CHAPTER 1

INTRODUCTION

1.1. Background of study

Technologically Enhanced Natural Occurrence Material (TENORM) is defined as materials, usually industrial wastes or by-products enriched with radioactive elements found in the environment and are brought to the surface through human activities such as oil and gas exploration or mining and through natural processes. In petroleum industry it is known as oil sludge which is the end product in petroleum refinery. These effluents must be treated through depuration processes. The composition ratio of oily sludge which often consists of various petroleum hydrocarbons (PHCs), heavy metal, and solid particles varies according to their origin, storage condition and treatment history (Guangji Hu, Jianbing Li, and Guangming Zeng, 2013). Petroleum hydrocarbons are among the most common environmental contaminants as they are highly toxic, mutagenic and carcinogenic to microorganisms as well as to higher systems including humans (Sudip K. Samanta, Om V. Singh and Rakesh K. Jain, 2002). Simply dumping these wastes or burning them with no previous treatment has serious environmental consequences and presents a risk to both ecosystems and human health.

There is a variety of oily sludge treatment methods that have been developed such as landfilling, incineration, co-processing in clinkerization furnaces, microwave liquefication, centrifugation, destructive distillations, low-temperature conversion, thermal plasma, incorporation in ceramic materials, development of impermeabilization materials, encapsulation, and the most commonly used in Malaysia is ‘landfarming’ method which offers a cost-effective, energy efficient, and environmentally friendly with minimal residue disposal problems (Ramzi F. Hejazi, Tahir Husain, and Faisal I. Khan, 2003). Although landfarming has reported to be a cost-effective and simple method in the treatment of petroleum waste, it also comes with a few operational and environmental drawbacks. One of the downside of using this method of treatment is that it creates a strong unpleasant odour originated from the hydrogen sulphide generated during the sludge processing causing the community to complaints.

Thus in order to address this problem, a study on the pre-treatment of the oily sludges (TENORM) to reduce or annihilate the odour of the oil sludges during the biodegradation process is to be carried out using a closed mechanical composting method.

1.2. Problem Statement

Petroleum storage and transportation facilities have often been a source of environmental pollution as they generate a number of hazardous waste during the operation. The petrochemical industry generates a series of liquid effluents during the petroleum-refining process. The sludges that result from this treatment process have a high content of petroleum-derived hydrocarbons, mainly alkanes and paraffins of 1-40 carbon atoms, along with cycloalkanes and aromatic compounds, making them a potentially dangerous waste product. Due to its content of harmful organic compounds, oil sludge has been recognized as a potentially dangerous waste product and categorized under scheduled waste under Environmental Quality Act 1984 Hence restricted to Environmental Quality Act 1974 where:

- Scheduled waste shall be disposed of at prescribed premises only
- Scheduled waste shall be rendered innocuous prior to disposal
- Scheduled waste shall be treated at prescribed premises or at on-site treatment facility only

The current treatment method that has been widely used in petroleum industry is land farming treatment method and it is proved to be economic and environmental friendly yet it still comes with some drawbacks which one of them is the unpleasant odour released to the surrounding area. To minimize or annihilate this problem, the biodegradation process of oil sludge will be carried out in a closed system whereby it will be called as the closed composting system. This is to control the release of odour from the mixture of oil sludge and the medium. Therefore, the present research is aimed to tackle the abovementioned limitation of the existing treatment method. This study is developed with the aim to provide an innovative treatment method which is related to human health, safety and environment implementation and beneficial to the industry in terms of waste management and is particularly applicable to be practised in Malaysia especially in the oil and gas industry.

1.4. Objective of study

The objectives of this study are as follows:

- To be able to treat TENORM in closed composting system.
- To be able to determine the optimum condition or environment for microorganism to degrade the hydrocarbon.
- To reduce the odour during the treatment.

1.5. Scope of Study

To develop the study, few parameters must be studied first in order to obtain the optimum condition for the hydrocarbons to degrade in a closed composting system and how they affect the biodegradation rate. These parameters are soil moisture, pH, mineral nutrients, micronutrients, organic supplements, and incubation temperature. Experiment will be done with various material and different composition of soil and the results from all the experiments will compared to choose the most effective parameters for the bioremediation of the oily sludge. As the rate of biodegradation is proportional to the reduction rate of oil sludge odour, hence theoretically the faster the biodegradation rate of TENORM the faster the reduction rate of the odour.

CHAPTER 2

LITERATURE REVIEW

This chapter outlines the fundamental concepts on oil sludge management and treatments. It reports on the previous studies done by other researcher on this aspect of the study. This information will be the benchmark for the evaluation of the biodegradation rate of oil sludge for this study.

2.1 Oil Sludge Composition

Oily sludge is a pasty, semisolid material made of sand which is contaminated by oil, and chemicals used in petroleum processing and it is the most abundant oil waste generated in refineries (Da Silva et al., 2012). In general, oily sludge is a recalcitrant residue characterized as a stable emulsion of water, solids, PHCs, and metals. The PHCs and other organic compounds in oily sludge can be generally classified into four fractions, including aliphatics, aromatics, nitrogen sulphur oxygen (NSO) containing compounds, and asphaltenes. The aliphatics and aromatic hydrocarbons usually account for up to 75% of PHCs in oily sludge, and their most common compounds include alkanes, cycloalkanes, benzene, toluene, xylenes, naphthalene, phenols, and various polycyclic aromatic hydrocarbons (PAH) while the rest is the NSO compound (Guangji Hu, Jianbing Li, and Guangming Zeng, 2013). This statement has been supported by Sugiura et al. where petroleum contains hundreds of significant compounds, which are generally grouped into four parts, according to their differential solubility in organic solvents: saturates, aromatics, resins and asphaltenes (Capelli, S. M., Busalmen, J. P., & Sã, S. R. De., 2001)

Asphaltenes and resins can be responsible for the stability of oily sludge emulsion since these constituents contain hydrophilic functional groups and consequently can act as lipophilic emulsifiers. Usually, the total petroleum hydrocarbon (TPH) contents in oily sludge can range from 5% to 86.2% by mass, but more frequently in the range of 15–50%, whereas the contents of water and solids are in the range of 30–85% and 5–46%, respectively. The nitrogen (N) content accounts for less than 3% in oily sludge and most of them are contained in the distillate residue as part of asphalt and resin fraction. The sulphur (S) content can be in the range of 0.3–10% whereas the oxygen (O) content is usually less than 4.8% (Guangji Hu, Jianbing Li, and Guangming Zeng, 2013).

The sludge from a different refinery plants varies in composition but they typically contains 10-30% hydrocarbons, 5-20% solids and 50-85% water. It is also widely accepted that the presence of polycyclic aromatic hydrocarbons (PAHs), which are organic micro-pollutant (xenobiotics) compounds, persistent with toxic and carcinogenic-mutagenic characteristics causes the harmful characteristics of the oil sludge (Pakpahan, 2011).

2.2 Existing Technological Solutions

Over the years, a wide range of technological solutions has been used in managing the petroleum wastes. According to Da Silva et al. (2012), there are many physical, physicochemical and biological processes are available to treat oily sludges, such as landfilling, incineration, co-processing in clinkerization furnaces, microwave liquefication, centrifugation, low-temperature conversion, thermal plasma, incorporation in ceramic materials, development of impermeabilization materials, encapsulation, biodegradation in landfarming, biopiles and bioreactor. Although physical and physicochemical proved to be effective, but on large scale it can cost a lot of money hence economically they are not applied on the field for oil sludge treatment and making the biological process popular choice in treatment plant (Da Silva, et al., 2012).

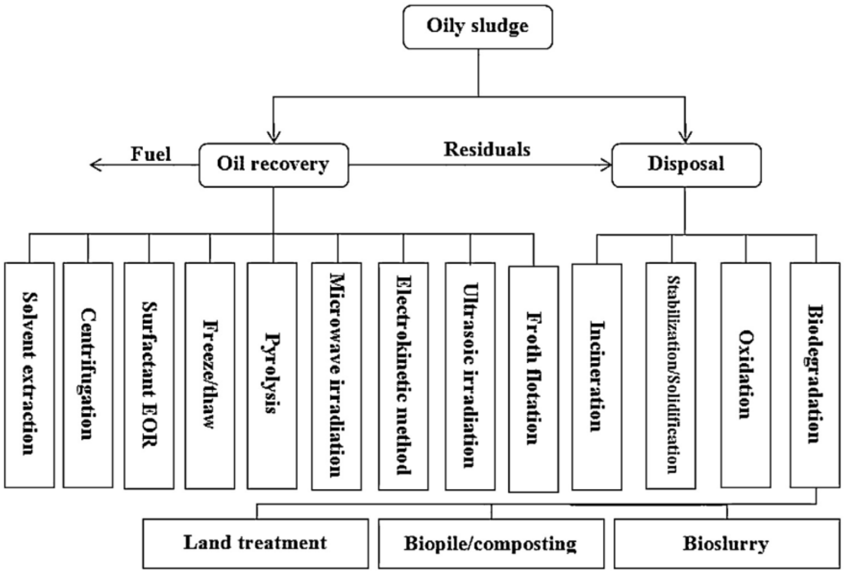

Figure 1: Oil Sludge Processing (Aramco, et al., 2004)

2.3 Biodegradation through Landfarming method

Of all the existing technological solutions around the world, landfarming is being used extensively. Being a cost-effective and easy-to-implement method of treatment, the oil and gas industry is using it as an in-house treatment for their oil sludge. It has been practised worldwide for over a century and by the petroleum industry for more than 25 years (Khan et al., 2004). Da Silva et al. stated that, landfarming is a bioremediation technique upon which oily sludges are scattered and mixed into the reactive soil layer in a controlled manner for the microorganism in the ground to act as a degrading agent and this is applied to a large areas because biodegradation occurs in the upper soil layer, where aerobiosis is guaranteed. The process involves the controlled application of waste on the surface in order to biodegrade the carbonaceous constituents by utilising the microorganisms that are naturally present in the soil and this technique has been effectively used for years in the management of disposal of oily sludge, other petroleum refinery wastes and other waste types (Dando, 2003).

Landfarming is designed to optimize degradation by application of an aerobic biological process while using the soil to support biological growth and the biodegradation process is also optimized by aerating the soil with addition of nutrients by agricultural tilling technique. The biodegradation process that occurs in landfarming is aerobic respiration. Aerobic process is a biological treatment that occurs in the presence of oxygen (Tchobanoglous, Burton, & Stensel, 2004).

Despite the fact that landfarming is relatively inexpensive compared to other method of treatments, there are a few downsides to this method which should be taken into consideration being it is being used. As stated by (Khan et al., 2004), listed below are the disadvantages of landfarming:

- A large amount of land is required.
- Volatile contaminants must be pre-treated because they would volatilize into the atmosphere and cause air pollution.
- It is not efficient in degrading the heavy components of petroleum.
- The presence of metal ions may be toxic to microbes and may leach from the contaminated soil into the ground.
- Dust and vapour generation during landfarm aeration may pose air quality concerns.

2.4 Factors affecting biodegradation of oil sludge

The oily sludge biodegradation can be affected by a variety of factors, such as the type of microorganisms, treatment duration, temperature, nutrients, concentration, loading rate and characteristics of oily sludge (J. T. Dieble and R. Bartha, 1979). This has been supported by Kretschek and Krupka where they state that various parameters that influence the biological process of hydrocarbons degradation includes moisture content, pH, temperature and microbial density and composition. Although the important parameters are the same for all biodegradation of hydrocarbons, its optimum condition may differ. (Aramco, Arabia, & Science, 2004).

a) Temperature

Temperature plays a significant role in controlling the nature and extent of microbial hydrocarbon metabolism. Temperature affects the rate of biodegradation, as well as the physical nature and chemical composition of hydrocarbons (Rowland et al., 2000). Thus, higher molecular reaction rates due to smaller boundary layers are expected at elevated temperatures.

To maintain microbial activity thus will break down the organic material. The ideal temperature range is needed, the mesophilic, 30 to 38°C, or the thermophilic, 55 to 60°C temperature regions. Within certain limits the rate of this biochemical reaction will about to double for each 10°C rise in temperature. If the temperature gets too high, more than 60°C, it can kill most of desirable microorganism responsible for decomposition. Changes in temperature are commonly used as a measure of microbiological activity underlying the composting process and the temperature profile of composting can be used to determine the stability of organic material (Andrew & Olli, 1991).

However, composting also can be done well in a low range temperature, which is 23- 25°C, lower than the normal temperature of composting pile (55-65°C), due to heat produced from biodegration of organic matter (Chua & Isa, 2006). These also supported by another study done by Van Gestel et al., where their compost piles operate in low range temperature. He found that more hydrocarbons were degraded through composting when the temperature profile was kept at 23°C rather than imposing a5 -day thermophilic plateau (50°C).

b) Nutrients

Additionally, soil hydrocarbon degradation can be increased by the addition of supplemental nutrients, particularly nitrogen and, to a lesser degree, phosphorus (Walworth and Reynolds, 1995). Determination of residual hydrocarbons confirmed that percent biodegradation was greatest at the intermediate fertilization level. At the highest level of fertilization, biodegradation was only slightly greater than in the control, which received no mineral nutrients. The optimal amount of C:N and C:P ratios for biodegradation process is of 60:1 and 200:1 (J. T. Dieble and R. Bartha, 1979). While other research done by George et al., state that the optimum range of carbon-to-nitrogen ratio (C: N) for most organic waste is from 20: 1 to 25: 1. This shows that the microorganisms need more carbon than nitrogen. The microorganism uses carbon as a source of energy and nitrogen for building cell structure. If the C: N ratio is below than 20: 1, the excess nitrogen will leave the compost as ammonia which contributes to odor problems. But if it is greater than 40: 1 it will takes much longer to compost (George et. all, 1993). Admon et al. and Yerushalmi et al. found that the removal of PHCs was observed only after nutrients were amended to oily sludge contaminated soil at a C:N:P ratio of 50:10:1. Roldán-Carrillo et al. investigated the biodegradation of oily sludge under different nutrient conditions, and they found that after 30 days of treatment, the highest TPH removal was 51% in the sludge which had a C:N:P ratio of 100:1.74:0.5. However, Tahhan et al. observed that adding nutrients caused the inhibition of oily sludge biodegradation probably because of the high nutrient concentration already present in the original sludge, and such inhibitory effect increased with the addition of nitrogen and phosphorous. The difference of C:N:

c) pH

Control of pH is another important parameter in evaluating the microbial environment and waste stabilization. The composting works the best when the pH stays between 6.5 and 8.0. The pH level can influence the availability of nutrients, activities and nature microbial populations. The pH level can be changes with lime to raise pH and sulfur to lower pH. A high pH, above 8.5, encourages the conversion of nitrogen compounds into ammonia gas, resulting in nitrogen loss from the compost, with losses of nitrogen in the form of ammonia to the atmosphere not only causes nuisance odors, but also reduces the nutrient value of the compost (HACH, 1999).

This has also been agreed by Dieble and Bartha where oil sludge biodegradation process is optimal at a pH of 7.5 to 7.8. Extremes of pH are inhibitory to the great majority of microbial degradation processes. Most fungi are less adversely affected by low pH values than are bacteria (J. T. Dieble and R. Bartha, 1979).

d) Soil Properties

Soil properties that are important in influencing the rate and extent of the remediation of petroleum contaminated soils include texture, bulk density, hydraulic conductivity, nutrient status, and soil microorganism's type and numbers (Atlas, 1981). The aerobic biodegradation of simple or complex organic material in soil is commonly greatest at 50 to 70% of the soil water-holding capacity. Inhibition at lower values is due to inadequate water activity, and higher values interfere with soil aeration. (J. T. Dieble and R. Bartha, 1979).

Kretschek and Krupka stated that the composition of sludge and the loading rate are important factors that affect the degradation process because the rate at which the compound is biologically broken down may increase or decrease depending on the presence of functional groups in the hydrocarbon chain or the aromatic ring (Aramco et al., 2004). The pattern of biodegradation of the hydrocarbon classes may be controlled by regulation on the oil sludge loading rate and frequency. Small charge size loadings resulted in a preferential utilization of the saturated hydrocarbon class and in a maximum overall rate and extent of biodegradation. Larger charge size loadings resulted in slightly lower overall biodegradation, but they favoured the net removal of asphaltic material (J. T. Dieble and R. Bartha, 1979).

e) Aerobic Respiration

In order for the aerobic respiration in the biodegradation process to occur, electron acceptor needs to be present and sufficient for the microbial activity. Being highly reduced substrates, hydrocarbons require an electron acceptor and molecular oxygen is the most common choice. A research done using an abiotic reactor which is vertically set up and equipped with continuous air flow had been done in order to avoid oxygen limitation to the biodegradation process (Koolivand et al., 2013). The growth rate increases depending on the availability of oxygen and yield of aerobic organisms. Mono-oxygenases and dioxygenases aerobes are two uniquely effective enzymes in the oxidation of hydrocarbons. The presence of oxygen, however, can suppress anaerobic processes, such as the degradation of halogenated pollutants, through the inhibition of reductive dehalogenation but as reported by Donald and Freeman, oxygen is rapidly depleted at heavily contaminated sites, in the case of biodegradation of hydrocarbons, thus resulting in anaerobic conditions (B. Antizar-Ladislao, 2010). It is important to maintain the biodegradation of oil sludge in aerobic respiration because in the absence of oxygen, the microbes will take sulfate ions (SO_4^{2-}) that is abundant in water as their source of oxygen for respiration and this will lead to the production of hydrogen sulphide (H_2S) which has a low solubility in the wastewater and a strong, offensive, rotten-egg odour (Zhang, Yan, Tyagi, & Surampalli, 2013). The unwanted production of hydrogen sulphide gas can be controlled by providing adequate oxygen supply to the biodegradation environment. Therefore, the presence of electron receptor is important in order to carry out the respiration in biodegradation process.

f) Moisture Content

Moisture content has a significant impact on the biodegradation rate, and indirectly affects the hydrocarbons contents in the sludge sample and other parameters as well. For instance, excessive amount of moisture can hinder the supply of oxygen and as a result will decrease the rate of biodegradation of oil sludge (Ho & Rashid, 2008). Air would usually be injected into or extracted from the vadose zone or soil with or without addition of nutrients to stimulate indigenous bacteria to biodegrade petroleum hydrocarbons in aerobic bioremediation treatment (Davis, Laslett, Patterson, & Johnston, 2013). Moisture content was also proven to have significant impact in regulating the temperature and air permeability of the biodegradation environment. According to Gajalakshmi and Abbasi, moisture content should be in between 45-60% in weight for an ideal biodegradation process because lots of moisture will be lost through evaporation and with the decrease in water content, the rate of biodegradation will decrease (Muktadirul Bari Chowdhury, Akratos, Vayenas, & Pavlou, 2013). However, according to Ho & Rashid (2008), the optimum range of moisture content is in between 30% to 40%. This is probably valid assuming that there is no loss of moisture content.

2.5 Biodegradation by composting

Composting of petroleum wastes has received increased attention as a substitute technology for landfarming which often requires a large land area. The piles may be static with installed aeration piping, or turned and mixed by special devices. Oil sludge biodegradation was monitored by CO2 evolution and by periodic analysis of residual hydrocarbons (J. T. Dieble and R. Bartha, 1979).). The bio-treatment efficiency can be improved with moisture adjustment, air blowing, and the addition of bulking agent and nutrients. Bulking agents usually include straw, saw dust, bark and wood chips, or some other organic materials. Addition of bulking agents results in increased porosity in soil–sludge piles, which leads to better air and moisture distribution in the matrix. This technology is termed as composting if organic material is added (J.A. Marín, J.L. Moreno, T. Hernández, and C. García, 2006).

A number of studies have been reported to use composting for refinery oily sludge treatment. Wang et al. found that during the composting process of aged oily sludge, microbial metabolic activity and diversity were significantly enhanced by the addition of bulking agent cotton stalk, but the application of large amounts of nutrient had a suppressing effect on the microbes (X. Wang, Q.H. Wang, S.J. Wang, F.S. Li, and G.L. Guo, 2012). Liu et al. found that the addition of manure to oily sludge significantly increased the microbial activity and diversity (W.X. Liu, Y.M. Luo, Y. Teng, Z.G. Li, L.Q. Ma, 2010). Kriipsalu et al. reported the aerobic biodegradation of oil refinery sludge in composting piles with four different amendments, and their results showed that after 373 days of treatment, the reduction of TPH was 62%, 51%, 74% and 49% in the piles with amendments of sand, matured oil compost, kitchen waste compost, and shredded waste wood, respectively (Kriipsalu, et al., 2007).

As compared to landfarming, biopile/composting is able to more efficiently remove PHCs in oily sludge and could treat more toxic compounds since it creates controlled conditions more favoured by biodegradation (Guangji Hu, Jianbing Li, and Guangming Zeng, 2013).

CHAPTER 3

METHODOLOGY

3.1 Methodology and Project Activity

The focus of this chapter is to create a procedure or method for this experiment to achieve the initial objective of this project. Since the major area of the study in dealing with the biodegradation of oil sludge, more concern is focused on the parameters such as the nutrients, temperature, moisture content and respiration condition.

These are the methodology used to conduct the study:

<u>i. Fabrication of drum composter prototype</u>

The design of the composter is a modification of garden compost tumbler and the design of the composting system will enhance the ability of the existing treatment method which is landfarming by addressing its primary downsides. This expected to eliminate the impact of TENORM towards the environment and to the people. The drum is built as a prototype with smaller scale due to limitation of samples and cost of fabrication as shown in figure below.

Figure 2: Designed Prototype of Compost Tumbler

A drum barrel is used as the closed system composter with two holes for oxygen (O_2) supply and discharge of carbon dioxide (CO_2) drilled at the two sides of the drum. The drum will be mechanically rolled at a constant speed periodically to encourage the homogeneous aeration of the microorganism inside it. Required equipment such as air compressor and gas flow meter will be connected to the composter to ensure that aerobic respiration will take place in the composter and also to measure the oxygen content in the drum.

ii. Selection of materials

Sample of oil sludge are collected from PETRONAS Refinery Melaka. As for the nutrient supplement, agricultural materials such as palm fronds and chicken manure are good alternatives to be used in providing necessary nutrition such as nitrogen and phosphorus for the microorganism during the biodegradation process as they are cheap and easy to get. Agricultural materials such as palm fronds and chicken manure are collected at BDE Poultry Farm at Bota, Perak while the palm fronds are collected at the palm oil farm along the road to Bota. The soil used as microbial source in this study is dug at the field behind block 13 UTP. The soil is then crushed and sieved to the size not exceeding 2mm. These items are then placed at Block 13 to ensure easy access to them.

Material	Acquired Place
Oil Sludges	• PETRONAS Penapisan Melaka Sdn. Bhd.
Manure	• Chicken poultry near Bota
Bulking Agent	• Palm Fronds near UTP
Soil	• UTP field

Table 1: List of Raw Material and Its Acquired Place

Figure 3: Materials used for this study (Oil Sludge, Soil, Palm Frond, and Manure)

iii. Laboratory set-up and experiment conduct

All test apparatus and equipment are to be calibrated with care so as to prevent systematic error during measurements. Any test or calibration will be based on ASTM standard method.

Moisture Content

Moisture content was measure by weighing the container with some amount of samples and dries it for 24 hours in a 105°C oven. Then reweight the samples by subtract the weight of the container and determine the moisture content using the equation 1.

$$M_n = \frac{W_w - W_w}{W_w} \times 100\%$$

Where,

M_n = moisture content (%)

W_w = wet weight of the sample

W_d = dry weight of the sample

pH analysis

Compost was spread into a thin layer in a pan, and dried for 24 hours in 105 - 110°C in the oven. 5g of sample of over-dried compost was weight and put into small containers and distilled water was added, it was mixed and stands for 10 minutes before measured using pH paper or calibrate meter. For digested sample of oil refinery sludge the measurement were done using calibrate pH meter.

Phosphorus Test

The samples were preheated for 30 minutes using a DRB200 reactor at 150^{o}C. The samples were mixed with Potassium Persulfate Powder Pillow for Phosphonate before heating begun. Sodium Hydroxide Standard Solution and PhosVer 3 Powder Pillow were added to the vial and readings were taken after 2 minutes to allow reaction of the mixtures. A spectrophotometer was used to determine the phosphorus content in the sample and materials.

Determination of Carbon and Nitrogen content in materials and samples

The total content of Carbon and Nitrogen in the oil sludge, coir and poultry manure were determined using CHNS Elemental Analyzer. This equipment provided a mean of determination of carbon, hydrogen, nitrogen and sulphur in organic matrices or other materials. In the combustion process, carbon was converted to carbon dioxide, while nitrogen is converted to nitrogen gas at a temperature of

1000^oC. Carbon and nitrogen content were determined in order to calculate the C:N:P ratio for the compost mix. . Below are the results for the analysis of the material.

Material	Moisture Content, %	C:N:P Ratio
Oil Sludge	71.4	100 : 0.72 : 0.508
Soil	66.3	100 : 1.38 : 0.016
Manure	48.75	100 : 2.66 : 0.9
Palm Fronds	9	100 : 107.5 : 6.03

Table 2: Analysis of Material Properties

Analysis of Total Petroleum Hydrocarbon (TPH) content

Samples of oil sludge (sweet) were collected directly and weighed (to the nearest 0.1 gram) EPA/VOA 40 ml vial. The sample should be about ¾ of the volume of the vial. The sample was weighed to the nearest 0.1 gram, subtracting the tare weight of the vial. 5 grams of sodium sulphate was added because the sample was wet and clumpy. Spatula was used to break up the clumps. The same amount of solvent (Hexane) as the weight of the sample in grams (weight of sodium sulphate is not included) was added. This will give a 1:1 extraction ratio. The vial was capped with the Teflon side of the liner toward the sample. The sample was then shaken vigorously for 2 minutes. A filter paper was placed in a filter funnel and approximately 1 teaspoon of silica gel is added. The sample was poured from the vial through the silica gel into a clean container. 50 micro litres of the sample was extracted using a pipette onto the centre of the HATR-T2 plate and the analysis is run. Results of analysis are as shown below. The readings were taken in triplicate to ensure accurate data.

Sample 1 (mg/g)	Sample 2 (mg/g)	Sample 3 (mg/g)	Avg. TPH Content (mg/g)
438	427	436	434

Table 3: initial TPH content of the mixture

The Total Petroleum Hydrocarbon (TPH) content will be measured by using TPH Analyzer. 3 samples are taken initially so that accurate measurement of TPH content of oil sludge can be determined. During the sampling, the sample's TPH also need to be measured, this will indicate the susceptibility of the biodegradation process.

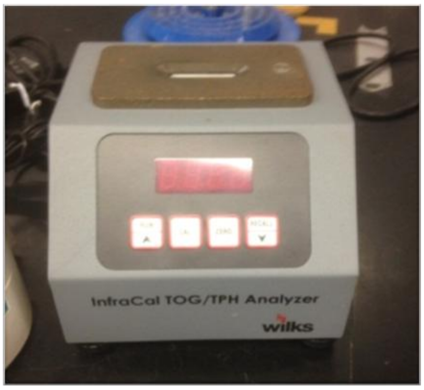

Figure 4: TPH Analyzer

iv. Mixing and Composting

The sample will be tested with different composition of soils with different C:N:P ratio, and the presence of bulking agent. According to the data collected from the literature research, optimum biodegradation happens in C:N:P ratio range of 100:20:1 and 100:4:0.6 . The study will have four different samples with different ratio within the optimum C:N:P ratio to determine the most optimum ratio for the oil sludge to biodegrade. The samples are then left in the composter for two weeks while the composters are being rolled every day during that period.

Sample	Oil Sludge	Soil	Poultry Manure	Palm Frond	C:N:P ratio
1	600g	100g	250g	50g	100 : 6.5 : 0.7
2	600g	250g	100g	50g	100 : 4.2 : 0.9
3	900g	500g	500g	100g	100 : 15 : 0.5
4	900g	1000g	750g	100g	100 : 17.5 : 2.1

Table 4: Samples Composition and its C:N:P ratio

v. Sampling

During the composting period, the performance of the compost was monitored by taking samples daily (50g) to measure the level of TPH using the TPH Analyzer and also to record the moisture content. The temperature of the compost mix was taken daily to monitor the performance of the compost tumbler experiment. The samples were also tested for the amount of moisture content to make sure that the level was within the optimum which has been set earlier. Since pH is also one of the most important factors in ensuring a good biodegradation environment, the pH of the compost mix will also be monitored regularly.

vi. Analysis and interpretation of the experimental results

The experimental data are to be processed by presenting it in a graphical method. These results are to be subsequently interpreted by proper engineering tool and judgment. The parameters that significantly affecting the biodegradation process of oil sludge are identified and subsequently considered as design parameters in the predictive models.

vii. Result Comparison

Efficiency of the closed composting method will be assessed by comparing the test results with those of the other existing oil sludge treatment.

Figure 6: Project Flow Diagram

3.2. Gant Chart & Key Milestone

FYP 1 Gant Chart:

The Gant Chart for the entire project period of FYP 1 is as shown in figure 4.

		Week													
ID	Task	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Selection of Project Title	■	■												
2	Appointment of Supervisor		■												
3	Literature Research			■	■	■	■								
4	Submission of Extended Proposal							■							
5	Methodology research for experiment								■	■					
6	Data gathering for model design									■	■				
7	Proposal Defence											■			
8	Design of prototype												■	■	
9	Material collection for prototype														■
10	Submission of Interim Report														■

Figure 7: FYP 1 Gant Chart

FYP 1 Key Mile Stones:

1) Title selection : Week 2

2) Submission of extended proposal : Week 7

3) Proposal defense : Week 11

4) Finalised Prototype Design : Week 13

5) Collection of Prototype Material : Week 14

5) Submission of interim report : Week 14

FYP 2 Gant Chart:

The Gant Chart for the entire project period of FYP 2 is as shown in figure 5.

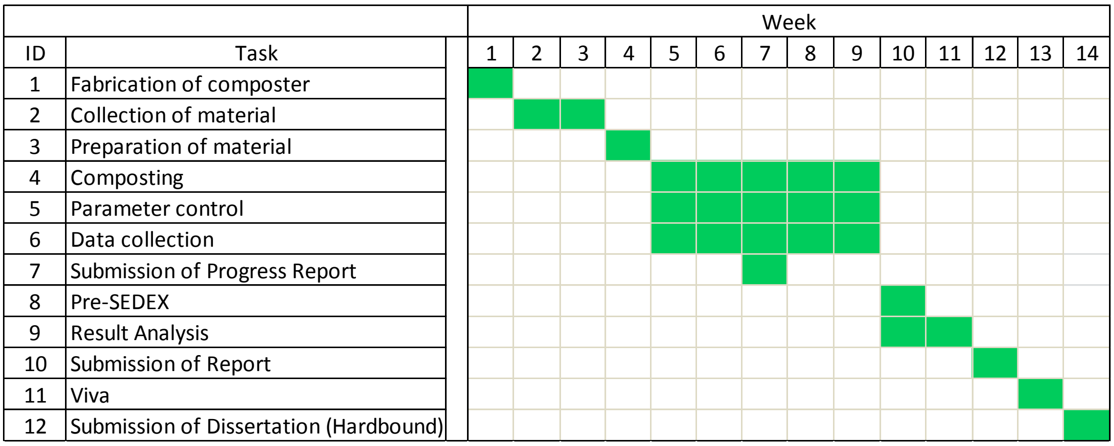

Figure 8: FYP 2 Gant Chart

FYP 2 Key Mile Stones:

1) Composter fabricated	: Week 1
2) Composting	: Week 5
3) Submission of progress report	: Week 7
4) Pre-SEDEX	: Week 10
5) Submission of technical report	: Week 12
6) Viva	: Week 13
7) Submission of Dissertion report	: Week 14

CHAPTER 4:

RESULT AND ANALYSIS

The parameters listed in previous chapter affects the rate of biodegradability of petroleum hydrocarbons which can also be used to identify the optimum condition to treat oil sludge. Above all, the content of oil sludge was the upmost important thing to ensure the success of the biodegradation process. For this research, four batches of biodegradation samples were prepared. For each sampling occasion, the sample was analyzed for its temperature, moisture content, total gas production and TPH content. The aims of these experiments are to determine the extent of rate of hydrocarbon biodegradation and to compare the effects of different C:N:P ratios to the biodegradation process.

4.1 Temperature

The temperature profiles of the samples are measured on a regular time intervals throughout the composting duration. In the beginning of the experiment, the temperature for all sample mixtures had slightly increased above the ambient, which indicated that biodegradation process was currently taking place vigorously. The ambient temperature of both of the composting environments was almost the same, whereby they ranged from $28^{o}C$ to $33^{o}C$. It had been fluctuating in between the range which was probably because of the moisture content in the mixture.

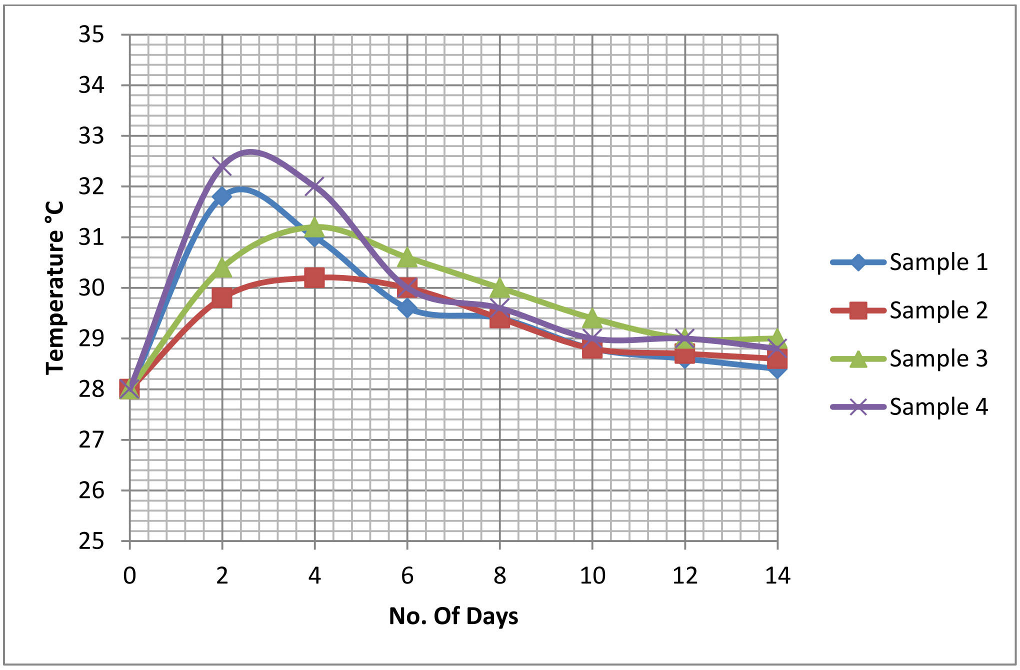

Figure 9: Temperature profile of the samples during biodegradation

From the result we can see that the temperature rises rapidly during the first 6 days of the composting and gradually decrease after the following days. The sudden rocket rise of the temperature might be because of the optimum condition for the microbial to degrade and after few days the nutrients are depleted and the microorganism's activity are decreased.

As expected, the temperature for the compost mixture in all samples increased after a few days of composting. However, the temperature never reached the thermophilic range (>45^{o}C) or in other word, both experimental mixes were always in mesophilic range. One of the factor that might contribute to this is because of low loading rate where the compost only occupy ¼ of the volume of the composter. Besides, the experiments have been conducted in a room temperature with air-conditioner at 28°C.

Even though the biodegradation of hydrocarbons can take place at a wide range of temperature, the rate of biodegradation generally decreases with a decrease in temperature.

4.2 Gas Production

Biodegradation products include carbon dioxide, water and other compounds. In order to ensure that there was biodegradation process that was taking place inside the composting reactors, the level of gas produced was measured by connecting an outlet to the compost reactors.

$$CH_3COOH + 2O_2 \rightarrow 2CO_2 + 2H_2O$$

The product of biodegradation process includes energy (heat) and carbon dioxide. However, the composition of the gas produced in this experiment may be consisting of carbon dioxide and also the volatilized compounds from the compost mixture. The percentage of volatilized compounds in the total gas production is probably of a small amount. Since carbon dioxide is one of the biodegradation product, the amount of carbon dioxide produced should increase when rate of TPH decrement increases.

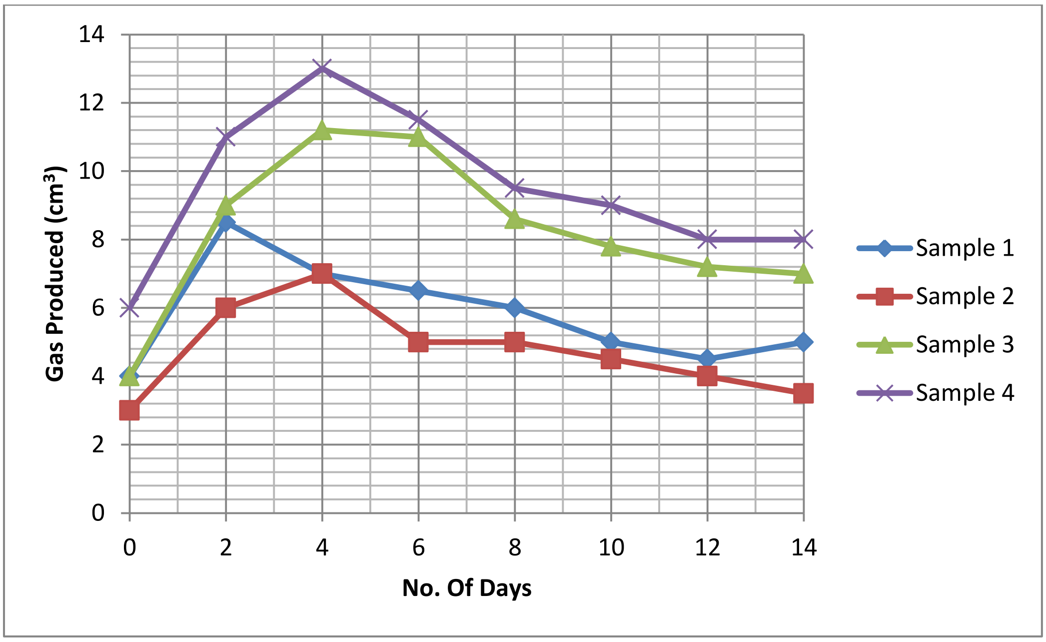

Figure 10: The gas production of the samples during composting

As can be seen from the graphs, the gas produced up until day 4 of experiment was the highest for all samples from 3 cm^3 minimum gas produced to over 12 cm^3. This was because at the beginning of the experiment, there was sufficient nutrient content in the compost mixture. Thus, it provided a suitable environment for biodegradation process to occur. However, the gas produced decreased from day 6 and day 8 respectively.

Over time, the nutrients provided by the compost mixture were eventually used by the indigenous bacteria in order to degrade hydrocarbons. Since the nutrients were not added, the biodegradation process slowed down due to insufficient nutrients. This caused the decrement in gas production. Other than that, the temperature recorded shows that it was almost impossible for the petroleum hydrocarbons to be volatilized under such condition. Since carbon dioxide is one of the biodegradation product, the amount of carbon dioxide produced should increase when rate of TPH decrement increases.

4.3 Total Petroleum Hydrocarbon (TPH) Content

The goal of this analysis was to quantify the rate and extent of hydrocarbons degradation under the provided biodegradation environment. In this analysis, the Total Petroleum Hydrocarbons (TPH) level is monitored on an alternate day basis in order to observe the trend in the decrement of the hydrocarbons.

The initial TPH content of the oil sludge is measured before the biodegradation assays are being carried out and then being monitored on an alternate day basis to observe the trend. According to previous research, the TPH content should decreases with an increased rate when the retention time increases. This is also dependent on the parameters mentioned earlier in Chapter 2.

The reduction of TPH content for all 4 samples after 14 days of biodegradation process is as tabulated below.

No. Of Days	Sample 1	Sample 2	Sample 3	Sample 4
0	442	442	442	442
2	413	418	408	403
4	393	398	382	376
6	388	390	362	340
8	380	387	354	333
10	373	383	349	329
12	369	382	345	324
14	365	379	339	318

Table 5: TPH content of the samples for 14 days

From the results tabulated above, it can be concluded that the compost mixture in Sample 4, which consisted of 100:17:2.1 of the C:N:P ratio, caused more decrement in the TPH content of the oil sludge. This might be because of higher C:N:P ratio and higher loading rate compared to the other samples.

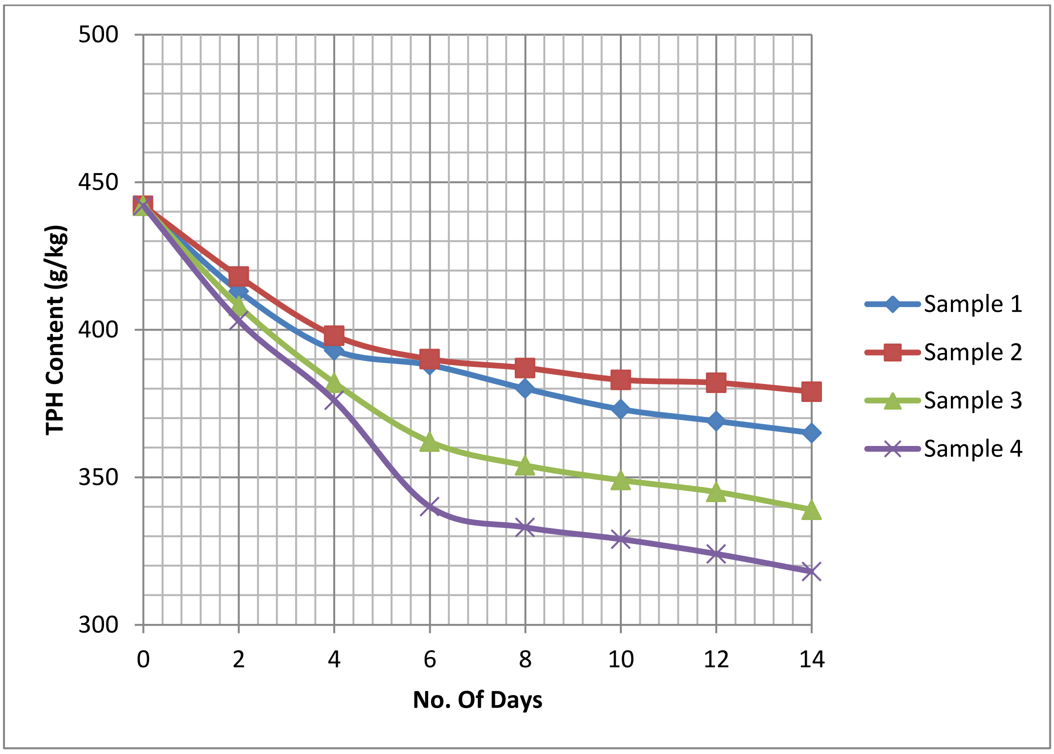

Figure 11: The decrement of TPH content over days

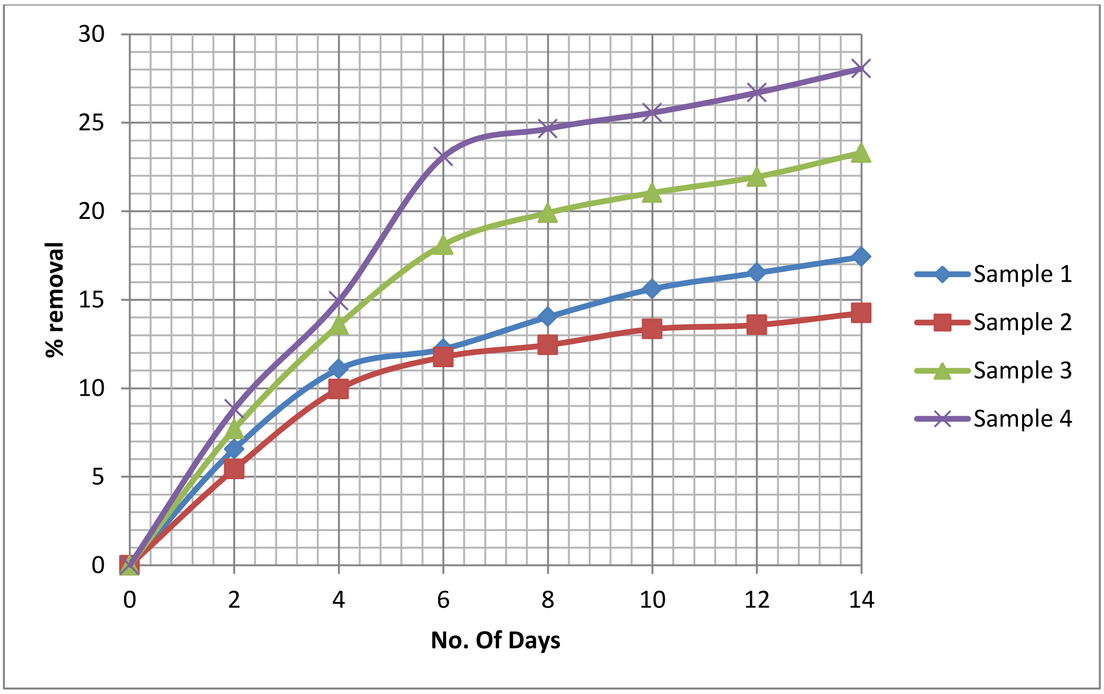

Figure 12: Comparison of percentage TPH removal between samples

The TPH content for the oil sludge for Sample 4 and Sample 3 decreased 28.05% and 23.3% followed by Sample 1 and with 17.4% and 14.3% respectively. In which Sample 4 with the highest removal of TPH and it can be derived that the C:N:P ratio in Sample 4 has increased the degradation of hydrocarbons with an increase in the nitrogen and phosphorus content in the mixture. This also concludes that the aeration, turning of compost tumbler and nutrients are enough to stimulate the microbial activity (Roldán-Carrillo et al., 2012).

CHAPTER 5:

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

In this paper, the closed composting treatment method which utilizes the biodegradation process has been carried out successfully with a significant result of TPH content being removed. By incorporating the concept of oil sludge biodegradation; closed composting systme can be used as oil waste treatment method given a suitable condition. Therefore, the important parameters of oil sludge biodegradation are being identified based on the previous researches done around the world in order to ensure the success of the lab-scale study.

The important parameters of biodegradation include:

- the availability of nutrients in the medium (soil),
- the optimum temperature of the biodegradation environment,
- the presence of oxygen for aerobic respiration
- the level of moisture content
- the usage of bulking agent

The parameters listed above affects the rate of biodegradability of petroleum hydrocarbons which can also be used to identify the optimum condition to treat oil sludge. Above all, the content of oil sludge is the upmost important thing to ensure the success of the biodegradation process. As it has been proven in this experiment, with a suitable amount of nutrients and the presence of indigenous bacteria, the biodegradation of hydrocarbons can be done at an optimized rate.

Sample 4 which had a higher C:N:P ratio as compared to the other samples resulted with a higher percentage of decrement in TPH content. Since no additional nutrients were added throughout both runs of experiments, the available nutrients in Sample 1 and 2 was used up at a faster rate because of the lower amount as compared to the nutrients content in Sample 3 and 4. In terms of temperature, Sample 4 experiment resulted in a higher peak temperature of 32.4˚C as compared to the other samples. This is because the biodegradation rate in Sample 4 is the highest among the other sample thus producing more energy compared to the others.

5.2 Recommendation

However, the experiment can further be improved by measuring the odour of oil sludge with appropriate standard technique such as the Threshold Odour Number test which can quantify and prove that the odour problem has lessened. Also, the samples should have the same weight in order to get the most optimum condition of the composure to biodegrade, and the loading rate should be more to ensure the temperature are at optimum level for the microorganism to degrade the hydrocarbons. Lastly, the period of the experiment should be lengthened to get a significant result of TPH content removal.

APPENDIX

Appendix I

Sample calculation of C:N:P ratio if the sample

Oil Sludge Moisture Content = 71.4% C:N:P ratio = 100 : 0.72 : 0.508	**Soil** Moisture Content = 66.3% C:N:P ratio = 100 : 1.38 : 0.016
Manure Moisture Content = 48.75% C:N:P ratio = 100 : 2.66 : 0.9	**Palm Fronds** Moisture Content = 9% C:N:P ratio = 100 : 107.5 : 6.03

1. Percentage of Composition for Oil Sludge, Soil, Manure, and Palm Fronds.

a) for 300g of Oil Sludge:	water content	: 300 (0.714) = 214.2g
	dry matter	: 300 - 214.2 = 85.8g
	C	: (100/101.228) 85.8 = 84.76g
	N	: (0.72/101.228) 85.8 = 0.610g
	P	: (0.508/101.228) 85.8 = 0.4305g
b) for 500g of Soil:	water content	: 500 (0.663) = 331.5g
	dry matter	: 500 – 331.5 = 168.5g
	C	: (100/101.396) 168.5= 166.18g
	N	: (1.38/101.396) 168.5= 2.293g
	P	: (0.016/101.396) 168.5= 0.0265g
c) for 500g of Manure:	water content	: 500 (0.663) = 331.5g
	dry matter	: 500 – 331.5 = 168.5g
	C	: (100/101.396) 168.5= 166.18g
	N	: (1.38/101.396) 168.5= 2.293g
	P	: (0.016/101.396) 168.5= 0.0265g
d) for 50g of Coir	water content	: 50 (0.09) = 4.5g
	dry matter	: 50 – 4.5 = 45.5g
	C	: (100/213.53) 45.5 = 23.18g
	N	: (107.5/213.53) 45.5 = 24.92g
	P	: (6.03/213.53) 45.5 = 1.398g

Mixture of these materials gives new ratio of C:N:P = 100 : 6.5 : 0.78
Need to increase C by adding more Soil or Oil Sludge because they have lower ratio of N and P and high C ratio.

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