THE UNIVERSITY OF CALGARY

Composting of Ethane Pyrolysis Quench Sludge

by

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ABSTRACT

The use of composting is investigated to biodegrade the quench sludge produced by the Joffre ethylene cracking plant. Various bulking agents have been tested. Highest microbial activity was obtained when a mixture of peat moss and Solv II was used as bulking agents. Using this mixture, hydrocarbon content was varied between 1.5% to 14% per dry mass. Significant decrease in microbial activity was observed when hydrocarbon content reached 7.5%. Highest activity was maintained in composters with 2.5% to 5% hydrocarbon content.

Composting experiments were conducted at 35°C. The 46% decrease in Total Extractable Hydrocarbon in control composters over one month was similar to the decrease found in active composters. Control composters also resulted in 89% dicyclopentadiene decrease in one month. Dicyclopentadiene losses were found to be partially due to air stripping (7%) but mostly due to mixing of the mixture. The effects of biodegradation could not be readily identified and non-reactor type composting does not present a suitable biodegradation technique for the quench sludge.

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DEDICATION

Dedicated to my parents,
Alain and Brigitte

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NOMENCLATURE

C_{DCPD}	Concentration of dicyclopentadiene in exhaust gas (mol/m^3)
C_G	Concentration of chemical in gas phase (mol/m^3)
C_L	Concentration of chemical in liquid phase (mol/m^3)
$C_{in\ CO2}$	Carbon present in carbon dioxide (g)
$C_{in\ CH4}$	Carbon present in methane (g)
$C_{loss\%}$	Percent carbon loss
F_{CO2}	Carbon dioxide flowrate in exhaust gas (mL/hr)
F_{O2}	Oxygen flowrate in exhaust gas (mL/hr)
H	Henry's constant (atm m^3/mol)
HC_{in}	Hydrocarbon content into composter (g)
HC_{left}	Hydrocarbon left after composting process (g)
HC_{loss}	Hydrocarbon lost during process (g)
$Mass_{DCPD}$	Mass of dicyclopentadiene in sampling bulb (g)
P_i	Partial pressure of a gas above a liquid (mmHg)
P_T	Total pressure (mmHg)
P_v	Vapour pressure (mmHg)
R	Universal gas constant (m^3 atm/mol K)
RF_{DCPD}	Response factor for dicyclopentadiene
S	Solubility of chemical in pure water (mg/mL)
T	Temperature (K)
V_{bulb}	Volume of gas sampling bulb (m^3)
X_i	Mole fraction of contaminant in the liquid phase
Y_i	Mole fraction of contaminant in the gas phase

CHAPTER ONE: BACKGROUND

Ethylene is the single most basic and important building block in the petrochemical industry (Albright et al, 1983). In North America, the pyrolysis of ethane or propane is often the process of choice for production of ethylene since the supply of natural gas is abundant and the pyrolysis of ethane or propane produces the lowest yield of by-products. Other possible feedstocks include naphtha, gas oil, and butane. For ethane pyrolysis, a major portion of the reaction is described by a single stoichiometric equation.

$$C_2H_6 \Leftrightarrow C_2H_4 + H_2 \qquad (1\text{-}1)$$

However, it is known that ethane pyrolysis is not as simple as the equation shown above. Many by-products are formed by mechanisms that are not fully understood. Rice and Herzfel (1934) suggested that pyrolysis occurs through free-radical reactions. These reactions are very complex as dozens of reactions can occur simultaneously. Free-radical reactions lead to a broad range of products. Larger molecules may be produced due to the coupling of free-radicals. Table 1.1 lists the pyrolysis products from various feedstocks. The pyrolysis reaction of choice when producing ethylene is one that minimizes the formation of methane, C^{4+} hydrocarbons and propylene. The reaction parameters that

most affect the selectivity of ethane production are temperature, hydrocarbon partial pressure, residence time, and feedstock composition.

Table 1.1: Pyrolysis Products from Various Feedstocks

Feedstock	Products (in kg/100 kg feedstock)				
	Ethylene	Propylene	Butadiene	BTX	Other
Ethane	82.3	1.8	2.6	0.7	12.6
Propane	43.7	21.2	4.1	4.8	26.2
Butane	42.2	14.6	3.9	4.8	34.5
Light naphtha	29.3	14.4	4.0	13.8	38.5
Full-range naphtha	27.2	12.8	4.5	11.3	44.2
Gas oil	25.0	12.4	4.8	11.2	46.6
Crude oil	25.2	8.3	3.5	15.3	47.7

From Albright et al. (1983).

The cracking of ethane at the Joffre plant operated by Nova produces a waste sludge, called quench sludge, which is currently trucked out of the province where it is treated by incineration. Landfarming the quench sludge is not an alternative due to its strong odour which tends to aggravate the public's perception of the waste and due to the production rate of the quench sludge. Figure 1.1 summarizes the process of the ethane cracking plant producing the quench sludge. To make ethylene, ethane gas is heated in a furnace at 800°C in the absence of oxygen. The effluent gases are passed through a transfer line heat exchanger and then to a quench tower where rapid cooling to ambient temperature occurs by direct contact with cold water. Here, the ethylene and some lighter hydrocarbons are removed as gas phase product. A liquid hydrocarbon stream called the C^{5+} stream and a water rich stream called the quench sludge are also produced. The water cannot be effectively separated from the hydrocarbon stream due to the formation of an

emulsion layer between the two phases. The quench sludge is a mixture of water, hydrocarbons, and fine solids. The hydrocarbons include many compounds, principally benzene, dicyclopentadiene, styrene and polyaromatic hydrocarbons. The solids are composed of primarily coke contaminated by adsorbed hydrocarbons and containing significant amounts of heavy metals, mostly nickel, iron and chromium. The production rate of the quench sludge is estimated to be 500 tonnes per year.

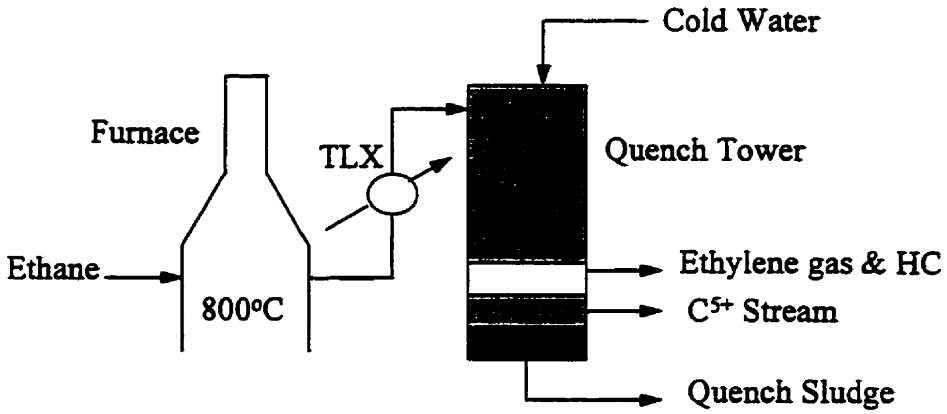


Figure 1.1: Flow Diagram of Ethane Cracking Plant

The quench sludge is currently trucked out of the province where it is treated by incineration in Ontario. Although similar petroleum wastes produced by Nova Chemicals in Ontario are treated by landtreatment, the smell associated with the quench sludge prevents such treatment. The quench sludge is a petroleum waste which may be considered hazardous based on its potential to exhibit toxic and flammable characteristics. The toxicity of the quench sludge has not been quantified. However, the sludge contains hydrocarbons such as benzene, which is a known carcinogen. Many petroleum wastes also cause a hazard since they are often readily ignitable. The pervasive odour of the quench sludge is caused by the presence of dicyclopentadiene (DCPD). Although DCPD has few acute toxic effects, public perception of the

seriousness and danger associated with it have been based on its smell. Very little has been published on the fate of DCPD in the environment and on its biodegradability potential. Stehmeier (1997) reported that preliminary work done on DCPD suggested that it is very recalcitrant and biodegradation would be difficult. It has been estimated that 50% conversion in the soil environment at 25°C could take 4 to 7 years (Stehmeier, 1997). The number of microorganisms capable of degrading DCPD is very limited. In his Ph.D. thesis, Stehmeier (1997) could not successfully find single strains of microorganisms capable of rapidly degrading DCPD. However, an active microbial population was sustained even when DCPD became the predominant substrate. He also concluded that DCPD could readily be biotransformed to intermediate products, but not be readily mineralized. However, if the transformation of DCPD into by-products eliminates the odour, part of the problem associated with the sludge disposal has been solved.

The processing of hydrocarbons leads to a vast array of petroleum wastes. Regulations restrict the disposal of liquid wastes into landfills. Incineration remains the only suitable disposal option but is very expensive and has air pollution implications. Biodegradation applications have also been considered for treatment to reduce the risk associated with oily wastes. Biodegradation techniques traditionally made use of landfarming and landspreading. In landspreading, the sludge is evenly spread over an area of land and is degraded by microorganisms present in the native soil. In landfarming, the sludge is actually mixed to the soil with mechanical equipment and fertilizers are usually added to increase the degradation rates. There are several disadvantages associated with landtreatment. Such methods require a lot of space and tie up the land for many years due to the low rates of biodegradation. New guidelines now require that the soil on which the sludge is applied be properly lined and a leachate control system must be installed. The large surface area required lead to a high cost associated with the lining of the land. A landtreatment facility may not be well accepted

by the community due to the lack of emission control. Other bioremediation techniques such as composting, biopiles and bioreactors offer several advantages over landtreatment since the waste is contained or placed in large piles requiring less land space and faster degradation rates are possible.

CHAPTER TWO: OBJECTIVES

The biodegradation of the quench sludge is an attractive alternative to incinerating the waste. The use of composting to degrade the waste offers several advantages over other biological techniques. The amendments added to the waste in composting aim to prevent limiting conditions from arising during the degradation process. The amount of water, nutrients, oxygen and bulking agents required are calculated to provide as high degradation rates as possible. A compost windrow can reach several meters in height and hence reduces the land space and lining required. The pile can also be covered to restrict gaseous emissions thereby controlling the odour problem.

The objective of this study is to evaluate the use of composting to biodegrade the sludge from the Joffre Nova Chemicals facility and especially its ability to transform dicyclopentadiene (DCPD) to remove the pervasive odour. It has already been shown that composting is capable of eliminating hydrocarbons from soils and sludges (Nordrum et al., 1992). In this research, the hydrocarbon degradation is to be monitored but the main focus will be on DCPD since no previous experiments have been done on the composting of that compound.

This research includes a study of the influence several factors have on the composting process. First, the most suitable amendments will be investigated. Bulking

agents such as wood chips, straw, peat moss, Sphag Sorb and Solv II will be tested. Previous work has shown that mixing a small amount of a contaminated soil or sludge with amendments can lead to successful degradation (Fyock et al., 1991). Increasing the hydrocarbon content in a mixture normally decreases biological activity. The amendments significantly increase the total volume to be treated and it is therefore necessary to determine the optimal sludge content of the compost mixture. It has already been established that maximum microbial activity occurs when the hydrocarbon content is maintained between 4% to 6% of the dry weight (Atlas, 1984). However, the degradation obtained when different amounts of sludge are mixed in the composters will be evaluated to see if successful degradation can be obtained at higher hydrocarbon contents. An evaluation of the degradation rates of the sludge will also be conducted.

In summary, the objective of this project is to reduce the toxic nature of the quench sludge and to study degradation rates of dicyclopentadiene through composting.

CHAPTER THREE: LITERATURE REVIEW

3.1 QUENCH SLUDGE DISPOSAL AND TREATMENT

For a petroleum waste to be considered hazardous, it must be specifically listed as a hazardous waste or must exhibit one of the following functional properties: flammability, corrosivity, reactivity, toxicity, radioactivity and infectious. The quench sludge may be considered hazardous based on its toxic and flammable characteristics. A toxic substance is one which causes adverse effects. The emphasis is generally on acute, or short term effects. Acute toxicity is defined in terms of lethal dose in the case of dermal or oral exposure. Although no lethal dose value is available for the quench sludge, it contains benzene which is a known to be toxic based on its chronic, or long term effects. A flammable waste is one that is readily ignitable, burns vigorously, causes fire or contributes to fire. A liquid waste containing solids in solution or suspension having a flash point less than 61 °C is considered flammable. The quench sludge contains a variety of hydrocarbons having low flash points and may therefore be flammable.

There are only a few alternatives available for the disposal of the ethane pyrolysis quench sludge. It is currently treated by incineration which remains the preferred method for the treatment of hydrocarbon sludges. Waste materials containing free liquids can no

longer be placed in landfills. Stabilization and solidification methods may be used to reduce the toxicity or to solidify waste materials. However, the high quench sludge production rate does not make these methods suitable. Biological treatment offers the advantage of potentially reducing the toxic nature of the sludge when the toxicity is a result of the hydrocarbon fraction.

3.1.1 Biological Treatment

Biological treatments utilize microorganisms to degrade organic wastes. Experience and research show that most synthetic organics are biodegradable, making biological treatment a technically feasible alternative. The inherent biodegradability of a chemical depends to a large extent upon its molecular structure. Biological treatment systems can be classified according to table 3.1.

Table 3.1: Classification of Biological Treatment Systems

System	Form of waste	Characteristics
Conventional liquid phase	Liquid	Attached or suspended growth, with or without recycle of cellular mass, and continuous or batch flow; principally aerobic, but anaerobic can play key role
In-situ	Liquid and contaminated soil	Treatment of ground water in its natural state below the surface and treatment of subsurface sources of ground water contamination
Slurry-phase	Sludge or solid (e.g., contaminated soil)	Similar to conventional systems for liquid treatment except that non-volatile solids content in the reactor may range from 5% to over 50% (dry weight basis)
Solid-phase	Sludge or solid (e.g., contaminated soil)	Unsaturated conditions if not minimal free moisture; land treatment, composting, and heaping are prime examples

From LaGrega et al. (1994).

The first two systems described in table 3.1 are not applicable to the treatment of industrial waste sludges. Wastes treated by these methods include contaminated groundwater, wastewater or contaminated soils.

In slurry-phase treatment, wastes can be sludges, solids or contaminated soils. Wastes are suspended with water or wastewater in a mixed reactor to form a slurry. The slurry-phase treatment systems are normally equipped with agitators and aeration devices. The agitation within the reactor promotes homogeneity, desorption of waste from solid particles, contact between organic waste and microorganisms, oxygenation of the slurry by aeration, volatilization of contaminants, and breaks down the solid particles (LaGrega et al., 1994). The three steps involved in the treatment of wastes using slurry-phase methods are mixing and aeration, desorption and biodegradation. The more simple systems occur in-place and are commonly called holding lagoons. These tend to be batch processes but can be modified for continuous flow. However, for continuous flow treatment, a multi-stage system is normally used. The advantage of the slurry-phase treatment is that it can degrade wastes at faster rates than solid-phase treatment while requiring less land area. Faster degradation rates are observed since the mixed and aerated slurry-phase offers an ideal media for bacterial growth.

Solid-phase treatment includes various methods capable of treating sludges, solids, and contaminated soils under minimal moisture conditions. The three categories of solid-phase treatment are landtreatment, composting and heaping.

Landtreatment includes land spreading and landfarming. The waste is mixed with the upper layer of the soil. The soil must be conditioned to obtain a relative uniform consistency with the removal of rocks and debris. Reduction in contaminant concentrations occurs due to degradation from native bacteria in the soil, aeration due to exposure and oxidation of the compounds due to contact with air. Landtreatment is

limited by the depth of soil that can be effectively treated because of limited oxygen diffusion. Although a popular biological treatment method over the last few decades, the use of landtreatment is decreasing due to stricter environmental regulations. The process ties up the land for many years while presenting a hazard due to the leaching of contaminants into the surrounding environment.

In composting, degradation is aided by the addition of amendments such as bulking agents which provide a more suitable environment for microbial activity. Composting can be performed in windrows, piles or in vessels. The composting process is able to maintain temperatures in the mesophilic region (30°C to 50°C) due to the size of the piles (Haug, 1993). Degradation rates are faster than those observed in landtreatment and less land is required.

Soil heaping, is the piling of a waste, normally contaminated soil over an air piping system and impermeable layer. This system is similar to composting since it provides favorable environments for microbial activity, but differs in that lesser quantities of bulking agents are used. It represents an effective method for treating large quantities of soil and other organic wastes containing low concentrations of organics (LaGrega et al., 1994). The piles can be covered to prevent precipitation penetration and volatile emissions. The air is normally drawn from the piles allowing for treatment of volatile emissions. Degradation rates are generally slower than landtreatment due to the low initial organic concentrations and since there is no mixing management. However, it provides the leachate and emission control that cannot be obtained with landtreatment.

3.1.2 Remediation Legislation

Regulations governing the remediation of contaminated soil and disposal of contaminated waste have undergone extensive review over the last few decades due to the

new information on environmental and health risks. In Canada, Environment Canada is the government department responsible for environmental quality. Although soil remediation legislation is provincially enforced, it is generally based on national guidelines called the "Canadian Council of Ministers of the Environment Interim Canadian Environmental Quality Criteria for Contaminated Sites". Soil remediation guidelines in the document are based on intended land use, giving numerical contaminant concentration targets for remediation in terms of agricultural, residential and commercial/ industrial land use applications.

In Alberta, a two-tier system for setting acceptable levels of residual contamination in remediated soil was developed by Alberta Environment. Alberta Tier 1 Criteria for Contaminated Soil Assessment and Remediation represent background levels used to indicate if remediation is needed and hence clean-up to Tier 1 levels is generally not attempted. In contrast, Tier 2 criteria are site-specific concerning protection of human health and the environment and generally represent the remediation levels to be met. Such criteria are based on acceptable risk specific to the site consideration of such variables as soil, geology, surface and groundwater, climate and land use. Tier 2 criteria are proposed by the proponent who is required to provide credible risk-based scientific documentation in support of their criteria and be willing to defend them.

3.2 PETROLEUM MICROBIOLOGY

The impact of petroleum hydrocarbons on the environment has probably been studied more extensively than any other single class of pollutants (Atlas, 1984). Large oil spills initiated the need to consider the bioremediation of hydrocarbons. The rate of microbial decomposition of organic compounds in soils is a function of three variables: (1) the availability of the chemicals to the microorganisms that can degrade them; (2) the

quantity of these microorganisms, and (3) the activity level of theses organisms. (Vecchioli et al., 1990).

3.2.1 Hydrocarbon-Utilizing Microorganisms

Biodegradation of hydrocarbons by natural populations of microorganisms represents one of the primary mechanisms by which petroleum and other hydrocarbon pollutants are eliminated from the environment. Hydrocarbon-utilizing bacteria and fungi are widely distributed in the marine, freshwater, and soil habitats. Microbial communities in soil typically are largely capable of degrading a wide variety of natural chemicals. This is particularly true for petroleum hydrocarbons (Atlas, 1984). The degrading capacity has made bioremediation techniques appealing since little intervention is required. The presence of appropriate microorganisms is established by testing their ability to remove the contaminant. Rates of biodegradation under optimal lab conditions range between 25 000 and 100 000 g/m^3d, whereas in-situ petroleum biodegradation rates range only between 0.001 to 60 g/m^3d (Atlas, 1981).

The ability to degrade petroleum hydrocarbons is not restricted to a few microbial genera; a diverse group of bacteria and fungi have been shown to have this ability (Atlas, 1981). More than 100 species representing 30 microbial genera, have been shown to be capable of degrading hydrocarbons. The most important genera of hydrocarbon-utilizing bacteria are *Pseudomonas, Achromobacter, Arthrobacter, Micrococcus, Nocardia* and *Acinetobacter*. A large number of *Pseudomonas* species have been isolated which are capable of utilizing petroleum hydrocarbons. The rates of degradation by bacteria are much lower in soil environments than in water. Fungi were also found to play an important role in the elimination of hydrocarbons in the soil environment. These include *Penicillium* and *Cunninghamella spp.*

3.2.2 Degradation of Individual Hydrocarbons

The type of hydrocarbons present in the soil affects the degradation rates. Straight chain alkanes are considered to be the easiest to remove. Compounds containing unsaturated bonds or rings are degradable but at slower rates. High molecular weight aromatics, resins and asphaltenes exhibit only very low rates of biodegradation. Completely different populations of microorganisms may carry out degradation of different classes of hydrocarbons.

Hydrocarbons within the aliphatic fraction include alkanes, alkenes, alkynes, and cycloalkanes (aliphatic cyclics or naphthenes). Oxygen is required for the bioremediation of aliphatics since the decomposition process is aerobic. The n-alkanes are generally considered to be the most readily biodegradable components in a petroleum mixture. Hydrocarbons with branched chains are degraded less readily than unbranched ones. Also, unsaturated aliphatics are less readily transformed than the saturated analogues. Those compounds exhibiting characteristics of both cyclic and aliphatic chemicals (alicyclic) are more resistant to microbial attack than most other groups of hydrocarbons. Cycloalkanes are particularly resistant to microbial attack when the compound is made up of four or more rings. However, alicyclic compounds do not accumulate in areas where microbial activity is abundant which indicates that biodegradation of these compounds is occurring. Degradation of substituted cycloakanes appears to occur more readily than the degradation of the unsubstituted forms, particularly if there is an n-alkane substituent of adequate chain length.

Aromatic compounds are those compounds containing a benzene ring. A large number of bacteria and fungi can oxidize aromatic compounds. These compounds are mineralized under aerobic metabolism and degraded under anaerobic metabolism mode. The anaerobic degradation of non-oxygen containing aromatic compounds requires the

incorporation of oxygen from water into the aromatic structure (Atlas, 1984). This may become the rate-limiting step. For single-ring aromatic compounds, the ease of degradation for both aerobic and anaerobic modes is influenced by the number, type, and position of substitutions. Simple aromatic compounds are usually degradable by several mechanisms of ring cleavage. The introduction of halogens will result in decreased biodegradability because halogens stabilize the ring. Multi-ring aromatics, or polycyclic aromatic hydrocarbons (PAH) are molecules containing two or more fused benzene rings. As for single-ring aromatics, the ease of degradation of a PAH is a function of substitution, and position of substitution but also of the number of fused rings. Two and three ring aromatics are readily degraded by soil bacteria and fungi. Aromatic compounds containing four and more rings are significantly more difficult to degrade. Some may even be recalcitrant and cometabolism appears important for their biodegradation. Methyl branching tends to inhibit biodegradation of aromatic compounds due to steric hindrance. Finally, increasing the degree of saturation significantly reduces the relative degree of degradation since more stable compounds are formed.

The metabolic pathways for the degradation of ashphaltic components of petroleum are probably the least understood. Their complex structures are difficult to analyze with common techniques.

3.2.3 Factors Influencing Biodegradation of Petroleum Hydrocarbons

The rate at which microorganisms can transform chemicals during bioremediation is dependent on two processes: (1) intrinsic activity and (2) mass transfer (Stehmeier, 1997). Mass transfer is in most cases the limiting factor in bioremediation due to desorption from soil, low solubility in water and diffusion transport. The fate of petroleum hydrocarbons in the environment is largely determined by abiotic factors

which influence the weathering, including biodegradation of the oil (Atlas, 1981). Any factor influencing the rate of microbial activity and enzyme production will have an effect on the rate of hydrocarbon degradation. Populations of indigenous hydrocarbon degrading microorganisms, physiological capabilities of populations and abiotic factors, determine rates of biodegradation.

Prior exposure of a microbial community to hydrocarbons is important to determine how rapidly subsequent hydrocarbon inputs can be biodegraded. An exposure results in adaptation, selective enrichment and genetic changes and an increase in the population of hydrocarbon degrading bacteria. In unpolluted environments, hydrocarbon degraders represent less than 1% of the microbial community, whereas in oil polluted soil, they can represent up to 10% (Atlas, 1984). An adapted community presents an advantage since it can respond to hydrocarbon pollutants within hours.

The physical state of petroleum hydrocarbons has a marked effect on biodegradation. A pollutant that has been in the soil for an extended period of time will be entrapped in the micropores and hence is no longer available to microorganisms. This process is called "contaminant aging". The degree of spreading of the contaminants determines the surface area available for the microorganisms. Availability of increased surface area should improve the rates of biodegradation since the hydrocarbon-degrading microorganisms act mainly at the oil-water interface (Atlas, 1984). The microorganisms have been found to grow over the entire surface area of an oil droplet, however, growth does not appear to take place within the droplet. Hence, the dissolution and emulsification of hydrocarbons appear to increase biodegradation rates.

The degradation of hydrocarbons can occur over a wide range of temperatures. Low temperatures lead to less spreading of the oil due to the increased viscosity. Degradation of hydrocarbons has been observed between 0°C and 70°C, although the

rates usually decrease significantly below 20°C (Atlas, 1984). Seasonal shifts to a microbial population capable of degrading hydrocarbons at low temperature are observed during winter months. The effect of temperature on degradation depends on the composition of the hydrocarbon mixture. Low temperatures retard the rates of volatilization of low molecular weight hydrocarbons, some of which are toxic to microorganisms. The presence of these compounds at low temperatures has been found to delay the onset of biodegradation. Hence, the toxic volatile compounds that cannot be released as readily at lower temperatures often hinder the biodegradation of lighter oils. However, heavier oils are not affected similarly by temperature if they do not have an associated volatile fraction (Atlas, 1984).

The amount of nutrients such as nitrogen and phosphorous can severely limit the extent of hydrocarbon degradation. Natural rates of replenishment of these nutrients are generally inadequate and additional nitrogen and phosphorous are generally added through the use of fertilizers.

Although the existence of anaerobic hydrocarbon degrading bacteria has been confirmed, aerobic degradation is generally preferred since it leads to much faster rates in nature. The importance of oxygen for hydrocarbon degradation is indicated by the fact that the major degradative pathways for both saturated and aromatic hydrocarbons involve oxygenases and molecular oxygen (Atlas 1981).

3.3 COMPOSTING

Composting is one of the many forms of biodegradation since it makes use of microorganisms to break down a waste product. Composting is an aerobic biological decomposition process which ultimately degrades organic material to carbon dioxide,

water, and a stabilized residue, principally humic substances, called compost (Haug, 1993). Although the decomposition of organic materials can occur under anaerobic conditions, aerobic composting is generally emphasized because decomposition of organic material occurs more rapidly and produces less odours. Composting of municipal sewage sludge has been widely practiced, however, treating chemical and industrial waste sludges by composting is a relatively innovative concept.

3.3.1 Composting Systems

Composting systems are divided into reactor and non-reactor types. A reactor type system is one which is often termed mechanical, enclosed or in-vessel. They are considered mechanical because most have agitators and forced aeration. Non-reactor systems include passive composting, windrows and aerated static piles.

Enclosed reactor systems can lead to the completion of the composting process in only a few days. Most in-vessel systems use sophisticated mixing equipment. The use of conveyors to transport material is a major difference between in-vessel composting and other composting configurations. The high-rate stage is always conducted in a closed reactor while the curing stage may be conducted in an exterior pile. Reactor processes are first classified according to the manner solids flow, either as vertical flow reactors or horizontal flow reactors. Vertical reactors are further divided by the bed conditions, either continuous or discontinuous. In the continuous vertical reactor, the composting mass is introduced in one operation whereas in the discontinuous process, masses are introduced at different times. The main disadvantage is the extreme difficulty of controlling the process, mainly the oxygenation of the mass. The lower part is usually overventilated, dried and cool whereas the upper part is insufficiently aerated, the air is warm and enriched in carbon dioxide with reduced oxygen content. Horizontal reactors are generally classified according to the type of agitation. In the horizontal type reactors,

it is possible to control under good conditions oxygenation of the mass, humidity and temperature. It is possible to turn the mass within the reactor and hence leads to a very uniform production of compost.

In passive composting, the organic material is placed into large piles and left to degrade over time with little or no mixing and management. Degradation rates are slow as anaerobic conditions develop. The windrow process shown in figure 3.1 is the most popular non-reactor agitated bed system (Haug, 1993). The mixture of waste and organic is piled in long rows and turned once or twice a week usually by mechanical equipment. A typical windrow turner is shown in figure 3.2. The turning aerates the mixture while releasing excess heat produced and increases the release of volatiles. Turning is conducted more frequently during the first weeks when the oxygen demand is high. The size and shape of the windrows depend primarily on the nature of the feed and on the equipment available for turning. The windrows are generally trapezoidal in shape, and can reach sizes of 6 m in width at the base, 2 m in width at the top and 2 m in height.

Static piles are similar to windrows but the piles are not turned. The piles are built on top of perforated pipes, and air is mechanically drawn or forced through the pile. The substrate of aerated static piles is mixed with a bulking agent. The bulking agent removes the need of periodical turning by providing structural stability to the material and maintaining air voids in the pile. Most piles or windrows are placed on a concrete or asphalt base pad. The base pad allows for placement of distribution pipes while collecting rain water running off the pile.

The advantage of the enclosed reactor system is that the operation can be optimized to complete the process in as little as three days compared with as much as thirty days with windrows. An enclosed reactor system also facilitates control of volatile

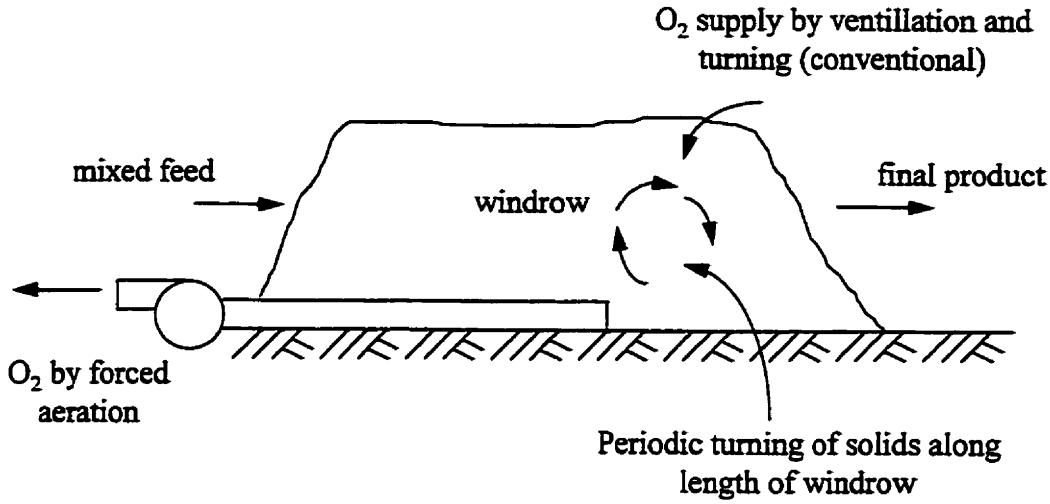


Figure 3.1: Windrow System: (1) conventional - agitation by periodic turning without forced aeration; (2) forced aeration - same as conventional with forced aeration.

Figure 3.2: Windrow Turner Used to Mix and Aerate Windrows

emissions. It can be operated as a batch or continuous system, with or without agitation. However, the capital and maintenance costs of non-reactor systems are much lower and are hence used more widely for remediation applications. It is also more difficult to bring a reactor system to a site, whereas windrows or static piles can easily be constructed on site when the space is available, removing the need to transport the waste.

3.3.2 Essential Factors

Essential factors are those features of the physical, chemical, and biological background that are necessary for the operation of the composting process. The following factors have become key design features in recent compost technology, namely, temperature, moisture content, oxygen availability (aeration), nutrients, and microorganism population.

It is well known that satisfactory composting and the attainment of high temperatures are mutually interdependent (Haug, 1993). Greatest microbial activity during composting is observed in the 30 to 50°C temperature ranges. Initially, the temperature in the compost pile will quickly rise due to the rapid degradation of the aliphatic compounds. The temperatures do not, however, exceed of 65°C since few thermophilic organisms can survive at such high temperatures (Golueke, 1987). When the readily metabolized hydrocarbons have been consumed, the rate of microbial activity decreases and the temperature begins to drop. When it reaches 55°C, other microbial groups, mesophilic bacteria, become active again. Towards the end of the process, at an advanced stage of stabilization, the fungi have their highest activity rate and bacterial activity begins to decline. Hence, the degradation of hydrocarbons requires thermophilic and mesophilic bacteria as well as fungi. The problem associated with composting in cold climates is mainly a kinetic one. Reaction rates are so slow that the rate of heat generation is less than the rate of heat loss to the cold surroundings. The energy is still

available in the substrate but is not released due to the low degradation rates. The best approach to overcome low temperature kinetic limitations in cold climates is to assure that any heat in the feed substrates is conserved to give as high a starting temperature as possible (McMillen et al., 1996). It may also be necessary to heat the air added to the pile at the start of the process to obtain higher initial degradation rates. Once the organic matter begins to degrade, the process will generate sufficient heat to sustain elevated temperatures in the pile. The heat is somewhat conserved due to the size of the pile which acts as an insulator (McMillen et al., 1996).

Water is both required for and produced by microbial activity. If the moisture content falls below 20%, the decomposition ceases (Golueke, 1987). If it exceeds 70%, water begins to fill the interstices between the particles of the biomass, reducing access to interstitial oxygen. The decrease in rate will reduce the temperature and may also lead to anaerobic conditions. For hydrocarbons, 60% moisture is recommended (Cookson, 1995). A water content of 40% to 60% should be maintained in the earlier stages of the composting process to compensate for water loss through evaporation due to the high initial temperatures. The large addition of water necessary to obtain the desired moisture content increases the overall mass of the compost mixture substantially. It is desirable to remove the water upon completion of the composting process since a dry residue is more easily screened, stored, transported and disposed of.

Oxygen is usually supplied as air and reaches the microorganisms through diffusion. Oxygen availability is a function of aeration through the pile. If moisture content is too high or the composting mass is compressed, oxygen may be used up faster than it can enter the bulk of the composting mass and anaerobic organisms will start to grow. Aeration and ventilation also play a crucial role in the removal of excess heat and water vapour. The optimal supply of oxygen lies between 15 and 20 volume percent of

the internal atmosphere. Aerobic composting is limited when oxygen is less than 10% by volume of the atmosphere within the biomass (Alberta Environmental Protection, 1993).

Bacteria use carbon as an energy source and nitrogen for cell building. The process of aerobic decomposition involves the reduction of the relative proportion of these elements, known as the carbon to nitrogen (C: N) ratio. This ratio is a deciding factor in the speed at which decomposition takes place. An ideal C: N mass ratio is approximately 30:1. Phosphorous is another nutrient that is also needed by the microorganisms. It is somewhat less important, since the optimum mass ratio of carbon to phosphorous is approximately 100:1 (Milne et al., 1996). Petroleum contaminated soils and sludges usually do not contain nitrogen and phosphorous. These elements are supplied to the compost using a suitable fertilizer. In soil remediation, the ratio of nutrients must be monitored periodically since adding all the nutrients necessary at once creates an undesirable environment.

Unlike in the composting of municipal solid wastes or crop residues, the type and size of the microbial population can be a limiting factor for industrial wastes and sludges (Golueke et al., 1987). Typical microbial counts for soil vary between 10^3 and 10^7 counts per gram of soil. Counts below 10^3 organisms per gram of soil in contaminated zones may indicate toxic conditions. The native soil must be analyzed for the presence of total heterotrophic and hydrocarbon degrading bacteria to determine if it is a suitable source of inoculum (McMillen et al, 1993). If it does not contain enough hydrocarbon degrading bacteria, another inoculum must be selected. A soil may be used as a source of inoculum if it contains at least 0.05 million of bacteria per gram of soil initially. This number should increase to well above 30 million within 10 days of exposure to the contaminant (McMillen et al, 1993).

Successful composting depends on the proper attainment of the essential factors listed above. The process is also dependent on bulking agents and the relative amounts of the waste and bulking agent in the compost pile.

3.3.3 Bulking Agents

The main problem associated with petroleum wastes is that they may not contain enough organic material to sustain composting. In such instances, highly biodegradable solids are mixed to small amounts of the waste (LaGrega et al., 1994). The biodegradable solids serve as a bulking agent and as a thermal source. As bulking agent, they provide void space for passage of air needed to supply the necessary oxygen, improve water holding capacity and improve the soil texture. It is not required that the solids added to as bulking agents be biodegradable. The solids can provide a thermal source since the biological decomposition releases large amounts of energy in the form of heat, which enhances biological activity. Usually, the solids added are a mixture of two different materials since a good bulking agent (wood chips) does not necessarily serve as an adequate thermal source. And on the other hand, a good thermal source (dry molasses) may make a poor bulking agent. The thermal source must not present a preferential carbon source, which prevents the degradation of the waste. Typical organic bulking agents include wood chips, shredded tree waste, straw, sawdust and peat moss. Bulking agents can represent between 20% to 40% of the overall mass of the compost mixture. As with water addition, bulking agents are beneficial but increase the overall mass to be composted.

There are several advantages to using organic bulking agents over inorganic ones such as sand or volcanic ash. Organic bulking agents are readily available, cheap and easy to handle. They decompose during the process removing the need of a separation process upon completion of composting. Organic bulking agents tend to improve the soil

characteristics during the process. Finally, the soil returns to (or close to) its original state having approximately the same volume as initially (Haug, 1993).

However, organic bulking agents are partially degraded during the composting process. Initial increase in oil content may be observed if bulking agent degradation is favoured to oil degradation. The decomposition of the organic bulking agent requires nutrients, air and water and hence there will be a competition for these elements with the contaminant, leading to slower remediation. The high microbial activity resulting from the decomposition of the bulking agent may lead to anaerobic conditions. Finally, straw and hay are very low in nitrogen. During the decomposition of straw, the microorganisms will use up the available nitrogen (Conklin, 1995).

3.3.4 Literature Review on the Composting of Oily Wastes

Although the use of composting for the disposal of oily wastes is a fairly recent concept, it has previously been reported to be successful in treating hydrocarbon wastes in laboratory studies and in the field. Some of the many studies done include the composting of flare pit soils, oily sludges, and various oil contaminated soils. The composting of oily wastes in cold a climate has also proved to be successful.

Holger et al. (1998) completed a study where petroleum based oil wastes were biodegraded through composting. The oil wastes from petroleum stations and petroleum residue from a refinery were mixed with horse manure in amounts varying from 1.8% to 7.1% by weight of dry matter. The mixture was placed in 280 L bins which were aerated and regularly mixed thoroughly. The amount of hydrocarbon in the compost air was evaluated by sucking a known volume of air through an active carbon trap. The carbon was then extracted and analyzed. Up to 78% mineralization was obtained after a four month treatment period with 2.1% by weight petroleum residues concentration.

Concentrations of aliphatic hydrocarbons decreased with time of composting, whereas aromatic hydrocarbons remained or decreased only slightly. Sampling of the compost air revealed that the concentrations of hydrocarbons lost due to aeration represented an overall loss of 0.2% of the oil content.

In a study conducted by Bengtsson et al. (1998), sludges with high oil content were treated by composting in lab scale composters (100 L) and outdoor compost piles (15 000 to 20 000 kg) using peat moss, straw and bark as bulking agents and manure or inorganics for nutrient source. Mixtures for lab experiments contained oil concentrations of 30 to 50 g/kg of dry matter. Depending on the conditions, the hydrocarbon concentrations were reduced by 55 to 90% during a period of 60 to 120 days. Using an activated carbon trap, loss of hydrocarbons due to volatilization was determined to be only 5%. Outdoor compost containing 40 to 80 g of oil per kg of dry matter resulted in 86 to 94% reduction of hydrocarbon in ten months. Prolonged treatment of five more months resulted in 97% decrease.

Milne et al. (1998) composted a heavy oil refinery sludge using various bulking agents. A Total Petroleum Hydrocarbon (TPH) decrease of 55% in five weeks was obtained using Solv II, a peat moss substitute manufactured for bioremediation applications, as the bulking agent. The final product was reported to be suitable for direct land disposal at an industrial site according to the Interim Canadian Environmental Quality Criteria for Contaminated Sites.

Composting for the biodegradation of oily wastes in northerly climates has been shown to provide a number of possible benefits, over previously used methods such as landfarming and landtreatment, including: 1) higher soil temperature which enhances biological activity and can extend the bioremediation period to twelve months of the year; 2) less land is required to treat the similar volumes of soil; and 3) less ongoing

maintenance may be required. The compost mixtures generate their own heat due to microbial breakdown of organic. This heat is somewhat conserved due to the size of the pile. A field study conducted by McMillen et al. (1996) in North Dakota over the winter months revealed that the temperature inside the windrows remained near 23°C even when the ambient temperature dropped to -3°C. The attainment of such temperatures over the winter months resulted in 44% to 72% TPH degradation in 14 weeks.

McMillen et al. (1993) found composting to be an effective biotreatment method for removing hydrocarbons from a crude oil production pit sludge. The composting mixture was composed of 55% sludge by weight, wood chips, manure and soil. The total extractable loss was 92% after 4 weeks of composting. The hydrocarbon distribution in terms of saturates, aromatics, resins and asphaltenes changed significantly with 97% of the saturates and 86% of the aromatics being lost during the process.

Nordrum et al. (1992) biodegraded tank bottom sludges and other oily wastes using composting. Mixing the sludge with 84% wood chips, 15% manure and 1% finished compost from previous operations resulted in a TPH decrease from 60 000 ppm to 20 000 ppm in just two weeks. Most of the compounds remaining were the branched alkanes and some heavier linear alkanes.

Fyock et al (1991) composted petroleum production sludges using a saw mill waste as a bulking agent. The sludge was applied at 20, 30, 40% volume. The best conditions were observed in the pile containing 20% sludge and led to a decrease in compost TPH from 10% to 2.7% by weight during the first ten days of composting then gradually to less than 1% over the next thirty days.

3.3.5 Advantages and Disadvantages of Composting

Non-reactor type composting has several advantages over other biodegradation techniques. The capital and operating costs of on-site composting are low since little equipment and management is necessary. The simple installation and maintenance of a windrow can be brought to a site, removing the need to transport the waste off site. The "low technology" nature of composting is particularly appropriate for use at small and/or remote facilities (Fyock et al., 1991). Composting offers the potential of completely destroying the waste and hence eliminating long term liability. The final state of the composting process is a stable product rich in nutrients and can be directly placed back into the environment or even sold as an organic fertilizer and soil conditioner. The time required to obtain a stable product is much shorter than previously commonly used methods such as landfarming or landtreatment. Less area is required for treatment since the compost is placed in large piles than can reach several meters in height and therefore reduces the costs involved in the protection of the underlying soil.

However, the main problem with non-reactor type composting is that it is still a relatively slow process. This makes composting unsuitable for wastes that are produced in large quantities if the rate of production of the waste exceeds the rate of degradation (Milne et al., 1996). Its applicability is also limited in cold climates since the microorganisms work best in a warm environment. The degradation will produce heat, but the air entering the windrow during aeration will lower the temperature within the pile and lead to lower degradation rates. Petroleum wastes need to be mixed with bulking agents, nutrients and water, making a large overall volume to compost and increasing the amount of space required. The need to amend the mass to be composted can cause a problem if composting is to be used in remote areas where bulking agents such as wood chips are not readily available. Bringing the amendments to the remote site may not be practical and may increase the cost of the remediation process.

3.4 DICYCLOPENTADIENE

Dicyclopentadiene (DCPD) represents the largest fraction of the quench sludge hydrocarbon phase. Its presence is primarily problematic due to its smell. Although a lethal dose value for DCPD is not available, recent investigation on its toxicity indicates that acute effects are minimal.

Dicyclopentadiene is a dimer of cyclopentadiene and is produced as a pyrolysis by-product in the production of hydrocarbon feed stocks in petrochemical plants. In such plants, the normal source of DCPD contamination is pyrolysis gas, a co-product of petrochemical monomer production. Only 5% to 13% DCPD is usually found in this stream, but due to the compound's ability to stimulate olfactory sensors, human perception of its presence is often as a greater percentage (Stehmeier, 1997). The threshold level for detection by the human nose is 5.7 ppb. Due to its pervasive odour, DCPD is placed in odour safety class A, meaning that more than 90% of distracted persons will perceive the threshold limit value in air.

3.4.1 Properties of Dicyclopentadiene

DCPD exists in 2 stereo-isomeric forms, the endo- and the exo-isomers. The endo-isomer is the most prevalent form and is formed at temperatures below 150°C by Diels Alder condensation. Figure 3.3 shows the structure of the isomer and table 3.2, its chemical and physical characteristics.

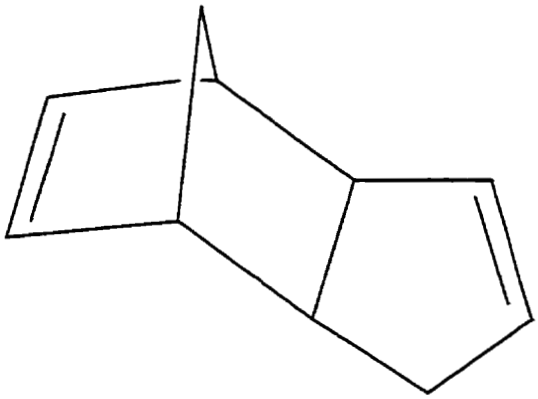


Figure 3.3: Structure of the Endo-isomer (compound I)

Table 3.2: Chemical and Physical Characteristics of Dicyclopentadiene

Property	Value
Physical State (20°C, 1 atm)	Colorless crystals
Molecular Weight	132.21
Boiling Point (°C)	170
Melting Point (°C)	33.6
Density (g/mL, 35°C)	0.98
Water Solubility (mg/mL, 25°C)	0.019
Log K_{oc} (organic carbon partition coefficient)	2.99
Vapour Pressure (mmHg, 20-25 °C)	1.7

The material safety data sheets suggest that DCPD is an irritant, primarily due to the exposure to vapours. Inhalation of vapours close to saturation may cause irritability, loss of appetite, nausea, vomiting, headache, weakness, sleeplessness or damage to liver, lungs or kidney. Chronic exposure may increase the acute effects.

The industrial use of DCPD has increased in the past 20 years to over 70,000,000 kg per year. Yet, little research has been done on the fate of DCPD in the environment. The adsorption coefficient of DCPD indicates that it will tend to sorb to soil more than other alicyclic compounds. The logarithmic of the organic carbon partition coefficient of

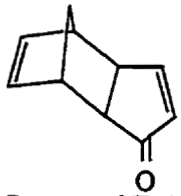
DCPD is 2.99. As a comparison, the logarithmic of the organic carbon partition coefficient of benzene is 1.9 meaning its tendency to adsorb to the soil will be lower than that of DCPD by a factor of 12.

3.4.2 Mineralization of Dicyclopentadiene

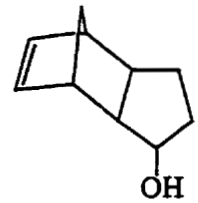
Stehmeier (1997) conducted many experiments to monitor the mineralization of DCPD to carbon dioxide using radiolabeled DCPD. The fraction of total radioactivity recovered as carbon dioxide was found to increase with time in all experiments. Equation (3-1) shows the theoretical balanced equation for the complete conversion of DCPD. According to the equation, the complete conversion of DCPD to CO_2 and H_2O, requires 1.3 moles of O_2 per mole of CO_2 produced.

$$C_{10}H_{12} + 13O_2 \rightarrow 10CO_2 + 6H_2O \qquad (3\text{-}1)$$

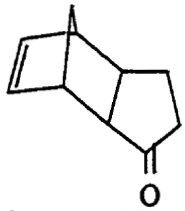
However, Stehmeier's experiments indicated that on average 19 moles of O_2 were required for every mole of CO_2 produced. The large excess in oxygen consumed suggests that oxygenated derivatives are formed in the initial process of DCPD degradation. Figure 3.4 lists the possible oxygenated derivatives. Comparing the experimental and theoretical values, it could be derived that when 1% of DCPD is converted to CO_2 approximately 25% is converted into mono-oxygenated DCPD derivatives. Although he found this ratio to vary, he could still conclude that a culture in which 5% of the DCPD has been converted to CO_2, very little DCPD is likely to remain and most of the remaining 95% will be present as oxygenated derivatives. The data suggests that DCPD is readily transformed but not mineralized. However, the intensity of the odour is known to be a function of the molecular structure of DCPD and bioxidation may be successful at removing the odour since it transforms the structure.



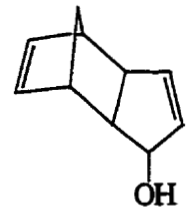
Compound II, 146 amu, $C_{10}H_{10}O$
endo-tricyclo[5.2.1.$0^{2,6}$]deca-4,8-diene-3-one



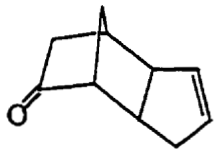
Compound III, 150 amu, $C_{10}H_{14}O$
endo-tricyclo[5.2.1.$0^{2,6}$]deca-8en-3-ol



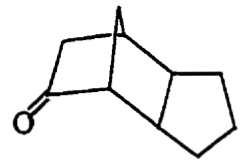
Compound IV, 148 amu, $C_{10}H_{12}O$
endo-tricyclo[5.2.1.$0^{2,6}$]deca-8-en-3-one



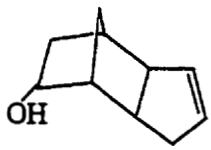
Compound V, 148 amu, $C_{10}H_{12}O$
endo-tricyclo[5.2.1.$0^{2,6}$]deca-4,8-dien-3-ol



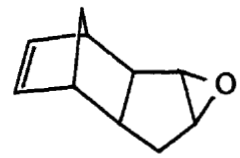
Compound VI, 148 amu, $C_{10}H_{12}O$
8-ketotriyclo[5.2.1.$0^{2,6}$]-4-decene



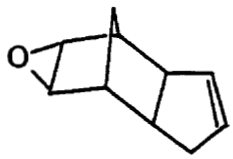
Compound VII, 150 amu, $C_{10}H_{14}O$
8-ketotriyclo[5.2.1.$0^{2,6}$]decane



Compound VIII, 150 amu, $C_{10}H_{14}O$
8-hydroxytricyclo[5.2.1.$0^{2,6}$]-4-decene



Compound IX, 148 amu, $C_{10}H_{12}O$
endo-4-oxatetracyclo[6.2.1.$0^{2,7}0^{3,5}$]dec-9-ene



Compound X, 148 amu, $C_{10}H_{12}O$
endo-9-oxatetracyclo[5.3.1.$0^{2,7}0^{8,10}$]dec-9-ene

amu: atomic mass unit

Figure 3.4: Structure of Oxygenated Derivatives of DCPD

A study of the oxygenated derivatives allowed Stehmeier to make the following proposal for the initial steps in DCPD degradation.

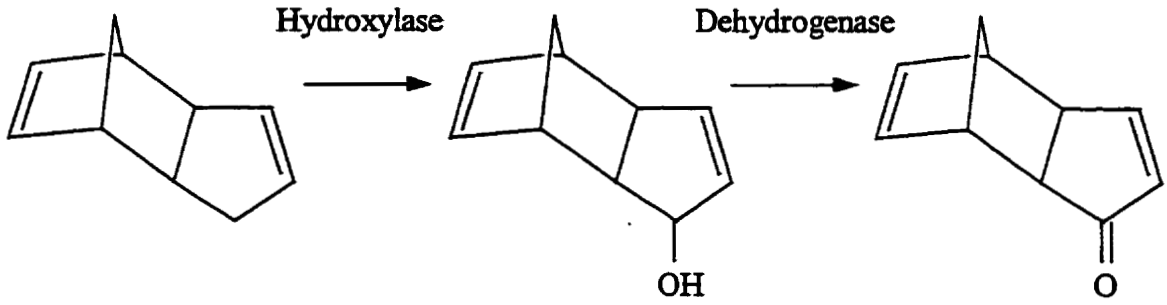


Figure 3.5: Proposed Initial Steps of DCPD Degradation

3.4.3 Biodegradation Potential of Dicyclopentadiene

The structure of DCPD indicates that mineralization may be difficult. The half life of DCPD in soil has been estimated to be 35 days (Stehmeier, 1997). Stehmeier attempted to single out strains of microorganisms capable of rapidly degrading DCPD without success. However, an active microbial population was sustained even when DCPD became the predominant substrate. Members of the DCPD degrading community include *Pseudomonas* specie and a *Sphingomonas* specie. He found that biodegradation rates could be increased by pre-exposure to DCPD.

Ideally, the goal of bioremediation is to convert the organic waste to CO_2 and H_2O. Mineralization is occurring, but at a slower rate than other organic wastes. The fact that DCPD is mostly transformed to oxygenated derivatives does not mean that bioremediation techniques cannot be applied. If bioremediation can remove the odor

associated with DCPD, one of the objectives has been met. However, little is known about the derivatives which may even be more toxic than the initial compound.

A review of case studies of in-situ bioremediation of DCPD compound in the soil shows that the loss of DCPD over time can be significant (Stehmeier, 1997). It was suggested that a site contaminated with 100 mg of DCPD per kg would take less than 2 years to remediate when the soil was placed in a soil pile. Nutrients appeared to increase the degradation rates in such a case. In a different study reviewed by Stehmeier (1997), DCPD was not the predominant hydrocarbon source and was only available in small quantities. In this case, it was found that the amount of DCPD present in the soil did not decrease substantially, possibly due to substrate preference. The low concentrations of DCPD can also be inhibitory because of the inaccessibility due to soil adsorption.

CHAPTER FOUR: MATERIALS AND METHODS

The use of composting for the biodegradation of the quench sludge was investigated using bench scale bioreactors. The composition of the compost mass was varied to study the effects of various parameters. The composters were designed and built to allow all aspects of the process to be monitored throughout the experiments. All streams and components entering the system were controlled to study the effects each factor has on the process.

4.1 EXPERIMENTAL APPARATUS

Bench scale composting was carried out in the laboratory in six bioreactors. The composting bioreactors were enclosed in an environmentally controlled chamber which was maintained at a fixed temperature using a conventional in-car heater and a controller panel. The Plexiglass chamber was 1.5 m long, 1 m wide and 1.5 m high, and was lined with a 3 cm layer of Styrofoam for insulation. Figure 4.1 shows the composters in the environmental chamber.

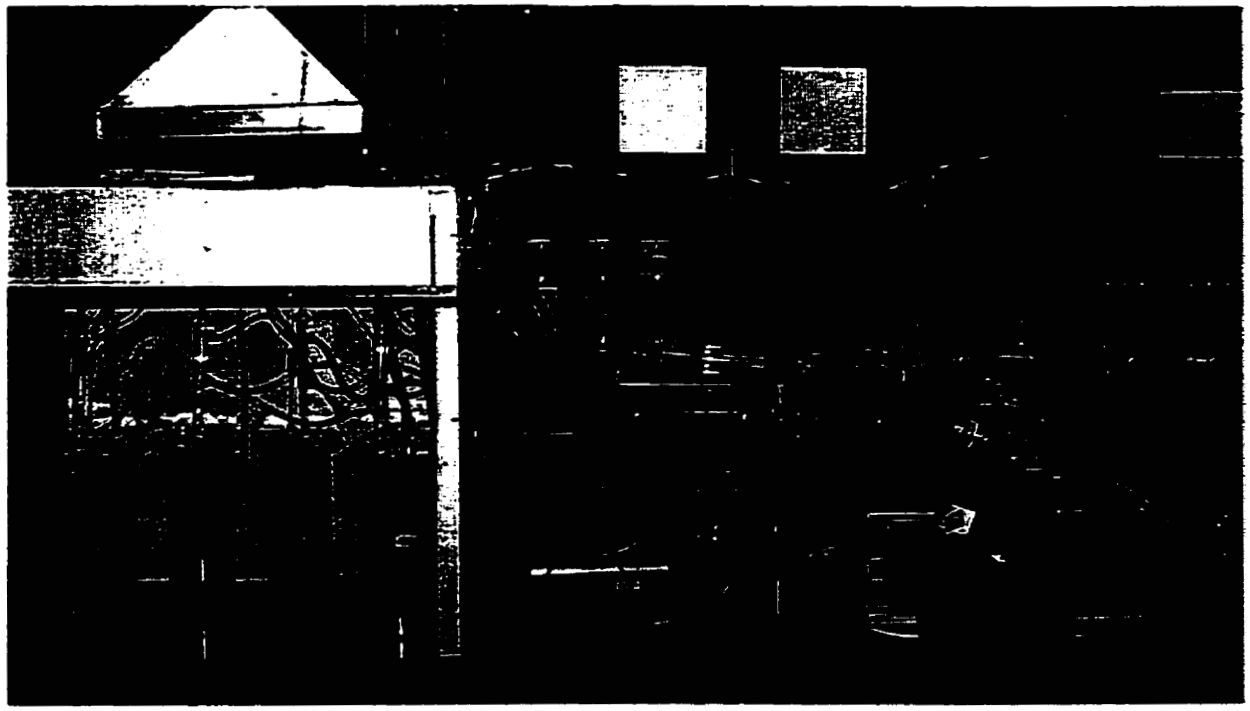


Figure 4.1: Composters in the Environmental Chamber

Each composter was made of a 11.5 cm in outer diameter Plexiglass cylinder having a total height of 30 cm and a wall thickness of 6 mm. The cylinder was sealed at the bottom and was closed at the top using a plexiglass plate. An aeration port was placed 1 cm from the bottom of the composter on the wall of the cylinder. The top plate had two openings, one through which a mini K type thermocouple (All Temp Sensors) was inserted 19 cm into the mass, and an exhaust air port. A Plexiglass plate was placed 3.5 cm above the base of the composter to support the composting mass and allow proper air distribution at the bottom of the composting mass. The support plate had 64, 6 mm holes and was covered my a thin aluminum mesh to prevent any of the composting mass from falling through. The schematic representation of each composter is shown in figure 4.2 while figure 4.3 shows an actual composter in the chamber.

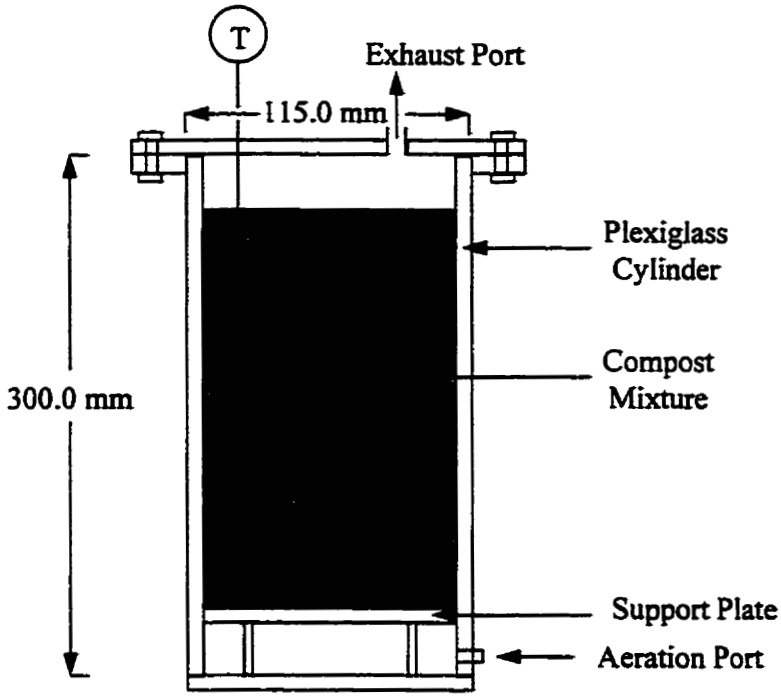


Figure 4.2: Schematic Representation of a Composter

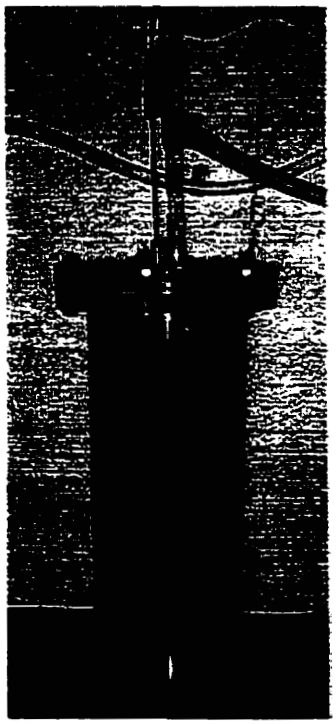


Figure 4.3: Actual Composter in Chamber

Air from a cylinder at atmospheric pressure was sent to a humidifier made of a Plexiglass cylinder, 10.7 mm in diameter and 36.5 mm high, filled with water. The air was forced to the bottom of the water using a bubbler. A scale was engraved on the cylinder to calculate the drop in the water level over the full experiment. The air stream entered a manifold which divided the flow equally to each composter. The air entered the composter, traveled upwards through the composting mass and out the exhaust port. The outlet gas stream was then passed through a small Kimax West condenser (190 mm) at 15°C to reduce loss of volatile hydrocarbons and moisture. The gas was directed through a 20 cm long and 3 mm diameter plastic tube containing indicating drierite (8 mesh size, BDH) to remove all water from the stream for GC analysis of the gas. The air passed through a nylon tee connector closed with a natural rubber septum. The septum was placed to allow gas samples to be drawn for Gas Chromatograph analysis. The gas was then sent through a 15 cm long tube (3 mm diameter) filled with Indicating Ascerite II (20-30 mesh size, Thomas) to absorb the carbon dioxide present in the stream. The tubes filled with drierite and ascerite were closed with a plastic cap lined with an O-ring on one side to be able to replace the materials during the process as needed. A 65 mm direct reading flowmeter with valve, for air flow rates of up to 7 mL/min (Cole Parmer), was placed at the end of each exhaust line to control the air flow rate through each composter. Finally, the gas stream was directed to a fume hood. Figure 4.4 shows a schematic flow diagram for the composting apparatus.

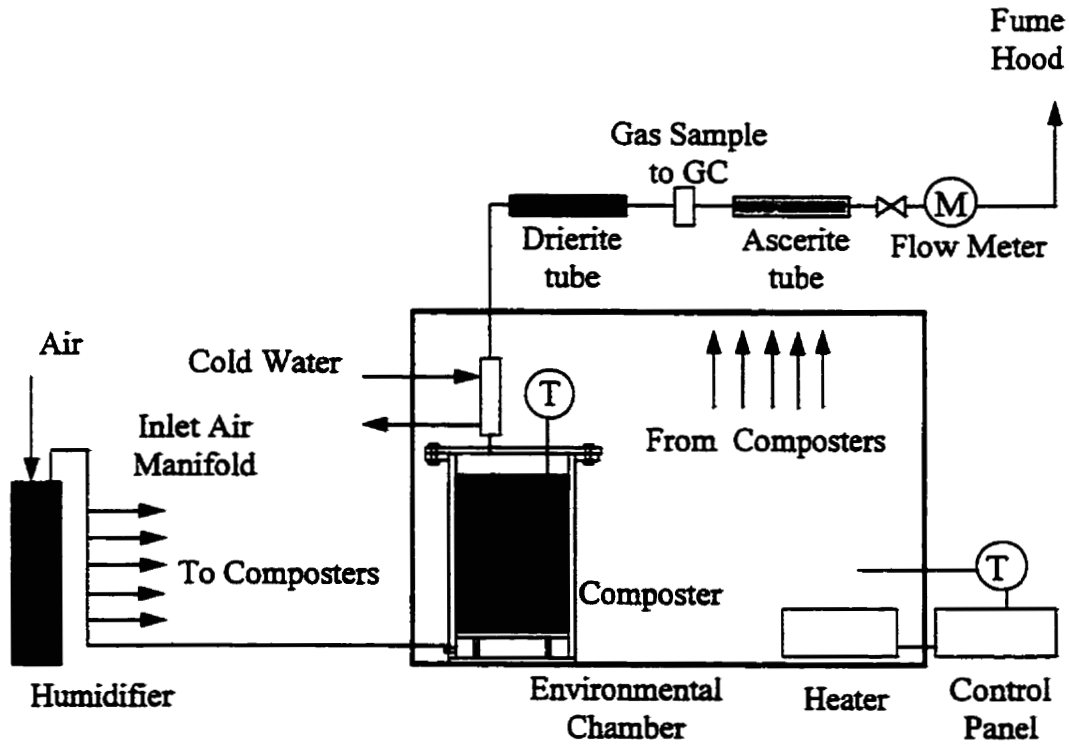


Figure 4.4: Schematic Flow Diagram of the Composting Apparatus

4.2 INGREDIENTS

The compost ingredients were altered to study what mixture composition would lead to the highest biological activity and degradation rates. The amendments significantly increase the mass of waste to be treated. The amount of sludge mixed with the bulking agents was therefore also varied to find a composition which would limit the mass to be composted while achieving high degradation rates. Table 4.1 lists the ingredients used for the compost preparation.

Table 4.1: List of Ingredients Used in Compost Preparation

Bulking agent	Nutrient	Others
Wood Chips	Urea	Soil
Straw	Triple Superphosphate	Sodium Azide
Peat Moss		
Sphag Sorb		
Solv II		

4.2.1 Bulking agents

Various organic bulking agents were investigated such as straw, peat moss, wood chips, Sphag Sorb, and Solv II. Straw, wood chips and peat moss are readily available and were purchased from Sunnyside garden stores. The other bulking agents are manufactured commercially and distributed in Canada for use in bioremediation and clean-up of contaminant spills. Peat moss, straw and wood chips offer the advantage of being cheap and readily available.

A heat treated peat moss, Sphag Sorb was purchased from Patron Equipment in Calgary. Sphag Sorb is an all natural product manufactured from sphagnum peat moss,

originating in the bogs of Canada. It outperforms all other types of absorbent materials. It is used to clean up major toxic chemical spills on water, oil in wetlands. The key to Sphag Sorb's effectiveness is the natural capillary and porous structure of the activated peat. It allows for rapid absorption of hydrocarbons, PCBs and solvents. The contaminant is then encapsulated in the peat. In bioremediation applications, it is not desirable to have the contaminant trapped in the matrix of a material as it is no longer accessible to the microorganisms. Sphag Sorb was used to increase the void space and the water holding capacity of the composting mixture, not simply to absorb the contaminant. Hence, the water necessary for the composting process was first added to the Sphag Sorb. This resulted in a wet matrix which no longer absorbed the contaminant into its matrix.

Solv II is a peat moss substitute produced by Control Inc. (Des Moines, IA), obtained from Pro Flow located in Medicine Hat. It is a complete product with dry microbes, nutrients, and absorbent that allows a one-time product application. This product is an advanced biotechnology material that has demonstrated the ability to degrade a broad spectrum of hydrocarbon compounds, crude oil, PCB's, and chlorinated solvents. Solv II provides an infusion of contaminant degrading organisms, rapid and slow release of nutrients, enhances the moisture-holding capability and aeration of the contaminated soil, and adsorbs and holds approximately four times its weight in hydrocarbons. It requires no additional ingredients other then water and the waste to be degraded.

Inorganic bulking agents such as ash or tire chips were not used since these would not likely be practical for a large scale composting facility. Inorganic bulking agents are not as readily available and require a separation process at the end of the operation. Finally, complications would arise during hydrocarbon extraction with dichloromethane if plastic parts were used as a bulking agents.

4.2.2 Fertilizers

Various sources of nutrients were considered for this study. Most fertilizers contain microorganisms and a source of organic matter. The addition of microorganisms and a carbon source was not desirable since a material balance around the bioreactor was to be made. Although the bacteria found in a fertilizer are unlikely to be hydrocarbon degrading, they will be able to use the organic matter in the fertilizer as a energy source. This additional bacterial activity may increase the amount of carbon dioxide produced from the composter and use water and nutrients.

It was recommended by a fertilizer manufacturer to use urea for a nitrogen source and Triple Superphosphate (TSP) for phosphorous, to avoid the addition of any undesirable organic matter and bacteria. However, the addition of organic matter from fertilizers was not found to be of great concern since organic bulking agents were used.

4.2.3 Hydrocarbon Content

Sludge samples were obtained from the Joffre ethylene cracking plant. It was necessary to determine the optimal amount of sludge that could be mixed into the compost mixture. A small ratio of sludge to overall mixture is known to give high degradation rates but is not desirable due to the large increase in the waste to be treated. Too much sludge however, can lead to a toxic environment for the microorganisms and lead to low degradation rates. Previous studies have shown that the maximum microbial activity occurs in a soil containing 5% to 6% hydrocarbons per dry weight (Atlas, 1984). Increasing the amount of hydrocarbon in the soil above this quantity tends to overload the system and prevent microbial growth. The hydrocarbon content was varied from 1.5% to 14% by weight of the dry matter once the most suitable using bulking agent was established.

4.2.4 Inoculation

Inoculation is the addition of microorganisms into an environment to ensure that enough are present for biodegradation to take place. The purpose of inoculation may also be to increase the degradation rates of biodegradable compounds that tend to persist in the soil environment. Such inoculation is usually called bioaugmentation. In circumstances in which the period for destruction of the chemicals is not important, it is likely that inoculation is not warranted because the initially small population will multiply to destroy the unwanted chemical (Alexander, 1994).

In this study, topsoil from the landfarm at the Nova Chemicals facility in Corunna, Ontario which treats various waste streams from the processing of hydrocarbons, was used as an inoculum. In Ontario, the ethylene is not produced from natural gas as in the Joffre plant. Ethylene is obtained by cracking oil and hence results in a richer and more complex waste material than the quench sludge. The materials placed on the soil include hydrocarbon contaminated water and tank bottom sludges. Hence a variety of hydrocarbons are present in the soil which should contain microbial populations capable of degrading the quench sludge. A source of inoculum was necessary since the sludge coming directly out of the plant did not likely contain oil degrading bacteria for biodegradation to take place in the composters. Although the soil was found to contain a large enough population of hydrocarbon degrading bacteria (0.5 million per gram of soil), it was incubated for a month in an Bushnell-Hass medium at mesophilic temperatures and in the dark with continuous aeration. At the end of the incubation, the medium was centrifuged to separate the bacteria from the nutrients. The microorganisms were then mixed with distilled water and added to composters. Incubation was used to reduce the lag period associated with the adjustment of the microorganisms to the new environment and to ensure that the size of the microbial population was not a limiting factor.

4.2.5 Control Composters

To study the losses of hydrocarbons in the composters due to effects other than degradation, some control composters were poisoned with sodium azide. Inoculum water was not added to the control composters to reduce the addition of bacteria. Sodium azide was mixed to the distilled water used to wet the bulking agent at a concentration of 10 g/L. The control composters were connected to the air line and mixed once a week like the active composters. To study the losses due to the mixing alone, a control composter was not connected to the air supply and only mixed once a week.

4.3 PREPARATION OF THE COMPOST MIXTURE

The bioreactors were designed to hold approximately 650 g (2.8 L) of compost mixture. For the biodegradation of hydrocarbons, it is recommended to maintain a moisture content of 60% (Cookson, 1995). The moisture content of each bulking agent and of the sludge were determined. The sludge was found to have a 53% moisture content and the bulking agents varied from 6% for the wood chips to 34.5% for Solv II. The following describes the steps that were taken to prepare the mixture using peat moss as the bulking agent containing 5% hydrocarbon per dry weight (approximately 33 g of sludge).

To obtain the desired 60% moisture in the mixture, the water contained in the peat moss was considered. The water contained in the small amount of sludge was ignored for simplicity. Drying the peat moss indicated that it contained 19% moisture. It was calculated that 329 g of distilled water were needed in combination with 321 g of peat moss to obtain the desired moisture content.

The solids content of the sludge was determined to be 8% and the ash content was less than 0.1%. Since another 53% of the sludge is water, the hydrocarbons only represent approximately 39% (or 13 g of the 650 g mixture). The mass of available hydrocarbons in the sludge was used to determine the amount of nutrients required. It was assumed that all hydrocarbons present were bioavailable. Using a carbon to nitrogen to phosphorous mass ratio of 100:3.3:1, it was calculated that 0.43 g and 0.13 g of nitrogen and phosphorous respectively were needed. 0.28 g of Triple Superphosphate (TSP) which contains only phosphorous in the form of phosphoric acid (46%), were added to obtain the 0.13 g of phosphorous needed. 0.81 g of urea was used as the nitrogen source. The amount of inoculum water was accounted for when measuring the distilled water to be added to the bulking agents.

Once all measurements were made, the nutrients were dissolved in 329 g of the mixture of distilled and inoculum water. The water was then mixed with 321 g of peat moss until a homogeneously wet mixture was obtained. 30 g of the inoculum soil was also added to the mixture. The sludge was then poured and mixed into the wet peat mixture using a large spoon. Previous work has shown that when the sludge is mixed to the dry bulking agent, the oil become trapped in the bulking agent particles and hence will be less available to the microorganisms (Milne et al., 1996). Therefore, it is best to first mix the water with the bulking agent prior to the sludge addition.

4.4 OPERATION

The prepared compost mixture was then transferred to the composter. The mixture was placed into the composter in small amounts using a large spoon without any compacting. The weight of the composter with and without the composting mass was measured and a 20 g sample was kept for analysis. All inlet and outlet streams were

connected and the process was operated for one to two months. The air flow rate was kept constant at 2.5 mL/min. Several parameters were recorded every second day. These include the temperature in the composters and in the chamber, the amount of carbon dioxide, oxygen and methane in the output gas stream as determined by Gas Chromatograph analysis, the air flow rate, and the weight of the drierite and ascerite tubes. Once a week, for up to seven weeks, the composters were opened so that the compost could be mixed and to take a 20 g sample for analysis. To mix the compost mixture, the content of each composter was emptied into a pale and mixed using a large spoon. The mixture was then placed back into the composter as done initially and the new weight was noted. The sample was used to determine the moisture content of the mixture, for extraction to determine the amount of hydrocarbons remaining in the composters and for bacteria enumeration. Additional water was added as deemed necessary from the moisture content or by the change in weight of the drierite tubes. At the end of the process, the drop in the water level of the humidifier was recorded and the composters were weighed to determine the final compost mass.

4.5 ANALYTICAL WORK

The primary objective of this study was to determine the ability of the microbes to degrade dicyclopentadiene. However, it was also necessary to evaluate the Total Extractable Hydrocarbon (TEH) throughout the composting process. The rate and mass of carbon dioxide evolved during the process can also quantify the amount of degradation that is taking place. However, carbon dioxide evolution does not represent the amount of hydrocarbon degradation alone. The degradation of the bulking agent itself increases the amount of carbon dioxide in the output gas stream. The composition of the exhaust gas was analyzed for carbon dioxide, oxygen and methane content. The other parameters monitored during the process include the moisture content and the microbial activity.

4.5.1 Hydrocarbon Content and Dicyclopentadiene Reduction

The Total Petroleum Hydrocarbon (TPH) or Total Extractable Hydrocarbon (TEH) content are the most widely used to quantify the amount of biodegradation that has occurred. TEH represents all hydrocarbons that are extractable using dichloromethane and analyzed using Gas Chromatography (GC). When the recovered oil from the dichloromethane extraction is cleaned using silica gel prior to GC analysis, the term TPH is used. Silica gel is used to remove polars not associated with hydrocarbons. Extractions of the pure bulking agents were conducted to see whether clean up of the extract using silica gel was necessary. A small residue was extracted from bulking agents such as peat moss and Solv II but when analyzed by GC, no peaks were observed. It was therefore concluded that silica gel clean up was not necessary since the presence of polars does not affect TEH values.

Two methods were investigated to analyze the compost samples for TEH and DCPD content. Since the sludge contained light hydrocarbons, it was initially decided to extract the compost sample directly with dichloromethane in a sealed jar to minimize losses. The results were then compared to values obtained using a Soxhlet extraction apparatus.

In the direct extraction method, the prepared compost sample was mixed with a solvent, dichloromethane, in a sealed jar. A 3 g compost sample was mixed with 6 g of sodium sulfate anhydrous in a sealed jar to remove the moisture. The mixture was kept aside for 24 hours to insure all moisture was removed. 25 mL of solvent was then added to the dried sample. The mixture was agitated vigorously and was left to stand for 48 hours in a refrigerator with occasional mixing. The contents were then poured into an autovial syringeless filter (Whatman) with 2 μm pores to separate the extract from solid particles.

For the Soxhlet extraction, a 10 to 15 g compost sample was first prepared for extraction. An equal weight of sodium sulfate anhydrous was mixed to the sample to remove the moisture. The mixture was kept aside until dry (24 hours), and then placed in a 33 x 80 mm Whatman single thickness cellulose extraction thimble of known weight. 250 mL of dichloromethane in a 500 mL round bottom flask was used for the extraction. Dichloromethane was used as the solvent because of its low boiling point of 36°C decreases the loss of the lighter hydrocarbons. The extraction ran for 16 hours. The 500 mL round bottom flask containing the diluted extract was evaporated in a Buchi 461 rotary evaporator to recover the solvent. The weight of the flask and solvent-free extract was noted. The extract was then redissolved in 5 mL of solvent for Gas Chromatograph analysis. The weight of oil recovered was converted to a weight of oil per gram of compost extracted. The oil residue obtained from dichloromethane extraction without any silica gel clean up is called the oil and grease fraction. The percent decrease in oil and grease can be evaluated over time by comparing the oil per gram ratio over time as shown in equation (4-1).

$$\%\text{Oil reduction} = \frac{\text{oil}/g_{(\text{initial})} - \text{oil}/g_{(\text{end})}}{\text{oil}/g_{(\text{initial})}} \times 100 \qquad (4\text{-}1)$$

The extracts obtained from both methods were analyzed using a Hewlett Packard 6890 Series Gas Chromatograph equipped with a Flame Ionization Detector (FID). A 30 m HP-1 capillary column (crosslinked methyl siloxane) from Hewlett Packard was used, and the FID output was connected to a GC ChemStation software package. Using the HP automatic liquid sampler, 1 μL samples were injected into the GC. The oven temperature was maintained at 35°C for 5 minutes, ramped at a rate of 30°C per minute to 75°C where it was held for one minute. The oven was then ramped again at the at a slow rate of 5°C per minute to a final temperature of 220°C and held for 15 more minutes. The injector and detector port temperatures were set at 220°C and 325°C respectively. The injector

temperature could not be set to a higher temperature since it was found that dicyclopentadiene starts to dissociate near 200°C. The helium gas flow rate was set to 30 mL/min. Only 2 mL/min of Helium was used as carrier gas, the excess was needed to make up the flow required by the detector. Hydrogen gas flowing at 30 mL/min and air at 400 mL/min were used as fuel and oxygen supply for the FID.

USEPA method 418.1 for hydrocarbon content analysis measures the infrared absorption of the extract from the soil sample. Other EPA analytical methods such as DHS 8015-modified pass the extract from the soil sample through a Gas Chromatograph and use a FID to measure contaminants according to retention time of the constituents. In a composting study conducted by Milne et al. (1996), the extract was analyzed using Fourier Transform Infrared Spectroscopy (FTIR). Relative decrease was estimated by comparison of absorbency at different times of the process. The extracts were then sent away for GC-FID analysis for comparison. The GC method calculated the total integrated area under the curve ignoring the solvent area. The areas were compared to evaluate the TPH decrease over time. Both the FTIR and GC-FID method produced similar results.

Hence, it was concluded that comparison of total integrated area over time could also indicate the relative decrease in TEH as shown in equation (4-2).

$$\%\text{TEH reduction} = \frac{\text{Area}/g_{\text{initial}} - \text{Area}/g_{\text{final}}}{\text{Area}/g_{\text{initial}}} \times 100 \qquad (4\text{-}2)$$

Because the response factor of dicyclopentadiene was not equal to one, the initial and final areas used in equation (4-2) were calculated using equation (4-3). The response factor of DCPD was found to be 1.8. It was required to adjust the total areas using the reference factor since DCPD represents such a large fraction of the hydrocarbon phase.

$$\text{Area} = \text{Area}_{DCPD} \times RF_{DCPD} + (\text{Area}_{total} - \text{Area}_{DCPD}) \qquad (4\text{-}3)$$

Diluted samples of the sludge were used as standards for the quantification of TEH in the compost extracts. Calibration curves were produced by plotting the areas of each diluted sample against concentration. The linear relationship obtained is shown in figure 4.5. An external calibration was also made for dicyclopentadiene. The calibrations allowed the integrated areas to be converted to concentrations.

4.5.1.1 Comparison of Extraction Procedures

The results from the direct and Soxhlet extraction methods were found to be significantly different and hence the Soxhlet extraction procedure was used for further experiments. Direct extraction resulted in much higher TEH reduction and was found to vary even when duplicate analyses were done. This variance is likely due to the high dilution of the oil that results from the direct extraction method. Figure 4.6 shows the difference obtained for TEH reduction at the end of an experiment from both extraction procedures.

The differences observed can be attributed to several factors. The percent decrease in TEH was found to be much larger using the direct extraction procedure. This is in part due to the fact that the light ends are lost during the Soxhlet extraction. Hence, the direct method shows the amount of all hydrocarbons while the Soxhlet extraction only the fraction that is still present at 35°C.

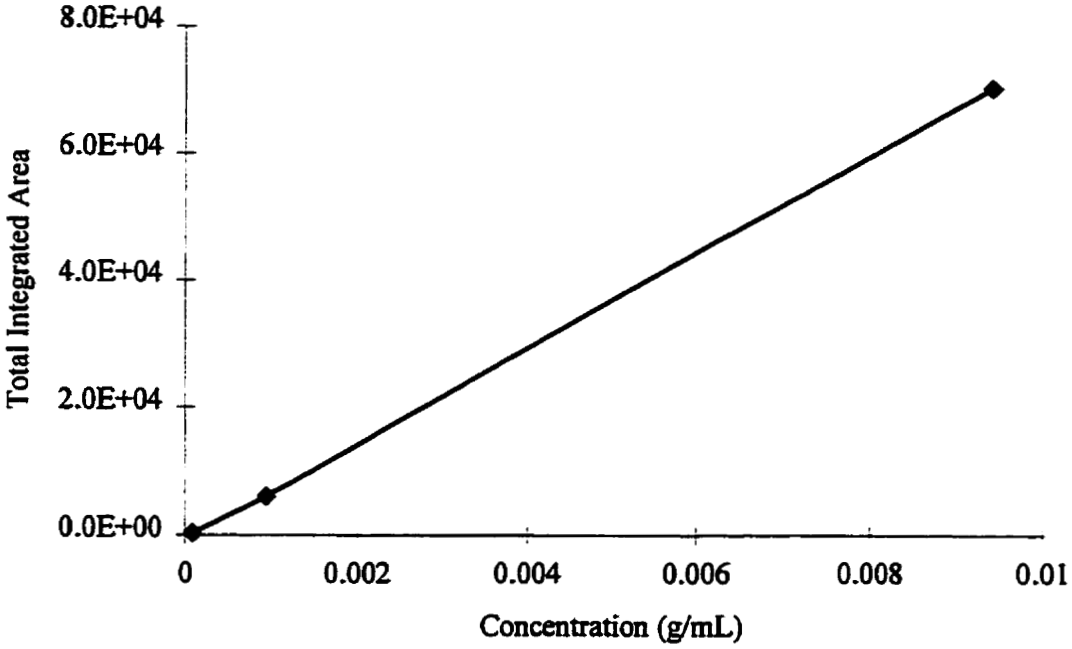


Figure 4.5: TEH Calibration Plot

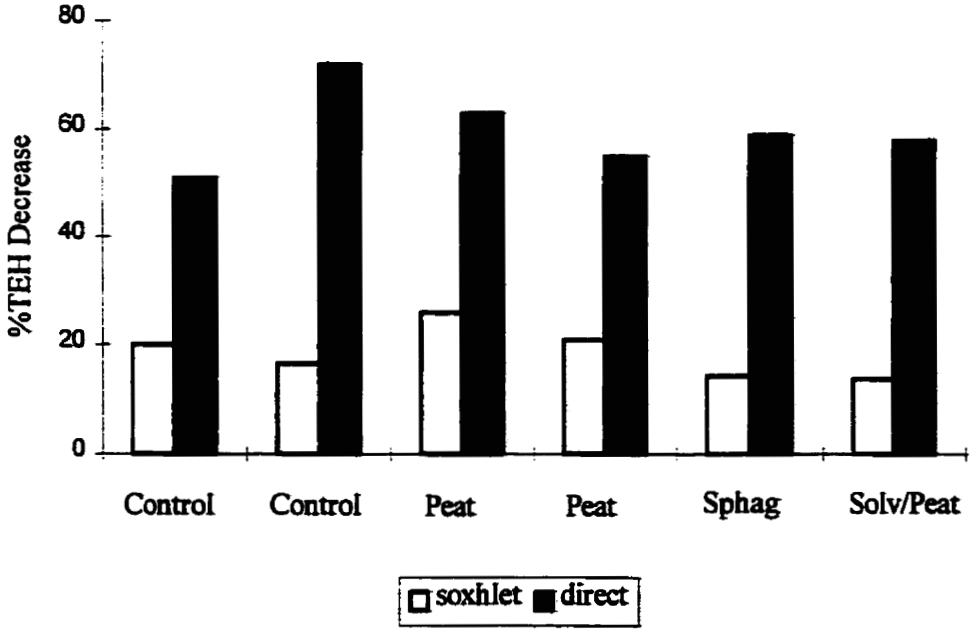


Figure 4.6: Comparison of Percent Decrease of TEH at the End of an Experiment Using the Direct and Soxhlet Extraction Procedures

The direct extraction method results in a very dilute extract and the hydrocarbon peaks were found to become too small for detection when lower sludge contents were investigated. The spectrum obtained from the diluted extracts containing low hydrocarbon content were no longer similar to the TEH calibration spectrum. The total area of the dilute extract was not representative of the sludge. This poor peak resolution was the main reason for switching to the Soxhlet extraction procedure. The sample taken for extraction is much smaller than for the Soxhlet extraction method which can result in more random error since the composting mixture cannot be perfectly mixed. All these factors resulted in numbers that fluctuated when duplicate samples were taken. Three samples from the same compost mixture were extracted using the Soxhlet apparatus. The oil per gram and total integrated area values varied at the most by 8% from the average values.

The Soxhlet extraction is a proven method and does not rely on equilibrium since clean solvent is recycled to the thimble every cycle. The direct extraction method, however, relies on an equilibrium and may therefore not represent accurately the decrease in the heavier hydrocarbons once the lighter components have been degraded.

4.5.2 Identification of Compounds in the Sludge

A sample of the quench sludge was placed in a separatory funnel to allow separation between the water and the hydrocarbons. The water was then drained and a known weight of the hydrocarbon phase was placed in a vial. A known weight of sodium sulfate anhydrous was added to the sludge to remove traces of water which may not have been separated. 25 mL of dichloromethane was added to the mixture for dilution. The sample was then placed in an autovial syringeless filter (Whatman) with 2 μm pores to remove the sodium sulfate and all other solid constituent.

The extract was then analyzed using a Hewlett Packard Gas Chromatograph 5890 series connected to a HP Mass Spectrometer 5970 series to identify the components. The output from the Mass Spectrometer was sent to a MS ChemStation software package. A 50m x 0.2 mm x 0.5 μm (film thickness) HP PONA column with crosslinked methyl silicone gum was used. Helium flowing at 0.5 mL/min was used as the carrier gas and the split flow was set at 30, equivalent to a split ratio of 62. The GC oven was maintained at 35°C for 10 minutes and was ramped at 15°C per minute to a final temperature of 220°C where it was held for 30 minutes. The injector and detector temperatures were 220°C and 250°C respectively.

A sludge sample was also sent to Maxxam Analytics Inc. for analysis. A PONAOX(U) analysis was completed for compound identification. Only compounds present in their data bank could be identified. An Iatroscan analysis was also done to determine the relative amounts of various hydrocarbon groups such as the saturates, aromatics and polars.

4.5.3 Carbon Dioxide Evolution and Output Gas Composition

The amount of microbial activity was monitored from the amount of carbon dioxide evolved during the process. Two methods were used to keep track of the evolved carbon dioxide. The output gas from each composter was directed through a tube filled with Indicating Ascerite II (Thomas) which adsorbs the carbon dioxide in the stream. The weight of the tube at various time intervals during the process was recorded. Knowing the density of carbon dioxide at room temperature, the weight of carbon dioxide absorbed could be converted to a flow rate as shown in equation (4-4). The overall change in mass of the ascerite tube during the process gave the total amount of carbon dioxide produced. This value was then used to complete mass balances around each composter. To use of equation (4-4), it is assumed that all carbon dioxide present in the

exhaust gas is adsorbed by the ascerite. Analysis of a gas leaving the ascerite tube revealed that carbon dioxide adsorption by ascerite was approximately 98.5%.

$$F_{CO_2} = \frac{\text{mass of } CO_2}{\text{density of } CO_2 \times \text{elapsed time}} \qquad (4\text{-}4)$$

The other method used to analyze the amount of carbon dioxide produced during the process involved the use of a Gas Chromatograph. The gas was analyzed using a Hewlett Packard Series 5890 equipped with a thermal conductivity detector (TCD). The TCD output was sent to a Hewlett Packard 3396A Integrator. A Carboxen 1000 (Supelco Canada), 15 ft packed column was used since it can analyze a wide range of gases such as carbon dioxide, oxygen, nitrogen, methane and ethane. Hence, while checking for the carbon dioxide content in the output stream, the amount of oxygen could also be obtained. The amount of oxygen in the stream served as an indicator to ensure that aerobic conditions were maintained in the composters. Methane content could also indicate if anaerobic conditions developed, and the amount evolved was used for carbon mass balances.

The program for the analysis was set using the recommendations made by Supelco. The oven temperature was kept at 30°C for 7 minutes, then increased to 225°C at a ramping rate of 45°C per minute. Once the final temperature was reached, it was maintained for 11 minutes. Helium was the carrier gas and was set at a flow rate 30 mL/min while the reference gas flow rate was set at 45 mL/min. The injector and detector temperatures were set at 170°C and 240°C respectively. The size of the sample used was 50 μL. The integrator was calibrated using a calibration gas prepared by Praxair, containing 20% oxygen, 50% nitrogen, 15% carbon dioxide, 4% methane and 1% ethane (weight percents).

Knowing the percent of carbon dioxide and oxygen in the stream and the flow rate of the gas through the composter from the flow meters, the carbon dioxide and oxygen flow rates could be calculated using equations (4-5) and (4-6) respectively.

$$F_{CO_2} = \text{flowmeter reading} \times \%CO_2 \qquad (4\text{-}5)$$

$$F_{O_2} = \text{flowmeter reading} \times \%O_2 \qquad (4\text{-}6)$$

4.5.4 Solid Phase Microextraction

To quantify and keep track of the losses of hydrocarbons escaping from the composters over the duration of the experiment, a Solid Phase Microextraction (SPME) device was used. The SPME manual holder assembly and 100 μm Poly Dimethyl Siloxane (PDMS) non-bonded fibre assembly were purchased from Supelco. The fibre was exposed to an exhaust gas sample contained in a 150 mL sampling bulb for 45 minutes. The compounds adsorbed onto the fiber were then analyzed using the same GC apparatus used for TEH analysis. The fiber was inserted in injector port set at 220°C for 5 minutes to ensure complete desorption. The oven was maintained at 35°C for 5 minutes, ramped at a rate of 10°C, and kept at 220°C for 10 minutes. Using a calibration done on dicyclopentadiene, the area recovered for DCPD was first converted to a concentration. The mass of DCPD lost over time was calculated knowing the concentration of the compound (C_{DCPD}) in the gas bulb, the volume of the bulb (V_{bulb}), the air flow rate through the composter and the total time elapsed as shown in equation (4-7).

$$Mass_{DCPD} = \text{flowrate} \times C_{DCPD} \times V_{bulb} \times \text{time elapsed} \qquad (4\text{-}7)$$

The calibration of the fibre was based on Henry's law shown in equation (4-8). Henry's law is used to describe the solubility of a gas in a liquid. It states that under equilibrium conditions, the partial pressure of a gas (P_i) above a liquid is proportional to the concentration of the chemical in the liquid (C_L). The proportionality constant is known as Henry's constant (H). Knowing the partial pressure of the gas, the mole fraction of DCPD in the bulb could be calculated and converted to a concentration. Equation (4-8) can be rewritten as equation (4-9) in terms of liquid and gas concentrations only if the definition of partial pressure is used.

$$P_i = H \times C_L \tag{4-8}$$

$$H = \frac{C_G \times RT}{C_L} \tag{4-9}$$

Since there was little information available on DCPD, the Henry's constant was estimated using the vapour pressure (P_v) and the solubility (S) at room temperature as shown in equation (4-10). Table 4.2 summarizes values used and calculated for the calibration of the fibre.

$$H = \frac{P_v}{S} \tag{4-10}$$

Table 4.2: Values Used for the Calibration of the SPME Fibre

Property	Value
Water solubility (mg/mL, 25°C)	0.019
Vapour pressure (mmHg)	1.7
Henry's Constant (m^3atm/mol)	1.556×10^{-2}

To calibrate the SPME fibre, a known amount of dicyclopentadiene was placed in 250 mL of water. The weight of DCPD placed into the water was maintained close to its solubility limit in water. The flask was connected to gas sampling bulb closed at one end and the system was allowed to reach equilibrium overnight. Using Henry's law, the amount of DCPD in the head space of known volume could be estimated. The bulb was closed off and the fibre was exposed to the gas and analyzed. A relationship between moles and area was then established.

4.5.5 Moisture Content

It was necessary to know the moisture content in the bulking agents and in the initial sludge to calculate how much additional water was required to obtain the desired moisture content in the mixture. Once the composting process was operating, compost samples were removed from the composters and tested for moisture content to ensure that the moisture content was remaining at a desired level.

A 3 g sample of the bulking agent was placed in a pre-weighed Pyrex dish. The sample was then placed in a drying oven at 65°C four 24 hours. The change in weight was assumed to be purely due to water loss. This simple procedure could not be used to measure the moisture content in the sludge due to the presence of volatile organic compounds in the sludge. A Dean-Stark distillation apparatus was used (Milne et al., 1996). A 30 g sample of sludge was mixed with toluene and boiled until all the water was collected. It was found that the water made up approximately 53% of the sludge by weight. Compost samples were tested for moisture content using the same method described to determine the moisture content of the bulking agent alone. Although the compost samples contained light hydrocarbons that disappeared during the drying, the percentage of light hydrocarbons in the sample was considered small enough to be insignificant compared to the water content.

Table 4.3: Moisture Content of Bulking Agents and Sludge

Material	Percent Moisture
Bulking agent	
Peat Moss	19
Wood Chips	6.7
Sphag Sorb	10.5
Solv II	34.5
Sludge	53

4.5.6 Microbial Count

Samples were again taken from the composters and were diluted several times before being placed on a plate with a Bushnell-Hass medium. The plates were placed for two weeks in the environmental chamber to keep them at the same temperature as the composters. The colonies formed by each bacteria could then be identified and counted. The compost sample was diluted using a mineral salt solution to reduce colonial growth on the plate to 20 to 300 colonies. Differentiation between bacteria types was not attempted. The primary energy source was hydrocarbons, and all heterotrophic bacteria were enumerated together.

The viable count method introduces several sources of error. The main problem results from the dilutions that are required due to the large population density of bacteria. Slight variations in dilution precision causes large differences in estimated propagule densities.

4.5.7 Metal and Solids Content

The amount of metals in the sludge could best be determined by ashing. A known weight of material was placed in a pre-weighed crucible. The material is then slowly

heated to 750°C and held there overnight in an oven equipped with a fume hood. The remaining particles are assumed to be completely metallic in nature. The sludge was found to have a very low ash content of less than 0.1%.

Another method was used to evaluate the fraction of overall solids content in the sludge since it was known that the solids were primarily coke. A known weight of sludge was placed on a pre-weighed filter paper. Toluene was added occasionally to aid in the filtration. The solids collected on the filter paper were then heated to 70°C for 24 hours to remove any remaining hydrocarbons and ensure that only solids were collected on the paper. The change in weight of the paper was noted and the percent solids content determined.

The solids fraction recovered from the filter paper was analyzed for metal content. The solids were placed in a tube with boiling chips and a 20 mL mixture of hydrochloric acid and nitric acid (1:1 volumetric ratio). The tube was heated over a heating plate for 3 hours. The light-coloured solution was collected in a volumetric flask and diluted to the desired concentration. The sample was stored at 4°C until ready for analysis. The solution was then analyzed with a Thermo Jarrell Atomscan 25 using the ThermoSPEC Spectrometer Operation System software package. Prior to analyzing the sample, distilled water and standard solutions for a wide range of heavy metals at 10 ppm were analyzed.

4.5.8 Removal of Polars From Oil and Grease

The fraction of polars present in the oil and grease obtained from soxhlet extraction was separated from saturates using methods described by Pollard et al., (1992). The separation was only conducted on extracts from compost samples containing n-

hexadecane to study the fraction of polars recovered during extraction due to organic bulking agents.

Recovered oil from extraction was diluted in 5 mL of dichloromethane and 5 mL of pentane. Asphaltenes precipitation was not necessary since only saturates were present in the sample. A 2 mL sample of the diluted oil was placed in a 20 mL Hamilton glass syringe with Luer-Lok connected to a silica cartridge (Waters Sep-Pak silica cartridge for rapid sample preparation). The cartridge was pre-eluted with n-pentane prior to sample analysis. The sample was then separated into component classes by use of an elution scheme: 30 mL of n-pentane for elution of saturated compounds followed by 30 mL of a solution of dichloromethane (50% volume) and methanol (50% volume) for polars. Fractions were collected in pre-weighed beakers and gravimetric recovery was calculated after removal of eluting solvent by evaporation to dryness in a fume hood.

4.6 EXPERIMENTAL PROTOCOL

The various experiments conducted are summarized in table 4.4. Sludge characterization was initially done to analyze the hydrocarbon phase, and to measure the water and solid content. Some background experiments were conducted to determine values such as the amount of carbon dioxide produced due to bulking agent partial degradation, the efficiency of the direct extraction procedure, and the possibility of increased adsorption of hydrocarbons onto bulking agent with time.

A bulking agent study was then conducted to evaluate which bulking agent, or mixture of, could lead to highest microbial activity and contaminant reduction. In this study, the hydrocarbon content in the compost mixture was maintained constant. Using the most suitable bulking agent, a hydrocarbon content study was then conducted. The

Table 4.4: Summary of Experiments

Study	Description of Experiments Conducted
Sludge characterization	Water content Solid and metal content Analysis of hydrocarbon phase Lab characterizations
Background	Bulking agent degradation at 35°C, using peat moss (70%) and solvII (30%) -14% hydrocarbon content for 2 weeks -2.5% n-hexadecane for 7 weeks Efficiency of direct extraction procedure Adsorption of hydrocarbon to bulking agent
Bulking agent	Constant sludge content, conducted for 5 weeks at 35°C -Wood chips -Peat moss x 2 composters -Solv II -Sphag sorb -50% solv II/ 50% peat moss -30% solv II/ 70% peat moss -Control (70% peat/ 30% solv) x 2 composters
Hydrocarbon content	Using peat moss/ solv mixture (85%/ 15%), conducted for 4 weeks and 35°C -1.5% hydrocarbon content -2.5% hydrocarbon content x 2 composters -5% hydrocarbon content -7.5% hydrocarbon content -Control with 5% hydrocarbon content
n-Hexadecane	Using peat moss/ solv mixture (85%/ 15%), conducted for 6 weeks and 35°C -2.5% n-hexadecane -5% n-hexadecane -Control with 5% n-hexadecane x 2 composters
Sludge volatilization	Non-aerated control composter (5% HC), mixed weekly for 5 weeks Aerated control composter (5% HC), not mixed for 4 weeks Sludge mixed to glass beads, 5 weeks

hydrocarbon content was varied between 1.5% and 7.5%. Due to problems encountered during the bulking agent and hydrocarbon content studies, n-hexadecane was composted to verify all methods and apparatus. Experiments were then conducted to evaluate where hydrocarbon losses were occurring. A control composter was mixed once a week but not continuously aerated and another was not mixed but was aerated. Finally, sludge was mixed to glass beads and placed in a composter to study its tendency to volatilize without organic matter interactions.

4.7 MASS BALANCES

A mass balance of carbon content in each composter was done to ensure that the decrease in hydrocarbon observed during the process was in fact due to biodegradation and not losses. Equation (4-11) shows the relationship used to establish the amount of carbon lost due to stripping and not accounted for.

$$HC_{in} = HC_{left} + C_{inCO_2} + C_{inCH_4} + C_{loss} \qquad (4\text{-}11)$$

HC_{in} is the mass of hydrocarbon placed in the composter initially. The amount of hydrocarbon left (HC_{left}) was calculated using the percent decrease in the Total Extractable Hydrocarbon content calculated from the extraction at the end of the process. The amount of carbon in the carbon dioxide evolved ($C_{in\,CO2}$) was calculated using the accumulated weight of carbon dioxide adsorbed on the ascerite throughout the whole process. Carbon represents 27.3% of the total weight of carbon dioxide collected. The amount of carbon present in the output stream as methane can be estimated from the percentage of methane in the gas stream from GC analysis. However, to obtain a mass from the flow rate of methane, a constant flow rate value must be assumed over a given time period.

Errors are introduced in the determination of hydrocarbon losses due to several reasons. The weight of hydrocarbons introduced in the composters is assumed to be equal to the weight of the carbon into the system. The weight of carbon dioxide produced is a result of hydrocarbon and bulking agent degradation. An experiment was conducted to establish the amount of carbon dioxide produced to due the bulking agent alone. However, the toxic nature of the sludge reduces the microbial activity and it was often found that contaminated composters resulted in less carbon dioxide production than in non-contaminated ones.

The percent losses of hydrocarbons due to factors that can not be calculated, such as loss during the mixing, can be calculated as shown in equation (4-12)

$$C_{loss\%} = \frac{C_{loss}}{HC_{in}} \times 100 \qquad (4\text{-}12)$$

The calculation of the percent carbon lost during the process was used to indicate the efficiency or problems of the experimental setup. Initial experiments were found to have percent losses as high as 65% due to the high air flow rates leading to stripping of the contaminants. The combination of high air flow rates and high condenser temperatures lead to the high losses.

CHAPTER FIVE: RESULTS AND DISCUSSION

5.1 SLUDGE CHARACTERIZATION

The sludge hydrocarbon content was analyzed using a Gas Chromatograph-Mass Spectrometer. Relatives amounts for some components were quantified and compared with values given by Nova. The sludge was sent to an analytical lab for compound identification. The water and solids content of the sludge were also determined.

5.1.1 Nova Characterization of C^{5+} Stream

The quench sludge is a mixture of water, hydrocarbons, and fine solids. The hydrocarbons include many compounds, principally benzene, dicyclopentadiene, styrene and polyaromatic hydrocarbons. The composition of the oil fraction of the sludge is similar to that of the C^{5+} stream. The solids are primarily coke, but are contaminated by adsorbed hydrocarbons and contain significant amounts of heavy metals, mostly nickel, iron and chromium. A break down of the hydrocarbon constituents of the C^{5+} stream was provided by Nova and is shown in table 5.1. The source of hydrocarbons in the sludge is the C^{5+} stream so similar compounds should be found in both but in different amounts.

Table 5.1: Main Hydrocarbon Constituents of the C^{5+} Stream

Component	Weight %
Benzene	45
Dicyclopentadiene	13
Cyclopentadiene	7
Toluene	6
C10 mixture	5.5
C6 mixture	3.5
Styrene	3
C5 mixture	2.8
Pentene-1	2.5
Cyclopentene	1.7
Others	10

5.1.2 Characterization Using GC-MS

A sludge sample of known weight was treated to remove the water content and diluted in dichloromethane for analysis by a Gas Chromatograph equipped with a Flame Ionization Detector. The spectrum obtained for the sludge is shown in figure 5.1. The width of the peaks indicate that the injector temperature should be raised for better resolution. However, due to the properties of DCPD, the temperature could not be increased. The same sample was also analyzed using a GC-MS apparatus to identify compounds present. Some of the peaks identified using GC-MS are shown on figure 5.1. The amounts of several compounds only could be obtained since external calibrations were only done for benzene, toluene, dicyclopentadiene, and styrene. Table 5.2 lists the compounds identified and the weight percentage values obtained for some of these.

GC-MS analysis revealed that cyclopentadiene could not be separated from the solvent peak since both had close retention times. Benzene was also difficult to analyze since it was overlapped by the solvent peak when the sample was diluted.

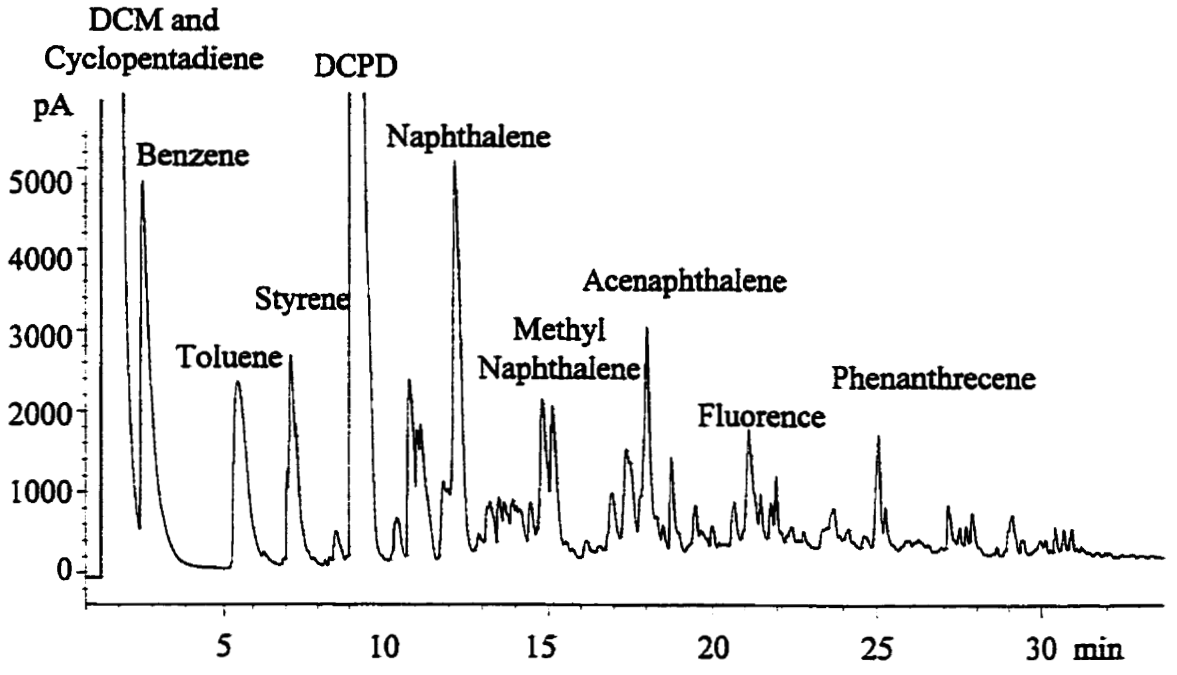


Figure 5.1: GC-FID Spectrum of Hydrocarbons in the Sludge

Table 5.2: Components Identified Using GC-MS

Component	Weight %
Benzene	8
Dicyclopentadiene	38
Cyclopentadiene	N/A
Toluene	7
Styrene	5
Paraxylene	N/A
Orthoxylene	N/A
Naphthalene	N/A
Methyl naphthalene	N/A
Acenaphthene	N/A
Anthracene	N/A
Fluorene	N/A
Phenanthrecene	N/A

The compounds detected using the GC-MS were similar to those presented in table 5.1. As expected, the composition of the hydrocarbon fraction did not match that of the C^{5+} stream. A direct comparison between the C^{5+} stream and the quench sludge cannot be done since the sludge is a mixture of several phases. It is only partially made up of the C^{5+} stream. The amount of benzene found to be present in the sludge was much lower than expected according to the amount found in the C^{5+} stream. The lower benzene content in the sludge is likely due to volatilization during transfer and storage. It can be seen that dicyclopentadiene becomes the most significant constituent of the hydrocarbon phase. The percentage values shown in table 5.2 are calculated for the hydrocarbon phase only which makes up 39% of the total weight of the sludge. Hence, 38% dicyclopentadiene in the hydrocarbon phase represents 15% of the total weight of a sludge sample.

5.1.3 Lab Characterization

The PONA analysis performed by Maxxam Anlytics Inc. was not found to give valuable information since only those compounds present in their data base could be identified. The compound present in the largest quantity could not be identified according to their data base but is likely to be dicyclopentadiene. Many of the compounds were listed with a question mark showing that there was little confidence to be placed in the results presented. Table 5.3 lists some of the compounds that were identified and their weight percents. The identified components were placed in group concentrations shown in table 5.4.

Table 5.3: Composition of Hydrocarbon Phase from PONA Analysis

Component	Weight %
Benzene	4.98
Dicyclopentadiene	41.9
Toluene	3.26
1-Methyl-1-cyclopentene	4.98
C12 Unknowns	1.57
C9 Paraffins	3.19
C11 Paraffins	2.79

Table 5.4: Identified Component Group Concentrations From PONA Analysis

Component Group	Weight %
Paraffins	20.44
Olefins	0.00
Naphthenes	44.73
Aromatics	11.57
Oxygenates	0.00

The Iatroscan analysis was done by Maxxam Analytics to obtain information about the component groups making up the sludge. Table 5.5 lists the results from the analysis. The "Polars B" material can be asphaltenes but cannot be reported conclusively as such.

Table 5.5: Results From Iatroscan Analysis

Component Group	Weight %
Saturates	12.9
Aromatics	68.8
Polars A	13.7
Polars B	4.6

5.1.4 Water and Solids Content

The fraction of water contained in the sludge was evaluated as described in section 4.5.5 using the Dean-Stark apparatus. The water content was measured to be 53%. The ashing method resulted in very low metal fraction of less than 0.1%. Using the filtration method, it was found that solids made up 8% of the sludge. The solids content of the sludge quickly precipitated to the bottom of the storage container. The solids content was significantly higher when only the bottom fraction of the sludge was analyzed. However, the sludge was well mixed with the solids prior to taking a sample for all experiments.

A nitric acid-chloric acid digestion done on the solids collected on the filter paper indicated that some heavy metals were present. The main heavy metals found were iron, nickel and chromium as expected according to the information provided by Nova. Table 5.6 lists the heavy metals obtained and their concentration in the sludge.

Table 5.6: Heavy Metal Concentration in Sludge

Heavy metal	Amount (ppm)
Nickel	72
Chromium	224
Iron	18

5.2 BACKGROUND EXPERIMENTS

Experiments were conducted to determine certain background values such as the amount of carbon dioxide produced due to bulking agent degradation, the efficiency of the direct extraction procedure, and the possibility of increased adsorption of hydrocarbons onto the bulking agent with time.

5.3.1 Bulking Agent Degradation

An experiment was done to establish the weight of carbon dioxide produced due to the degradation of the pure bulking agent. The mixture was prepared following the same procedure as for other composters but no contaminants were added. The bulking agent mixture used for this experiment was 85% peat moss and 15% Solv II by weight.

It was found that a significant amount of carbon dioxide was evolved due to the degradation of the bulking agent. Figure 5.2 shows the carbon dioxide production rate calculated for a composter without contaminants compared to one which was contaminated with 2.5% n-hexadecane per dry weight. Peat moss obviously provides an energy source and hence more nitrogen and phosphorous should be added to account for the bulking agent degradation.

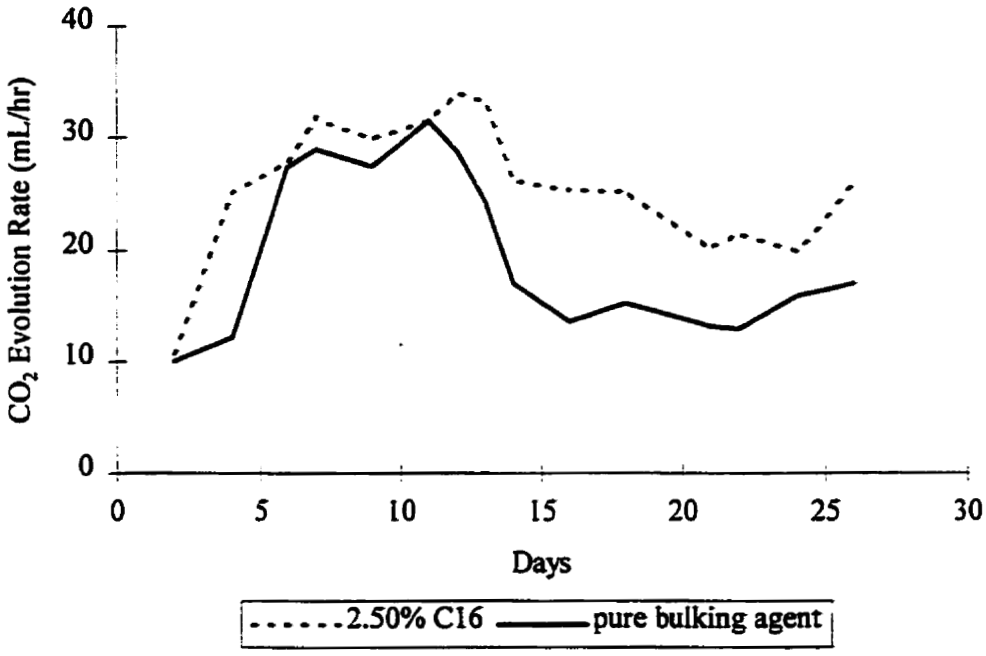


Figure 5.2: Carbon Dioxide Production Rate From Bulking Agent Degradation Compared to a Composter Contaminated with 2.5% n-Hexadecane

The amount of carbon dioxide collected during the experiment using ascerite is shown in table 5.7. Ideally, the amount of carbon dioxide produced due to contaminant degradation should be equal to the carbon dioxide collected from the contaminated composters less the amount produced from the bulking agent degradation. Carbon dioxide produced from contaminant degradation is needed to complete mass balance calculations. It was therefore attempted to establish a background amount of carbon dioxide produced from bulking agent degradation. This value was established using the total weight change of the ascerite tube during the whole process.

Table 5.7: Weight of Carbon Dioxide Produced From Bulking Agent Degradation

Week	Cumulative Mass of CO_2 Produced (g)
1	5.36
2	12.73
3	18.3
4	23.13
5	26.34
6	28.73

Some experiments were carried out with high hydrocarbon content. For these experiments, a background amount of carbon dioxide production could not be subtracted from the contaminated composters since the carbon dioxide production rates were significantly lower than in the non-contaminated composter. This is shown in figure 5.3. The experiment was only carried out for two weeks since it was obvious that a background value could not be obtained.

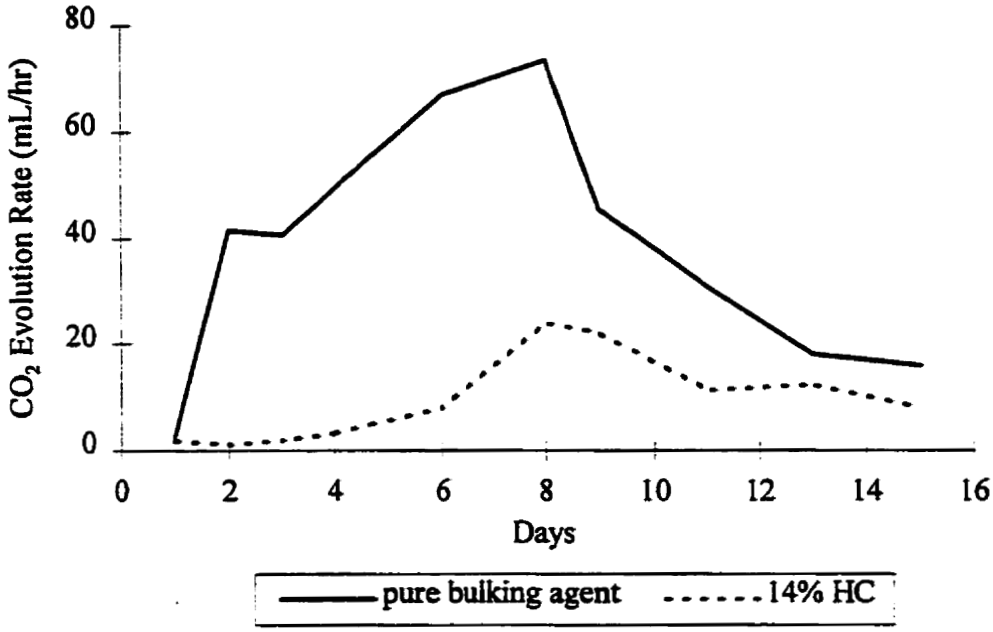


Figure 5.3: Carbon Dioxide Production Rate of Bulking Agent Compared to Highly Contaminated Composter

Although large amounts of carbon dioxide were produced from bulking agent degradation, the weight of the non-contaminated compost mixture did not change significantly. As shown in table 5.8, there was only a 17.7 g decrease in weight in the mixture weighing initially 579.3 g. This decrease corresponds only to a 3% weight change.

Table 5.8: Change in Weight of Bulking Agent With Time

Week	Weight Change (g)
1	3.5
2	3.7
3	2.9
4	3.1
5	2.1
6	2.4
total	17.7

Partial degradation of bulking agents can cause problems when analyzing for oil content in a compost mixture. If the decomposition of compost mass is more intensive than oil decomposition, oil concentrations increase in the remaining mass although there is an actual breakdown of oil (Holger et al., 1998). Total organic content in the compost material can monitor carbon content decrease and explain an unexpected increase in oil concentration. Even if oil content decreases, the degradation may be underestimated due to bulking agent degradation. Total organic content was not monitored since equipment was not available.

5.3.2 Efficiency of Extraction Procedure

Since the direct extraction method described in section 4.5.1 initially used is not a standard method, it was necessary to establish the efficiency of the extraction procedure. The percent recovery of hydrocarbons during the extraction was based on the concentration obtained for dicyclopentadiene and on the TEH calibration plot. A known mass of the sludge was mixed with a bulking agent and extracted. Knowing the concentration of DCPD in the sludge and the volume of solvent used, the maximum attainable concentrations of DCPD and TEH were calculated and compared to the concentrations actually obtained from the GC analysis. The efficiency of the extraction procedure was verified using different bulking agents. Experiments were carried out for compost mixtures containing at least 10% hydrocarbon per dry mass. Table 5.9 lists the efficiency of the extraction using various bulking agents. Once the hydrocarbon content was lowered, it was found that peaks were not well resolved and the method did not seem suitable for mixtures containing less than 7.5% hydrocarbon.

The recovery of dicyclopentadiene varied between 76% and 97% depending on the bulking agent. The fraction that could not be recovered was likely due to adsorption of the contaminants onto the bulking agents or losses due to volatilization during the extraction procedure. The recovery of the TEH was found to be similar, ranging between 81% and 95%. Peat moss was found to allow the highest recovery while Sphag Sorb resulted in the lowest percent recovery which could be expected due to its absorbent nature. Assuming that adsorption of contaminants on bulking agents did not increase with time, the small unrecovered fraction of contaminants should not affect the evaluation of relative decrease in TEH in the compost mixture.

Table 5.9: Efficiency of Extraction Procedure Using Different Bulking Agents

Bulking Agent	DCPD % Recovery	TEH % Recovery	% Error
Peat moss	97	95	7
Sphag sorb	76	81	4
Solv II	87	84	8

The values shown above were found to vary from sample to sample since the calculations assume that the compost mixture is perfectly mixed. The samples taken for extraction were small (3.000 g) which increased the likelihood that the sample was not well representative of the mixture. Percent errors shown in table 5.8 were calculated by averaging three different samples taken from the same mixture and taking the maximum deviation between the average and any one value.

5.3.3 Adsorption of Hydrocarbons Onto Bulking Agents With Time

The change in adsorption of hydrocarbons onto the bulking agent over time was also investigated to ensure that the decrease in TEH and DCPD was not due to gradual adsorption of the contaminants onto the bulking agent. Poisoned compost samples were stored in a refrigerator at 4°C to minimize losses and were extracted every second week for up to one month (approximately the duration of an experiment). The results are shown in table 5.10. It was found that the concentration of contaminants remained relatively constant during the month, suggesting that the adsorption of the hydrocarbons on the bulking agent did not change throughout the experiment. TEH and DCPD values were not found to decrease with time and the DCPD values were even found to increase slightly (shown by the negative value). The small increase was likely due to shifts in moisture content of the mixture. Even though the mixture was stored in the refrigerator, water collected on the cap of the vial indicating that moisture content may have varied

slightly. The extraction is strongly dependent on moisture content since 60% of the sample mass was water.

Table 5.10 TEH and DCPD Reduction Obtained for Poisoned Mixture Placed in a Refrigerator for One Month

Days	% TEH Reduction	% DCPD Reduction
14	-2.5	-1.5
35	6.9	-10.0

5.3 BULKING AGENT STUDY

Different bulking agents were tested to investigate which could lead to highest degradation rates. The hydrocarbon concentration in the compost mixture was maintained constant using different bulking agents. The organic bulking agents studied include straw, peat moss, wood chips, Sphag Sorb, and Solv II. Different combinations of bulking agents were also tested. The efficiency of each bulking agent, or mixture of, was evaluated according to its capability to maintain high microbial activity and to lead to high TEH reduction. The environmental chamber was maintained at 35°C for all experiments. Composting was carried out for five weeks and duplicate experiments were done on the control and for composters containing peat moss. Control composters contained a mixture of 30% peat moss and 70% Solv II and were aerated and mixed like the active ones.

5.3.1 Carbon Dioxide Production

The production rate of carbon dioxide was monitored to see which bulking agent provided the most suitable environment for microbial activity. Figure 5.4 shows the

carbon dioxide evolution rates with time for different bulking agents and mixtures of bulking agents. The evolution rates shown in figure 5.4 were calculated using the GC results.

Figure 5.4 shows that mixtures of Solv II and peat moss lead to the highest microbial activities. The same was observed when Sphag Sorb was used in combination with Solv II. Sphag Sorb, peat moss and wood chips alone resulted in low carbon dioxide productions. However, the low rates obtained for these bulking agents were due to the high hydrocarbon content in the mixture. Solv II alone does not represent an ideal bulking agent because it does not keep its porous structure during the process and results in ineffective aeration of the compost materials. Within a week, the mixture compacted and reduced in volume. Figure 5.5 shows the bulking agents before the composting process. Figure 5.6 shows that a mixture prepared using peat moss (70%) with Solv II (30%) does not change in texture after 35 days of composting. It can be said that Sphag Sorb and peat moss act as better bulking agents over time since they maintain their porous structure and do not compact.

The total amount of carbon dioxide collected during the composting process using ascerite is shown below in table 5.11. These amounts were used to calculate mass balances of carbon for each composter.

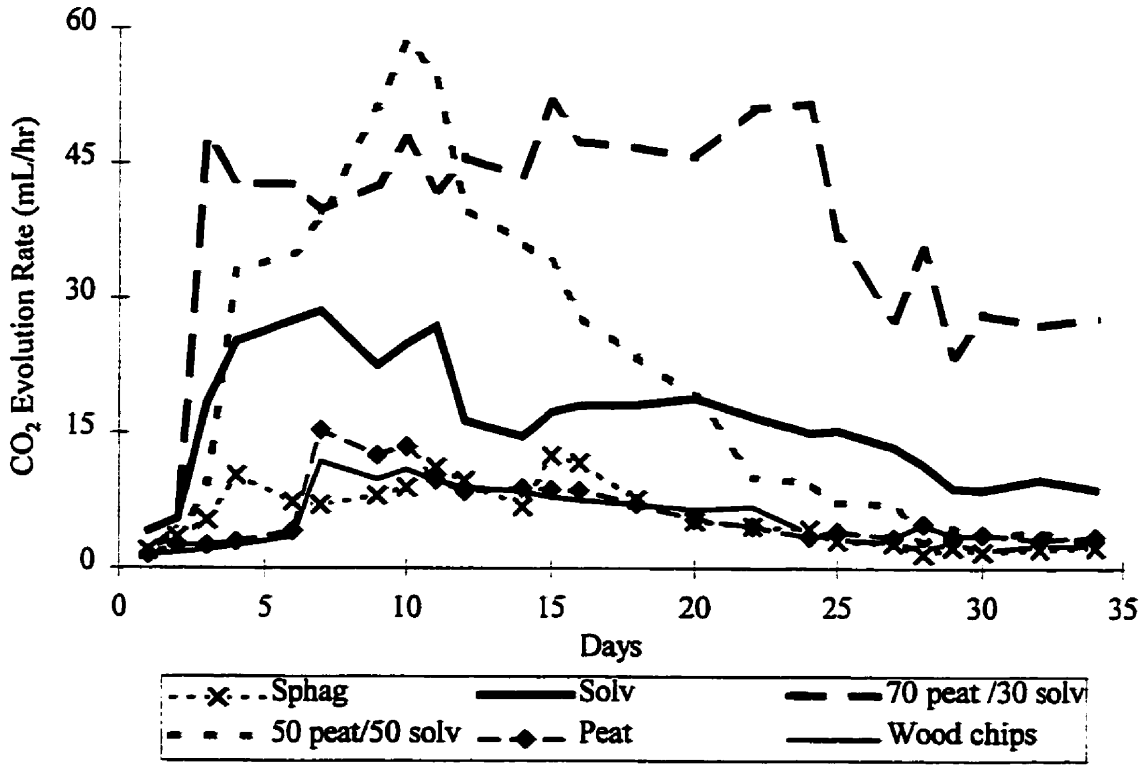


Figure 5.4: Carbon Dioxide Evolution Rate Using Different Bulking Agents

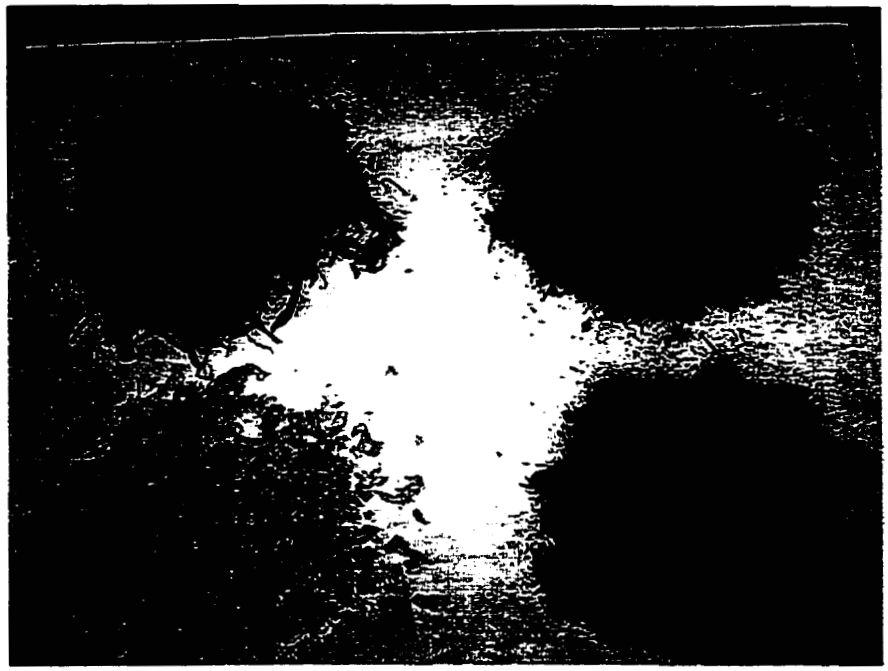


Figure 5.5: Bulking Agents Before Composting Process (Clockwise Starting Top Left: Solv II, Peat Moss, Sphag Sorb, Wood Chips)

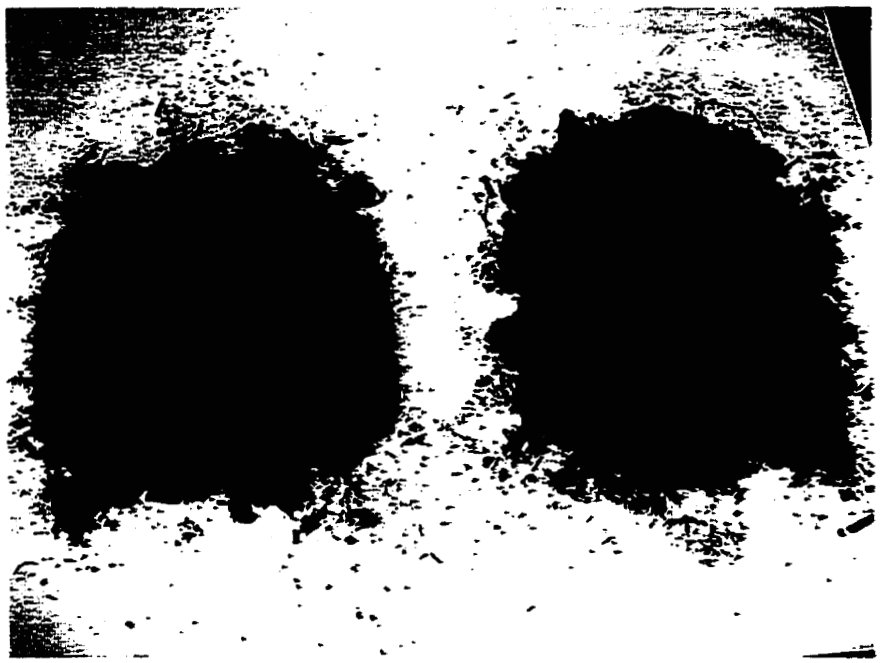


Figure 5.6: Peat Moss and Solv II mixture Before (left) and After (right) Composting Process

Table 5.11: Carbon Dioxide Collected After 35 Days of Operations

Bulking Agent	Weight of CO_2 (g)
Control (30% Solv II/ 70% peat)	1.44
Control (30% Solv II/ 70% peat) (duplicate)	1.29
Wood Chips	6.59
Peat moss	8.63
Peat moss (duplicate)	9.01
Sphag Sorb	9.25
Solv II	24.39
50% Solv II/ 50% peat moss	31.45
30% Solv II/ 70% peat moss	56.78

5.3.2 Oxygen and Methane Content

The amount of oxygen in the output stream was also monitored. Ideally, the air input into the composters should be adjusted so that the oxygen content makes up at least 12% of the air space in the composters. However, initial experiments indicated that volatile losses were of concern and it was therefore decided to maintain the air flow rate at a constant low value of 2.5 mL/min. 12% oxygen in a gas flowing at 2.5 mL/hr is equivalent to an oxygen flow rate of 18 mL/hr. Figure 5.7 shows the oxygen and carbon dioxide flow rates in the output stream for the composter containing 50% Solv II and 50% peat moss. The low air input resulted in low oxygen content for the most active weeks of the process as seen in figure 5.7. Even after mixing, the oxygen content decreased rapidly to insufficient levels for composters containing mixtures of Solv II and peat moss.

Only the most active composters were expected to have reduced oxygen levels. The GC was calibrated to analyze methane content in the gas. No methane peak was detected even when the oxygen content had dropped to a level that could no longer be

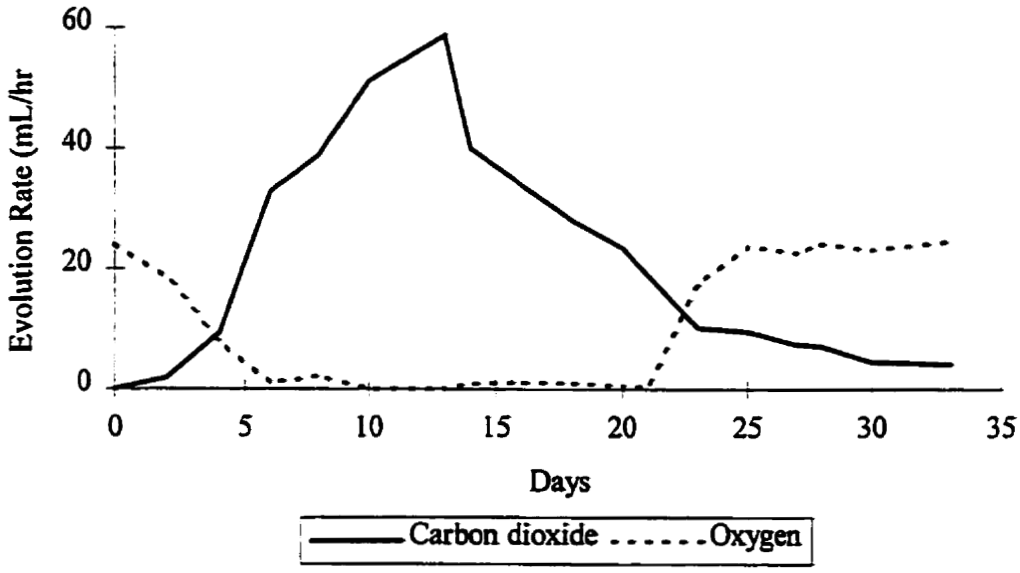


Figure 5.7: Oxygen and Carbon Dioxide Evolution Rate in Output Stream of Composter Containing 50% Solv II and 50% Peat Moss

detected. Figure 5.8 shows a spectrum obtained from a gas analysis where the oxygen peak has disappeared and yet no methane peak is observed. In comparison, figure 5.9 shows the spectrum obtained from the calibration gas containing both methane and oxygen.

5.3.3 Oil and Grease Reduction

Figure 5.10 shows the oil and grease reduction obtained after five weeks of operation. The oil and grease content decreased by 8% in the control composter. The oil and grease in composters containing wood chips, peat moss, Sphag Sorb and mixtures of peat moss and Solv II resulted in similar decreases, ranging between 7% and 13%. The largest decrease was observed for composters containing peat moss. The small difference between the control composter and other active ones prevents conclusions to be made about the effects of biological activity.

The oil and grease recovered from the Soxhlet extraction resulted in variable results. Extraction of pure bulking agents gave oily residues which indicates that polars are present in the bulking agents. The amount of residue was found to vary and hence affected the amount of oil and grease recovered from a compost sample. The decrease in oil and grease was not as significant as the decrease observed in TEH. A large fraction of the extracted oil was found to be polars from bulking agents. Hence, the change in the small oil fraction may have been masked by the presence of the larger, variable polar fraction. Even when the oil per gram ratio did not show much of a decrease after composting, GC analysis revealed a more significant decrease in TEH. The GC did not analyze polars present in the extract and specifically quantified hydrocarbons extracted. The large presence of polars in the bulking agents makes the quantification of hydrocarbon reduction by oil and grease determination difficult if they are not removed.

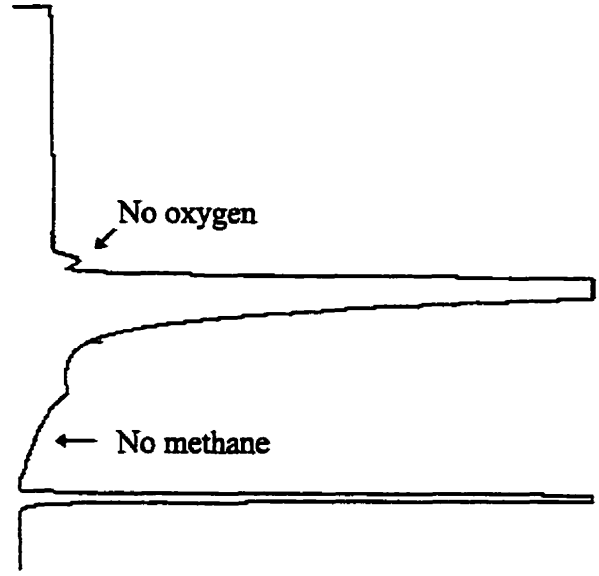


Figure 5.8: Spectrum From GC Analysis of Gas Sample Containing no Oxygen and no Methane

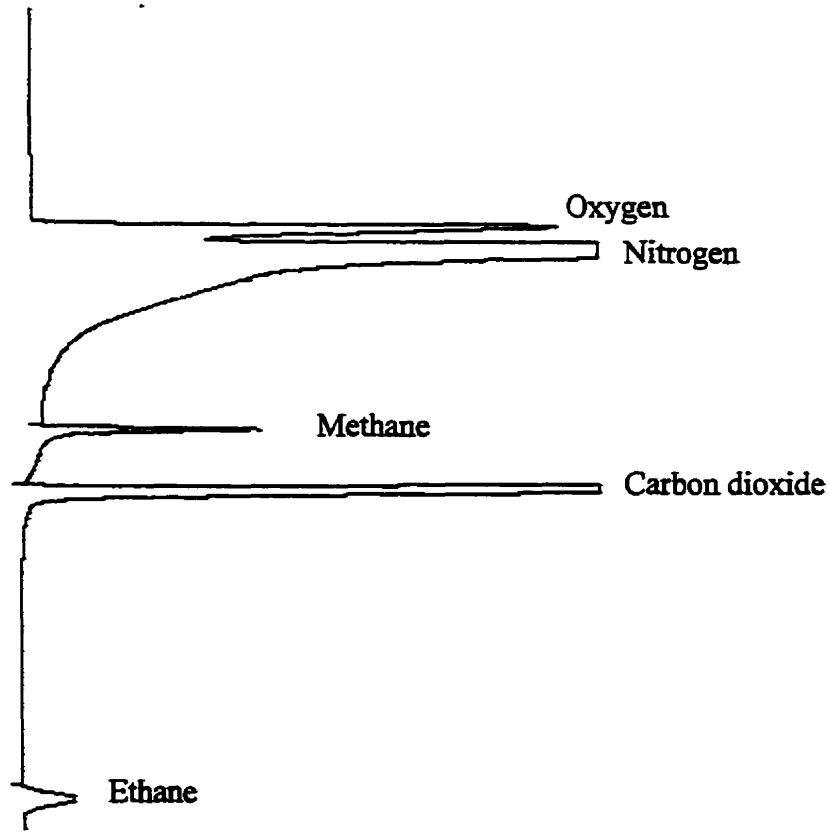


Figure 5.9: Spectrum From GC Analysis of Calibration Gas

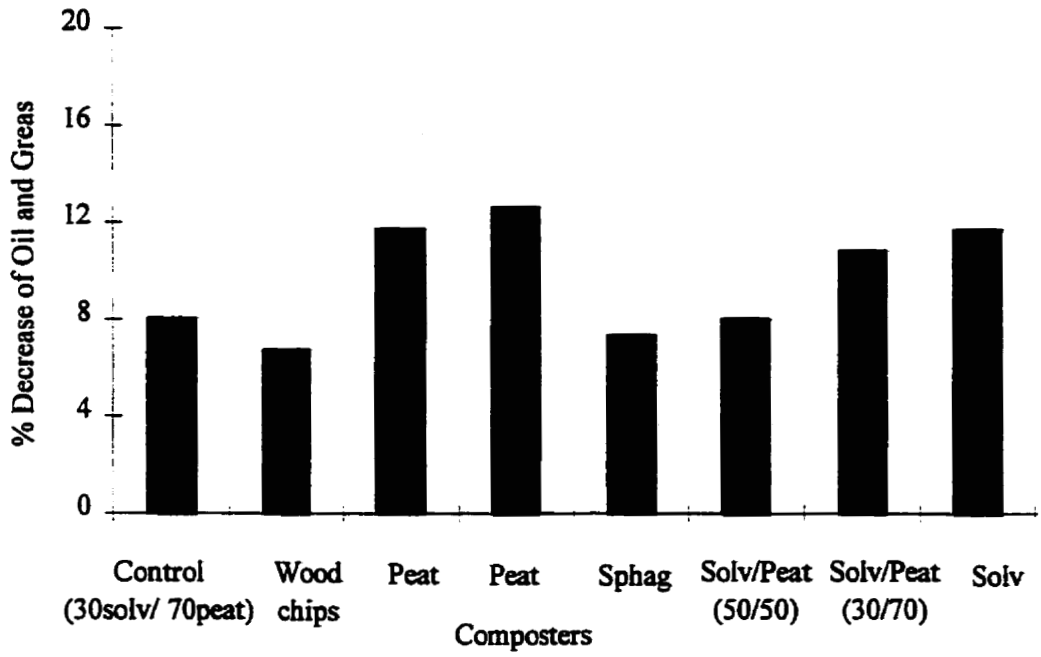


Figure 5.10: Total Oil and Grease Reduction Using Various Bulking Agents After Five Weeks of Operation

5.3.4 TEH and DCPD Reduction

The reduction of Total Extractable Hydrocarbon content (TEH) and dicyclopentadiene were recorded weekly for different bulking agents. Figure 5.11 shows the overall decrease in hydrocarbon content and DCPD after five weeks of operation. There was a 38% decrease in hydrocarbon content and a 83% DCPD reduction in the control composter. The highest TEH decrease was 41% when peat moss was used as a bulking agent. The large decrease observed in the control composters prevent conclusions to be drawn about biodegradation of the hydrocarbons since the 6% difference falls within the error of the extraction procedure.

Figure 5.12 shows the spectrum of the extract obtained from GC analysis for the control composter at the start of the process. Figure 5.13 is the spectrum of the extract of the same compost mixture after five weeks of operation. It can be seen that most of the peaks have decreased in size. The first large peak shown in the figures represents dicyclopentadiene which is significantly reduced during the composting process. A new peak increasing in size was not found when initial chromatograms were compared to ones obtained later in the process, indicating that oxidation of DCPD due to aeration cannot account for the reduction of DCPD.

All the experiments conducted for the bulking agent study contained a high hydrocarbon content of 14% of the dry mass due to an error in calculation. This large concentration of hydrocarbon in the mixture was likely limiting the microbial activity. The main problem was found to be the large decrease in contaminants observed in the control composters and was not likely due to the high hydrocarbon content. However, the hydrocarbon content study was conducted using lower hydrocarbon contents to verify that the problems encountered were not simply due to the high hydrocarbon content.

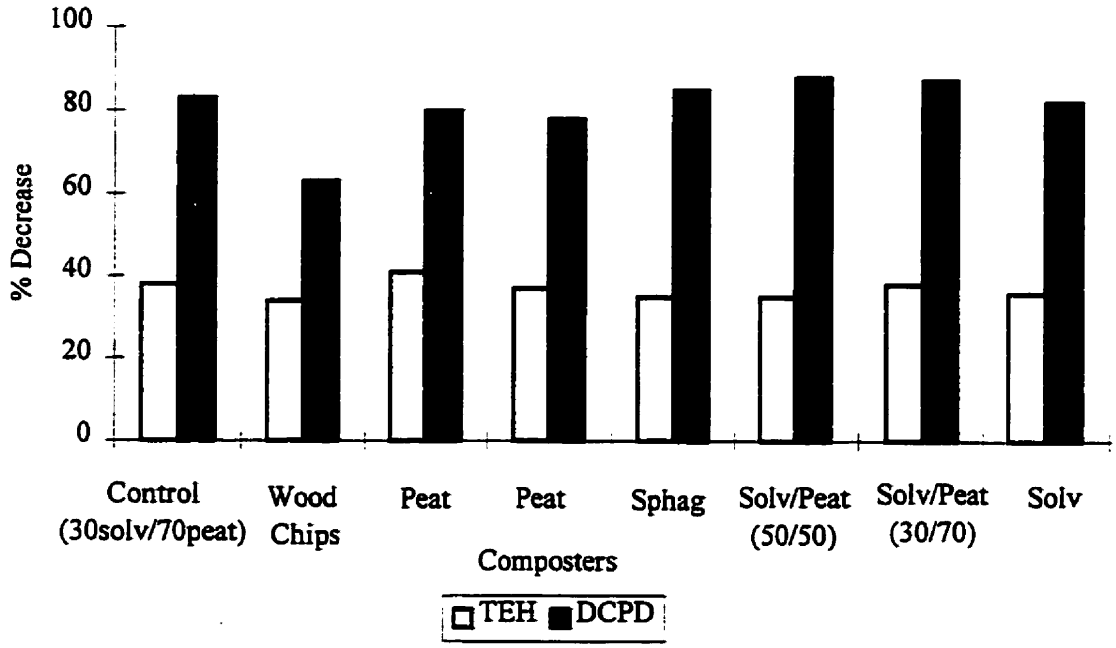


Figure 5.11: Total Decrease in TEH and DCPD Using Different Bulking Agents After Five Weeks Operation

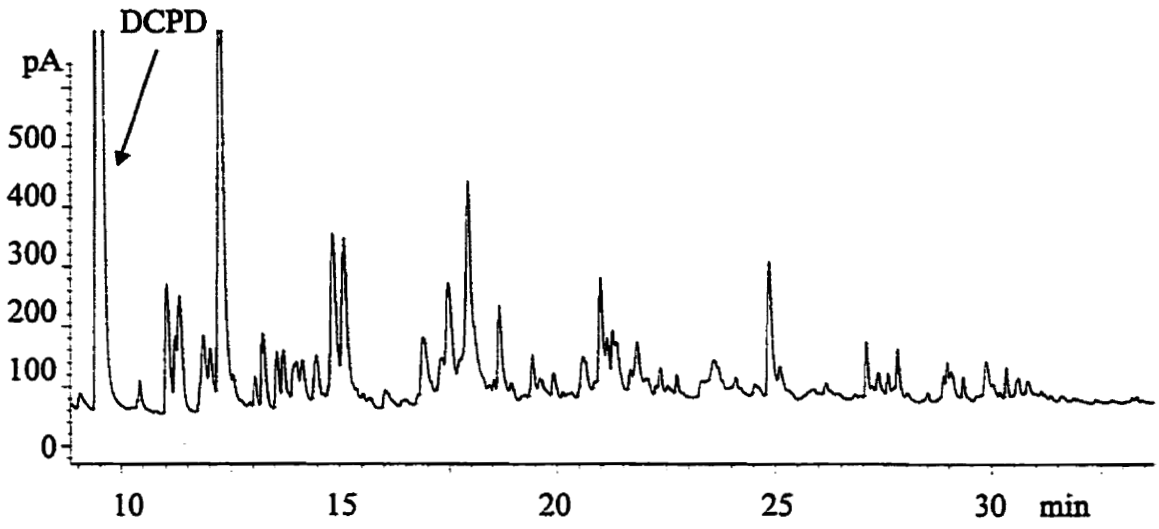


Figure 5.12: GC Spectrum of Control Composter Extract at Start of Process

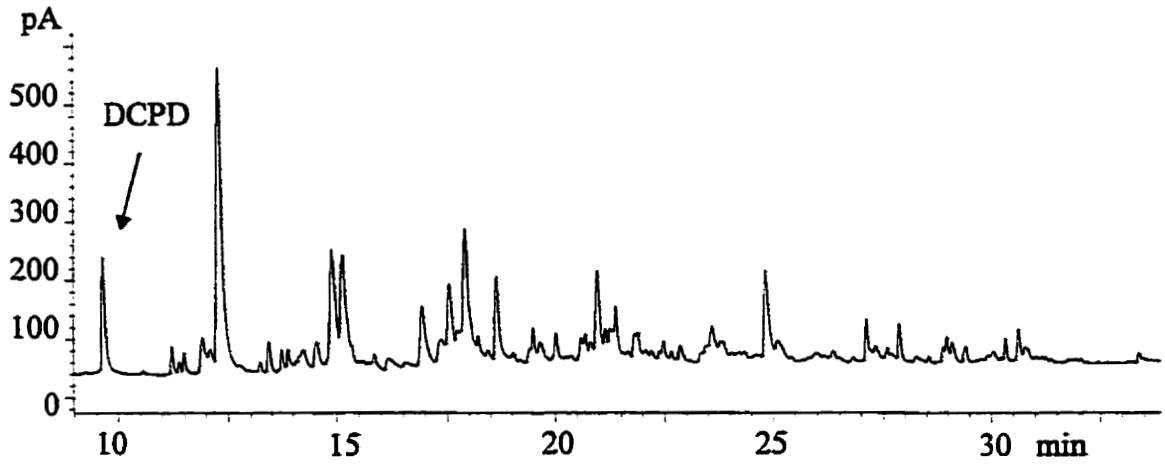


Figure 5.13: GC Spectrum of Control Composter Extract After Five Weeks

5.3.5 Bacteria Counts

Bacteria counts were done on the initial compost mixtures and after two weeks of composting. Table 5.12 shows the bacteria counts, or colony forming units (CFU), calculated at the two time intervals. Most composters showed a decrease in bacteria population while some increased slightly. However, the increase observed for some of the composters is not significant. Populations should reach numbers well above 30 million within a couple of weeks of exposure to a contaminant. The decrease in bacteria counts indicated that toxic conditions were present in the composters. This was due to the high sludge concentration placed in the mixture which resulted in toxic conditions.

Table 5.12: Bacteria Counts For Various Bulking Agents at the Start and After Two Weeks of Composting

Composter Description	Bacteria Count (million/g) Initially	Bacteria Count (million/g) Day 14
Control (30 solv/70 peat) (duplicate)	0.003	0
Control (30 solv/70 peat)	0	0
Peat moss	0.02	0
Peat moss (duplicate)	0.02	0.001
Sphag sorb	0.03	0.001
Solv II	0.9	0.6
30% solv/70% peat	0.05	0.09
50% solv/50% peat	0.04	0.2

5.4 HYDROCARBON CONTENT STUDY

Hydrocarbon content in the compost mixture was varied between 1.5% and 7.5% of the dry mass to study the optimal concentration of hydrocarbon in the mixture. Two

composters were contaminated with 2.5% hydrocarbon to verify reproducibility. A mixture of peat moss (85% by weight) and Solv II (15% by weight) was used for all experiments while the temperature within the chamber was maintained at 35°C. The control composter was contaminated with 5% hydrocarbon.

5.4.1 Carbon Dioxide Evolution and Output Gas Composition

As for the bulking agent study, the amount of carbon dioxide evolved throughout the process was monitored. The results calculated from GC analysis are shown in figure 5.14. It can be seen that when the amount of hydrocarbon within the composting mixture is set to 7.5% and above, a significant decrease in carbon dioxide production was observed. The highest activity was obtained at the lowest sludge concentration indicating that the sludge is toxic especially when applied at high concentrations. However, the high initial carbon dioxide production rates observed with 1.5% hydrocarbon content was not maintained. Although composters containing 2.5% and 5% hydrocarbon showed slightly lower carbon dioxide production rates than the composter containing only 1.5%, the difference became less obvious after two weeks of operation. Two composters were contaminated at 2.5% to test the reproducibility of the process. As can be seen in figure 5.14, both composters resulted in similar carbon dioxide evolution rates.

Figure 5.15 shows the difference in the results obtained for the production of carbon dioxide using the ascerite and Gas Chromatograph methods. The results shown are only those obtained for the two composters contaminated with 2.5% hydrocarbon for clarity and to show reproducibility. It can be seen that both techniques used to evaluate carbon dioxide production rates gave similar results. Production rates were always found be slightly lower and less consistent using the ascerite method. The ascerite tubes plugged up when large concentrations of carbon dioxide were detected in the exhaust gas for the most active composters. Even though the ascerite was replaced occasionally, the

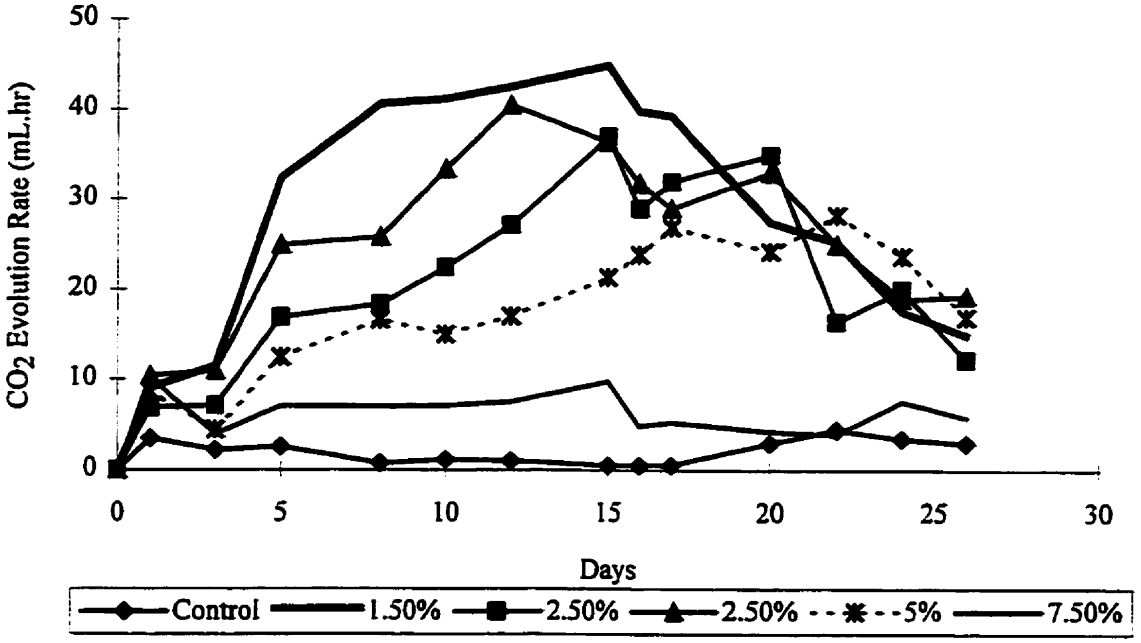


Figure 5.14: Carbon Dioxide Evolution at Various Hydrocarbon Concentrations

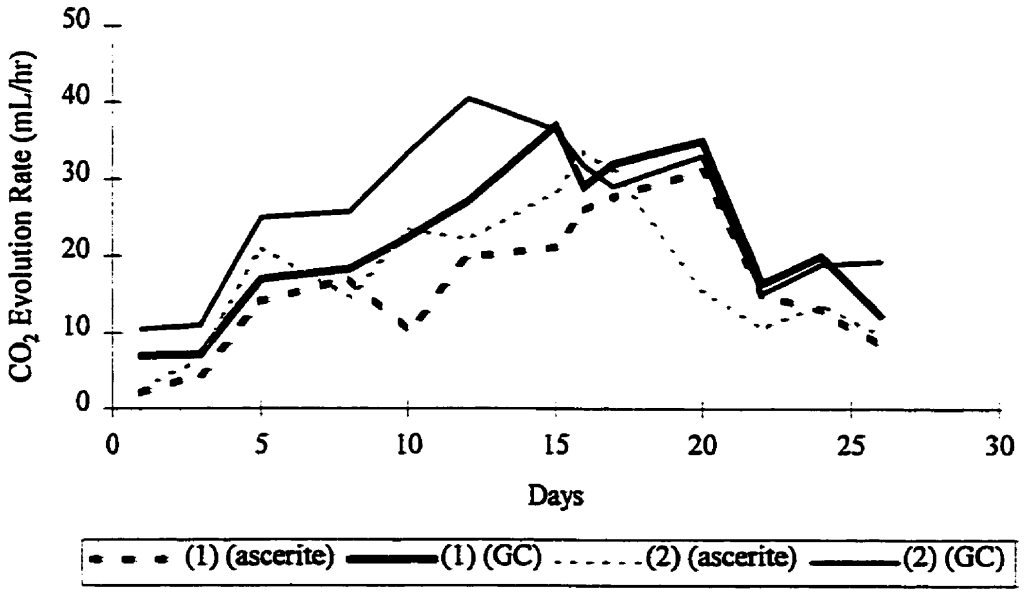


Figure 5.15: Comparison of CO_2 Evolution Rates From GC and Ascerite Method

plugging of the tubes resulted in lower air flowrate through the composters and hence in less carbon dioxide adsorption in the tubes. The lower flowrates calculated from the ascerite method can also be attributed to the small percentage of carbon dioxide that was found to pass through the ascerite tubes. The total weight of carbon dioxide collected during the process in the ascerite tubes is shown in table 5.13.

Table 5.13: Total Carbon Dioxide Produced Over Four Weeks Using Different Hydrocarbon Contents

Hydrocarbon Content	Weight of CO_2 (g)
Control (5%)	3.91
1.50%	25.65
2.50%	20.22
2.50%	21.84
5%	16.82
7.50%	8.16

As in the bulking agent study, the amount of oxygen became limited for the most active composters but no methane was detected from GC analysis. Less than 24 hours after mixing, the amount of oxygen dropped to nearly zero for the active composters containing 5% and less hydrocarbon content. The oxygen flow rate in the output stream for composters containing 1.5%, 2.5% and 5% hydrocarbon content is shown in figure 5.16. The dark line in the figure represents the minimum oxygen content required for the composter containing 1.5% hydrocarbon. The limiting flow rate of oxygen was calculated by setting the minimal oxygen content in the output stream to 8%. The curve is not represented by a straight line since the flow rate through the composter varied slightly with time and could not be maintained at exactly 2.5 mL/min due to plugging of the ascerite tubes. Both the carbon dioxide and oxygen flow rate curves for the composter containing 5% hydrocarbon indicate that microbial activity reaches a peak after two weeks of operation. The carbon dioxide evolution rate surpasses that of the

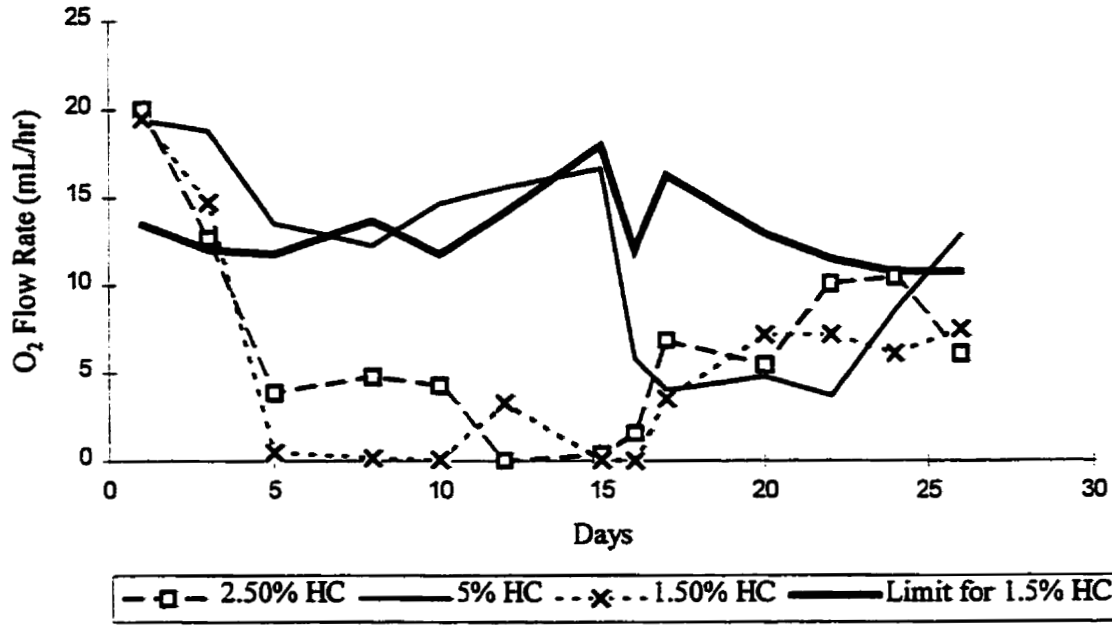


Figure 5.16: Oxygen Flow Rate in Exhaust Gas of Composters Containing 1.5%, 2.5% and 5% Hydrocarbon

composter containing only 1.5%, while the oxygen content decreases below the level of the initially most active composters.

5.4.2 Oil and Grease Reduction

The change in oil and grease content in the composters over time is shown in figure 5.17. The difference between the control composter and the active ones is not significant. The oil and grease content in the control composter (contaminated with 5% hydrocarbon) decreased by 27%. The composter contaminated with 1.5% hydrocarbon resulted in the largest decrease of 30% and the lowest decrease of 13% was observed in the composter containing 7.5% hydrocarbon. The 13% decrease in oil and grease was lower than the decrease obtained in the control composter. This result is surprising and seems to indicate that direct comparison of oil and grease content may not be valid here as discussed previously. It was found that results obtained from oil and grease content calculations fluctuated. The poor results obtained from oil and grease calculations are again likely due to the polars contained in the bulking agent. Even though polars do not affect the TEH value obtained from GC analysis, they do have a marked effect on the oil and grease value.

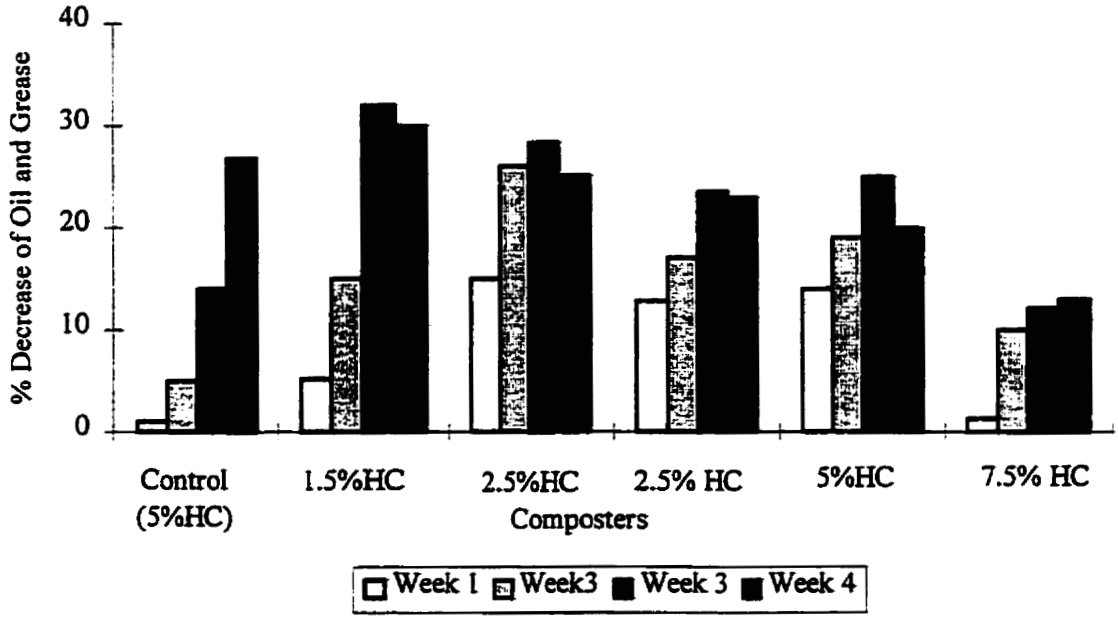


Figure 5.17: Oil and Grease Reduction for Composters with Various Hydrocarbon Content

5.4.3 TEH and DCPD Reduction

Similar problems as were found during the bulking agent study were encountered when TEH and DCPD contents were analyzed. As shown in figure 5.18, a 46% decrease in total extractable hydrocarbon was obtained in the control composter which was contaminated with 5% hydrocarbon. No other active composter showed a higher decrease. Very little carbon dioxide was collected from the control composter (as shown in table 5.13), indicating that the decrease in TEH was not due to microbial activity. Partial degradation of the bulking agent may explain the higher reduction observed in the control composter than in the active ones. Even if the hydrocarbons were being consumed due to microbial activity, the simultaneous degradation of the bulking agent resulted in an smaller decrease of the hydrocarbon to total weight ratio.

The decrease in DCPD was found to be once again significant even in the control composter as shown in figure 5.19. Within two weeks of operation, the loss of DCPD was approximately 70% and after four weeks reached 89% in the control composter. Reduction values in the active composters were in the same range, varying by no more than 10%. The large losses of both TEH and DCPD in the control composter prevent any conclusions to be drawn about the effects of biological activity due to the small difference observed between the control and the active composters.

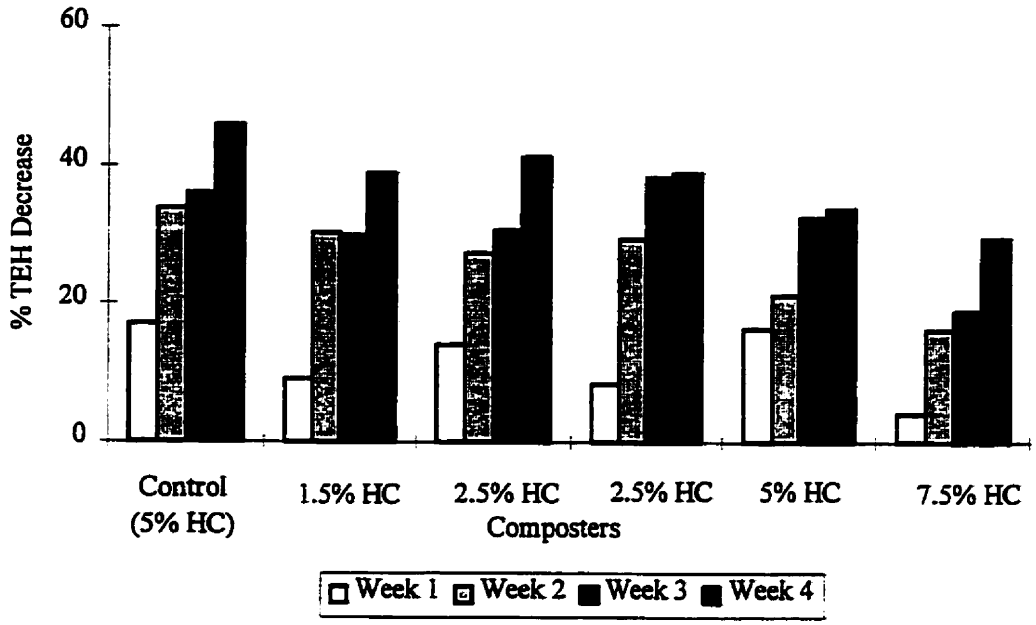


Figure 5.18: Reduction in TEH for Various Hydrocarbon Concentrations Over Four Weeks

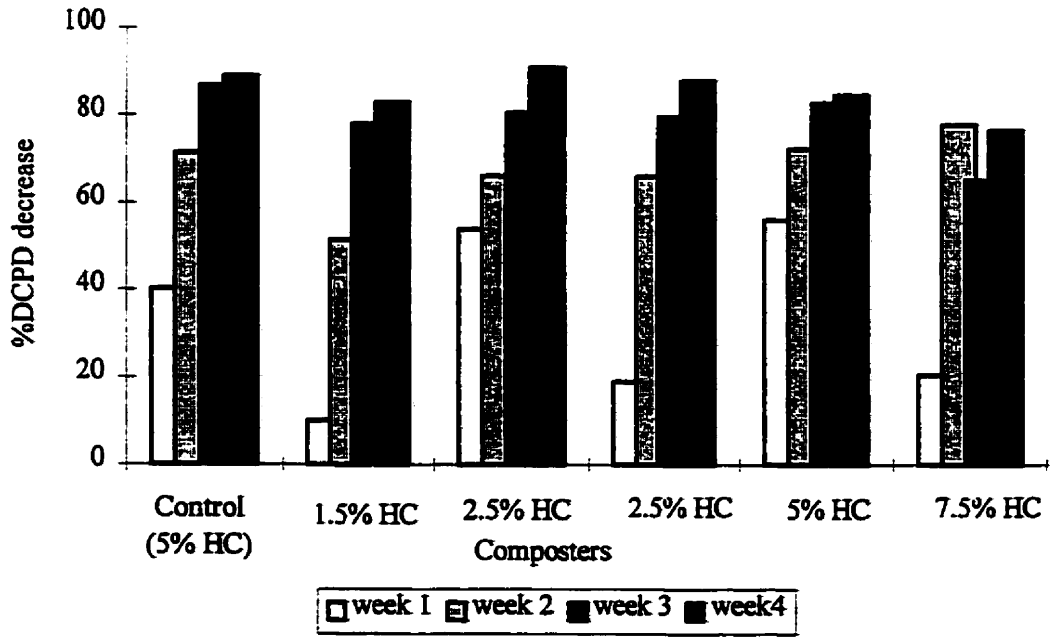


Figure 5.19: Decrease in DCPD for Various Hydrocarbon Concentrations Over Four Weeks

5.4.4 Bacteria Counts

Bacteria enumeration revealed that the toxic conditions previously encountered were reduced since bacterial growth was observed. Table 5.14 shows the increase in bacteria counts after two weeks of composting. It can be seen that even if the number of bacteria per gram of compost mixture increased after two weeks, the population did not increase to the high value that is normally expected. Even at the lowest hydrocarbon concentration bacteria counts did not reach 30 million indicating that the sludge is toxic and can only be applied at low concentrations. Increasing the hydrocarbon content to 7.5% limits bacterial growth as was deduced from the low carbon dioxide production curves.

Table 5.14: Bacteria Population at Beginning and After Two Weeks of Composting

Composter Description	Bacteria Count (million/g) Initially	Bacteria Count (million/g) Day 14
5% HC poisoned	0.004	0.001
1.5% HC	1.2	10.6
2.5% HC	0.4	7.1
2.5% HC	0.5	5.9
5% HC	0.1	1.6
7.5% HC	0.2	0.7

5.4.5 Moisture Content

The moisture content was monitored weekly but only the initial and final values are shown in table 5.15 since little change was observed over time. Negative values indicate an increase in the moisture content. The moisture content was monitored since a small change in moisture content can have a significant influence of the TEH value obtained from extraction. If the moisture content decreases over time, more dry mass will

be placed in the extraction thimble and the TEH value will increase. If the moisture content of a sample is 60% initially, a 1% decrease in moisture will increase the amount of TEH by 2.5%. Hence a variance in moisture of only 3% can become significant.

The changes in moisture content for this experiment do not explain the large decrease in TEH observed for the control composter. According to table 5.15, moisture in the poisoned composter decreased by 2.4% which implies that the decrease in TEH was actually underestimated by a value of 6%. However, TEH decrease for the composter contaminated with 5% hydrocarbon should be lowered by another 7.3% to accommodate for the small increase in moisture content.

Table 5.15: Decrease in Moisture Content After Four Weeks of Operation

Days	Control	1.5% HC	2.5% HC	2.5% HC	5% HC	7.5% HC
0	0	1	0	0	0	0
28	2.4	-1.2	0.3	0.4	-2.9	-0.3

The top thin layer of the composting materials in the control composter was uniformly wet. This wetness was circumstantial evidence that the outlet gas was saturated. As the gas emerges from the mixture, it encounters lower bulkhead temperatures due to the condensers. This causes condensation onto the top material. A layer of material a few centimeters thick just above the distributing plate, where the air first entered the composting matrix was dry. Otherwise, the bulk of the material in the control and less active composters appeared to be uniform with respect to moisture content. The top layer of the materials in the most active composters with less hydrocarbon content was also wet but the bulk of the material was not found to be as uniform. A few days after mixing, a large portion of the materials at the bottom appeared dry (up to 10 cm). The reduction in moisture content at the base of the composters was a result of microbial activity since the drying was not observed in the control composters.

Fungal growth was observed in the dry material since fungi need less moisture for metabolic activity and can grow faster than bacteria at lower moisture contents. The change in uniformity of the materials indicated that mixing at least once a week was required for the most active composters.

5.5 n-HEXADECANE STUDY

Due to the large unexpected decrease in TEH and DCPD found in the control composters, the composting apparatus and analytical methods were verified using a readily biodegradable, non volatile compound. n-Hexadecane was chosen due to its low vapour pressure (0.00496 mmHg at 35°C) and its linear chemical structure for ease of biodegradation. The goal of this experiment was to verify that the amount of n-hexadecane would not decrease in the control composters and show degradation in the active ones. If successful, conclusions about the applicability of composting for the degradation of the quench sludge could be made.

Four composters were prepared. Two were poisoned and two were maintained active with 2.5% and 5% n-hexadecane per dry weight. The poisoned composters contained 5% n-hexadecane. The experiments were conducted at 35 °C for six weeks using a mixture of peat moss (85% by weight) and Solv II (15% by weight). The same methods and equipment were used as previously described. Only the GC-FID settings were altered to accommodate the higher boiling point of n-hexadecane. The injector temperature was raised to 300°C and the final oven temperature was raised to 300°C. All other settings were maintained. Calibration for n-hexadecane was done using two dilutions of 0.38 g/L and 1.86 g/L in dichloromethane.

5.5.1 Carbon Dioxide Production and Output Gas Composition

The amount of carbon dioxide produced during the process was again monitored. Figure 5.20 shows the evolution rate of carbon dioxide and oxygen for composters containing 2.5% and 5% n-hexadecane. The production rate of carbon dioxide for the control composters is not shown since the rates were on average lower than 1 mL/hr and once reached a maximum value of 2.3 mL/hr at the start of the experiment. It can be seen once again that the oxygen content in the composters quickly dropped below desired levels but the air flow rate was not increased to remain consistent with previous experiments for comparison. Once again, methane was not detected using GC even when the oxygen content was minimal during the most active weeks of the process. The composter contaminated with 2.5% hexadecane resulted in the highest carbon dioxide evolution rates initially. The carbon dioxide production rate decreased after 30 days and the amount of oxygen in the output stream increased. The composter contaminated with 5% showed a slightly lower initial carbon dioxide production rate but maintained a higher rate after one month of operation. The oxygen was still utilized quickly upon entering the composter since the oxygen content in the output remained at a low value. The total carbon dioxide collected during the six weeks of operation for all composters is shown table 5.16.

Table 5.16: Carbon Dioxide Collected During n-Hexadecane Study

n-Hexadecane Content	Weight of CO_2 (g)
Control (5%)	2.43
Control (5%) (duplicate)	2.49
2.50%	26.74
5%	21.25

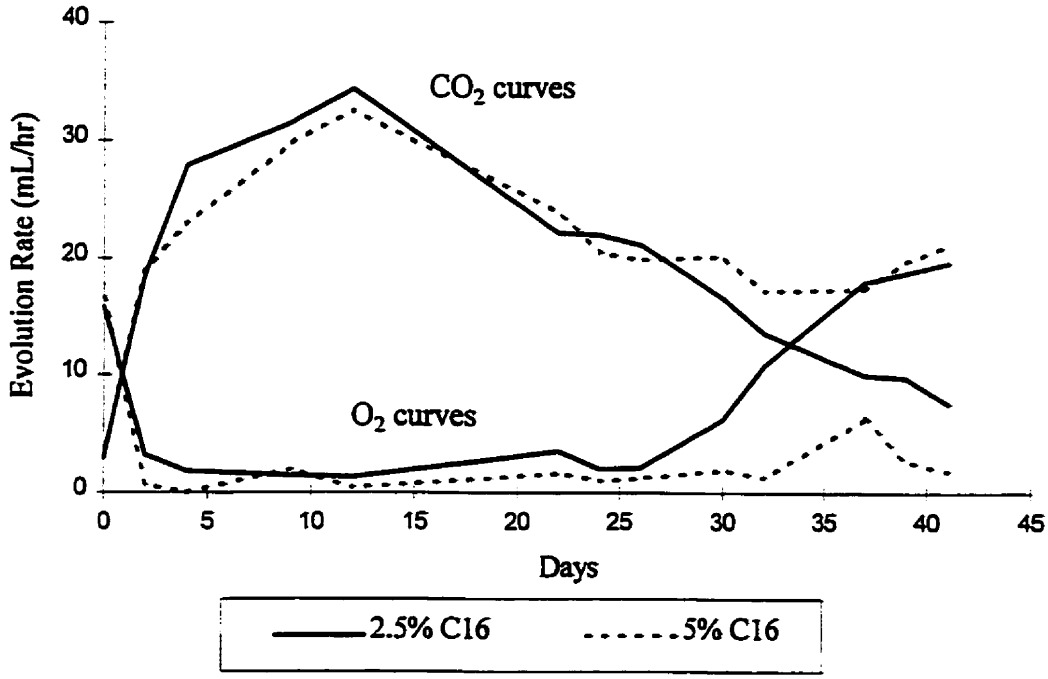


Figure 5.20: Carbon Dioxide and Oxygen Evolution Rates for Composters Containing n-Hexadecane

5.5.2 n-Hexadecane Reduction

Figure 5.21 shows the decrease of n-hexadecane observed during six weeks of operation. A small increase in hexadecane was observed in one of the control composters. The moisture content of the composting mixture was monitored and the drop in moisture over the duration of the experiment was taken into account when calculating the total decrease in the contaminant. Table 5.17 shows the decrease in moisture content in the composters during the experiments. The appearance of the materials in the active composters changed within a few days of composting. The bottom portion of the material was dry a couple of days after mixing, showing the need for mixing, especially during the most active weeks of the process.

Table 5.17: Percent Decrease in Moisture Content During Composting of n-Hexadecane

Week	Control	Control	2.5% C16	5% C16
1	1.4	-0.2	0.6	-2.1
2	3.2	1.2	2.2	1.7
3	3.4	1.7	2.8	-2.1
4	4.3	1.7	2.2	0.8
5	4.1	5.2	2	1.5
6	5.1	3.9	2.6	3.3

As seen on figure 5.21, a decrease in contaminant was observed as expected in the active composters whereas the control composters maintained their level of contamination. The results of only one of the poisoned composters are shown since both gave very similar results.

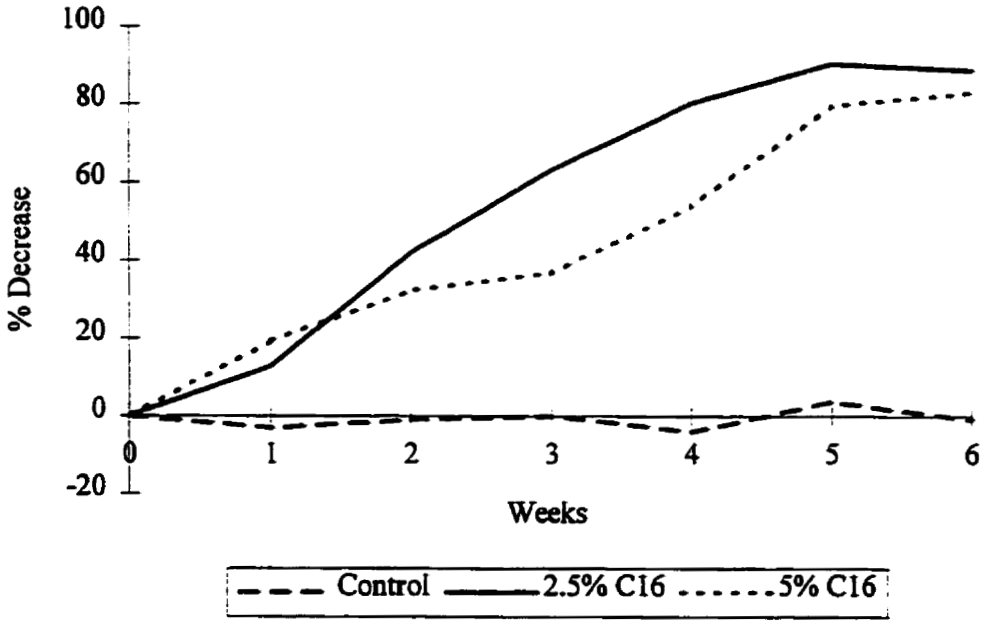


Figure 5.21: Decrease in n-Hexadecane Content Over Six Weeks

5.5.3 Separation of Polars

The extracts recovered for the composter contaminated with 2.5% n-hexadecane at the beginning and after six weeks of operation were further analyzed to study their polar content. Polar content was analyzed in compost samples containing only saturates for ease of separation. Using a silica cartridge, the saturates (hexadecane) were separated from the polars and weight percents were determined gravimetrically. The polar fraction in the extracts was found to be 72% initially and 78% at the end of the process once the saturates content had decreased. These values indicate that the polar fraction in the oil extract is significant and should have been removed for all samples prior to gravimetric analysis. The decrease in saturates was found to be only 50%. However, the separation method was not perfected and was only done to verify that the polar fraction was significant and possibly skewing oil and grease values obtained previously from compost samples containing sludge.

5.6 SLUDGE VOLATILIZATION

Due to the large decrease observed for both TEH and DCPD values, experiments on the volatilization of the sludge were carried out. To study the extent of the sludge volatilization alone, a known weight of sludge was left open in a fume hood and the weight change was noted after a week. It was found that 59% of the weight was lost due to venting. The sludge residue was a dry black powder since the large water fraction disappeared. The remaining sludge was analyzed using the GC. The chromatogram revealed that the lighter hydrocarbons such as toluene and styrene were no longer present in the remaining sludge. The DCPD peak still appeared in the chromatogram after evaporation but was reduced in size and no longer represented a main constituent of the hydrocarbon phase.

Further experiments were conducted to attempt to quantify the losses observed in both TEH and DCPD from the extraction procedure and to understand where the losses were occurring. A Solid Phase Microextraction apparatus was used to detect the hydrocarbons present in the exhaust gas of the composters. A control composter was not aerated but was still opened and mixed once a week. Another control composter was aerated but was not mixed weekly. Finally, the sludge was mixed with glass beads and placed in an aerated composter to study the effects of volatilization without organic matter interference.

5.6.1 SPME Results

Bengtsson et al (1998) found that hydrocarbons corresponding from n-C_{13} to n-C_{14} originating from light fuels were found in the offgas during enclosed composting. Based on the sludge characterization, several hydrocarbons were expected to escape the system. The hydrocarbons present in the exhaust gas stream of the control composter from the bulking agent study were analyzed using a Solid Phase Microextraction (SPME) apparatus. An exhaust gas sample could not simply be drawn and analyzed using GC-FID since the column was sensitive to oxygen. The column in the GC equipped with TCD could separate oxygen but could only separate hydrocarbon compounds lighter than ethylene.

The gas from a control composter during the bulking agent study was analyzed every couple of days and it was assumed that the losses over the two days were constant. The amount of DCPD escaping the system was cumulated and compared to the initial amount of DCPD placed in the composter. Figure 5.22 shows the percent DCPD lost over three weeks according to the SPME fibre. While other hydrocarbons were found to exit the system, dicyclopentadiene and benzene were most significant. It can be seen that

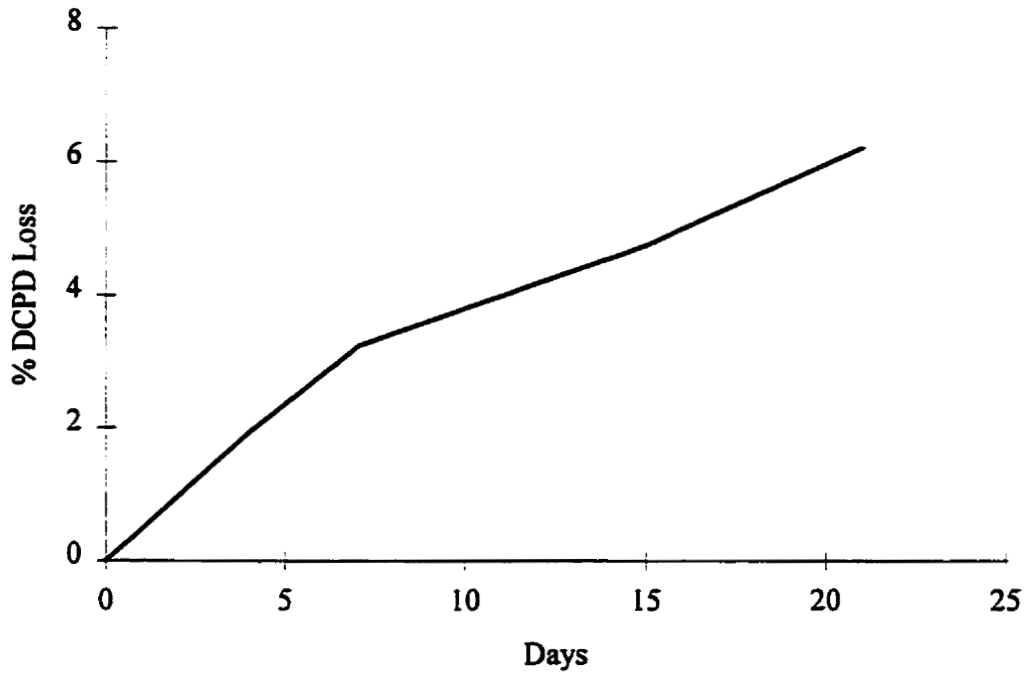


Figure 5.22: Percent DCPD Lost in Exhaust Gas According to SPME Fibre for Control Composter During Bulking Agent Study

after three weeks, approximately 6.2% of DCPD was lost in the exhaust gas. However, as seen previously in figure 5.11, there was a 65% to 85% decrease of DCPD in the composting mixture determined from extraction. Hence, not all losses observed in DCPD and TEH could be attributed to air stripping alone.

Figure 5.23 shows a typical spectrum from SPME fibre analysis using GC-FID. Benzene was always present in the largest concentration but the peak size decreased with time as the amount in the compost mass depleted. DCPD, naphthalene and other compounds were present in much smaller amounts. The release of DCPD was found to remain relatively constant and did not level off as fast a benzene. This could be due to the increased adsorption of DCPD on the fibre as the amount of benzene in the exhaust gas decreased, leaving more available adsorption sites on the fibre.

5.6.2 Expected Losses Using Raoult's Law

The losses of dicyclopentadiene calculated using the SPME fibre were verified by performing a calculation knowing the vapour pressure of DCPD in the composter at 35°C. DCPD has a vapour pressure of 5 mmHg at 34.1°C, and the air was fed into the composters at atmospheric pressure (680 mmHg). The moles of air passing through one composter over three weeks were calculated. The calculations were done over a duration of three weeks for comparison with the results shown in figure 5.22.

Calculations were done using Raoult's and Dalton's laws shown by equations (5-1) and (5-2) respectively. Raoult's law can be used when a solution consists of substances with nearly identical molecules. It states that the partial pressure of a contaminant (P_i) is equal to the mole fraction of the contaminant in the liquid phase (X_i) multiplied by its vapour pressure (P_v) at a given temperature. The mole fraction of DCPD was taken as the fraction in the hydrocarbon phase, which was calculated to be

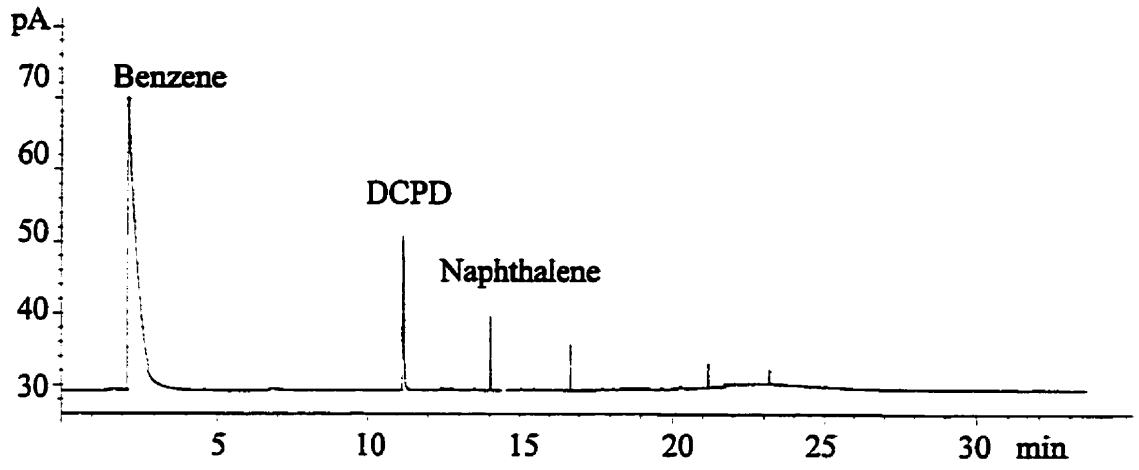


Figure 5.23: Typical GC-FID Output From SPME Analysis

46%. Since Raoult's law applies to molecules in miscible phases, the water and hydrocarbon phases cannot be both considered. Although the use of Raoult's law is extended for this calculation it still represents the best approximation for the determination of the partial pressure of DCPD in the exhaust gas. The mole fraction of DCPD in the exhaust gas can be found using Dalton's law. Dalton's law states that the mole fraction of the contaminant in the gas phase is equal to the ratio of the partial pressure of that contaminant to the total pressure of the system.

$$P_i = P_v \times X_i \qquad (5\text{-}1)$$

$$P_i = P_T \times Y_i \qquad (5\text{-}2)$$

The assumption made for the calculations is that the air passing through the composting mass is in equilibrium with the hydrocarbon phase at all times. The loss calculated should therefore represent the maximum possible loss.

When the calculations were done, it was found that after a 21 day operation a maximum of 13.1% DCPD should escape the system due to air stripping. However, the actual loss due to volatilization is likely to be less than the value calculated since the exhaust gas was passed through a condenser at 15°C prior to SPME analysis. The losses due to volatilization at 15°C could not be repeated since DCPD has a melting point of 32.9°C and hence vapour pressure values cannot be obtained below that temperature. Figure 5.22 shows that a 6.2% decrease in DCPD was observed from the SPME. The lower value was expected since the condensers reduced the output stream temperature and hence prevented all DCPD vapourized from escaping the system.

Using the same principles, the amount of water gain to be expected during the process could also be calculated. Water accumulation in the composters was expected

since saturated air enters the composters at room temperature and exits at 15°C in the condenser. The mole fraction of vapour in the input and output gas stream can be calculated knowing the vapour pressure of water at both temperatures. The mole fraction in each stream was converted to a mass of water and the net gain of water in the composter over a 30 day operation was found to be approximately 1 g. Hence, the water gain from the humidified air is not significant.

5.6.3 Non-Aerated Control Composter

A composter was poisoned as the other control composters but was not continuously aerated. The bulking agent used was 85% peat moss and 15% Solv II and the mixture was contaminated with 5% hydrocarbon. It was opened and mixed once a week to study the losses of contaminants due to the mixing alone. Composters were always cooled to room temperature prior to opening for mixing. Figure 5.24 shows the TEH and DCPD decrease observed in the non-aerated control composter.

These results show that mixing alone leads to 40% and 78% losses in TEH and DCPD respectively. The aerated control composter resulted in 46% and 89% losses in TEH and DCPD over the same duration. Hence, the losses observed in the bulking agent and hydrocarbon content studies are mostly due to opening, emptying and mixing of the compost material. The higher losses observed for the aerated composter can be attributed to air stripping. As predicted by Raoult's law and shown from SPME analysis, the losses due to air stripping should not be significant.

The moisture content of the poisoned composter was also monitored weekly. The decrease in moisture is shown in table 5.18. The water content decreased by 2% at the most during the experiment and should result in a 4.8% increase in TEH. The values for

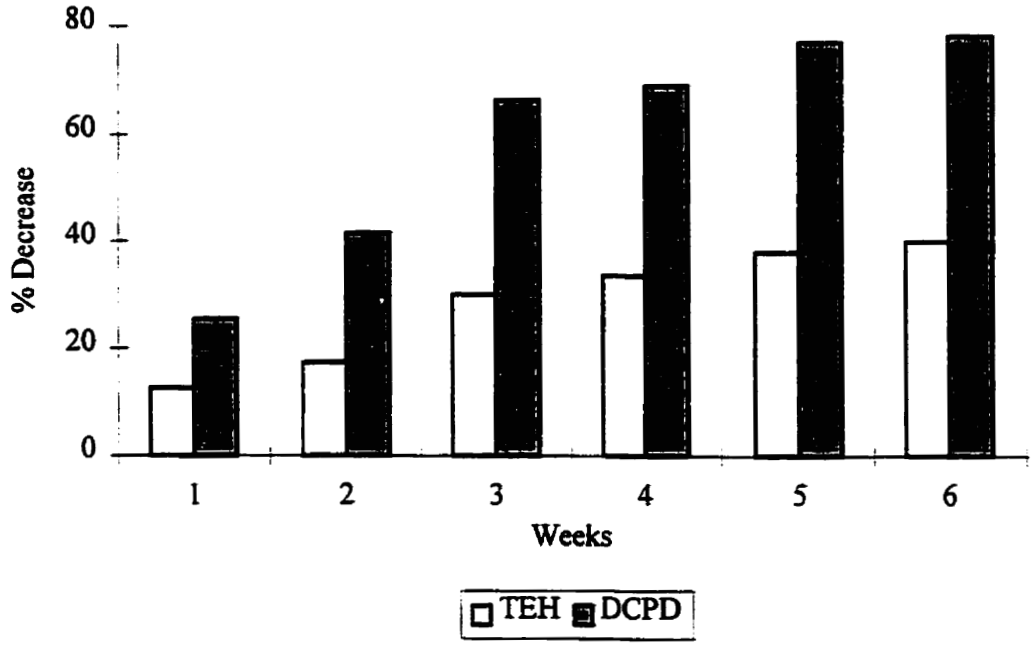


Figure 5.24: Decrease in TEH and DCPD for a Non-Aerated Control Composter

TEH percent decrease shown in figure 5.24 were not corrected for the change in moisture content and hence represent a slightly underestimated value.

Table 5.18: Moisture Content of Control Non-Aerated Composter

Week	% Moisture Decrease	% Increase in TEH Due to Moisture Decrease
1	0.6	1.4
2	1.1	2.6
3	1.5	3.6
4	2	4.8
5	2	4.8
6	1.9	4.6

The decrease in TEH and DCPD observed in the non-aerated control composter were much larger than expected. The composters were only opened for short periods of time during mixing. If such losses occur while the compost materials are mixed and opened to atmosphere, the use of composting to biodegrade the quench sludge does not seem to present a viable solution.

5.6.4 Aerated Control Composter Without Mixing

Another control composter was prepared using 85% peat moss and 15% Solv II and contaminated with 5% hydrocarbon. The composter was aerated for four weeks but was never opened during the process and the compost mass never mixed. The purpose of this experiment was to verify that if the mixture was not stirred every week, losses would be minimized at the end of the process. Table 5.19 lists the decrease observed in TEH and DCPD after four weeks of aeration.

Table 5.19: TEH and DCPD Decrease in Aerated Control Composter Without Mixing Over Four Weeks

Week	% DCPD Decrease	% TEH Decrease
4	48	28

The decrease shown in table 5.19 for DCPD and TEH do not represent the losses due to aeration alone since the mixture was emptied into a pale and mixed at the end of the four weeks prior to extraction. The losses should be compared to the ones observed for an aerated control composter sampled after one week of operation. Figures 5.18 and 5.19 show that the losses were found to be 40% and 17% for DCPD and TEH respectively for the aerated control composter after one week. These values indicate that the losses observed for the control composter that was not mixed weekly were primarily due to the mixing prior to sampling at the end of the process.

5.6.5 Volatilization of Sludge on Glass Beads

To study the effects of volatilization of the sludge in the composter without organic matter interference, the sludge was mixed with glass beads (2 to 2.5 mm in diameter) and enclosed in an aerated composter. The SPME fibre was used to analyze the composition of the exhaust gas. The exhaust gas was then passed through an activated charcoal trap (Sigma-Aldrich, untreated 8-20 mesh size) to measure hydrocarbon losses gravimetrically. The glass beads and sludge mixture was not mixed every week to minimize the amount of sludge lost to the mixing container and spatula.

The weight of the activated charcoal trap did not change during the six weeks of operation. The insignificant weight change implies that the amount of hydrocarbons escaping the system was negligible. SPME analysis revealed that benzene was escaping readily while dicyclopentadiene and other components were found but in lesser amounts.

Figure 5.25 shows the DCPD losses calculated from the SPME. The amount of DCPD calculated in the output stream may have been underestimated because the fibre was calibrated when DCPD only was present in the gas phase. Benzene is likely to be more readily adsorbed onto the fibre since it is a smaller molecule. Its presence in the exhaust stream may have hindered the adsorption of DCPD onto the fibre. Figure 5.25 shows that after six weeks of operation approximately 5.7% of the DCPD escaped due to aeration. According to Raoult's law, a 14% loss of DCPD could be expected without condensers and if the air reached equilibrium with the hydrocarbon phase while passing through the composter. The lower loss of 5.7% obtained from the SPME analysis is likely due to the effects of the condenser, the high benzene content in the output stream and failure to reach equilibrium with the air passing through the composter. Since the mixture of beads and sludge contained initially 15.8 g of DCPD, the corresponding loss was 0.9 g loss. The benzene represented approximately 2 g of the sludge added to the beads and was expected to entirely escape the system according to Raoult's law. However, the weight of benzene and DCPD escaping the system was not observed from with the activated charcoal trap.

Finally, extraction was done on the bead mixture to quantify the drop in total hydrocarbons during the process. Results from the extraction were not expected to provide accurate information since each mixing resulted in significant losses of sludge to the bucket and mixing spatula. Figure 5.26 shows the decrease in TEH and DCPD observed over time. According to figure 5.26 the losses are in the same range to those observed during the composting experiments for both TEH and DCPD values, with TEH values decreasing by 36% and DCPD by 60%.

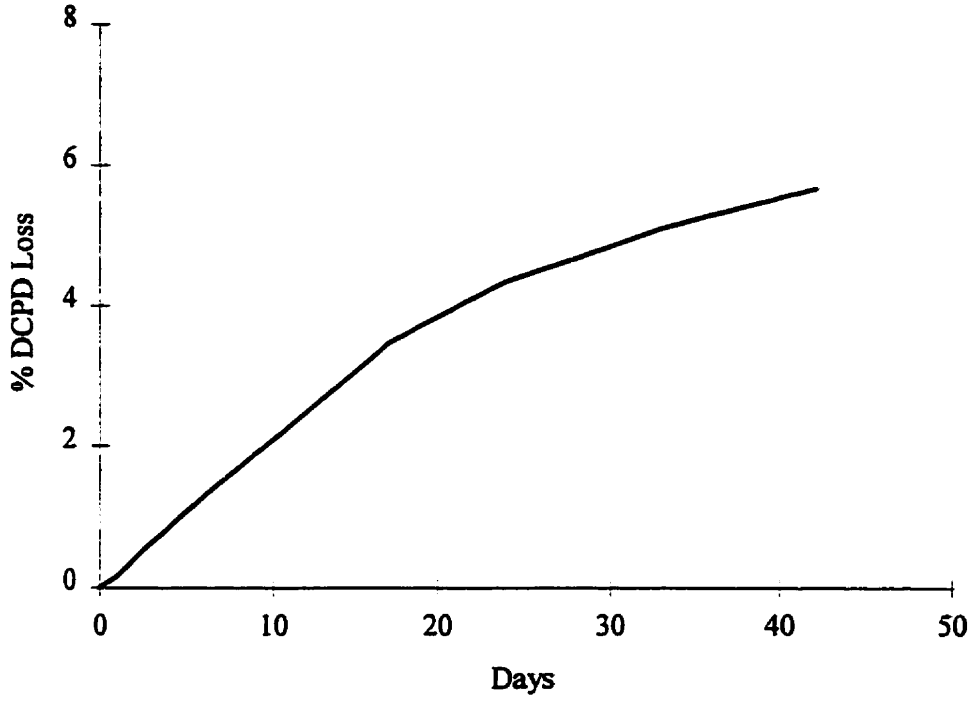


Figure 5.25: DCPD Losses From Bead/Sludge Mixture According to SPME Analysis

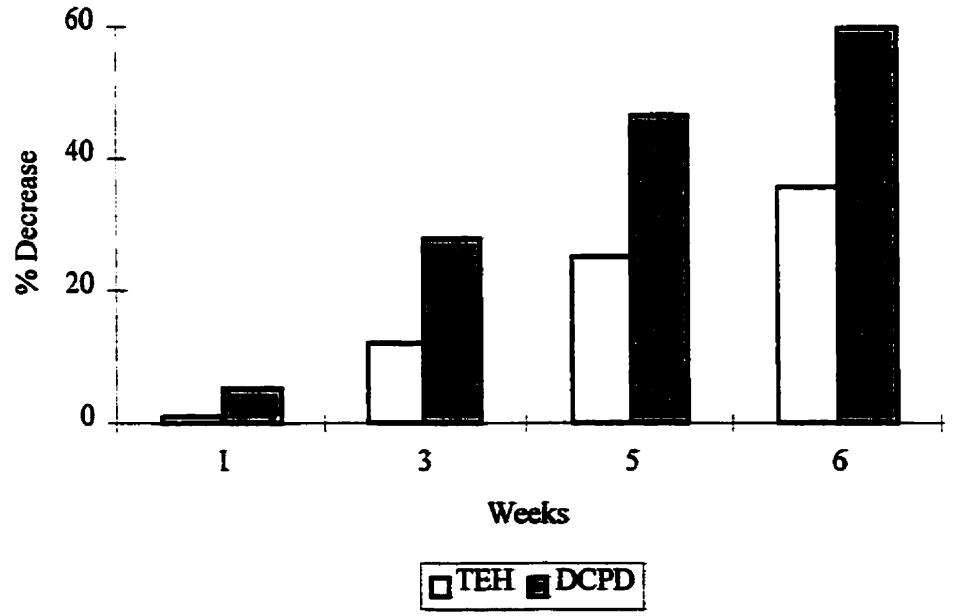


Figure 5.26: Decrease in TEH and DCPD for the Sludge/Bead Mixture

5.7 MASS BALANCE CALCULATIONS

Carbon mass balance calculations did not result in closure and indicated large losses. It was obvious that losses occurred for control composters showing a 46% decrease in TEH. Mass balance calculations on control composters resulted only in a 39% loss since some carbon dioxide was collected. However, closure on the carbon balance could not be obtained even from the n-hexane study which showed that abiotic losses were not significant. The unexplained losses obtained from the mass balance calculations are due to the difficulty in isolating the amount of carbon dioxide evolved due to contaminant degradation. Carbon dioxide from contaminant degradation could not be identified separately from carbon dioxide production due to bulking agent degradation. Taking the difference of carbon dioxide produced between a contaminated and non contaminated composter is not in an accurate estimate of the carbon dioxide produced from contaminant degradation. This is clear according to the results presented in table 5.20.

Table 5.20 shows the values used for mass balance calculations done to determine the percent carbon losses for the composters from the n-hexadecane study. The weight of n-hexadecane at the start of the process is shown and knowing the percent degradation, the weight of carbon remaining in the composters could be determined. The table also shows the amount of carbon dioxide produced during the process which was used for the calculation. The carbon content in n-hexadecane was calculated to be 91.4% by weight and 28.73 g (from table 5.7) of carbon dioxide was subtracted from the total weight collected to account for bulking agent degradation. This amount was not subtracted from the control composter so that a value could be calculated. The negative value obtained for the control composter is due to the small amount of carbon dioxide produced which was likely due to bulking agent degradation and not contaminant degradation. This low value confirms that abiotic losses of carbon during the n-hexadecane study were

negligible. The mass balance calculations done by subtracting the amount of carbon dioxide due to bulking agent degradation show that the subtraction is not valid to differentiate between carbon dioxide from bulking agent and contaminant. Composters contaminated with 2.5% and 5% n-hexadecane resulted in 55% and 60% carbon loss respectively, according to mass balance calculations. The large losses calculated in the active composters were not likely to have occurred since closure was obtained on the control composter which underwent the same treatment. Hence, when dealing with organic bulking agents, carbon mass balances cannot be done unless it is possible to differentiate between carbon dioxide mass produced from the contaminant.

The most active composters indicated that oxygen levels became limiting for aerobic activity. Although methane was not detected using GC it is suspected that it was present. Some of the losses could be due to the failure of quantifying methane in the output stream.

Table 5.20: Percent Carbon Losses According to Mass Balance Calculations Done on n-Hexadecane Study

Composter Description	Weight of C_{16} Initially (g)	% C_{16} Reduction	CO_2 Produced (g)	% Losses from Mass Balance
Control	12	-1	2.43	-7.0
2.5% C_{16}	6.2	89	35.71	55.4
5% C_{16}	12	83	37.88	60.2

CHAPTER 6: CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

The composition of the ethane pyrolysis quench sludge produced by Nova Chemicals at the Joffre plant indicates that it has the potential for biological treatment. However, the experiments done on the composting of the sludge do not provide much information on its biodegradability potential.

A study of the bulking agents revealed that a mixture of the manufactured Solv II and peat moss resulted in the highest microbial activity according to carbon dioxide production rates. Solv II alone compacted during the process and did not maintain its structure, preventing proper aeration of the materials. A mixture of 70% peat moss and 30% Solv II resulted in the highest microbial activity for prolonged periods of time. Peat moss, Sphag Sorb and wood chips alone were able to sustain microbial activity when low hydrocarbon content was placed in the mixture. The advantage of using Solv II as part of the bulking agent is that it contains a wide range of bacteria and fungi and hence served mostly as another source of inoculum. TEH decrease in the control composter was significant indicating that volatile losses were occurring. The control composter resulted in a 38% decrease in TEH and 83% reduction in DCPD. In the active composters, TEH and DCPD contents decreased between 34% to 41% and 62% to 85% respectively. The

high reductions in the control composter prevent conclusions to be drawn about biodegradation effects. All experiments were conducted at 35°C and contained up to 14% hydrocarbon content per dry weight. The high hydrocarbon content was limiting microbial activity. Bacteria counts revealed that the high concentration of hydrocarbon in the composters resulted in toxic conditions.

Experiments on the effect of hydrocarbon content in the composters were conducted using a mixture of 85% peat and 15% Solv II by weight. Hydrocarbon content was varied between 1.5% to 7.5% per dry mass and experiments were again conducted at 35°C. The highest carbon dioxide production rate was observed in the composter containing 1.5% hydrocarbon but the evolution rate was found to decrease within two weeks of the operation. Composters contaminated with 2.5% and 5% hydrocarbon also resulted in high carbon dioxide evolution rates and the high rates were maintained for a longer period of time. Oxygen content fell below limits but the air flow rate was not increased to minimize volatile losses. Once hydrocarbon content was set to 7.5% and higher, carbon dioxide production rates were significantly reduced. Bacteria counts were consistent with results obtained from carbon dioxide evolution. The largest population growth was observed in the 1.5% hydrocarbon mixture, reaching 11 million bacteria per gram of mixture after a two week exposure. Growth was significantly reduced when hydrocarbon content was increased to 7.5% since bacteria counts only reached 0.7 millions per gram. However, even at low hydrocarbon content, the bacterial growth after two weeks of operation was lower than expected. TEH decreased by 46% and DCPD by 89% in the control composter after one month. Again, the active composters did not decrease in hydrocarbon content any more than the control.

The methods and apparatus were verified by composting n-hexadecane. n-Hexadecane was chosen since it is readily biodegradable and should not be lost to volatilization. The poisoned composters maintained their initial concentration of n-

hexadecane whereas the composters contaminated with 2.5% and 5% hexadecane resulted in 90% and 85% decrease respectively after 42 days of operation. This experiment was conducted to ensure that the unexpected decrease observed in the control composters during previous experiments was not due to experimental set up and procedures.

A problem associated with the use of organic bulking agents is that they degrade during the process. Partial degradation of bulking agents utilizes nitrogen and phosphorous and more nutrients must be added to the compost mixture. The decrease in bulking agent content may also mask the effect of biodegradation of hydrocarbons, if decomposition of bulking agent is more intensive than oil decomposition. As a result, oil concentration may increase although there is an actual breakdown of oil. Finally, degradation of the bulking agent results in large carbon dioxide production making carbon mass balance calculations difficult. An experiment conducted using non contaminated bulking agent revealed that most of the carbon dioxide collected from the composting process was due to bulking agent degradation.

Mass balance calculations were attempted using the results from the n-hexadecane study since it was known that abiotic losses were not significant. The amount of carbon dioxide produced due to bulking agent degradation was subtracted from the amount collected from the contaminated composters. This method resulted in large percent losses of 55% and 62% for the composters contaminated with 2.5% and 5% n-hexadecane respectively. These values are not representative since it was previously shown that abiotic losses were negligible. The calculated losses imply that a background amount of carbon dioxide associated with bulking agent degradation cannot be identified using methods presented in this work. It became obvious that a background amount could not be established when the hydrocarbon content in the composters was increased and resulted in lower carbon dioxide production than in the non-contaminated composters.

A Solid Phase Microextraction apparatus was used to analyze hydrocarbon compounds escaping in the exhaust gas. SPME analysis indicated that 6.2% of DCPD was lost due to air stripping after 21 days of operation of a control composter. Extraction of the same compost mixture indicated that there was a 83% decrease in DCPD during that time. Hence, air stripping effects were not leading to the high losses observed. SPME results were verified using Raoult's law. The maximum losses that can be expected due to volatilization were calculated to be 13%. Lower actual losses were expected due to the cooling effect of the condensers not included in the calculation.

A composter was poisoned and not aerated but was opened and mixed once a week to study the losses due to mixing. TEH and DCPD values decreased by 40% and 78% respectively after 42 days of operation. Previous experiments were carried out to verify that the hydrocarbons were not simply adsorbing onto the bulking agent with time. Hence, the losses observed from the bulking agent and hydrocarbon content studies were mostly due to the mixing of the material.

Sludge was mixed with glass beads and placed in an aerated composter to study the losses without organic matter interactions. The activated charcoal trap placed at the output of the composter did not increase in weight indicating that hydrocarbons lost from air stripping were negligible. However, SPME analysis revealed that up to 5.7% DCPD was lost during a 42 day operation which was equivalent to 0.9g. Extraction of the beads resulted in high losses of 36% in TEH and 60% in DCPD, but these can mostly be attributed to the loss of sludge to the bucket and spoon during mixing.

Composting does not seem to provide a viable waste management alternative for the quench sludge due to the high abiotic losses of dicyclopentadiene and total hydrocarbons. An enclosed system may be more suitable to address the concern of volatile losses.

6.2 RECOMMENDATIONS FOR FUTURE WORK

The following recommendations are made taking into consideration problems encountered during this work:

1. The use of organic bulking agents is convenient for large scale composting operations but presents problems due to their tendency to biodegrade. The degradation of bulking agent material increases carbon dioxide production. This is mainly a problem for lab work when attempting mass balance calculations. The degradation of bulking agents may also lead to underestimation of oil degradation. Total Organic Content should be monitored to account for dry mass reduction when using organic bulking agents. The use of inorganic bulking agents such as tire chips should be considered since they are essentially inert and pass through the composting process virtually unchanged. Because they do not decompose, they can be recovered by screening, saving composting facilities money by reducing the purchase costs of other bulking agents. However, they present a problem when extracting the compost material for hydrocarbon content using dichloromethane.

2. Polars recovered during extraction should be removed from the oil to obtain more accurate oil and grease content values when using organic bulking agents.

3. Lab scale composters were built to hold approximately 650 g of material (3L). Larger bioreactors (10 - 100 L) are recommended since literature review on the comparison between lab scale and pilot scale composting indicates significant differences in results.

4. The composition of the quench sludge suggests that it should be biodegradable. Other biological treatments should be investigated. The large fraction of DCPD

present in the sludge suggests that an aerobic process is favourable since oxidation has been shown the be the first step in DCPD biodegradation. Based on the high losses observed due to volatilization during mixing, the following systems and changes are recommended for the treatment of the quench sludge:

- The use of hydrogen peroxide or pure oxygen under controlled feed in response to oxygen needs is recommended since it can minimize volatile losses due to lower aeration requirements.
- Mixing of DCPD to activated charcoal has been found to reduce volatility of the substrate. It is recommended to mix the sludge with activated charcoal prior to any biological treatment method to reduce volatilization although it is not know how it will interfere with other compounds or solids and water found in the sludge.
- The large losses during mixing indicate that an enclosed compost reactor system may be more suitable. The built-in agitator removes the need to open the reactor and mix the materials. Enclosed reactors allow for better control of volatile emissions.
- Slurry-phase treatment also offers the advantage of mixing the material during the process but tends to promote volatilization of contaminants.
- For any enclosed system equipped with agitators, recirculation of the exhaust gas should be considered since volatilization of contaminants will be increased due to mixing effects. The use of a gas-recirculation system removes the need for off gases processing and allows for a better estimate of the extent of bioremediation.
- Biopiles present an advantage since the material is not mixed during the process. They do not however, provide much control of volatile losses.
- Static piles use perforated pipes on which the materials are placed. The pipes supply the oxygen while removing the need for occasional mixing. Unlike

biopiles they offer better control of volatile losses if the air is drawn from the pile and collected.

5. The hydrocarbon content study indicated that the sludge is toxic when applied at concentrations near 7.5% (or 75 000 ppm). Optimal microbial activity was observed below 5% hydrocarbon content. The ratio of bulking agents to sludge needed to obtain this concentration is very large (10% w/w), indicating that bulking agents should be recycled to minimize operating costs. The increase in material to be treated may make any type of composting unsuitable if the production rate of the sludge is faster than remediation rates.

REFERENCES

Alberta Environmental Protection, "Sustainable Composting Options in the province of Alberta, Final report", (1993).

Albright, L., B. Crynes and W. Corcoran, "Pyrolysis: Theory and Industrial Practice", Academic Press, Toronto, (1983).

Alexander, Martin, "Biodegradation and Bioremediation", Academic Press, Toronto, (1994).

American Society for Testing and Materials, "Standard Practice for Extraction of Solid Waste Samples for Chemical Analysis Using Soxhlet Extraction", designation D 5369-93, (1993).

Anderson, William, "Bioremediation: Innovative Site Remediation Technology", Springer-Verlag, New York, (1995).

Anon, "Successful Bioremediation with Compost", *Biocycle*, **36**(2), 57-59, (1995).

Atlas, Ronald. "Microbial Degradation of Petroleum Hydrocarbons: Environmental Perspective", *Microbiological Reviews*, **45**(1), 180-209, (1981).

Atlas, Ronald, "Petroleum Microbiology", Macmillan Publishing Company, New York, (1984).

Atlas, Ronald, "Handbook of Microbiological Media", CRC Press, Boca Raton Fla., (1993).

Bengtsson, A. et al., "Composting of Oily Sludges - Degradation, Stabilized Residues, Volatiles and Microbial Activity", *Waste Management & Research*, **16**(3), 273-284, (1998).

Benton, C. and J. Gage, "A Look at In-Vessel Composting", *Solid Waste Technologies*, **12**(3), 14-21, (1998).

Brinton, William and Mary Droffner, "Microbial Approaches to Characterization of Composting Process", *Compost Science and Utilization*, **2**(3), 12-17, (1994).

Canadian Council of Ministers of the Environment, "Interim Canadian Environment Quality Criteria for Contaminated Sites", CCME Subcommittee on Environmental Quality Criteria for Contaminated Sites, (1991).

Canadian Council of Ministers of the Environment, "National Guidelines for the Landfilling of Hazardous Waste", Report CCME-WM/TRE-028E, April (1991).

Cheremisinoff, P.,"Thermal Treatment of Hazardous Wastes", Encyclopedia of Environmental Control Technology; v.1, Gulf Publishing Company Book Division, Houston, (1989).

Conklin, Alfred Jr., "To Bulk or not to Bulk? Some Soils Respond to Bulking, Some Don't", *Soil and Groundwater Cleanup*, 44-46, Dec. (1995).

Cookson, John Jr., "Bioremediation Engineering: Design and Applications", McGraw-Hill Inc., Toronto, (1995).

Deipser, A., "Biodegradation of Volatile CFCs, H-CFCs and VC in Compost and Marl", *Waste Management & Research*, **16**(4), 330-341, (1998).

Fyock. O., S. Nordrum, S. Fogel and M. Findlay, "Pilot Scale Composting of Petroleum Production Sludges", presented at the Third Annual Symposium on Environmental Protection in the Energy Industry: Treatment and Disposal of Petroleum Sludges, University of Tulsa, Oklahoma, Dec. 12, (1991).

Golueke, C. and L. Diaz, "Composting and The Limiting Factor Principle", *BioCycle*, **28**(4), 22-25, (1987).

Gomez, A., "The Evaluation of Compost Quality", *Trends in Analytical Chemistry*, **17**(5), 310-314, (1998).

Haug, Roger, "The Practical Handbook of Compost Engineering", Lewis Publishers, Ann Arbor, (1993).

Holger, K. and E. Wasiyhun, "Biodegradation of Petroleum-based Oil Wastes Through Composting", *Biodegradation*, **9**(2), 151-156, (1998).

LaGrega, M., P. Buckingham and J. Evans, "Hazardous Waste Management", McGraw-Hill Inc., Toronto, (1994).

McMillen, S.J et al., "Composting in Cold Climates: Results from Two Field Trials", paper SPE 35578, presented at the The Third International Conference on Health, Safety & Environment in Soil & Gas Exploration & Production, New Orleans, 9-12, (1996).

McMillen, S., N. Gray, J.Kerr and M. Findlay, "Composting of a Production Pit Sludge", Houston, Exxon Production Research Company, (1993).

Milne, B. and P. Fedorak, "Composting of Heavy Oil Refinery Sludge", Final report, Report for Consumer's Cooperative Refineries Ltd., June (1996).

Milne, B., H. Baheri and G. Hill, "Composting of a Heavy Oil Refinery Sludge", *Environmental Progress*, **17**(1), 24-27, (1998).

Nordrum, S., L. Fyock, and M. Findlay, "Treatment of Production Tank Bottom Sludge by Composting", Paper SPE 24568, presented at the 67th Annual Technical Conf., Society of Petroleum Engineers, Washington D.C., 181-190 (1992).

Perry, Jerome, "Isolation and Characterization of Thermophilic Hydrocarbon-Utilizing Bacteria", *Advances in Aquatic Microbiology*, **3**, 109-139, (1985).

Pollard, S., S. Hrudey, B. Fuhr, et al., "Hydrocarbon Wastes at Petroleum- and Creosote-Contaminated Sites: Rapid Characterization of Component Classes by Thin-Layer Chromatography with Flame Ionization Detection", *Environmental Science & Technology*, **26**(12), 2528-2534, (1992).

Shen, Y., L. Stehmeier and G. Voordouw, "Identification of Hydrocarbon-Degrading Bacteria in Soil by Reverse Sample Genome Probing", *Applied and Environmental Microbiology*, **64**(2), 637-645, (1998).

Sitting, M., "Incineration of Industrial Hazardous Wastes and Sludges", Pollution Technology Review No. 63, Noyes Data Corporation, New York (1979).

"Standard Methods For the Examination of Water and Wastewater", Sixteenth Edition, prepared and published by American Public Health Association, American Water Works Association, and Water Pollution Control Federation, American Public Health Association, Washington, (1985).

Stehmeier, Lester, "Fate of Dicyclopentadiene in the Environment", Ph.D. thesis, University of Calgary, (1997).

Vecchioli G., M. Del Panno and M. Painceia, "Use of Selected Autochthonous Soil Bacteria to Enhance Degradation of Hydrocarbons in Soil", *Environmental Pollution*, **67**, 249-258, (1990).

van Breemen, R., C. Fenselau and R. Cotter, "Derivatives of Dicyclopentadiene in Groundwater", *Biomedical and Environmental Mass Spectrometry*, **14**, 97-102, (1994).

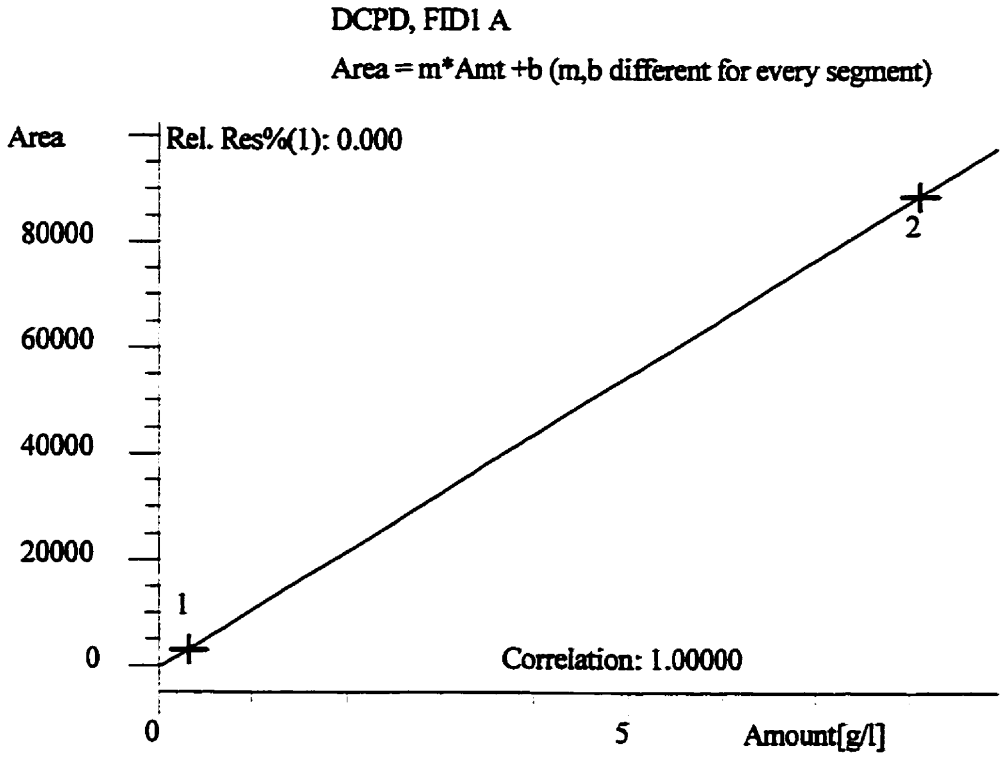
van Breemen, R., Y. Tsou and G. Connolly, "Oxidation of Dicyclopentadiene in Surface Water", *Biological Mass Spectrometry*, **22**(10), 579-584, (1993).

Zappi, M., B. Rogers, A. Brad et al., "Bioslurry Treatment of a Soil Contaminated with Low Concentration of Total Petroleum Hydrocarbons", *Journal of Hazardous Materials*, **46**(1), 1-12, (1996).

APPENDIX A: GC AND FLOWMETERS CALIBRATION CURVES

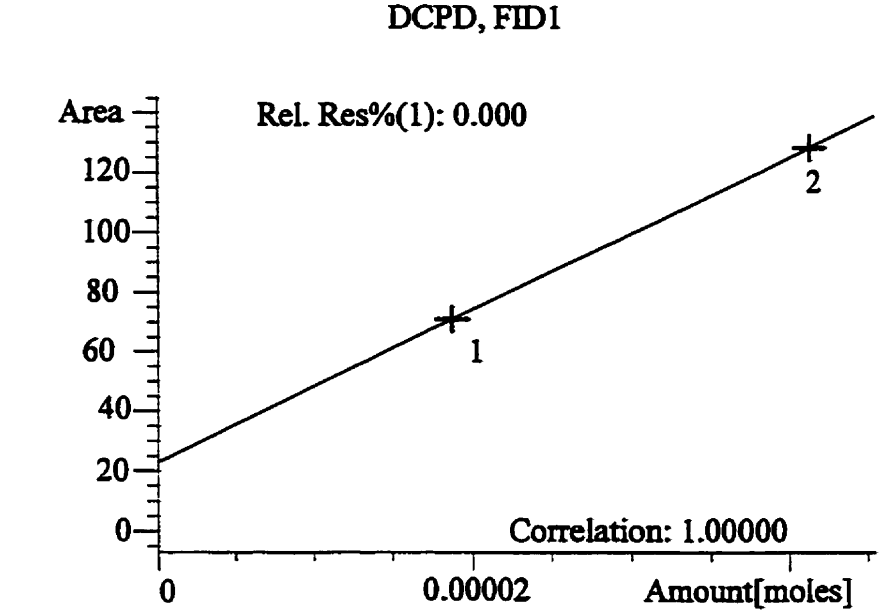
Calibration for Sludge Extract Analysis Using GC-FID

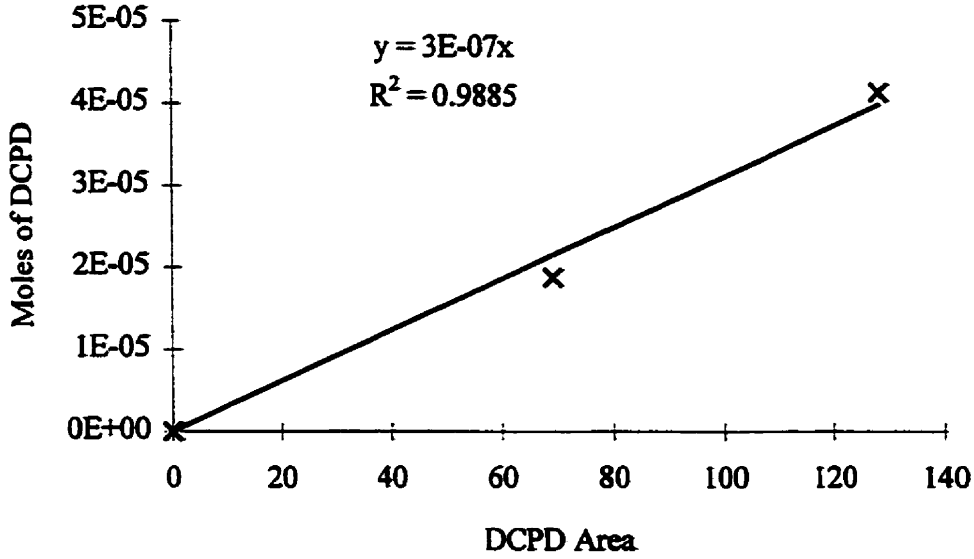
The calibration plot for Total Extractable Hydrocarbon content was shown in chapter 4. Dicyclopentadiene calibration plot used to quantify the amount of DCPD present in the extract is shown below.



SPME Calibration

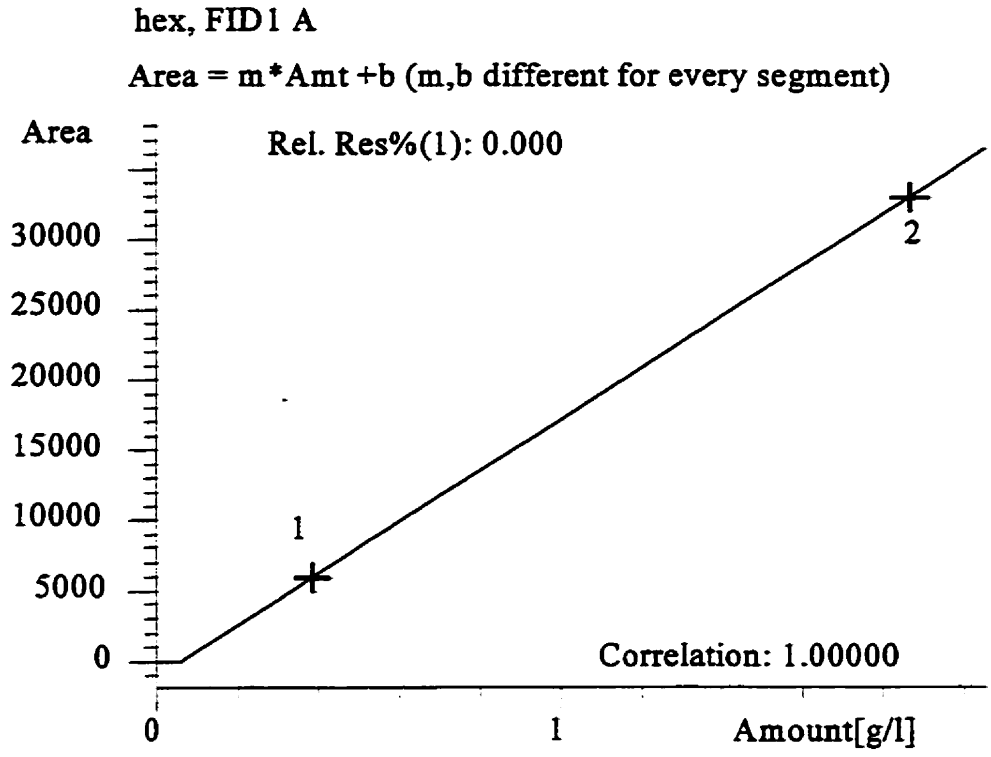
The calibration plot obtained for the concentration of dicyclopentadiene in a gas sampling bulb using the SPME fibre is shown next. The second figure shows the calibration and linear regression actually used once the line was forced to pass through the origin.





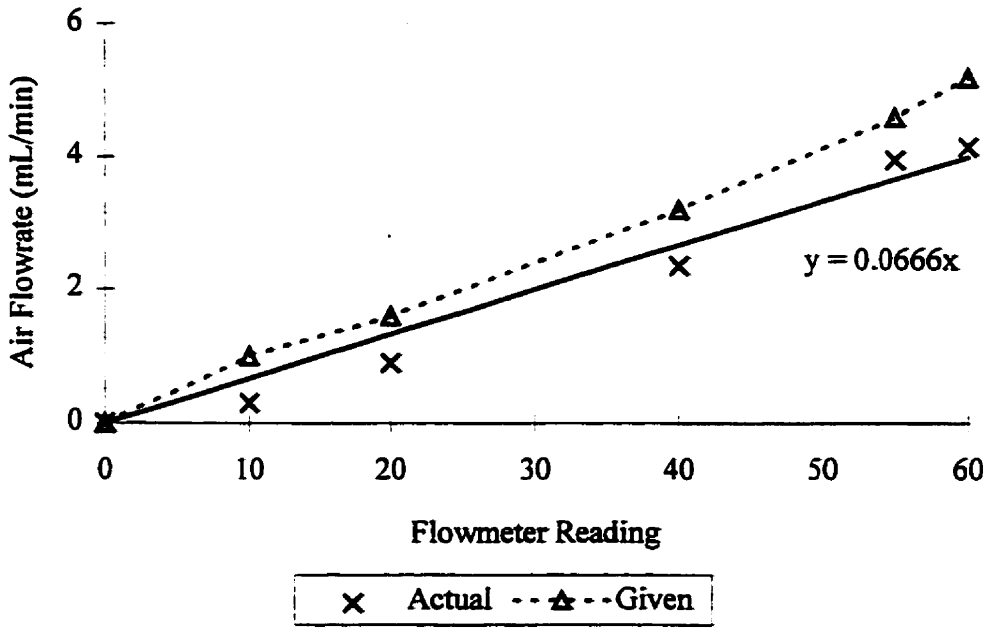
n-Hexadecane Calibration Curve

A calibration was done for n-hexadecane using concentrations of 0.38 g/L and 1.86 g/L in dichloromethane. The following figure shows the calibration plot obtained from GC-FID for n-hexadecane.



Flowmeter Calibration

The flowmeters were provided with a calibration table. The values given in the table were verified using a digital flowmeter (J&W Scientific ADM 1000 Intelligent Flowmeter). The following figure shows the difference between the given values and the ones observed using the digital flowmeter. The linear regression for the actual values was used to convert the flowmeter reading to air flow rates.



APPENDIX B: MAXXAM ANALYTICS RESULTS

MAXXAM ANALYTICS Inc.

CHEMEX LABS ALBERTA Inc.

CERTIFICATE OF PONAOX(U) ANALYSIS

Container I.D.:	Glass	**Contact Name:**	Estelle Ducatel
Project No.:	99-22066-01	**Contact Phone:**	1-403-220-8409
Date Received:	98-12-03	**Contact Fax:**	1-403-220-1061
Company:	University Of Calgary		
Plant:			
Sample Point:	Quench Sludge		
Date Sampled:	N/A	**Sampled By:**	U of C
Sample Description:	Sludge		
Date Reported:	99-01-11	**Analyzed By:**	PW

*** information not available**

Component	Weight %	Liquid Volume %
Methane	<0.01	<0.01
Ethene	<0.01	<0.01
Ethane	<0.01	<0.01
Propene	<0.01	<0.01
Propane	<0.01	<0.01
Isobutane	<0.01	<0.01
Methanol	<0.01	<0.01
Isobutene	<0.01	<0.01
1-Butene	<0.01	<0.01
1,3-Butadiene	<0.01	<0.01
n-Butane	<0.01	<0.01
trans-2-Butene	<0.01	<0.01
2,2-Dimethylpropane	<0.01	<0.01
cis-2-Butene	<0.01	<0.01
1,2-Butadiene	<0.01	<0.01
Ethanol	<0.01	<0.01
3-Methyl-2-butene	<0.01	<0.01
Isopentane	<0.01	<0.01
1,4-Pentadiene	<0.01	<0.01
2-Butyne	<0.01	<0.01
1-Pentene	<0.01	<0.01
Isopropanol	<0.01	<0.01
2-Methyl-1-butene	<0.01	<0.01
n-Pentane	<0.01	<0.01
2-Methyl-1,3-butadiene	<0.01	<0.01
trans-2-Pentene	<0.01	<0.01
1-Pentyne	<0.01	<0.01

Component	Weight %	Liquid Volume %
cis-2-Pentene	<0.01	<0.01
2-Methyl-2-butene	<0.01	<0.01
trans-1,3-Pentadiene	<0.01	<0.01
3-Methyl-1,2-butadiene	<0.01	<0.01
Cyclopentadiene	<0.01	<0.01
cis-1,3-Pentadiene	<0.01	<0.01
1,2-Pentadiene	<0.01	<0.01
2,2-Dimethylbutane	<0.01	<0.01
Cyclopentene	<0.01	<0.01
4-Methyl-1-cyclopentene	<0.01	<0.01
2,3-Pentadiene	<0.01	<0.01
n-Propanol	<0.01	<0.01
Cyclopentane	<0.01	<0.01
2,3-Dimethylbutane	<0.01	<0.01
C6-Olefin	<0.01	<0.01
Methyl-tert-butyl ether	<0.01	<0.01
C6-Olefin	<0.01	<0.01
2-Methylpentane	<0.01	<0.01
C6-Olefin	<0.01	<0.01
Methyl ethyl ketone	<0.01	<0.01
3-Methylpentane	<0.01	<0.01
C6-Olefin?	<0.01	<0.01
C6-Olefin	<0.01	<0.01
1-Hexene	<0.01	<0.01
C6-Olefin?	<0.01	<0.01
C6-Olefin?	<0.01	<0.01
2-Butanol	<0.01	<0.01
n-Hexane	<0.01	<0.01
C6-Olefin	<0.01	<0.01
trans-2-Hexene	<0.01	<0.01
2-Methyl-2-pentene	<0.01	<0.01
C6-Olefin	<0.01	<0.01
C6-Olefin	<0.01	<0.01
cis-2-Hexene	<0.01	<0.01
C6-Olefin	<0.01	<0.01
C6-Olefin	<0.01	<0.01
Methylcyclopentane	<0.01	<0.01
2,2-Dimethylpentane	<0.01	<0.01
Isobutanol	<0.01	<0.01
C6-Olefin	<0.01	<0.01
2,4-Dimethylpentane	<0.01	<0.01
C6-Olefin	<0.01	<0.01
2,2,3-Trimethylbutane	<0.01	<0.01
C6-Olefin?	<0.01	<0.01
C6-Olefin?	<0.01	<0.01
C6-Olefin?	<0.01	<0.01
C6-Olefin	<0.01	<0.01
C6-Olefin	<0.01	<0.01

Component	Weight %	Liquid Volume %
C6-Olefin	<0.01	<0.01
Benzene	4.98	4.45
1-Methyl-1-cyclopentene	<0.01	<0.01
C7-Olefin?	<0.01	<0.01
3,3-Dimethylpentane	<0.01	<0.01
Cyclohexane	<0.01	<0.01
C7-Olefin?	<0.01	<0.01
C7-Olefin?	<0.01	<0.01
n-Butanol	<0.01	<0.01
C7-Olefin	<0.01	<0.01
C7-Olefin	<0.01	<0.01
C7-Olefin	<0.01	<0.01
C7-Olefin	<0.01	<0.01
C7-Olefin?	<0.01	<0.01
C7-Olefin	<0.01	<0.01
2-Methylhexane	<0.01	<0.01
2,3-Dimethylpentane	<0.01	<0.01
1,1-Dimethylcyclopentane	<0.01	<0.01
C7-Olefin	<0.01	<0.01
C7-Olefin	<0.01	<0.01
3-Methylhexane	<0.01	<0.01
C7-Olefin	<0.01	<0.01
C7-Olefin	<0.01	<0.01
cis-1,3-Dimethylcyclopentane	<0.01	<0.01
trans-1,3-Dimethylcyclopentane	<0.01	<0.01
3-Ethylpentane	<0.01	<0.01
trans-1,2-Dimethylcyclopentane	<0.01	<0.01
C7-Olefin	<0.01	<0.01
C7-Olefin	<0.01	<0.01
2,2,4-Trimethylpentane	<0.01	<0.01
1-Heptene	<0.01	<0.01
C7-Olefin	<0.01	<0.01
C7-Olefin	<0.01	<0.01
C7-Olefin	<0.01	<0.01
C7-Olefin	<0.01	<0.01
trans-3-Heptene	<0.01	<0.01
n-Heptane	<0.01	<0.01
cis-3-Heptene	<0.01	<0.01
C7-Olefin	<0.01	<0.01
C7-Olefin	<0.01	<0.01
trans-2-Heptene	<0.01	<0.01
C7-Olefin	<0.01	<0.01
C7-Olefin	<0.01	<0.01
C7-Olefin	<0.01	<0.01
C7-Olefin	<0.01	<0.01
cis-2-Heptene	<0.01	<0.01
C7-Olefin	<0.01	<0.01
Methylcyclohexane	<0.01	<0.01

Component	Weight %	Liquid Volume %
2,2-Dimethylhexane	<0.01	<0.01
C8-Olefin?	<0.01	<0.01
C8-Olefin	<0.01	<0.01
C8-Olefin?	<0.01	<0.01
Ethylcyclopentane	<0.01	<0.01
C8-Olefin?	<0.01	<0.01
C8-Olefin?	<0.01	<0.01
2,5-Dimethylhexane	<0.01	<0.01
2,2,3-Trimethylpentane	<0.01	<0.01
2,4-Dimethylhexane	<0.01	<0.01
C7-Olefin	<0.01	<0.01
trans,cis-1,2,4-Trimethylcyclopentane	<0.01	<0.01
C8-Paraffin	<0.01	<0.01
C8-Olefin?	<0.01	<0.01
C8-Olefin?	<0.01	<0.01
trans,cis-1,2,3-Trimethylcyclopentane	<0.01	<0.01
C8-Olefin?	<0.01	<0.01
C8-Olefin?	<0.01	<0.01
C8-Olefin?	<0.01	<0.01
2,3,4-Trimethylpentane	<0.01	<0.01
C7-Olefin?	<0.01	<0.01
C8-Olefin?	<0.01	<0.01
C8-Olefin?	<0.01	<0.01
Toluene	3.26	2.95
2,3,3-Trimethylpentane	<0.01	<0.01
C8-Olefin?	<0.01	<0.01
C8-Olefin?	<0.01	<0.01
C8-Olefin?	<0.01	<0.01
C8-Olefin?	<0.01	<0.01
C8-Olefin?	<0.01	<0.01
2,3-Dimethylhexane	<0.01	<0.01
2-Methyl-3-ethylpentane?	<0.01	<0.01
C8-Olefin?	<0.01	<0.01
C8-Olefin?	<0.01	<0.01
C8-Olefin?	<0.01	<0.01
C8-Olefin?	<0.01	<0.01
2-Methylheptane	<0.01	<0.01
4-Methylheptane	<0.01	<0.01
cis,trans-1,2,4-Trimethylcyclopentane	<0.01	<0.01
C8-Olefin?	<0.01	<0.01
3,4-Dimethylhexane?	<0.01	<0.01
C8-Olefin?	<0.01	<0.01
3-Methylheptane	<0.01	<0.01
trans-1,4-Dimethylcyclohexane	<0.01	<0.01
3-Ethylhexane	<0.01	<0.01
1-Methyl-2-ethylcyclopentane?	<0.01	<0.01
C8-Olefin?	<0.01	<0.01
C8-Olefin?	<0.01	<0.01

Component	Weight %	Liquid Volume %
C8-Olefin?	<0.01	<0.01
C8-Olefin?	<0.01	<0.01
1,1-Dimethylcyclohexane?	<0.01	<0.01
2,2,5-Trimethylhexane?	<0.01	<0.01
cis-1-Ethyl-2-methylcyclohexane?	<0.01	<0.01
C8-Olefin?	<0.01	<0.01
cis-1-Ethyl-3-methylcyclohexane?	<0.01	<0.01
1-Methyl-1-ethycyclopentane	<0.01	<0.01
1-Octene	<0.01	<0.01
C8-Olefin?	<0.01	<0.01
trans-1,2-Dimethylcyclohexane	<0.01	<0.01
C8-Olefin?	<0.01	<0.01
1-Methyl-trans-3-ethylcyclopentane?	<0.01	<0.01
C9-Paraffin?	<0.01	<0.01
C8-Olefin?	<0.01	<0.01
C8-Olefin?	<0.01	<0.01
cis,cis-1,2,3-Trimethylcyclopentane	<0.01	<0.01
n-Octane	<0.01	<0.01
C8-Olefin?	<0.01	<0.01
C8-Olefin?	<0.01	<0.01
trans-2-Octene	<0.01	<0.01
Isopropylcyclopentane	<0.01	<0.01
C9-Olefin?	<0.01	<0.01
C9-Olefin?	<0.01	<0.01
C9-Olefin?	<0.01	<0.01
C9-Olefin?	<0.01	<0.01
2,2,4-Trimethylhexane?	<0.01	<0.01
2,4,4-Trimethylhexane?	<0.01	<0.01
C9-Olefin?	<0.01	<0.01
2,3,5-Trimethylhexane?	<0.01	<0.01
cis-2-Octene	<0.01	<0.01
2,2,3,4-Tetramethylpentane?	<0.01	<0.01
C9-Paraffin?	<0.01	<0.01
2,2,Dimethylheptane?	<0.01	<0.01
2,4-Dimethylheptane?	<0.01	<0.01
cis-1,2-Dimethylcyclohexane	<0.01	<0.01
C9-Olefin?	<0.01	<0.01
Ethylcyclohexane	<0.01	<0.01
Propylcyclopentane	<0.01	<0.01
cis-1,3,5-Trimethylcyclohexane	<0.01	<0.01
C9-Olefin?	<0.01	<0.01
C9-Olefin?	<0.01	<0.01
1,1,3-Trimethylcyclohexane?	<0.01	<0.01
C9-Olefin?	<0.01	<0.01
C9-Olefin?	<0.01	<0.01
1,1,4-Trimethylcyclohexane	<0.01	<0.01
3,3-Dimethylheptane	<0.01	<0.01
C9-Olefin?	<0.01	<0.01

Component	Weight %	Liquid Volume %
2,5-Dimethylheptane	<0.01	<0.01
C9-Olefin?	<0.01	<0.01
C9-Paraffin?	<0.01	<0.01
C9-Olefin?	<0.01	<0.01
2,3,3-Trimethylheptane?	<0.01	<0.01
C9-Olefin?	<0.01	<0.01
Ethylbenzene	<0.01	<0.01
trans-1,2,4-Trimethylcyclohexane	<0.01	<0.01
C9-Olefin?	<0.01	<0.01
2,3,4-Trimethylhexane?	<0.01	<0.01
C9-Olefin?	<0.01	<0.01
3,3,4-Trimethylhexane?	<0.01	<0.01
m-Xylene	<0.01	<0.01
p-Xylene	<0.01	<0.01
3,5-Dimethylheptane	<0.01	<0.01
2,3-Dimethylheptane	<0.01	<0.01
3,4-Dimethylheptane	<0.01	<0.01
C9-Olefin?	<0.01	<0.01
C9-Olefin?	<0.01	<0.01
3-Methylethylhexane?	<0.01	<0.01
C9-Olefin?	<0.01	<0.01
4-Ethylheptane?	<0.01	<0.01
4-Methyloctane?	<0.01	<0.01
2-Methyloctane	<0.01	<0.01
C9-Olefin?	<0.01	<0.01
C9-Paraffin?	<0.01	<0.01
C9-Olefin?	<0.01	<0.01
C9-Olefin?	<0.01	<0.01
C9-Paraffin?	3.19	3.47
3-Methyloctane	<0.01	<0.01
cis,1,2,4-Trimethylcyclohexane	<0.01	<0.01
3,3-Diethylpentane	<0.01	<0.01
o-Xylene	<0.01	<0.01
1,1,2-Trimethylcyclohexane	<0.01	<0.01
C9-Olefin?	<0.01	<0.01
C9-Olefin?	<0.01	<0.01
C9-Paraffin?	<0.01	<0.01
trans-1-Ethyl-4-methylcyclohexane?	<0.01	<0.01
cis-1-Ethyl-4-methylcyclohexane?	<0.01	<0.01
C9-Paraffin?	<0.01	<0.01
1-Nonene	<0.01	<0.01
Isobutylcyclopentane	<0.01	<0.01
C9-Paraffin?	<0.01	<0.01
trans-3-Nonene	<0.01	<0.01
cis-3-Nonene	<0.01	<0.01
C9-Paraffin?	<0.01	<0.01
n-Nonane	<0.01	<0.01
C10-Olefin?	<0.01	<0.01

Component	Weight %	Liquid Volume %
1-Methyl-1-ethylcyclohexane?	<0.01	<0.01
trans-2-nonene	<0.01	<0.01
1-Methyl-2-propylcyclopentane?	<0.01	<0.01
C10-Olefin?	<0.01	<0.01
C10-Paraffin?	<0.01	<0.01
C10-Paraffin?	<0.01	<0.01
Isopropylbenzene	<0.01	<0.01
cis-2-Nonene	<0.01	<0.01
tert-Butylcyclopentane?	<0.01	<0.01
C9-Olefin?	<0.01	<0.01
Isopropylcyclohexane	<0.01	<0.01
3,3,5-Trimethylheptane?	<0.01	<0.01
2,2-Dimethyloctane	<0.01	<0.01
2,4-Dimethyloctane?	<0.01	<0.01
1-Methyl-4-isopropylcyclohexane?	<0.01	<0.01
sec-Butylcyclopentane?	<0.01	<0.01
2,6-Dimethyloctane?	<0.01	<0.01
2,5-Dimethyloctane?	<0.01	<0.01
Butylcyclopentane	<0.01	<0.01
Propylcyclohexane?	<0.01	<0.01
3,3-Dimethyloctane	<0.01	<0.01
1-Methyl-2-ethylcyclohexane?	<0.01	<0.01
C10-Olefin?	<0.01	<0.01
Propylbenzene	<0.01	<0.01
3,6-Dimethyloctane?	<0.01	<0.01
3-Methyl-5-ethylheptane?	<0.01	<0.01
C10-Olefin?	<0.01	<0.01
1-Ethyl-3-methylbenzene	<0.01	<0.01
1-Ethyl-4-methylbenzene	<0.01	<0.01
Naphthene?	<0.01	<0.01
1,3,5-Trimethylbenzene	<0.01	<0.01
2,3-Dimethyloctane	<0.01	<0.01
5-Methylnonane?	<0.01	<0.01
3,3,4-Trimethylheptane?	<0.01	<0.01
2-Methylnonane	<0.01	<0.01
1-Ethyl-2-methylbenzene	<0.01	<0.01
3-Ethyloctane	<0.01	<0.01
Naphthene?	<0.01	<0.01
3-Methylnonane	<0.01	<0.01
C10-Olefin?	<0.01	<0.01
C10-Paraffin?	<0.01	<0.01
C10-Paraffin?	<0.01	<0.01
1,2,4-Trimethylbenzene	<0.01	<0.01
C10-Paraffin?	<0.01	<0.01
C10-Paraffin?	<0.01	<0.01
Isobutylcyclohexane	<0.01	<0.01
C10-Paraffin?	<0.01	<0.01
C10-Paraffin?	<0.01	<0.01

Component	Weight %	Liquid Volume %
1-Decene	<0.01	<0.01
C10-Paraffin?	<0.01	<0.01
C10-Paraffin?	<0.01	<0.01
C10-Aromatic?	<0.01	<0.01
C10-Paraffin?	<0.01	<0.01
Naphthene?	<0.01	<0.01
Isobutylbenzene	<0.01	<0.01
trans-1-Methyl-2-propylcyclohexane?	<0.01	<0.01
C10-Paraffin?	<0.01	<0.01
sec-Butylbenzene	<0.01	<0.01
n-Decane	<0.01	<0.01
C11-Paraffin?	<0.01	<0.01
C11-Paraffin?	<0.01	<0.01
1,2,3-Trimethylbenzene	<0.01	<0.01
1-Methyl-3-isopropylbenzene	<0.01	<0.01
C11-Paraffin?	<0.01	<0.01
1-Methyl-4-isopropylbenzene	<0.01	<0.01
C11-Paraffin?	<0.01	<0.01
C11-Paraffin?	<0.01	<0.01
2,3-Dihydroindene?	<0.01	<0.01
sec-Butylcyclohexane? (Indene ????)	41.90	41.09
4-Methyldecane?	<0.01	<0.01
1-Methyl-2-isopropylbenzene	<0.01	<0.01
3-Ethylnonane?	<0.01	<0.01
Naphthene?	2.83	2.78
C11-Paraffin?	<0.01	<0.01
C11-Paraffin?	<0.01	<0.01
1,3-Diethylbenzene?	<0.01	<0.01
1-Methyl-3-propylbenzene	<0.01	<0.01
1,4-Diethylbenzene?	<0.01	<0.01
1-Methyl-4-propylbenzene	0.54	0.49
Butylbenzene	<0.01	<0.01
1,3-Dimethyl-5-ethylbenzene	<0.01	<0.01
1,2-Diethylbenzene?	<0.01	<0.01
C11-Paraffin?	<0.01	<0.01
Isobutylcyclohexane?	<0.01	<0.01
5-Methyldecane?	<0.01	<0.01
C10-Aromatic?	<0.01	<0.01
C10-Aromatic?	<0.01	<0.01
1-Methyl-2-propylbenzene	<0.01	<0.01
C10-Aromatic?	<0.01	<0.01
C11-Paraffin?	<0.01	<0.01
C11-Paraffin?	<0.01	<0.01
trans-1-Methyl-2-methyl-4-propylcyclopentane	<0.01	<0.01
C11-Paraffin?	<0.01	<0.01
C11-Paraffin?	<0.01	<0.01
1,4-Dimethyl-2-ethylbenzene	<0.01	<0.01
1,3-Dimethyl-4-ethylbenzene	<0.01	<0.01

Component	Weight %	Liquid Volume %
C11-Paraffin?	<0.01	<0.01
C11-Paraffin?	<0.01	<0.01
1,2-Dimethyl-4-ethylbenzene	<0.01	<0.01
1,3-Dimethyl-2-ethylbenzene	<0.01	<0.01
C11-Paraffin?	2.79	2.95
C11-Paraffin?	<0.01	<0.01
C11-Paraffin?	<0.01	<0.01
1-Methyl-4-tert-butylbenzene?	<0.01	<0.01
1,2-Dimethyl-3-ethylbenzene	1.31	1.15
1-Ethyl-2-isopropylbenzene?	<0.01	<0.01
n-Undecane	<0.01	<0.01
1-Ethyl-4-isopropylbenzene?	<0.01	<0.01
Unknowns - C12	3.16	3.31
1,2,4,5-Tetramethylbenzene	<0.01	<0.01
2-Methylbutylbenzene	<0.01	<0.01
1,2,3,5-Tetramethylbenzene	<0.01	<0.01
C12-Paraffin?	<0.01	<0.01
C11-Aromatic?	<0.01	<0.01
C11-Aromatic?	<0.01	<0.01
C11-Aromatic?	<0.01	<0.01
C11-Aromatic?	<0.01	<0.01
tert-1-Butyl-2-methylbenzene	<0.01	<0.01
C11-Aromatic?	<0.01	<0.01
1-Ethyl-2-propylbenzene?	<0.01	<0.01
C11-Aromatic?	<0.01	<0.01
C11-Aromatic?	<0.01	<0.01
C11-Aromatic?	<0.01	<0.01
1-Methyl-3-butylbenzene?	0.88	0.81
1,3-Diisopropylbenzene?	<0.01	<0.01
Unknowns - C12	1.02	1.06
Unknowns - C12	0.34	0.35
trans-1-Methyl-2-(4-methylpentyl)-cyclopentane	<0.01	<0.01
C11-Aromatic?	<0.01	<0.01
Unknowns - C12	0.99	1.04
C11-Aromatic?	<0.01	<0.01
C12-Paraffin?	<0.01	<0.01
1,2,3,4-tetrahydronaphthalene?	<0.01	<0.01
tert-1-Butyl-3,5-dimethylbenzene	<0.01	<0.01
Unknowns - C12	0.21	0.22
C12-Paraffin?	14.28	14.94
C11-Aromatic?	<0.01	<0.01
C11-Aromatic?	<0.01	<0.01
C12-Paraffin?	0.19	0.20
C12-Paraffin?	<0.01	<0.01
C11-Aromatic?	<0.01	<0.01
C12-Paraffin?	<0.01	<0.01
1,3-Diisopropylbenzene?	<0.01	<0.01
n-Dodecane	<0.01	<0.01

Component	Weight %	Liquid Volume %
Unknowns - C13	0.22	0.23
C11-Aromatic?	<0.01	<0.01
C11-Aromatic?	<0.01	<0.01
1,3,5-Triethylbenzene	<0.01	<0.01
C11-Aromatic?	0.59	0.53
Unknowns - C13	0.20	0.21
tert-1-Butyl-4-ethylbenzene?	<0.01	<0.01
Unknowns - C13	0.80	0.83
Unknowns - C13	1.12	1.16
Unknowns - C13	0.52	0.54
Unknowns - C13	0.32	0.33
Unknowns - C13	0.74	0.77
Unknowns - C13	4.15	4.30
Unknowns - C13	3.89	4.03
Unknowns - C13	0.17	0.17
1-Methylnaphthalene	<0.01	<0.01

Component	Weight %	Liquid Volume %

IDENTIFIED COMPONENT GROUP CONCENTRATIONS

Paraffins	20.44	21.56
Olefins	0.00	0.00
Napthenes	44.73	43.87
Aromatics	11.57	10.38
Oxygenates	0.00	0.00

UNIDENTIFIED COMPONENT GROUP CONCENTRATIONS

C4 Unknowns	<0.01	<0.01
C5 Unknowns	<0.01	<0.01
C6 Unknowns	<0.01	<0.01
C7 Unknowns	<0.01	<0.01
C8 Unknowns	<0.01	<0.01
C9 Unknowns	<0.01	<0.01
C10 Unknowns	<0.01	<0.01
C11 Unknowns	<0.01	<0.01
C12 Unknowns	5.71	5.98
C13 Unknowns	12.14	12.59
C13+ Unknowns	5.42	5.62

**Detection Limit: 0.01

Note: The identification of components is based on relative retention time data. Identification in some cases is speculative.

Re: Sludge Sample
MAXXAM File No.: 99-22066-01

The Iatroscan analysis we discussed has been completed. The results are of the Carbon Disulfide soluble material only. Normally, a % Recovery is reported but without proper sample preparation and more cost to you, the % Recovery was not determined. The "Polars B" material can be asphaltenes but cannot be report conclusively as such. You have to analyse the sample using an asphaltene method to be 100 % sure. The data are tabulated below:

SATURATES (Weight %)	AROMATICS (Weight %)	POLARS A (Weight %)	POLARS B (Weight %)
12.9	68.8	13.7	4.6

APPENDIX C: ATOMSCAN 16/25 RESULTS

Blank run: Distilled water

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Method: ENVIRO2 Standard: blank

Elem	Be2348	Mg2802	V 3110	Cr2677	Mn2576	Fe2539	Co2286
Avge	D.0123	D.0409	D1.039	D1.103	D.0465	D.3856	D.3646
SDev	.0004	.0001	.003	.005	.0005	.0029	.0022
%RSD	3.114	.2823	.3314	.4603	1.024	.7424	.6125
#1	D.0120	D.0410	D1.039	D1.108	D.0468	D.3876	D.3664
#2	D.0128	D.0410	D1.034	D1.097	D.0460	D.3830	D.3668
#3	D.0120	D.0408	D1.039	D1.105	D.0452	D.3834	D.3632
#4	D.0124	D.0406	D1.043	D1.102	D.0470	D.3856	D.3622

Elem	Ni2316	Cu3247	Zn2138	Al3092	B_2497	Se1960	As1890
Avge	D.3758	D.4163	d.0650	D2.188	d.3318	D.4541	\.2235
SDev	.0032	.0013	.0004	.006	.0028	.0055	.0052
%RSD	.8516	.3101	.5618	.2752	.8492	1.219	2.341
#1	D.3790	D.4148	d.0646	D2.181	d.3332	D.4560	.2270
#2	D.3766	D.4158	d.0652	D2.194	d.3280	D.4536	.2264
#3	D.3714	D.4178	d.0654	D2.186	d.3344	D.4500	.2198
#4	D.3762	D.4168	d.0646	D2.193	d.3314	D.4488	.2250

Elem	Cd2265	Pb2203	Mo2045	Ba4554	Hg1942	Na5895	K_7664
Avge	d.1325	D1.043	D.4238	D1.097	/.4510	1.475	D1.175
SDev	.0008	.011	.0064	.005	.0153	.010	.002
%RSD	.5713	1.027	1.520	.4919	3.388	.6777	.1491
#1	d.1330	D1.048	D.4242	D1.091	/.4284	1.466	D1.172
#2	d.1330	D1.042	D.4322	D1.095	.4560	1.469	D1.176
#3	d.1326	D1.041	D.4206	D1.097	.4576	1.486	D1.175
#4	d.1314	D1.064	D.4172	D1.104	.4620	1.479	D1.175

Elem	Ca3933
Avge	d.0168
SDev	.0001
%RSD	.5970
#1	d.0166
#2	d.0168
#3	d.0168
#4	d.0168

Standard 1: Various elements at 10 ppm

Method: ENVIRO2 Standard: std1

Elem	Be2348	Cr2677	Fe2599	Co2286	Ni2316	Cu3247	Zn2138
Avge	22.48	28.99	31.33	23.22	14.61	18.36	23.35
SDev	.11	.10	.12	.09	.05	.15	.09
%RSD	.4827	.3383	.3840	.3988	.3567	[illegible]	.3382
#1	22.65	28.85	31.36	23.16	[illegible]	[illegible]	23.48
#2	22.41	28.98	31.28	23.27	14.61	18.55	23.27
#3	22.44	29.04	31.40	23.12	14.55	18.38	23.30
#4	22.43	29.08	31.20	23.31	14.58	18.21	23.36

Elem	[illegible]	[illegible]	Se1960	As1890	Cd2265	Pb2203	Na5895
Avge	13.80	37.97	5.180	4.819	18.12	4.169	33.52
SDev	.05	.17	.028	.045	.10	.078	.20
%RSD	.3703	.4391	.5454	.9311	.5396	1.860	.6022
#1	13.81	37.83	5.196	4.857	18.00	4.285	33.28
#2	13.87	38.09	5.138	4.796	18.09	4.133	33.56
#3	13.99	38.14	5.190	4.766	18.23	4.127	33.48
#4	13.94	37.82	5.196	4.856	[illegible]	[illegible]	[illegible]

Elem	K_7664	Ca3933
Avge	2.465	13.30
SDev	.006	.15
%RSD	.2427	1.097
#1	2.459	13.19
#2	2.473	13.15
#3	2.467	13.41
#4	2.462	13.44

Standard 3: Magnesium, Manganese and Mercury at 10 ppm

Method: ENVIRO2 Standard: std3

Elem	Mg2802	Mn2576	Hg1942
Avge	22.17	20.38	19.32
SDev	.08	.09	.07
%RSD	.3691	.4176	.3574
#1	22.15	20.42	19.25
#2	22.12	20.47	19.40
#3	22.14	20.27	19.36
#4	22.29	20.36	19.27

Standard 4: Vanadium and Molybdenum at 10 ppm

Method: ENVIRO2 Standard: std4

Elem	V_3110	Mo2045
Avge	23.38	15.58
SDev	.09	.09
%RSD	.4004	.5816
#1	23.41	15.47
#2	23.50	15.65
#3	23.32	15.53
#4	23.29	15.65

Standard 4b: Barium at 10 ppm

Method: ENVIRO2 Standard: std4ba

Elem	Ba4554
Avge	578.70
SDev	.24
%RSD	.3047
#1	578.86
#2	578.34
#3	578.79
#4	578.79

Solids Samples

Method: ENVIRO2 Sample Name: Sample-2 Operator:
Run Time: 05/04/99 09:21:34
Comment:
Mode: CONC Corr. Factor: 1

Elem	Be2348	Mg2802	V_3110	Cr2677	Mn2576	Fe2599	Co2286
Units	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Avge	D.0020	2.786	D.0167	6.746	.9196	S25.23	.1276
SDev	.0001	.012	.0022	.043	.0049	.00	.0004
%RSD	2.510	.4259	13.07	.6423	.5285	.0061	.3423
#1	D.0020	2.777	D.0187	6.767	.9216	S25.23	.1275
#2	D.0020	2.803	D.0166	6.690	.9232	S25.23	.1276
#3	D.0021	2.786	D.0137	6.736	.9213	S25.23	.1272
#4	D.0021	2.778	D.0178	6.790	.9124	S25.22	.1282

Elem	Ni2316	Cu3247	Zn2138	Al3092	B_2497	Se1960	As1890
Units	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Avge	35.77	.3710	.7942	2.616	2.107	D.0160	.0986
SDev	.13	.0023	.0056	.010	.010	.0087	.0045
%RSD	.3662	.6266	.7065	.3714	.4944	54.56	4.579
#1	35.72	.3728	.8011	2.620	2.119	D.0184	.0998
#2	35.88	.3699	.7904	2.614	2.094	D.0133	.1006
#3	35.87	.3682	.7964	2.604	2.106	D.0265	.0919
#4	35.61	.3730	.7889	2.627	2.109	D.0057	.1020

Elem	Cd2265	Pb2203	Mo2045	Ba4554	Hg1942	Na5895	K_7664
Units	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Avge	d.0088	1.369	.0737	.8037	.0109	8.275	d-2.023
SDev	.0008	.036	.0014	.0041	.0015	.044	.040
%RSD	9.580	2.643	1.886	.5154	14.23	.5370	1.973
#1	d.0082	1.403	.0725	.7985	.0101	8.274	d-1.963
#2	d.0081	1.363	.0730	.8023	.0101	8.253	d-2.047
#3	d.0097	1.389	.0756	.8059	.0132	8.337	d-2.039
#4	d.0094	1.321	.0737	.8079	.0102	8.235	d-2.042

Elem	Ca3933
Units	ppm
Avge	17.62
SDev	.04