2,100.00	2,100.00	2,100.00	2,221.49	0.00	11.03	11.08	40.63
4200.75	2,100.00	2,100.00	2,100.00	2,251.60	0.00	10.83	10.81	40.63
4210.37	2,100.00	2,100.00	2,100.00	2,223.28	0.00	11.11	11.10	40.63
4221.19	2,100.00	2,100.00	2,100.00	2,176.58	0.00	10.71	10.80	40.70
4230.80	2,100.00	2,100.00	2,100.00	2,209.01	0.00	10.45	10.42	40.63
4240.35	2,100.00	2,100.00	2,100.00	2,182.10	0.00	10.61	10.60	40.70
4251.17	2,100.00	2,100.00	2,100.00	2,230.87	0.00	10.34	10.42	40.63
4260.79	2,100.00	2,100.00	2,100.00	2,262.89	0.00	10.05	10.03	40.70
4270.34	2,100.00	2,100.00	2,100.00	2,264.96	-0.06	10.22	10.14	40.70
4281.16	2,100.00	2,100.00	2,100.00	2,235.70	-0.05	10.01	10.06	40.55
4290.78	2,100.00	2,100.00	2,100.00	2,219.78	-0.03	9.62	9.57	40.70

4300.39	2,100.00	2,100.00	2,100.00	2,199.16	-0.04	9.83	9.70	40.63
4311.15	2,100.00	2,093.00	2,100.00	2,269.25	-0.02	11.53	10.91	40.70
4320.77	2,100.00	2,100.00	2,100.00	2,266.35	-0.05	11.26	11.35	40.63
4330.38	2,100.00	2,100.00	2,100.00	2,215.80	-0.07	10.81	10.75	40.78
4341.14	2,100.00	2,100.00	2,100.00	2,321.88	-0.04	10.73	10.71	40.63
4350.75	2,100.00	2,100.00	2,100.00	2,259.17	-0.05	10.12	10.07	40.78
4360.37	2,100.00	2,100.00	2,100.00	2,144.22	-0.05	10.19	10.10	40.63
4371.13	2,100.00	2,100.00	2,100.00	2,195.86	-0.05	10.29	10.23	40.63
4380.74	2,100.00	2,100.00	2,100.00	2,329.12	-0.04	9.69	9.70	40.78
4390.36	2,100.00	2,100.00	2,100.00	2,278.49	-0.05	9.65	9.57	40.70
4401.18	2,100.00	2,100.00	2,100.00	2,289.95	-0.06	9.71	9.67	40.70
4410.73	2,100.00	2,100.00	2,100.00	2,270.73	-0.08	10.15	9.98	40.63
4420.35	2,100.00	2,100.00	2,100.00	2,483.83	-0.07	11.09	10.95	40.63
4431.17	2,100.00	2,100.00	2,100.00	2,207.21	-0.05	11.37	11.31	40.63
4440.72	2,100.00	2,100.00	2,100.00	2,219.87	-0.05	11.14	11.15	40.70
4450.33	2,100.00	2,100.00	2,100.00	2,230.09	-0.08	10.78	10.72	40.70
4461.15	2,100.00	2,100.00	2,100.00	2,252.42	-0.05	10.84	10.80	40.70
4470.71	2,100.00	2,100.00	2,100.00	2,152.09	-0.03	10.76	10.75	40.63
4480.32	2,100.00	2,100.00	2,100.00	2,254.58	-0.03	11.44	11.43	40.63
4491.14	2,100.00	2,100.00	2,100.00	2,220.81	-0.02	10.50	10.54	40.63
4500.76	2,100.00	2,100.00	2,100.00	2,178.81	-0.01	10.24	10.27	40.70
4510.31	2,100.00	2,100.00	2,100.00	2,204.02	0.00	9.43	9.47	40.78
4521.13	2,100.00	2,100.00	2,100.00	2,122.87	0.00	9.41	9.40	40.63
4530.75	2,100.00	2,100.00	2,100.00	2,244.40	0.00	9.39	9.39	40.63
4540.30	2,100.00	2,100.00	2,100.00	2,262.35	0.00	8.68	8.78	40.70
4551.12	2,100.00	2,100.00	2,100.00	2,249.40	0.00	8.61	8.61	40.70
4560.73	2,100.00	2,100.00	2,100.00	2,281.89	0.00	8.75	8.74	40.63
4570.35	2,100.00	2,100.00	2,100.00	2,217.99	0.00	8.28	8.40	40.78
4581.11	2,100.00	2,100.00	2,100.00	2,235.16	0.00	8.14	8.11	40.70
4590.72	2,100.00	2,100.00	2,100.00	2,244.08	0.00	8.53	8.50	40.63
4600.34	2,100.00	2,100.00	2,100.00	2,222.97	0.00	8.28	8.37	40.78
4611.10	2,100.00	2,100.00	2,100.00	2,249.36	0.00	8.10	8.06	40.70
4620.71	2,100.00	2,100.00	2,100.00	2,237.30	0.00	8.38	8.36	40.78
4630.33	2,100.00	2,100.00	2,100.00	2,236.89	0.00	8.46	8.49	40.70
4641.09	2,100.00	2,100.00	2,100.00	2,197.00	0.00	9.41	9.29	40.70
4650.70	2,100.00	2,100.00	2,100.00	2,226.47	0.00	9.87	9.87	40.78
4660.31	2,100.00	2,100.00	2,100.00	2,198.99	0.00	9.66	9.72	40.70
4671.08	2,100.00	2,100.00	2,100.00	2,236.48	0.00	8.88	8.90	40.70
4680.69	2,100.00	2,100.00	2,100.00	2,267.89	0.00	8.94	8.93	40.78
4690.30	2,100.00	2,100.00	2,100.00	2,265.89	0.00	8.86	8.88	40.78
4701.12	2,100.00	2,100.00	2,100.00	2,230.34	0.00	8.23	8.24	40.78
4710.68	2,100.00	2,100.00	2,100.00	2,264.74	0.00	8.46	8.44	40.78
4720.29	2,100.00	2,100.00	2,100.00	2,236.99	0.03	8.45	8.49	40.70
4731.11	2,100.00	2,100.00	2,100.00	2,243.53	0.08	7.83	7.94	40.70
4740.67	2,100.00	2,100.00	2,100.00	2,227.03	0.09	8.03	8.09	40.70
4750.28	2,100.00	2,100.00	2,100.00	2,259.29	0.09	11.17	10.98	40.78
4761.10	2,100.00	2,100.00	2,100.00	2,202.98	0.03	11.82	11.90	40.70
4770.71	2,100.00	2,100.00	2,100.00	2,249.03	0.04	11.76	11.79	40.70
4780.27	2,100.00	2,100.00	2,100.00	2,235.10	0.04	11.91	11.94	40.63
4791.09	2,100.00	2,100.00	2,100.00	2,222.58	0.04	11.61	11.73	40.78

4800.70	2,100.00	2,100.00	2,100.00	2,241.23	0.04	11.19	11.23	40.70
4810.26	2,100.00	2,100.00	2,100.00	2,225.26	0.03	12.26	11.96	40.78
4821.08	2,100.00	2,100.00	2,100.00	2,203.36	0.05	11.63	11.84	40.78
4830.69	2,100.00	2,100.00	2,100.00	2,212.85	0.05	10.55	10.64	40.70
4840.31	2,100.00	2,100.00	2,100.00	2,262.66	0.06	10.49	10.55	40.63
4851.07	2,100.00	2,100.00	2,100.00	2,212.00	0.06	10.36	10.46	40.78
4860.68	2,100.00	2,085.00	2,100.00	2,225.79	0.06	3.41	9.76	40.70
4870.29	2,100.00	2,100.00	2,100.00	2,223.19	0.07	11.84	11.87	40.70
4881.06	2,100.00	2,100.00	2,100.00	2,230.05	0.07	11.28	11.40	40.63
4890.67	2,100.00	2,100.00	2,100.00	2,262.19	0.07	10.46	10.63	40.78
4900.28	2,100.00	2,100.00	2,100.00	2,264.11	0.07	10.23	10.29	40.70
4911.05	2,100.00	2,100.00	2,100.00	2,431.38	0.06	10.27	10.33	40.70
4920.66	2,100.00	2,100.00	2,100.00	1,839.42	0.07	9.80	9.96	40.78
4930.27	2,100.00	2,100.00	2,100.00	2,166.94	0.07	9.32	9.39	40.63
4941.09	2,100.00	2,100.00	2,100.00	2,397.64	0.07	9.98	9.92	40.78
4950.65	2,100.00	2,100.00	2,100.00	2,267.04	0.07	10.56	10.69	40.63
4960.26	2,100.00	2,100.00	2,100.00	2,255.93	0.07	10.04	10.12	40.78
4971.08	2,100.00	2,100.00	2,100.00	2,227.46	0.06	10.02	10.08	40.70
4980.64	2,100.00	2,100.00	2,100.00	2,253.16	0.05	9.87	9.97	40.63
4990.25	2,100.00	2,100.00	2,100.00	2,184.30	0.05	9.18	9.26	40.78
5001.18	2,100.00	2,100.00	2,100.00	2,202.35	0.04	9.70	9.62	40.78
5010.74	2,100.00	2,100.00	2,100.00	2,235.89	0.04	10.49	10.51	40.70
5020.35	2,100.00	2,100.00	2,100.00	2,193.74	0.03	9.91	10.02	40.70
5031.17	2,100.00	2,100.00	2,100.00	2,271.20	0.02	9.98	9.97	40.78
5040.73	2,100.00	2,100.00	2,100.00	2,143.99	0.01	10.03	10.05	40.70
5050.34	2,100.00	2,100.00	2,100.00	2,154.14	0.00	9.41	9.50	40.70
5061.16	2,100.00	2,100.00	2,100.00	2,293.07	0.00	9.42	9.40	40.78
5070.77	2,100.00	2,100.00	2,100.00	2,253.19	0.00	9.51	9.51	40.70
5080.33	2,100.00	2,100.00	2,100.00	2,107.72	0.00	9.05	9.13	40.78
5091.15	2,100.00	2,100.00	2,100.00	2,294.21	0.00	9.09	9.05	40.70
5100.76	2,100.00	2,100.00	2,100.00	2,191.68	0.00	9.25	9.25	40.78
5110.32	2,100.00	2,100.00	2,100.00	2,291.84	0.00	8.88	8.99	40.78
5121.14	2,100.00	2,100.00	2,100.00	1,752.38	0.00	8.84	8.81	40.70
5130.75	2,100.00	2,100.00	2,100.00	2,225.65	0.00	9.04	9.02	40.85
5140.36	2,100.00	2,100.00	2,100.00	2,303.44	0.00	8.77	8.90	40.70
5151.13	2,100.00	2,100.00	2,100.00	2,244.26	0.00	8.60	8.55	40.78
5160.74	2,100.00	2,100.00	2,100.00	2,268.15	0.00	8.98	8.95	40.78
5170.35	2,100.00	2,100.00	2,100.00	2,486.41	0.00	8.94	9.00	40.78
5181.12	2,100.00	2,100.00	2,100.00	2,265.56	0.00	10.50	10.12	40.78
5190.73	2,100.00	2,100.00	2,100.00	2,333.13	0.00	11.92	11.79	40.63
5200.34	2,100.00	2,100.00	2,100.00	2,230.17	0.00	12.30	12.28	40.70
5211.11	2,100.00	2,100.00	2,100.00	2,238.88	0.00	11.77	11.80	40.70
5220.72	2,100.00	2,100.00	2,100.00	2,197.40	0.00	11.78	11.77	40.78
5230.33	2,100.00	2,100.00	2,100.00	2,233.04	0.00	11.97	11.94	40.85
5241.10	2,100.00	2,100.00	2,100.00	2,241.81	0.00	11.49	11.56	40.70
5250.71	2,100.00	2,100.00	2,100.00	2,249.14	0.00	11.40	11.39	40.70
Pump B empty and Pump A starts automatically								
5260.32	2,092.00	2,050.00	2,100.00	2,231.91	1.18	0.00	0.02	40.70
5271.14	2,100.00	2,057.00	2,100.00	2,207.29	11.25	0.00	11.25	40.63
5280.70	2,100.00	2,057.00	2,100.00	2,240.26	10.35	0.00	10.42	40.63

5290.31	2,100.00	2,058.00	2,100.00	2,198.32	10.55	0.00	10.54	40.70
5301.13	2,100.00	2,058.00	2,100.00	2,156.35	10.22	0.00	10.29	40.63
5310.69	2,100.00	2,057.00	2,100.00	2,212.05	10.11	0.00	10.09	40.55
5320.30	2,100.00	2,058.00	2,100.00	2,221.14	10.37	0.00	10.34	40.70
5331.12	2,100.00	2,057.00	2,100.00	2,198.92	9.99	0.00	10.06	40.78
5340.73	2,100.00	2,058.00	2,100.00	2,196.59	9.87	0.00	9.83	40.70
5350.29	2,100.00	2,058.00	2,100.00	2,209.16	10.06	0.00	10.06	40.70
5361.11	2,100.00	2,058.00	2,100.00	2,196.04	9.76	0.00	9.83	40.78
5370.72	2,100.00	2,056.00	2,100.00	2,186.25	11.29	0.00	11.04	40.63
5380.28	2,100.00	2,058.00	2,100.00	2,120.24	12.30	0.00	12.24	40.63
5391.10	2,100.00	2,058.00	2,100.00	2,119.42	12.17	0.00	12.23	40.63
5400.71	2,100.00	2,058.00	2,100.00	2,183.42	12.06	0.00	12.06	40.70
5410.32	2,100.00	2,058.00	2,100.00	2,126.79	12.33	0.00	12.30	40.78
5421.09	2,100.00	2,058.00	2,100.00	2,140.63	12.02	0.00	12.09	40.48
5430.81	2,100.00	2,058.00	2,100.00	2,197.03	11.87	0.00	11.83	40.70
5440.37	2,100.00	2,058.00	2,100.00	2,205.13	12.08	0.00	12.07	40.70
5451.19	2,100.00	2,058.00	2,100.00	2,200.72	11.78	0.00	11.85	40.70
5460.80	2,100.00	2,058.00	2,100.00	2,218.29	11.53	0.00	11.51	40.63
5470.41	2,100.00	2,058.00	2,100.00	2,158.64	11.69	0.00	11.65	40.85
5481.18	2,100.00	2,058.00	2,100.00	2,171.78	11.39	0.00	11.47	40.63
5490.79	2,100.00	2,058.00	2,100.00	2,177.26	11.10	0.00	11.08	40.93
5500.40	2,100.00	2,059.00	2,100.00	2,227.00	11.38	0.00	11.32	40.63
5511.17	2,100.00	2,059.00	2,100.00	2,169.61	11.14	0.00	11.24	40.70
5520.78	2,100.00	2,059.00	2,100.00	2,223.12	10.86	0.00	10.83	40.70
5530.39	2,100.00	2,059.00	2,100.00	2,166.33	11.04	0.00	11.01	40.63
5540.00	2,100.00	2,059.00	2,100.00	2,166.14	10.93	0.00	11.02	40.63
5550.77	2,100.00	2,059.00	2,100.00	2,211.93	10.49	0.00	10.48	40.70
5560.38	2,100.00	2,059.00	2,100.00	2,159.63	10.75	0.00	10.70	40.93
5571.14	2,100.00	2,059.00	2,100.00	2,189.72	10.56	0.00	10.62	40.70
5580.76	2,100.00	2,059.00	2,100.00	2,208.35	10.29	0.00	10.27	40.70
5590.37	2,100.00	2,059.00	2,100.00	2,186.98	10.51	0.00	10.50	40.55
5601.19	2,100.00	2,059.00	2,100.00	2,223.94	10.44	0.00	10.49	40.78
5610.75	2,100.00	2,059.00	2,100.00	2,172.86	10.06	0.00	10.06	40.70
5620.36	2,100.00	2,059.00	2,100.00	2,174.93	10.31	0.00	10.27	40.70
5631.18	2,100.00	2,060.00	2,100.00	2,201.16	10.27	0.00	10.34	40.85
5640.73	2,100.00	2,060.00	2,100.00	2,172.83	9.81	0.00	9.81	40.63
5650.35	2,100.00	2,060.00	2,100.00	2,182.47	9.97	0.00	9.96	40.70
5661.17	2,100.00	2,060.00	2,100.00	2,147.68	10.06	0.00	10.10	40.70
5670.78	2,100.00	2,060.00	2,100.00	2,178.28	9.62	0.00	9.62	40.70
5680.34	2,100.00	2,060.00	2,100.00	2,161.68	9.85	0.00	9.80	40.78
5691.16	2,100.00	2,060.00	2,100.00	2,175.04	10.01	0.00	10.03	40.70
5700.77	2,100.00	2,060.00	2,100.00	2,185.17	9.57	0.00	9.58	40.85
5710.33	2,100.00	2,060.00	2,100.00	2,181.25	9.80	0.00	9.75	40.70
5721.15	2,100.00	2,060.00	2,100.00	2,196.78	10.21	0.00	10.20	40.70
5730.76	2,100.00	2,060.00	2,100.00	2,197.59	9.87	0.00	9.89	40.78
5740.37	2,100.00	2,060.00	2,100.00	2,160.29	10.22	0.00	10.16	40.78
5751.14	2,100.00	2,060.00	2,100.00	2,178.44	10.35	0.00	10.36	40.78
5760.75	2,100.00	2,060.00	2,100.00	2,170.62	9.90	0.00	9.97	40.70
5770.36	2,100.00	2,061.00	2,100.00	2,238.76	10.16	0.00	10.10	40.70
5781.12	2,100.00	2,061.00	2,100.00	2,218.05	10.54	0.00	10.53	40.70

5790.74	2,100.00	2,061.00	2,100.00	2,198.66	10.27	0.00	10.36	40.93
5800.35	2,100.00	2,061.00	2,100.00	2,155.61	9.94	0.00	9.91	40.78
5811.11	2,100.00	2,061.00	2,100.00	2,206.92	10.13	0.00	10.11	40.70
5820.73	2,100.00	2,061.00	2,100.00	2,188.43	9.91	0.00	10.00	40.85
5830.34	2,100.00	2,061.00	2,100.00	2,177.21	9.52	0.00	9.49	40.70
5841.16	2,100.00	2,061.00	2,100.00	2,231.78	10.36	0.00	10.27	40.70
5850.71	2,100.00	2,061.00	2,100.00	2,203.27	10.67	0.00	10.71	40.70
5860.33	2,100.00	2,061.00	2,100.00	2,185.28	10.13	0.00	10.16	40.70
5871.15	2,100.00	2,061.00	2,100.00	2,201.73	10.38	0.00	10.34	40.78
5880.70	2,100.00	2,061.00	2,100.00	2,195.19	10.42	0.00	10.42	40.78
5890.32	2,100.00	2,061.00	2,100.00	2,198.75	10.46	0.00	10.44	40.63
5901.14	2,100.00	2,061.00	2,100.00	2,205.83	10.71	0.00	10.71	40.78
5910.69	2,100.00	2,061.00	2,100.00	2,191.67	10.79	0.00	10.79	40.70
5920.31	2,100.00	2,061.00	2,100.00	2,161.90	10.61	0.00	10.64	40.63
5931.13	2,100.00	2,061.00	2,100.00	2,183.23	10.44	0.00	10.46	40.63
5940.74	2,100.00	2,061.00	2,100.00	2,181.34	10.36	0.00	10.37	40.55
5950.29	2,100.00	2,062.00	2,100.00	2,180.38	10.39	0.00	10.38	40.55
5961.12	2,100.00	2,062.00	2,100.00	2,170.78	10.27	0.00	10.30	40.48
5970.73	2,100.00	2,062.00	2,100.00	2,180.70	10.15	0.00	10.20	40.55
5980.28	2,100.00	2,062.00	2,100.00	1,806.14	9.96	0.00	9.98	40.48
5991.10	2,091.00	2,051.00	2,088.00	1,753.46	10.29	0.00	9.42	40.48
6000.72	2,088.00	2,051.00	2,100.00	2,180.80	1.53	0.00	10.13	40.55
6010.33	2,100.00	2,055.00	2,100.00	2,131.45	11.19	0.00	11.24	40.55
6021.09	2,100.00	2,060.00	2,100.00	2,108.85	9.84	0.00	9.89	40.63
6030.71	2,100.00	2,061.00	2,100.00	2,111.12	9.78	0.00	9.80	40.48
6040.32	2,100.00	2,062.00	2,100.00	2,196.12	9.18	0.00	9.21	40.55
6051.08	2,100.00	2,062.00	2,100.00	2,244.07	9.33	0.00	9.31	40.55
6060.70	2,100.00	2,062.00	2,100.00	2,203.07	9.59	0.00	9.57	40.55
6070.31	2,100.00	2,062.00	2,100.00	2,240.14	9.31	0.00	9.40	40.33
6081.07	2,100.00	2,061.00	2,100.00	2,151.67	10.43	0.00	10.09	40.55
6090.68	2,100.00	2,061.00	2,100.00	2,206.19	12.23	0.00	12.07	40.55
6100.30	2,100.00	2,062.00	2,100.00	2,181.69	12.67	0.00	12.67	40.48
6111.12	2,100.00	2,063.00	2,100.00	2,195.41	12.07	0.00	12.11	40.40
6120.67	2,100.00	2,063.00	2,100.00	2,217.63	12.11	0.00	12.10	40.40
6130.29	2,100.00	2,063.00	2,100.00	2,187.48	12.34	0.00	12.34	40.48
6141.11	2,100.00	2,063.00	2,100.00	2,309.38	11.90	0.00	12.00	40.48
6150.66	2,100.00	2,063.00	2,100.00	2,022.44	11.74	0.00	11.73	40.48
6160.28	2,100.00	2,063.00	2,100.00	2,269.17	11.85	0.00	11.85	40.55
6171.10	2,100.00	2,063.00	2,100.00	2,254.94	11.99	0.00	11.98	40.40
6180.65	2,100.00	2,063.00	2,100.00	1,829.96	12.16	0.00	12.14	40.48
6190.26	2,100.00	2,063.00	2,100.00	2,057.27	12.32	0.00	12.33	40.40
6201.08	2,100.00	2,063.00	2,100.00	1,682.50	12.45	0.00	12.43	40.25
6210.70	2,100.00	2,063.00	2,100.00	1,867.05	12.68	0.00	12.65	40.40
6220.25	2,100.00	2,063.00	2,100.00	2,571.97	12.84	0.00	12.84	40.40
6231.07	2,100.00	2,063.00	2,100.00	1,723.40	13.03	0.00	13.03	40.33
6240.69	2,100.00	2,063.00	2,100.00	1,752.33	12.30	0.00	12.38	40.33
6250.24	2,100.00	2,063.00	2,100.00	2,179.19	11.54	0.00	11.62	40.25
6261.17	2,100.00	2,064.00	2,100.00	2,483.54	10.13	0.00	10.24	40.33
6270.79	2,100.00	2,064.00	2,100.00	2,083.36	9.37	0.00	9.44	40.18
6280.34	2,100.00	2,062.00	2,100.00	2,293.39	10.56	0.00	10.21	40.25

6291.16	2,100.00	2,063.00	2,100.00	1,859.59	11.14	0.00	11.14	40.18
6300.77	2,100.00	2,063.00	2,100.00	2,303.57	11.06	0.00	11.07	40.18
6310.39	2,100.00	2,063.00	2,100.00	2,026.76	10.95	0.00	10.98	40.25
6321.15	2,100.00	2,063.00	2,100.00	2,185.06	10.72	0.00	10.74	40.11
6330.76	2,100.00	2,063.00	2,100.00	2,542.35	10.32	0.00	10.37	40.11
6340.38	2,100.00	2,063.00	2,100.00	2,433.63	9.93	0.00	9.97	40.18
6351.14	2,100.00	2,064.00	2,100.00	2,257.43	9.47	0.00	9.53	40.33
6360.75	2,100.00	2,064.00	2,100.00	2,329.76	9.03	0.00	9.06	40.11
6370.37	2,100.00	2,064.00	2,100.00	2,373.34	8.73	0.00	8.79	40.03
6381.13	2,100.00	2,064.00	2,100.00	2,013.68	8.82	0.00	8.85	40.18
6390.74	2,100.00	2,064.00	2,100.00	2,379.07	8.66	0.00	8.67	40.03
6400.35	2,100.00	2,064.00	2,100.00	1,871.88	8.60	0.00	8.61	39.96
6411.12	2,100.00	2,064.00	2,100.00	1,983.12	8.31	0.00	8.32	40.03
6420.73	2,100.00	2,064.00	2,100.00	2,253.43	8.45	0.00	8.49	39.96
6430.34	2,100.00	2,064.00	2,100.00	1,782.38	8.37	0.00	8.22	40.11
6441.16	2,100.00	2,064.00	2,100.00	2,438.35	9.29	0.00	9.27	40.11
6450.72	2,100.00	2,064.00	2,100.00	2,183.23	9.40	0.00	9.42	40.18
6460.33	2,100.00	2,064.00	2,100.00	2,275.61	9.12	0.00	9.17	40.11
6471.15	2,100.00	2,063.00	2,100.00	2,166.21	10.15	0.00	10.02	40.03
6480.71	2,100.00	2,064.00	2,100.00	2,190.03	10.91	0.00	10.86	40.18
6490.32	2,100.00	2,064.00	2,100.00	2,194.66	10.84	0.00	10.88	39.96
6501.14	2,100.00	2,064.00	2,100.00	2,185.49	10.32	0.00	10.41	39.96
6510.75	2,100.00	2,064.00	2,100.00	2,209.03	10.00	0.00	9.99	40.03
6520.31	2,100.00	2,064.00	2,100.00	2,191.92	10.02	0.00	10.03	40.11
6531.13	2,100.00	2,064.00	2,100.00	2,227.13	9.65	0.00	9.70	40.03
6540.74	2,100.00	2,064.00	2,100.00	2,209.16	8.65	0.00	8.77	39.96
6550.30	2,100.00	2,064.00	2,100.00	2,228.70	8.62	0.00	8.61	40.11
6561.12	2,100.00	2,064.00	2,100.00	2,193.41	8.64	0.00	8.64	40.03
6570.73	2,100.00	2,064.00	2,100.00	2,192.74	8.66	0.00	8.72	40.18
6580.35	2,100.00	2,064.00	2,100.00	2,190.10	8.36	0.00	8.32	40.11
6591.11	2,086.00	2,051.00	2,100.00	2,196.39	2.47	0.00	10.14	39.96
6600.72	2,100.00	2,058.00	2,100.00	2,188.10	11.75	0.00	11.88	39.96
6610.33	2,100.00	2,063.00	2,100.00	2,190.09	9.89	0.00	9.65	40.18
6621.10	2,100.00	2,064.00	2,100.00	2,173.92	9.60	0.00	9.54	40.03
6630.71	2,100.00	2,064.00	2,100.00	2,179.35	9.72	0.00	9.75	40.03
6640.32	2,100.00	2,064.00	2,100.00	2,199.36	9.36	0.00	9.44	40.03
6651.09	2,100.00	2,065.00	2,100.00	2,200.61	8.76	0.00	8.73	40.03
6660.70	2,100.00	2,065.00	2,100.00	2,196.91	9.12	0.00	9.10	40.03
6670.31	2,100.00	2,065.00	2,100.00	2,196.53	9.28	0.00	9.29	40.03
6681.08	2,100.00	2,065.00	2,100.00	2,201.12	9.83	0.00	9.79	39.96
6690.69	2,100.00	2,065.00	2,100.00	2,190.95	10.10	0.00	10.06	40.03
6700.30	2,100.00	2,065.00	2,100.00	2,189.63	10.23	0.00	10.22	40.03
6711.12	2,100.00	2,065.00	2,100.00	2,175.38	10.01	0.00	10.08	40.11
6720.68	2,100.00	2,065.00	2,100.00	2,088.09	9.47	0.00	9.42	40.03
6730.29	2,100.00	2,064.00	2,100.00	2,221.44	10.92	0.00	10.79	40.03
6741.11	2,100.00	2,065.00	2,100.00	2,169.27	11.36	0.00	11.38	40.03
6750.67	2,100.00	2,065.00	2,100.00	2,159.90	10.78	0.00	10.86	39.96
6760.28	2,100.00	2,065.00	2,100.00	2,257.53	10.64	0.00	10.63	39.96
6771.10	2,100.00	2,065.00	2,100.00	2,157.57	10.73	0.00	10.73	39.89
6780.71	2,100.00	2,065.00	2,100.00	2,250.53	10.62	0.00	10.66	39.96

6790.27	2,100.00	2,065.00	2,100.00	2,541.97	9.93	0.00	10.00	40.03
6801.09	2,100.00	2,065.00	2,100.00	2,031.04	9.94	0.00	9.90	40.03
6810.70	2,100.00	2,065.00	2,100.00	2,250.70	10.03	0.00	10.04	40.18
6820.26	2,100.00	2,065.00	2,100.00	2,162.59	9.88	0.00	9.94	40.03
6831.08	2,100.00	2,065.00	2,100.00	2,228.41	9.34	0.00	9.34	40.03
6840.69	2,100.00	2,066.00	2,100.00	2,226.01	9.47	0.00	9.47	40.11
6850.30	2,100.00	2,066.00	2,100.00	2,219.62	9.98	0.00	9.96	40.03
6861.07	2,100.00	2,066.00	2,100.00	2,290.53	9.50	0.00	9.51	39.96
6870.68	2,100.00	2,066.00	2,100.00	1,954.63	10.30	0.00	10.18	40.11
6880.29	2,100.00	2,065.00	2,100.00	2,480.30	11.53	0.00	11.43	40.03
6891.06	2,100.00	2,066.00	2,100.00	2,429.58	11.66	0.00	11.73	40.03
6900.67	2,100.00	2,066.00	2,100.00	2,282.75	11.25	0.00	11.23	39.96
6910.28	2,100.00	2,066.00	2,100.00	2,180.67	11.48	0.00	11.46	40.11
6921.05	2,089.00	2,052.00	2,084.00	2,215.11	11.42	0.00	10.35	39.96
6930.66	2,100.00	2,062.00	2,100.00	2,202.60	11.61	0.00	12.27	40.11
6940.27	2,100.00	2,064.00	2,100.00	2,147.49	11.18	0.00	11.21	40.11
6951.04	2,100.00	2,065.00	2,100.00	2,115.64	11.22	0.00	11.22	39.96
6960.65	2,100.00	2,065.00	2,100.00	2,126.13	10.87	0.00	10.96	40.03
6970.26	2,100.00	2,066.00	2,100.00	2,192.90	10.39	0.00	10.39	40.03
6981.08	2,100.00	2,066.00	2,100.00	2,205.97	10.47	0.00	10.47	40.03
6990.64	2,100.00	2,066.00	2,100.00	2,179.78	10.43	0.00	10.46	40.03
7000.25	2,100.00	2,066.00	2,100.00	2,195.20	9.75	0.00	9.79	40.03
7011.07	2,100.00	2,066.00	2,100.00	2,249.41	9.89	0.00	9.86	40.03
7020.63	2,100.00	2,066.00	2,100.00	2,172.80	9.95	0.00	9.95	40.03
7030.24	2,100.00	2,066.00	2,100.00	2,240.90	9.74	0.00	9.81	39.96
7041.06	2,100.00	2,066.00	2,100.00	2,244.67	9.19	0.00	9.17	40.03
7050.67	2,100.00	2,066.00	2,100.00	2,208.11	9.41	0.00	9.40	40.18
7060.23	2,100.00	2,066.00	2,100.00	2,185.11	9.57	0.00	9.55	40.03
7071.05	2,100.00	2,066.00	2,100.00	2,229.49	9.14	0.00	9.19	39.96
7080.66	2,100.00	2,066.00	2,100.00	2,211.56	9.27	0.00	9.24	40.03
7090.22	2,100.00	2,066.00	2,100.00	2,188.97	9.52	0.00	9.52	39.96
7101.04	2,100.00	2,066.00	2,100.00	2,247.95	9.38	0.00	9.44	39.96
7110.65	2,100.00	2,066.00	2,100.00	2,186.28	8.94	0.00	8.95	40.11
7120.26	2,100.00	2,066.00	2,100.00	2,185.33	9.26	0.00	9.21	40.03
7131.03	2,100.00	2,066.00	2,100.00	2,203.99	9.51	0.00	9.49	40.03
7140.64	2,100.00	2,066.00	2,100.00	2,199.99	9.14	0.00	9.16	39.89
7150.25	2,100.00	2,065.00	2,100.00	2,188.01	12.12	0.00	11.99	39.96
7161.02	2,100.00	2,066.00	2,100.00	2,208.53	13.00	0.00	12.96	40.03
7170.63	2,100.00	2,066.00	2,100.00	2,196.47	12.98	0.00	13.03	39.96
7180.24	2,100.00	2,066.00	2,100.00	2,193.56	12.66	0.00	12.66	39.96
7191.01	2,100.00	2,066.00	2,100.00	2,210.58	12.49	0.00	12.50	40.03
7200.62	2,100.00	2,067.00	2,100.00	2,237.71	12.01	0.00	12.10	40.03
7210.23	2,100.00	2,067.00	2,100.00	2,194.98	10.80	0.00	10.92	40.03
7221.00	2,100.00	2,066.00	2,100.00	2,193.09	10.28	0.00	10.30	40.11
7230.61	2,100.00	2,067.00	2,100.00	2,198.16	10.31	0.00	10.32	39.96
7240.22	2,100.00	2,067.00	2,100.00	2,199.51	10.01	0.00	10.09	39.96
7251.04	2,100.00	2,067.00	2,100.00	2,207.34	9.33	0.00	9.33	40.03
7260.60	2,100.00	2,066.00	2,100.00	2,214.35	9.71	0.00	9.54	40.11
7270.21	2,100.00	2,067.00	2,100.00	2,187.35	11.17	0.00	11.12	39.96
7281.03	2,100.00	2,067.00	2,100.00	2,222.70	10.69	0.00	10.77	40.03

7290.59	2,100.00	2,067.00	2,100.00	2,203.48	10.65	0.00	10.64	39.96
7300.20	2,100.00	2,067.00	2,100.00	2,179.63	10.76	0.00	10.76	40.11
7311.02	2,100.00	2,067.00	2,100.00	2,172.41	10.28	0.00	10.40	40.03
7320.63	2,100.00	2,067.00	2,100.00	2,216.03	10.17	0.00	10.14	40.03
7330.19	2,100.00	2,067.00	2,100.00	2,187.44	10.23	0.00	10.24	40.03
7341.01	2,100.00	2,068.00	2,100.00	2,213.69	9.93	0.00	10.01	39.96
7350.62	2,100.00	2,067.00	2,100.00	2,195.13	9.27	0.00	9.28	40.03
7360.18	2,100.00	2,067.00	2,100.00	2,179.32	9.68	0.00	9.62	39.96
7371.00	2,100.00	2,067.00	2,100.00	2,185.87	9.80	0.00	9.88	40.03
7380.61	2,100.00	2,067.00	2,100.00	2,173.34	9.05	0.00	9.03	40.03
7390.22	2,100.00	2,067.00	2,100.00	2,190.22	10.50	0.00	10.37	39.96
7400.99	2,100.00	2,067.00	2,100.00	2,165.45	10.96	0.00	10.98	40.11
7410.60	2,100.00	2,067.00	2,100.00	2,199.01	10.38	0.00	10.47	39.96
7420.21	2,100.00	2,068.00	2,100.00	2,206.93	10.29	0.00	10.25	40.11
7430.98	2,100.00	2,067.00	2,100.00	2,205.21	10.91	0.00	10.86	39.96
7440.59	2,100.00	2,068.00	2,100.00	2,233.74	10.58	0.00	10.68	39.96
7450.20	2,100.00	2,068.00	2,100.00	2,212.43	10.09	0.00	10.07	40.03
7460.97	2,100.00	2,068.00	2,100.00	2,173.05	10.45	0.00	10.42	39.96
7470.58	2,100.00	2,068.00	2,100.00	2,232.22	10.35	0.00	10.40	39.96
7480.19	2,100.00	2,068.00	2,100.00	2,175.59	9.91	0.00	9.91	40.03
7490.95	2,100.00	2,068.00	2,100.00	2,242.73	10.17	0.00	10.13	40.03
7500.57	2,100.00	2,068.00	2,100.00	2,174.58	10.50	0.00	10.50	40.03
7510.18	2,100.00	2,067.00	2,100.00	2,187.00	10.00	0.00	9.99	39.96
7521.00	2,100.00	2,067.00	2,100.00	2,242.94	10.81	0.00	10.72	40.03
7530.56	2,100.00	2,068.00	2,100.00	2,276.09	11.03	0.00	11.03	39.96
7540.17	2,100.00	2,068.00	2,100.00	2,208.53	10.61	0.00	10.68	39.96
7550.99	2,100.00	2,068.00	2,100.00	2,144.99	10.46	0.00	10.43	39.89
7560.55	2,100.00	2,068.00	2,100.00	2,204.47	10.72	0.00	10.70	39.89
7570.16	2,100.00	2,068.00	2,100.00	1,900.63	10.63	0.00	10.69	39.96
7580.98	2,100.00	2,068.00	2,100.00	2,213.54	10.20	0.00	10.19	39.89
7590.59	2,100.00	2,068.00	2,100.00	2,183.92	10.39	0.00	10.38	40.11
7600.15	2,100.00	2,068.00	2,100.00	2,260.44	10.51	0.00	10.51	40.03
7610.97	2,100.00	2,068.00	2,100.00	2,215.30	9.87	0.00	9.94	40.03
7620.58	2,100.00	2,068.00	2,100.00	2,193.69	10.02	0.00	9.97	40.11
7630.14	2,100.00	2,068.00	2,100.00	2,115.94	10.31	0.00	10.31	40.03
7640.96	2,100.00	2,068.00	2,100.00	2,220.29	9.89	0.00	9.96	40.03
7650.57	2,100.00	2,068.00	2,100.00	2,170.33	9.99	0.00	9.95	40.03
7660.18	2,100.00	2,067.00	2,100.00	2,160.62	10.25	0.00	10.22	40.03
7670.95	2,100.00	2,064.00	2,100.00	2,171.46	10.91	0.00	11.29	40.18
7680.56	2,100.00	2,067.00	2,100.00	2,212.78	10.56	0.00	10.60	39.96
7690.17	2,100.00	2,068.00	2,100.00	2,212.98	10.54	0.00	10.54	40.18
7700.94	2,100.00	2,068.00	2,100.00	2,246.57	10.50	0.00	10.54	39.96
7710.55	2,100.00	2,068.00	2,100.00	2,199.55	9.97	0.00	10.01	40.03
7720.16	2,100.00	2,068.00	2,100.00	2,175.51	10.19	0.00	10.16	40.11
7730.92	2,100.00	2,068.00	2,100.00	2,176.08	10.37	0.00	10.35	39.89
7740.54	2,100.00	2,068.00	2,100.00	2,187.83	9.98	0.00	10.04	39.96
7750.15	2,100.00	2,068.00	2,100.00	2,237.64	10.15	0.00	10.12	40.03
7760.91	2,100.00	2,068.00	2,100.00	2,194.78	10.47	0.00	10.43	40.11
7770.53	2,100.00	2,068.00	2,100.00	2,179.91	10.36	0.00	10.43	40.03
7780.14	2,100.00	2,068.00	2,100.00	2,244.14	9.93	0.00	9.93	40.03

7790.96	2,100.00	2,068.00	2,100.00	2,224.25	10.27	0.00	10.20	40.03
7800.52	2,100.00	2,068.00	2,100.00	2,198.61	10.43	0.00	10.43	39.96
7810.13	2,100.00	2,068.00	2,100.00	2,193.69	9.93	0.00	9.95	40.11
7820.95	2,100.00	2,068.00	2,100.00	2,237.07	10.20	0.00	10.17	40.03
7830.50	2,100.00	2,068.00	2,100.00	2,163.46	10.30	0.00	10.29	40.03
7840.12	2,100.00	2,068.00	2,100.00	2,208.28	10.16	0.00	10.21	40.03
7850.94	2,088.00	2,055.00	2,085.00	2,168.36	9.05	0.00	6.90	39.96
7860.55	2,100.00	2,066.00	2,100.00	2,180.27	11.31	0.00	11.25	39.96
7870.11	2,100.00	2,068.00	2,100.00	2,183.04	10.80	0.00	10.89	39.96
7880.93	2,100.00	2,068.00	2,100.00	2,211.64	10.17	0.00	10.16	39.96
7890.54	2,100.00	2,068.00	2,100.00	2,212.25	10.31	0.00	10.31	40.03
7900.09	2,100.00	2,068.00	2,100.00	2,163.91	10.44	0.00	10.43	40.03
Pump A empty and refilling pump A. Pressurized flow closed to the vessel								
7910.92	2,100.00	2,072.00	2,100.00	2,226.62	-2.06	0.00	5.50	39.96
7920.53	867.00	2,079.00	867.00	2,217.45	204.11	0.00	204.04	40.03
7930.14	867.00	2,082.00	869.00	2,232.85	204.07	0.00	203.87	40.03
7940.90	871.00	2,083.00	871.00	2,222.94	204.09	0.00	204.02	40.03
7950.52	872.00	2,084.00	872.00	2,192.18	204.10	0.00	203.78	40.11
Re-pressurizing Pump A with pressurized flow closed to the vessel								
7960.13	1,006.00	2,084.00	938.00	2,229.30	195.85	0.00	195.82	40.11
7970.89	1,992.00	2,084.00	1,945.00	2,181.68	30.35	0.00	47.39	40.11
7980.51	2,100.00	2,083.00	2,100.00	2,216.79	9.28	0.00	12.27	40.03
7990.12	2,100.00	2,061.00	2,100.00	2,213.14	6.70	0.00	7.00	40.11
8000.88	2,087.00	2,033.00	2,087.00	2,146.30	14.46	0.00	11.91	39.89
Pressurized flow opened to the vessel								
8010.50	2,100.00	2,045.00	2,100.00	2,157.92	20.13	0.00	20.08	39.74
8020.11	2,100.00	2,046.00	2,100.00	2,151.28	19.56	0.00	19.64	39.89
8030.93	2,100.00	2,047.00	2,100.00	2,146.23	19.15	0.00	19.15	39.89
8040.48	2,100.00	2,047.00	2,100.00	2,184.61	19.18	0.00	19.17	39.89
8050.10	2,100.00	2,048.00	2,100.00	2,156.41	18.97	0.00	19.04	39.81
8060.92	2,100.00	2,048.00	2,100.00	2,165.23	18.50	0.00	18.51	40.11
8070.47	2,100.00	2,048.00	2,100.00	2,173.39	18.50	0.00	18.51	39.89
8080.09	2,100.00	2,041.00	2,100.00	2,139.49	18.41	0.00	18.44	39.89
8090.91	2,100.00	2,048.00	2,100.00	2,168.98	18.75	0.00	19.20	39.81
8100.46	2,100.00	2,048.00	2,100.00	2,166.31	18.45	0.00	18.53	39.96
8110.08	2,100.00	2,048.00	2,100.00	2,162.45	18.18	0.00	18.22	40.03
8120.90	2,100.00	2,048.00	2,100.00	2,174.21	17.61	0.00	17.63	39.96
8130.51	2,100.00	2,048.00	2,100.00	2,165.05	17.73	0.00	17.69	39.81
8140.06	2,100.00	2,048.00	2,100.00	2,169.64	17.79	0.00	17.81	39.89
8150.88	2,100.00	2,048.00	2,100.00	2,157.08	17.35	0.00	17.36	39.89
8160.50	2,100.00	2,048.00	2,100.00	2,135.71	17.48	0.00	17.46	39.96
8170.05	2,100.00	2,048.00	2,100.00	2,171.25	17.55	0.00	17.58	40.03
8180.87	2,100.00	2,048.00	2,100.00	2,181.84	17.16	0.00	17.15	39.96
8190.49	2,100.00	2,048.00	2,100.00	2,186.82	17.35	0.00	17.31	39.89
8200.10	2,100.00	2,050.00	2,100.00	2,161.64	15.63	0.00	16.66	39.89
Dynamic extraction finished and Lab View program still running. Depressurization of the vessel starts								
8210.86	2,100.00	2,057.00	2,100.00	2,150.43	0.00	0.00	-0.22	40.03
8220.48	2,110.00	2,056.00	2,109.00	2,174.96	0.00	0.00	0.00	39.89
8230.09	2,114.00	2,057.00	2,114.00	2,129.88	0.00	0.00	0.00	39.96
8240.85	2,114.00	2,059.00	2,114.00	2,134.44	0.00	0.00	0.00	39.81

8250.46	2,113.00	2,059.00	2,113.00	2,134.54	0.00	0.00	0.00	39.81
8260.08	2,110.00	2,059.00	2,111.00	2,144.60	0.00	0.00	0.00	39.89
8270.84	2,107.00	2,057.00	2,107.00	2,126.25	0.00	0.00	0.00	39.89
8280.45	2,100.00	2,054.00	2,100.00	2,082.33	0.00	0.00	0.00	39.67
8290.07	2,100.00	2,050.00	2,100.00	1,508.25	0.00	0.00	0.00	37.55
8300.89	2,094.00	2,047.00	2,100.00	1,291.61	0.00	0.00	0.00	33.60
8310.44	2,090.00	2,045.00	2,091.00	1,202.81	0.00	0.00	0.00	31.63
8320.06	2,087.00	2,043.00	2,087.00	1,161.91	0.00	0.00	0.00	30.59
8330.88	2,083.00	2,040.00	2,083.00	1,173.62	0.00	0.00	0.00	30.70
8340.43	2,080.00	2,037.00	2,080.00	1,158.62	0.00	0.00	0.00	30.53
8350.04	2,076.00	2,035.00	2,077.00	1,132.94	0.00	0.00	0.00	30.08
8360.86	2,073.00	2,031.00	2,073.00	1,121.69	0.00	0.00	0.00	29.74
8370.42	2,070.00	2,028.00	2,070.00	1,106.54	0.00	0.00	0.00	29.36
8380.03	2,067.00	2,025.00	2,067.00	1,091.88	0.00	0.00	0.00	29.08
8390.85	2,064.00	2,022.00	2,064.00	1,092.99	0.00	0.00	0.00	28.75
8400.47	2,061.00	2,020.00	2,061.00	1,071.33	0.00	0.00	0.00	28.97
8410.02	2,059.00	2,018.00	2,059.00	1,066.13	0.00	0.00	0.00	29.03
8420.84	2,055.00	2,014.00	2,056.00	1,036.52	0.00	0.00	0.00	29.03
8430.46	2,053.00	2,012.00	2,053.00	996.50	0.00	0.00	0.00	29.14
8440.01	2,051.00	2,009.00	2,051.00	994.98	0.00	0.00	0.00	29.25
8450.83	2,048.00	2,006.00	2,048.00	938.23	0.00	0.00	0.00	29.19
8460.44	2,045.00	2,004.00	2,046.00	909.83	0.00	0.00	0.00	29.14
8470.06	2,043.00	2,001.00	2,043.00	873.02	0.00	0.00	0.00	29.08
8480.82	2,040.00	1,999.00	2,041.00	852.38	0.00	0.00	0.00	29.03
8490.43	2,038.00	1,997.00	2,039.00	808.39	0.00	0.00	0.00	28.97
8500.05	2,036.00	1,995.00	2,036.00	776.67	0.00	0.00	0.00	29.03
8510.81	2,034.00	1,993.00	2,034.00	731.75	0.00	0.00	0.00	29.14
8520.42	2,032.00	1,991.00	2,032.00	707.14	0.00	0.00	0.00	29.25
8530.04	2,029.00	1,988.00	2,030.00	669.46	0.00	0.00	0.00	29.36
8540.80	2,027.00	1,985.00	2,028.00	642.98	0.00	0.00	0.00	29.52
8550.52	2,025.00	1,982.00	2,025.00	617.83	0.00	0.00	0.00	29.58
8560.13	2,023.00	1,980.00	2,023.00	583.68	0.00	0.00	0.00	29.74
8570.90	2,020.00	1,977.00	2,020.00	505.80	0.00	0.00	0.00	29.25
8580.51	2,017.00	1,975.00	2,017.00	472.27	0.00	0.00	0.00	28.26
8590.23	2,014.00	1,973.00	2,015.00	401.46	0.00	0.00	0.00	27.57
8601.00	2,011.00	1,971.00	2,012.00	341.02	0.00	0.00	0.00	27.04
8610.61	2,008.00	1,968.00	2,009.00	319.58	0.00	0.00	0.00	26.78
8620.22	2,006.00	1,966.00	2,006.00	289.95	0.00	0.00	0.00	26.68
8630.99	2,003.00	1,964.00	2,003.00	256.07	0.00	0.00	0.00	26.68
8640.60	2,000.00	1,961.00	2,000.00	216.80	0.00	0.00	0.00	26.83
8650.21	1,997.00	1,955.00	1,998.00	223.13	0.00	0.00	0.00	27.09
8661.03	1,994.00	1,952.00	1,994.00	146.95	0.00	0.00	0.00	26.88
8670.59	1,991.00	1,949.00	1,991.00	113.28	0.00	0.00	0.00	26.36
8680.20	1,988.00	1,946.00	1,988.00	121.05	0.00	0.00	0.00	26.36
8691.02	1,985.00	1,942.00	1,985.00	115.14	0.00	0.00	0.00	26.78
8700.58	1,982.00	1,940.00	1,982.00	131.91	0.00	0.00	0.00	27.41
8710.19	1,979.00	1,938.00	1,979.00	117.14	0.00	0.00	0.00	28.05
8721.01	1,976.00	1,935.00	1,976.00	102.61	0.00	0.00	0.00	28.75
8730.57	1,974.00	1,933.00	1,974.00	121.10	0.00	0.00	0.00	29.36
8740.18	1,971.00	1,931.00	1,971.00	120.66	0.00	0.00	0.00	29.91

8751.00	1,968.00	1,929.00	1,968.00	113.45	0.00	0.00	0.00	30.48
8760.61	1,966.00	1,927.00	1,966.00	114.42	0.00	0.00	0.00	30.88
8770.17	1,964.00	1,925.00	1,964.00	123.93	0.00	0.00	0.00	31.40
8780.99	1,961.00	1,922.00	1,961.00	88.93	0.00	0.00	0.00	31.86
8790.60	1,959.00	1,921.00	1,959.00	129.99	0.00	0.00	0.00	32.16
8800.16	1,957.00	1,919.00	1,957.00	118.81	0.00	0.00	0.00	32.45
8810.98	1,954.00	1,916.00	1,955.00	112.22	0.00	0.00	0.00	32.81
8820.59	1,952.00	1,914.00	1,952.00	119.60	0.00	0.00	0.00	33.12
8830.20	1,950.00	1,912.00	1,950.00	103.07	0.00	0.00	0.00	33.36
8840.97	1,947.00	1,906.00	1,948.00	126.81	0.00	0.00	0.00	33.60
8850.58	1,945.00	1,903.00	1,945.00	95.49	0.00	0.00	0.00	33.85
8860.19	1,942.00	1,901.00	1,943.00	101.89	0.00	0.00	0.00	33.98
8870.96	1,940.00	1,899.00	1,940.00	104.02	0.00	0.00	0.00	34.16
8880.57	1,937.00	1,896.00	1,938.00	121.14	0.00	0.00	0.00	34.35
8890.18	1,935.00	1,894.00	1,936.00	111.99	0.00	0.00	0.00	34.48
8900.95	1,933.00	1,892.00	1,933.00	129.77	0.00	0.00	0.00	34.66
8910.56	1,930.00	1,890.00	1,931.00	108.91	0.00	0.00	0.00	34.79
8920.17	1,929.00	1,888.00	1,929.00	107.68	0.00	0.00	0.00	34.85
8930.99	1,926.00	1,886.00	1,926.00	111.42	0.00	0.00	0.00	34.98
8940.55	1,924.00	1,884.00	1,924.00	115.02	0.00	0.00	0.00	35.11
8950.16	1,922.00	1,882.00	1,922.00	91.03	0.00	0.00	0.00	35.24
8960.98	1,919.00	1,880.00	1,920.00	68.36	0.00	0.00	0.00	35.17

Depressurization finished and Lab View program stopped

Appendix B

Appendix B1 Sample GC data and chromatogram

Title :
Experiment File : C:\Star\\Jairo Lopez\Jairo data\2003-6-26 New Calibration Curve # second method\10, 3, 6-27-03, 4; 49; 30 am. Run
Method File : C:\STAR\JAIRO LOPEZ\JAIRO METHOD\MODIFIED NEW FINAL CCME METHOD W 30 ML FID FLOW (10ML, 50SP, SP-SP.LESS INJ, 2UL).MTH
Sample ID : 10

Injection Date : Friday Jun 27 04:49:30 2003 Calculation: Friday Jun 27 10:11:33 2003

Operator : Jairo López
Workstation : VARIAN 3400
Instrument : 3800 GC
Channel : Rear = FID

Detector Type : 3800
Bus Address : 44
Sample rate : 10.000 Hz
Run Time : 26.973 min.

Star Chromatography Workstation (Demo) Version 5.50 ** 05000-1A68-DA2-3be9

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

Peak No.	Peak Name	Result ( )	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1 / 2 (sec)	Status Codes
1		0.0000	0.023	0.0000	144	BB	0.0	
2		0.0002	0.317	0.0000	1646	BV	1.6	
3		0.0003	0.350	0.0000	2213	VV	0.0	
4		0.0023	0.436	0.0000	18378	VV	3.0	
5	Solvent peak	98.5462	1.213	0.223	804035712	VP	79.5	
6		0.0005	1.904	0.0000	3906	TF	0.0	
7		0.0020	1.916	0.0000	16268	TF	0.0	
8		0.0001	1.967	0.0000	1075	PV	0.0	
9		0.0011	2.123	0.0000	8719	VV	0.0	
10	C_{10} Decane	0.0007	2.141	-0.179	5606	VB	0.0	
11		0.7967	4.648	0.0000	**6500420**	**GR**	0.0	
12	C_{16} Hexadecane	0.0184	7.037	-0.044	150181	VV	0.0	
13		0.6315	11.753	0.0000	**5152769**	**GR**	0.0	
14	C_{34} Tetratriacontane		16.489					M
15	C_{50} Pentacontane		20.908					M
	Totals :	100.0000		0.0000	815897037			

Status Codes:
M – Missing peak

Total Unidefined Counts : 11705539

Detected Peaks: 119 Rejected Peaks: 0 Identified Peaks: 5

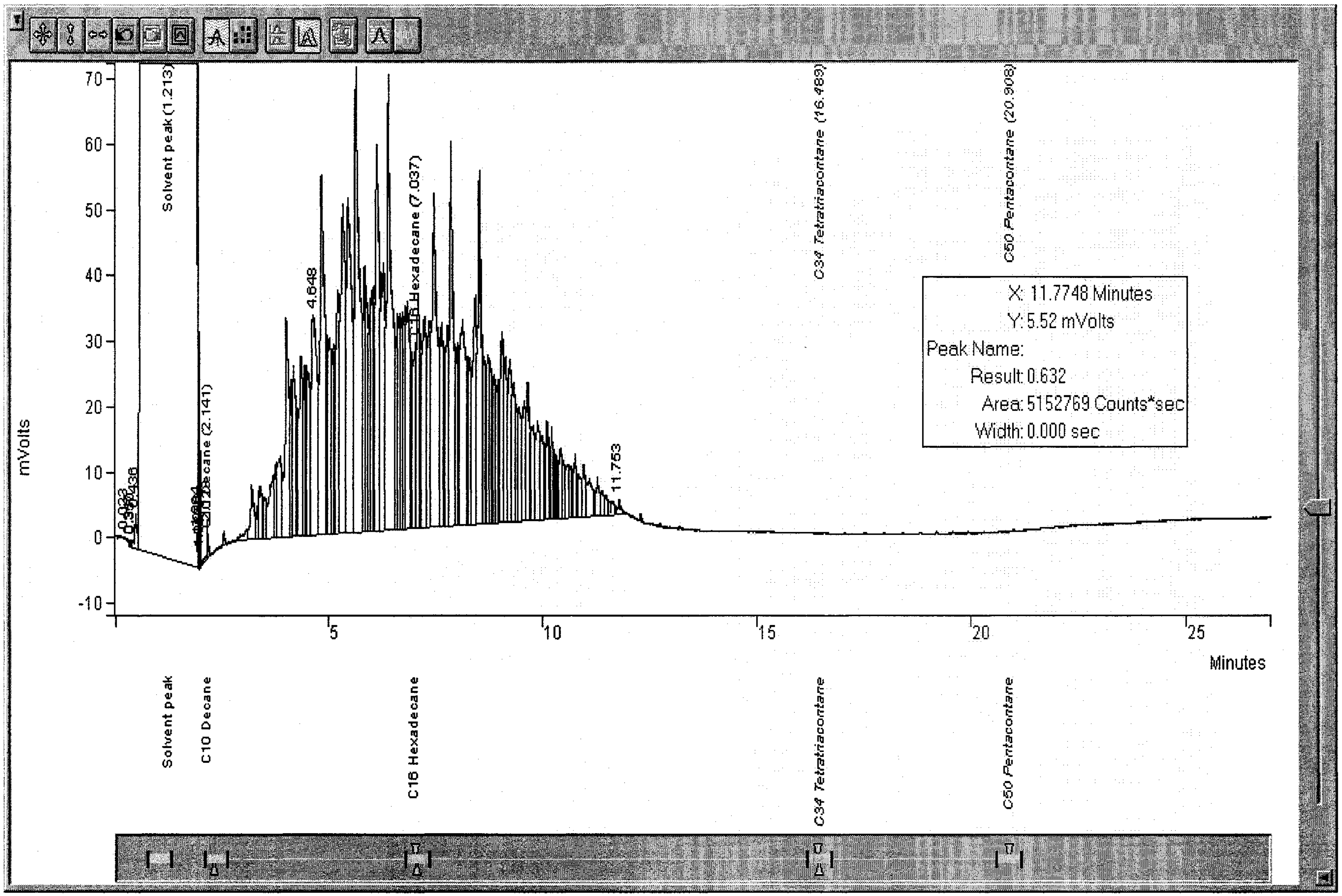
Multiplier: 1 Divisor: 1 Unidefined Peak Factor: 0

Baseline Offset: -382 microvolt

Noise (used): 180 microvolt – monitored before this run

Vial: 5 Injection Number: 3 Volume: 2.0 uL Position: 1

Data handling: Non-reference peak no identified
Data handling: Non-reference peak no identified



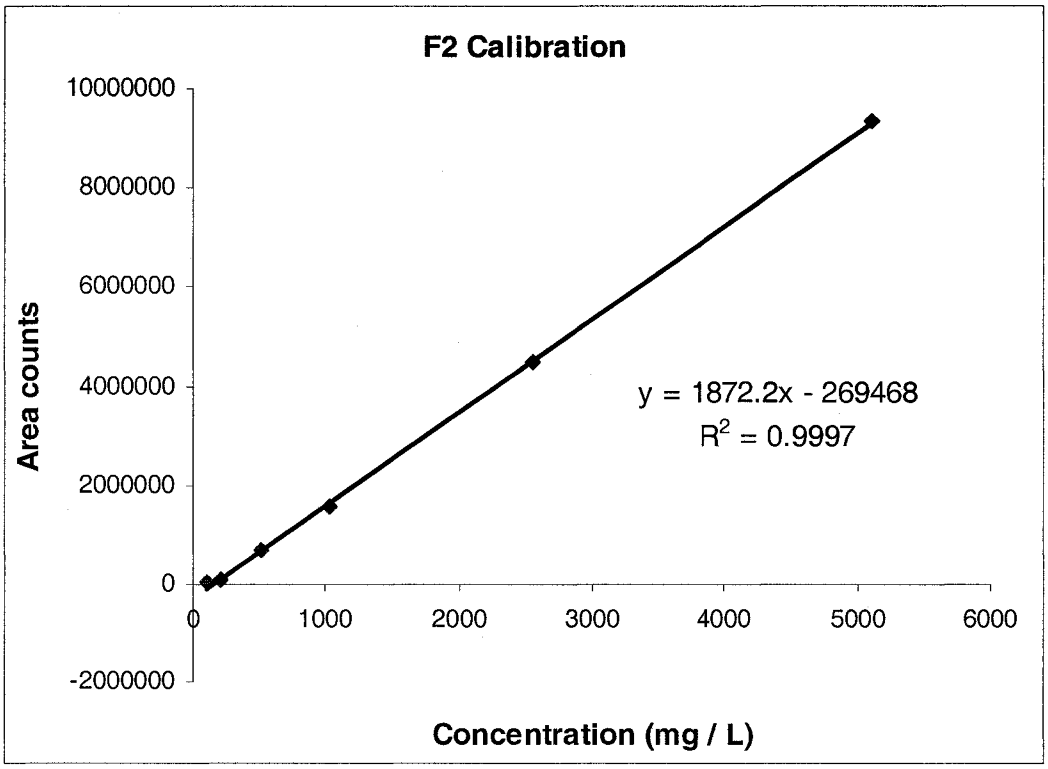
X: 11.7748 Minutes
Y: 5.52 mVolts
Peak Name:
Result: 0.632
Area: 5152769 Counts*sec
Width: 0.000 sec

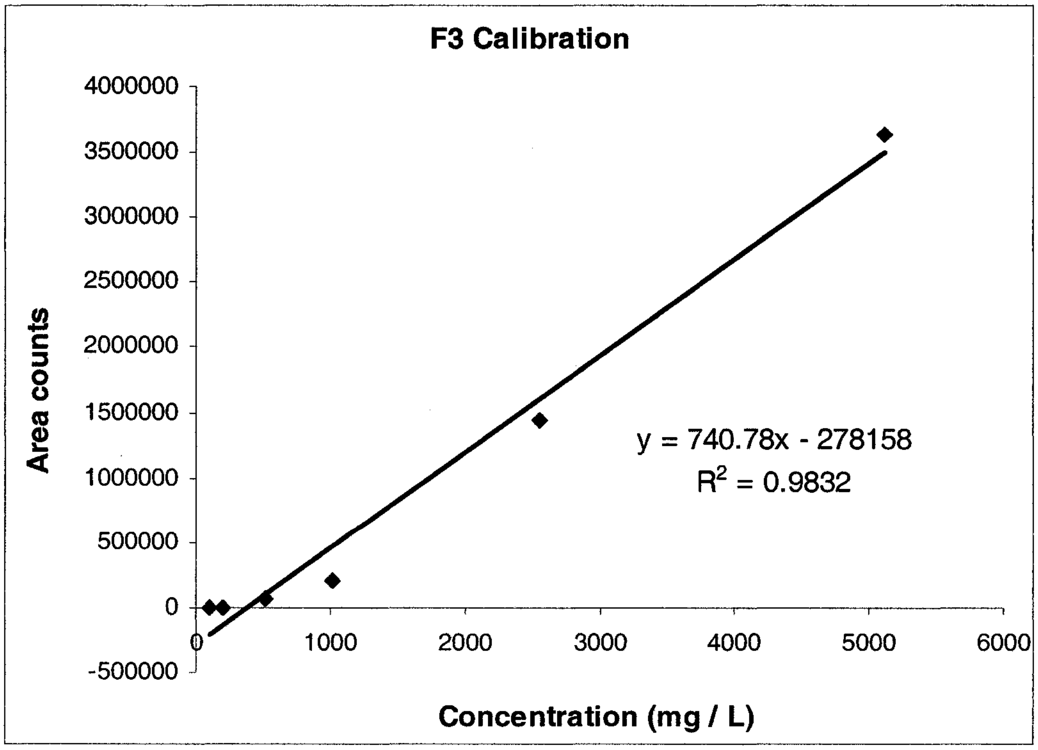
Appendix B2 Diesel Standard Calibration Curves

Calibration # 1 valid for all experiments carried out prior to June 25, 2003

Diesel Standard Concentration (mg diesel/ L toluene)	# Injections	Area F2	Average F2	Area F3	Average F3	Total Hump Area
102.20	1	61,570.00	30,680.40	2,216.00	2,216.00	32,896.40
	2					
	3	19,481.00				
	1	50,427.00				
	2	1,141.00				
	3	20,783.00				
204.40	1	38,571.00	87,385.33	1,435.00	4,723.50	92,108.83
	2	205,163.00		2,863.00		
	3	91,322.00		11,477.00		
	1	115,331.00				
	2	22,703.00				
	3	51,222.00		3,119.00		
511.00	1	780,742.00	685,752.00	54,216.00	68,298.50	754,050.50
	2	168,778.00		7,219.00		
	3	480,447.00		13,889.00		
	1	755,000.00		89,724.00		
	2	871,276.00		73,738.00		
	3	1,058,269.00		171,005.00		
1,022.00	1	2,063,597.00	1,565,035.17	354,016.00	212,543.67	1,777,578.83
	2	989,907.00		119,611.00		
	3	1,376,756.00		161,982.00		
	1	1,450,944.00		129,373.00		
	2	1,948,100.00		446,415.00		
	3	1,560,907.00		63,865.00		
2,555.00	1	660,897.00	4,479,020.67	196,735.00	1,444,935.00	5,923,955.67
	2	6,626,617.00		2,106,657.00		
	3	4,122,752.00		1,698,165.00		
	1	4,158,694.00		1,205,562.00		
	2	6,088,396.00		1,508,385.00		
	3	5,216,768.00		1,954,106.00		
5,110.00	1	11,320,982.00	9,329,553.00	4,528,382.00	3,639,175.17	12,968,728.17
	2	8,003,458.00		3,189,545.00		
	3	8,199,585.00		3,116,525.00		
	1	10,148,915.00		4,120,008.00		
	2	9,568,623.00		3,629,935.00		
	3	8,735,755.00		3,250,656.00		

Calibration curves valid for all experiments carried out prior to June 25, 2003

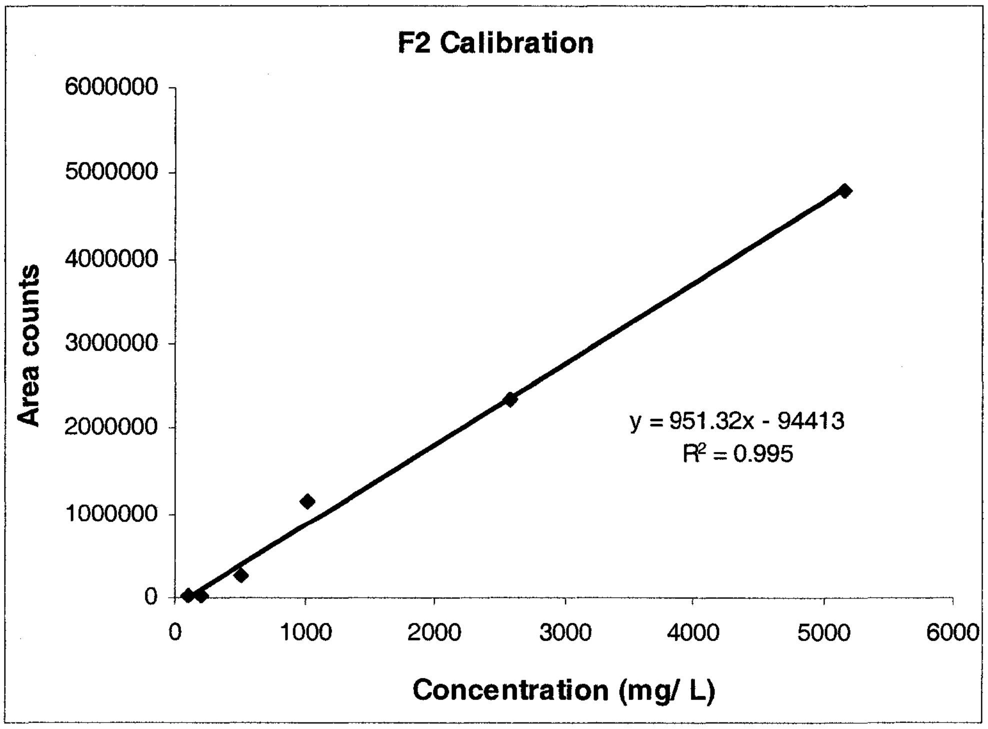


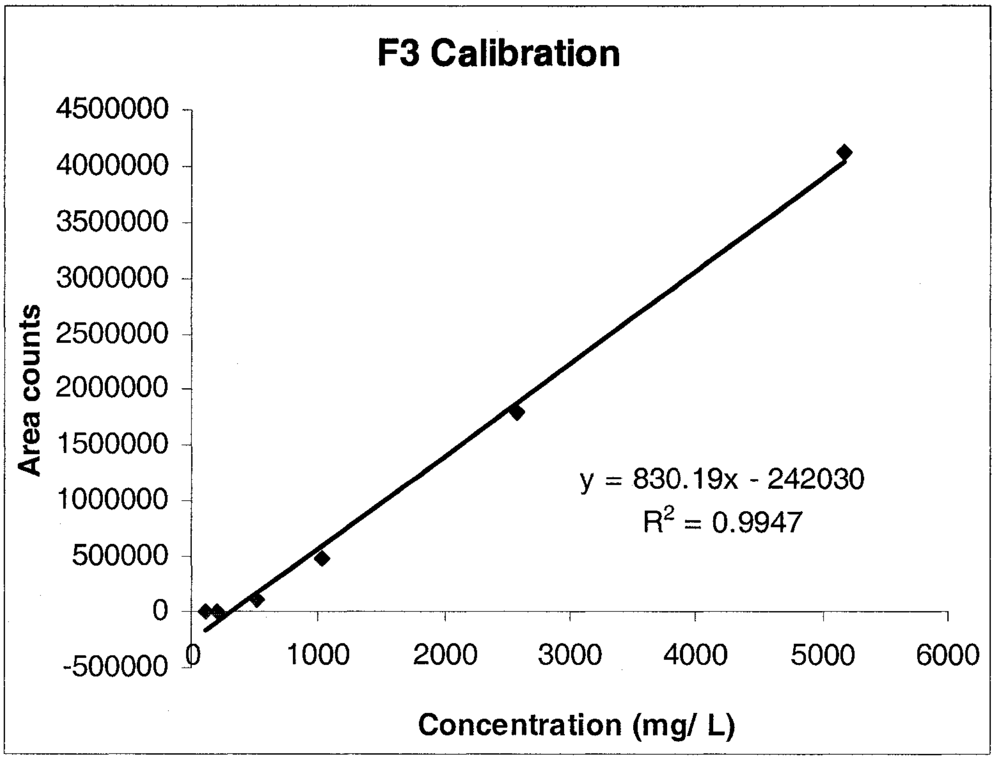


Calibration # 2 valid for all experiments carried out after June 25, 2003

Diesel Standard Concentration (mg diesel/ L toluene)	# Injections	Area F2	Average F2	Area F3	Average F3	Total Hump Area
103.34	1	23,216.00	18,287.00	3,662.00	3,220.00	21,507.00
	2	12,540.00		2,256.00		
	3	19,105.00		3,742.00		
206.68	1	48,983.00	34,397.33	7,182.00	6,617.33	41,014.67
	2	25,406.00		5,312.00		
	3	28,803.00		7,358.00		
516.70	1	258,569.00	249,691.33	71,163.00	101,732.00	351,423.33
	2	392,281.00		199,596.00		
	3	98,224.00		34,437.00		
1,033.40	1	979,538.00	1,135,692.00	187,754.00	483,458.67	1,619,150.67
	2	1,489,329.00		694,399.00		
	3	938,209.00		568,223.00		
2,583.50	1	1,807,802.00	2,335,479.33	1,629,531.00	1,807,503.33	4,142,982.67
	2	3,395,526.00		2,588,964.00		
	3	1,803,110.00		1,204,015.00		
5,167.00	1	3,410,866.00	4,802,733.33	3,382,451.00	4,123,919.67	8,926,653.00
	2	4,496,914.00		3,836,539.00		
	3	6,500,420.00		5,152,769.00		

Calibration curves valid for all experiments carried out after June 25, 2003

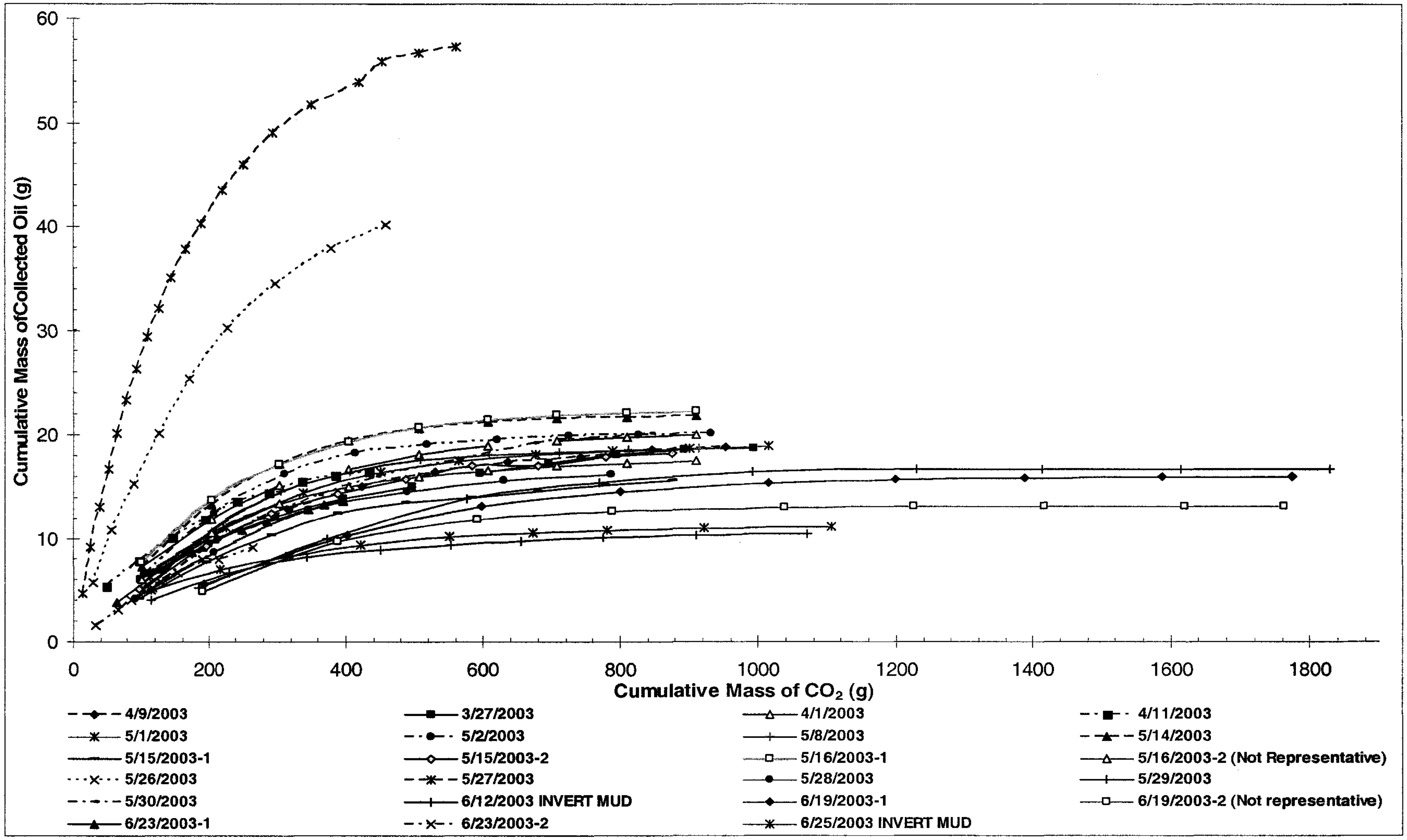



F3 Calibration
Area counts
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
0
1000
2000
3000
4000
5000
6000
Concentration (mg/ L)
y = 830.19x - 242030
R2 = 0.9947

Appendix B3 Sample experiment data

5/16/2003		Average Flow (mL/min)	10.5	Average Pressure Transducer (PSI)	2,227	Density CO_2 at 7.5 °C and 2100 psi (g/mL)	0.963
Density CO_2 at 40°C and average pressure psi (g/ml)	0.785	Mass of cuttings added to the vessel (g)		101.189	Average mass of CO_2 added to each vial (g)		101.119
Time (min)	Vial Number #	Collected oil mass per vial (g)	Cumulative Volume of CO_2 (mL)	Cumulative mass of collected oil per vial (g)	Cumulative Mass of CO_2 (g)	Solubility by vial (g collected oil / g of CO_2	Concentration in Supercritical phase (g of collected oil /mL of CO_2)
			15 min Static Period				
25	1	7.681	105	7.681	101.119	0.075	0.073
35	2	6.012	210	13.693	202.238	0.059	0.057
45	3	3.523	315	17.216	303.357	0.034	0.033
55	4	2.091	420	19.307	404.476	0.020	0.019
65	5	1.353	525	20.661	505.596	0.013	0.012
75	6	0.812	630	21.473	606.715	0.008	0.007
85	7	0.435	735	21.909	707.834	0.004	0.004
95	8	0.272	840	22.182	808.953	0.002	0.002
105	9	0.009	945	22.191	910.072	9.394E-05	9.047E-05
Total mass of collected oil		22.191			Average	0.024	

Appendix B4 Graphical results



Appendix B5 Raw Data

Date	Mass added to the vessel (g)	Pump pressure (PSI)	Temp. (oC)	RPM by cycle	# static period	Duration of static period (min)	# dynamic period	Duration of dynamic period (min)	Ave. flow rate (mL/ min)	Approx. mass of collected oil	η according to the mass of collected oil (%)	General comments of the experimentation
12/23/02	76.903	1800	60	120	1	15	1	30	10.5	-	-	Testing period
12/24/02	82.637	1800	60	300	1	15	1	30	10.5	-	-	Testing period
12/25/02											-	Experiment Cancelled -Vial Exploded
1/7/03	102.85	1800	60	500/550	2	15	2	30	10.5	14.00	70.89	Dark treated cuttings needs more time. Wet particles at the bottom of the vessel were found due to low rpms.
1/9/03	100.15	1800	60	800	3	15	3	30	8.5	10.65	55.38	Completely mixed but the treated cuttings was still dark.
1/10/03	99.638	1800	60	800	3	15	3	30	10.5	22.15	115.81	Completely mixed but the treated cuttings was still dark. Suspicious measurement of the weight of oil.
1/11/03	100.18	1800	60	800	3	15	3	30	11	14.69	76.42	Same as above but again not well weighted the collected oil

1/14/03	100.45	2000	60	800	3	15	3	30	10.5	-	-	Same as above
1/16/03	100.33	2000	60	800	3	15	3	30	11.5	21.94	113.89	The cuttings looked better and a high amount of oil was collected -Light and soft in texture.
1/17/03	100.05	2000	60	800	3	15	3	30	11	22.65	117.95	The cuttings looked better and high amount of oil was collected -Light and soft in texture.
2/5/03											-	Experiment Cancelled
2/7/03	101.65	2200	60	800	3	15	3	30	11	20.45	104.80	Increasing in the pressure did not affect the quality - Same quality.
3/27/03	100.47	2000	60	800	2	15	2	45	11.5	18.68	96.85	Not good quality. It looked darker
3/28/03	100.44	2100	60	800	2	15	2	45	12	-	-	Same as above
4/1/03	100.87	2100	60	800	3	15	3	30	10.5	19.96	103.06	Good quality. Valves not working properly
4/9/03	100.25	2100	60	800	1	15	1	90	11	18.82	97.77	Good quality but wet chunks were found. Valves not working properly
4/11/03	100.72	2100	60	800	1	15	1	90	5	16.39	84.78	Not soft powder - slightly dark. Valves not working properly.
4/14/03	100.38	2100	60	800	1	15	1	90	5	13.05	67.718	Good quality -Loss of oil in the traps. Valves not working properly

4/16/03	100.52	2100	60	800	1	15	1	90	10.5	10.60	54.928	Good quality but a low mass of oil was collected. Valves not working properly.
5/1/03	99.998	2000	60	800	1	15	1	90	11.75	18.94	98.66	Good Quality and average quantity of oil was collected
5/2/03	99.883	2100	60	800	1	15	1	90	10.75	20.11	104.88	Excellent quality. It looked dry, soft and light in color
5/8/03	100.51	2200	60	800	1	15	1	90	10.5	18.70	96.91	Excellent quality. It looked dry, soft and lighter color due to irregularities in the flow at the beginning
5/14/03	100.07	2100	60	800	1	15	1	90	10.5	21.77	113.31	Excellent quality. It looked dry, soft and light in color
5/15/03-1	99.614	1300	40	800	1	15	1	90	10.5	15.56	81.381	Not good quality. It looked darker and had wet chunks
5/15/03-2	99.679	1300	40	800	1	15	1	90	10.5	18.22	95.21	Not good quality. It looked darker and had wet chunks.
5/16/03-1	101.19	2100	40	800	1	15	1	90	10.5	22.19	114.22	Excellent quality. It looked dry, soft and light in color

5/16/03-2	99.271	2100	40	800	1	15	1	90	10.5	17.48	91.739	Excellent quality. It looked dry, soft and light in color. Loss of oil at the beginning of the experiment
5/26/03	203.22	2100	40	800	1	15	1	90	2.5 to 8.5	40.18	102.99	Good quality. The flow started at 2.5 and increased gradually to 8.5 mL/min at the end due to a clogging. It must have been left some oil in the cuttings because the extraction was stopped at 90 minutes
5/27/03	285.72	2100	40	800	1	15	1	200	1.2 to 5.85	57.26	104.396	Good quality. The flow started at 1.2 and increased gradually to 5.85 mL/min at the end due to a clogging in the system.
5/28/03	100.09	2100	40	800	1	15	1	60	8.5 to 15.85	16.15	84.07	System not working properly. Bad batch.
5/29/03	100.2	2100	40	800	1	15	1	90	20	16.72	86.91	Good quality. There were chunks in the treated cuttings but once touched they got destroyed. The final cuttings looked good but the low quantity of oil collected might be due to losses in the traps because of excessive flow and turbulence.

5/30/03	100.44	2100	40	800	1	15	1	90	1 to 25	20.06	104.05	The flow was extremely unstable. Despite of this, the flow in average was around 10 mL/min and at the end, the treated cuttings looked good. This experiment was wanted to have 5mL/min but was not possible.
6/12/03 Invert Cuttings	100.82	2100	40	800	1	15	1	90	11 mL/min and the last three vials went to 15 mL/min due to an instability with the metering valve	10.42	69.89	The flow was stable for almost all the experiment but in the last there vials the system got unstable. Despite of this, the treated invert cuttings looked excellent. It had crusts adhered to the walls of the vessel but once it was peeled it and macerated, it was noticed that the oil had been extracted.

6/19/03-1	100.37	2100	40	800	1	15	1	90	20	15.99	82.99	Regular quality. There were chunks in the treated cuttings but once touched they got destroyed. The final cuttings looked good but sticky. The low quantity of oil collected might be due to losses in the traps due to an excessive flow.
6/19/03-2	99.602	2100	40	800	1	15	1	90	20	13.14	68.74	At the end of the experiment, the cuttings looked better than the first experiment because it was necessary to depressurize the vessel and tide the bolts again due to a leak. This depressurization produced a loss of oil at the beginning and therefore the collected oil was less. Because of this, the cuttings looked better and the oil collected was less. Also, the low quantity of oil collected might be due to losses in the traps because of excessive flow and turbulence.

6/23/03-1	100.31	2100	40	800	1	15	1	90	4.57	13.63	70.79	The experiment indicated that it could be extracted more with more time but not with too much time because at the end of the experiment the gradient force gets weak due to the low flux of CO_2. As a result, the CO_2 is not able to take out the oil as normal. It can be done but with a lot of time and with difficulty. At the end of the experiment the cuttings looked light but sticky. The curves demonstrate that at low flow rates the extractions of oil gets irregular and do not present the gradual decreasing in the weight.
6/23/03-2	99.589	2100	40	800	1	15	1	90	3.06	9.11	47.65	The same as above but more unstable due to the extremely low flow.

6/25/03 Invert Cuttings	100.69	2100	40	800	1	15	1	90	12.55	11.12	74.67	The quality was good. The invert cuttings looked dry and light. As waited, this cuttings was stuck to the wall of the vessel but was well treated.
7/09/03 Invert Cuttings	99.845	2100	40	800	1	15	1	90	11	7.98	54.08	The quality was good. The invert cuttings looked dry and light. As waited, this cuttings was stuck to the wall of the vessel but was well treated. Despite of this, the amount of collected oil was low and might have been due to the instability of the flow.

Appendix B6 Solubility Calculation

Data.

Average flow for the vial (F): 1.949 mL /min.

Volume of toluene added to the vial (V_T) : 20 mL

Density of toluene at 20°C: 0.8667 g toluene / mL toluene

Duration of collection of oil for this vial (T_V): 5 min

Density of CO2 at 7.5 °C and 2100 psi (ρCO_2): 0.963 (g/ mL)

Hump area in chromatogram (HA): 125,291,680.00

Correlation used from the GC (Calibration # 1): $HA = 2613.1 * C - 547627$

C: Concentration for the vial in mg diesel oil / L of toluene

Therefore $C = (HA + 547627)/2613.1$

Calculation

$$C = \{\frac{(125{,}291{,}680.00 + 547{,}627)}{2{,}613.1}\}/\{10^6 * \frac{0.8667 g\_Toluene}{ml\_Toluene}\} = 0.055 \frac{g\_Diesel}{g\_Toluene}$$

Mass of toluene for the vial (M_T) = 20 mL * 0.8667 = 17.33g Toluene

Mass of diesel added to the vial (M_D) = *(0.055g diesel /g toluene)*17.33g toluene = 0.96g diesel.*

Mass of CO_2 to the vial (M_{CO_2}) = $F*T_V*\rho CO_2 = 1.949\ mL/min*5\ min*0.963g/mL = 9.38g\ CO_2$.

Therefore the solubility is $M_D / M_{CO_2} = 0.96g\ diesel / 9.38g\ CO_2 = 0.102g\ diesel / g\ CO_2$.

Appendix B7 Sample CCME calculation

Data for one injection of raw cuttings.

For F2 concentration

$$C_{10} - C_{16}\ Hydrocarbons\ (mg/kg) = \frac{A_{C10-C16} * Vol * F}{RF_{avg} * Wd}$$

$A_{C10-C16} = 22{,}171{,}954$

$Vol = 2.90\ mL$

$F = (Dilution\ volume / Aliquot) = 10 / 0.25 = 40$

$RFavg = 3{,}564{,}859{,}482.90732$

$Wd = 5.0073g$

Therefore $C_{C10-C16} = 144{,}084.06\ mg / kg$

For F3 concentration

$$C_{16} - C_{34}\ Hydrocarbons\ (mg/kg) = \frac{A_{C16-C34} * Vol * F}{RF_{avg} * Wd}$$

$A_{C16-C34} = 7{,}467{,}942$

$Vol = 2.90\ mL$

$F = (Dilution\ volume / Aliquot) = 10 / 0.25 = 40$

$RFavg = 3{,}564{,}859{,}482.90732$

$Wd = 5.0073g$

Therefore $C_{C10-C16} = 48{,}530.29\ mg / kg$

F4 concentration

$$C_{34} - C_{50}\ Hydrocarbons\ (mg/kg) = \frac{A_{C34-C50} * Vol * F}{RF_{avg} * Wd}$$

$A_{C34-C50} = 0$

$Vol = 2.90\ mL$

$F = (Dilution\ volume / Aliquot) = 10 / 0.25 = 40$

$RFavg = 3{,}564{,}859{,}482.90732$

$Wd = 5.0073g$

Therefore $C_{C34-C50} = 0\ mg / kg$

The total concentration is:

$TC_{C10-C50} = C_{C10-C16} + C_{C16-C34} + C_{C34-C50} = (144{,}084.06 + 48{,}530.29 + 0)\ mg / kg =$ $192{,}614.35\ mg / kg$ *dry cuttings*

Therefore,

$[\{(192{,}614.35\ mg / kg) * (5.0073\ g/1000\ g/\ 1\ mg)\} / 1000g/1kg] / [5.0073g] = 0.1926$

therefore the percentage of oil is 19.26%.

Appendix B8 Sample CCME results

Date of Extraction	Pump Pressure (PSI)	Ave. F2 (mg Hc/Kg Dry Cuttings)	Ave. F3 (mg Hc/Kg Dry Cuttings)	Ave. F4 (mg Hc/Kg Dry Cuttings)	Ave. Total (mg HC/Kg Cuttings)	Number of Injections	Average (% HC)	Standard Deviation (%HC)	Relative Standard Deviation (RSD)	Efficiency (%)	General Comments
2/7/03	2,200.00	490.29	1,381.95	-	1,872.24	9.00	0.19	0.07	37.65	99.04	-
4/1/03	2,100.00	6,511.29	7,119.33	-	13,630.62	5.00	1.36	0.13	9.57	92.98	Valves were not working properly
4/9/03	2,100.00	7,358.60	-	-	15,532.31	6.00	1.55	0.47	30.36	92.00	Valves were not working properly
4/14/03	2,100.00	4,845.12	6,502.74	-	11,347.86	6.00	1.13	0.23	20.16	94.16	Valves were not working properly
Centrifuge Underflow Raw	-	147,700.13	46,527.14	-	194,227.27	30.00	19.42	3.52	18.14	-	The final volume could not be reduced to less than 2 mL of toluene. The high boiling point of the additives produced this impasse. The rotovap was heated up to 80oC approximately
4/11/03	2,100.00	8,193.23	7,231.65	-	15,424.88	6.00	1.54	0.34	21.86	92.06	Valves were not working properly

4/16/03	2,100.00	22,693.75	24,197.65	-	46,891.40	6.00	4.69	0.52	11.04	75.86	This high percentage of oil can also be compared with the low quantity of oil extracted. Valves were not working properly
5/1/03	2,000.00	1,751.29	4,326.11	-	6,077.41	6.00	0.61	0.24	39.24	96.87	-
5/2/03	2,100.00	645.85	1,618.23	-	2,264.09	6.00	0.23	0.08	36.22	98.83	-
5/14/03	2,100.00	1,079.75	2,349.88	-	3,429.63	6.00	0.34	0.03	8.84	98.23	Experiment performed with UNOTEC Staff
5/16/2003-1	2,100.00	1,976.61	2,069.00	-	4,045.61	6.00	0.40	0.04	9.59	97.92	-
5/16/2003-2	2,100.00	2,154.94	2,107.75	-	4,262.69	6.00	0.43	0.08	18.73	97.81	The efficiency remained the same since the content of oil in the cuttings did not change. The point was that there was a spill of extracted oil at the beginning of the extraction and therefore was not able to quantify it using the vials.
5/15/2003-1	1,300.00	29,827.76	30,466.13	-	60,293.89	6.00	6.03	0.11	1.83	68.96	The results are according to the collected diesel
5/15/2003-2	1,300.00	20,519.65	23,781.92	-	44,301.57	6.00	4.43	0.37	8.25	77.19	The results are according to the collected diesel

5/29/03	2,100.00	680.28	1,522.53	-	2,202.81	6.00	0.22	0.06	26.71	98.87	-
5/30/03	2,100.00	3,094.90	4,276.27	-	7,371.17	6.00	0.74	0.16	21.47	96.20	-
5/26/03	2,100.00	8,756.65	5,600.92	-	14,357.57	6.00	1.44	0.33	22.64	92.61	-
INVERT CUTTINGS RAW	-	90,897.85	56,318.62	693.41	147,909.88	9.00	14.79	4.90	33.10	-	-
6/25/2003 INVERT CUTTINGS	2,100.00	834.40	2,391.45	806.55	4,032.40	9.00	0.40	0.32	78.15	97.27	The extremely high deviation standard might have been due to certain injections that were strange and also because the oil content was low. The GC was operated closed to the MDL; where the linearity is low. Despite of this the results were good