Middle-East Journal of Scientific Research 24 (S1): 240-244, 2016

ISSN 1990-9233

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DOI: 10.5829/idosi.mejsr.2016.24.S1.49

Experimental Analysis of Smouldering Combustion as a Remediation Technology for Treating Petroleum Products Contaminated Soil

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Abstract: The petroleum industry effluents like oily sludge and oil spills cause a serious threat to the environment since their constituents are toxic, mutagenic and carcinogenic. Safe disposal of these wastes nowadays is a serious concern faced by industrial people all over the world. This report details about the removal of petroleum wastes found on the soil by shouldering combustion concept called sustaining thermal active remediation (STAR). This technique is a novel technology employed to decompose the contaminants dumped on the soil particles into volatile gases, carbon dioxide and water vapor under the influence of heat treatment to elevated temperature. Shouldering combustion initiated inside the soil facilitating the decomposition of contaminants since the combustion process release lot of energy sufficient to sustain the decomposition process. Combustion unit used in this work has been designed and fabricated by employing components like coal stove, air compressor, heating coil, thermocouple, etc. After loading the contaminated soil in the coal stove, the heating coil was introduced into the middle of contaminants and heated up to 650° C. Finally, effectiveness of the removal of hydrocarbons available on the contaminants was checked by Fourier transform infrared spectrometry (FTIR).

Key words: Petroleum industry effluents · Oil sludge · Contaminated soil · Smoulderingcombustion

INTRODUCTION

Petroleum refineries usually generate enormous quantity of wastes in the form of sludge generated by effluent treatment plant (ETP) and oil contaminated soil in their day to day refining process. Oil contaminated soil lose its fertility and have impact on seed germination. Hence disposal of the oily waste in an improper manner may cause a serious environmental problem. Various conventional methods like land filling, incineration, air splurging, etc. have been applied since early times for remediation of oily waste. It is observed that none of the conventional methods is environment friendly solution. The common drawback is that they are not the permanent solution for the environmental pollution and sometimes they are not cost effective. All fossil fuels primarily consist of a compel mixture of molecules called hydrocarbons as major constituents [1]. However, many countries including India designated oily waste originated from petroleum products as hazardous wastes

Usually oil spills have been considered as serious environmental problem that often requires cleaning up of the contaminated sites. The hazardous oily waste is composed of total petroleum hydrocarbons (TPH), water and sediments.

The Total petroleum hydrocarbons (TPH) constitute a complex mixture of alkanet, aromatic, nitrogen, sulfur and containing compounds. Abatement environmental pollution with those petroleum and petrochemical products has attracted great attention in recent decades. Especially oil contamination has severe impacts in the plant and animal ecosystem including human health and many living beings including those lived in aquatic condition too [2]. Sometimes untreated crude oil also may cause damage to lungs, liver, kidneys, intestines and other internal organs. In addition to that, one of the major constituents found in petroleum products like polycyclic aromatic hydrocarbons (PAH) may lead to cancer, Inhalation leads to headache, nausea, dizziness, respiratory irritation, etc. More often the volatile constituents such as benzene, toluene, ethyl benzene and xylem, etc, cause mutations, cancers, birth defects, nervous disorders and liver disease, depression, irregular heartbeats etc. In fact, whatever be the constituents found on petroleum products, all are greatly alter the quality of the environment. Different technologies are available for the cleanup of petroleum contaminated sites but most of them are not effective with respect to the time required, the amount of contamination removed or the overall cost [3]. In India, the soils contaminated by the petroleum products are commonly treated bioremediation, chemical oxidation, excavation, incineration, soil vapor extraction etc. However in bioremediation one of the problem encountered by the researchers are in ability of microbes above certain critical concentration of pollutants. In chemical oxidation, incineration and soil vapor extraction heat energy was used to remove the contaminants but these processes need more energy to remove the contaminants. In addition to that, shouldering combustion is a self-sustaining thermal active remediation (STAR) a novel technology that employs shouldering concept for the remediation of subsurface contamination. Shouldering combustion is a flameless form of combustion generates the sufficient quality of heat for long time [4]. By applying shouldering combustion unit concept, the oil sludge on the contaminated soil is able to decompose in the form of volatile gaseous and water vapor. Recently many researches were undergoing studies related to the reduction of toxic and harmful wastes into the environment by utilizing many strategies.

MATERIALS AND METHODS

Coarse sand collected from agricultural land, Cuddlier was used for the purpose of making artificially contaminated soil. 2T engine oil with the specification of 10W-30, density 0.8322 (g/cm³) @ 100 °C was purchased from a retail store located in Virudhunagar and mixed with the coarse sand. Prototype unit of shouldering combustion includes coal stove with a capacity of 5 Kg soil.



Fig. 1 Artificial contaminated soil

The heater coil and mini air compressor was purchased from an automobile spares store located in Savakis. The specification of heater coil was 320 watts, 220 volts capacity and the specification of mini air compressor was 250 (psi) pressure. Artificially contaminated soil was prepared for smoldering combustion process by mixing 3 kg of coarse sand and 300 ml of engine oil.

Prototype of Smouldering Combustion Unit: The experimental setup designed for this work is shown in Fig. 5 with the following components like coal stove (Beaker model indigenously designed), heater coil, thermocouple, mini air compressor.

Coal Stove: Coal stove was designed to conduct combustion process in which constant temperatures have to be maintained for certain period. The maximum temperature to be maintained by inside the coal stove was 1000°C. However, during the shouldering process the maximum temperature may attained up to above 650°C



Fig. 2: Coal stove (Beaker model)

In general the temperature required for a shouldering combustion was 400°C - 700°C. This type of coal stove is generally applicable for a laboratory experimental only. The total reaction time for the shouldering combustion in the coal stove was 2-3 hours and the temperature can reach maximum up to 650°C.

Heater Coil: Heater coil was used to heat the contaminated soil in the coal stove to remove the petroleum hydro- carbons present in the soil. This type of heater coil was used in the laboratory purposes and the temperature can rise up to 1000°C. After attaining that temperature the heater coil was immediately removed from the coal stove.



Fig. 3: Heater coil with thermocouple

The thermocouple probe was fixed to the heater coil with data logger assembled. The loggers were display the temperature range from 0°C-999°C. The thermocouple probe withstand up to the temperature range of 700°C made up of nickel chrome alloy it fixed at the centre of the coal stove. Heater coil was designed in the shape of round spiral type with four rings.

Mini Air Compressor: Air compressor was used to circulate the uniform air inside the coal stove to sustain the temperature for maximum hours. Shouldering combustion was mainly propagated by the circulation of air.



Fig. 4: Mini air compressor

Whenever ignition was started, simultaneously the air compressor was also switched on to flow uniform air supply inside the contents. Usually the ignition temperature of petroleum contaminated soil was around 300°C-400°C. The air compressor designed with the maximum pressure of 250 (psi) and the inner line of air compressor was made up of stainless steel. Through this inner line air was circulated into the coal stove. The air compressor was connected with 12 volts DC power supply with the designed current of 1 Ampere. The air compressor line was attached to the bottom hole of coal stove. The compressor was switched on only when the ignition takes place.

Experimental Setup and Procedure: An experimental setup consists of coal stove, heater coil, air compressor and thermocouple is shown in the Fig.5

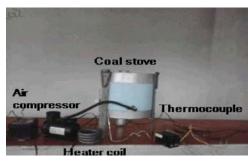


Fig. 5: Experimental set up

Coal stove was used for attaining the shouldering combustion. Clean sand and the contaminated sand were filled inside the coal stove. Heater coil was used to heat the contaminated soil and air compressor was used to propagating the shouldering combustion. Thermocouple was used to measure the temperature inside the coal stove. 2 kg of clean coarse sand was filled in the bottom of the coal stove above that 1 kg of artificially contaminated sand was filled in the middle of the coal stove and 1 kg of clean sand was filled at the top of the coal stove. This arrangement was used to prevent the contaminated soil which escapes out due to the flow of heat. Heater coil was fixed in the middle of the coal stove and initial temperature was noted at 25°C and final temperature attained up to 650°C. The ignition temperature was recorded at 400°C during the process. Heater was switched off when the ignition temperature occurs and compressor was switched on for propagating the shouldering combustion. The velocity of inlet air flow was set at the flow of 7 cm/sec. The temperature was slowly increased from 400°C – 650°C with the time period of 45 minutes by the circulation of air supply without heat supply.

The total time attained for purify the 1 Kg of artificially contaminated soil was 3 hours with a maximum temperature of 650°C. At the end of the process petroleum contaminants present in the coal stove were escaped out in the form of volatile gases and water vapor. After the shouldering process, the temperature of the system gets automatically reduced.



Temp 25°C @ 0 (mines)
Fig. 6 (a): Shouldering combustion at initial stage



Temp 400°C @ 80 (mines)

Fig. 6 (b): Shouldering combustion at intermediate stage



Temp 651 °C @ 170 (mines) Fig. 7: Shouldering



Temp > 651 °C @180 (mines) combustion on final stage

The initial, final and the intermediate stage of shouldering process is photographed and illustrated in the Fig 6, 7. After the reaction process the top layer of the sand was not disturbed and the bottom layer was ignited lightly and the middle layer got completely ignited and burned. As mention in earlier the contaminated sand was filled in the middle layer and the presence of hydrocarbon was more and there found to burn completely in the middle layer of the coal stove.

Determination of Petroleumhydrocarbons on the Soil by Using Fourier Transform Infrared Spectrometry: Fourier transform infrared spectroscopy (FT-IR) is a technique which is used to obtain the infrared spectrum of absorption of a solid, liquid or gas. An FTIR spectrometer simultaneously spectral data in a wide spectral range. This confers a significant advantage over a dispersive spectrometer which measures intensity over a narrow range of wavelengths at a time. It provides vital information about the skeleton, functional group and orbital frequencies of atom exist in the molecule which attached with another atom. Following Table 1 details about the characteristic group as well as individual frequencies of C-C, C-H, C=C, etc., usually exist any organic molecules (John Coates, "Interpretation of infrared spectra", A practical Encyclopedia of analytical chemistry, approach, pp. 10815-10837:2000).

Table 1: Saturated aliphatic (alkanet/alkyl) group frequency

Group frequency	Functional group/assignment
	Methyl (-CH3)
2970-2950/2880-2860	Methy l C=H asym./sym. stretch
1470-1430/1380-1370	Methyl C=H asym./sym. bend
385-1380/1370-1365	gem-Dimethyl or iso-(doublet)
1395–1385	Trimethyl or ,,,,tert-butyl (multiplet)
	Methylene (CH2)
2935-2915/2865-2845 M	Methylene C=H asym./sym. stretch
1485–1445	Methylene C=H bend
750–720	Methylene = $(CH2)n$ = rocking
1055-1000/1005-925	Cyclohexane ring vibrations Methyne (CH-)
2900-2880	Methyne C=H stretch

Naturally, petroleum products are hydrocarbons containing carbon and hydrogen in the form of chemical compounds like methane, propane, butane, benzene, etc. All these molecules are having C-C, C-H bonds etc., as major constituents. It will be characterized by [5] analyzing the FT-IR spectra of molecules. FTIR analysis of petroleum hydrocarbon exist on the soil has been recorded and given in the Figure 8. A peak at wavelength 2920.08 cm⁻¹ and 2853.83 cm⁻¹ were attributable to the stretching vibrations of aliphatic C-C peak found in the hydrocarbon. These stretching vibration corresponding to the ethylene group present in the petroleum hydrocarbon which was coated on the soil particle

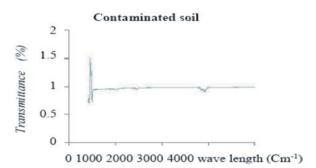


Fig. 8: FTIR Spectra of engine oil in coarse sand (Before treatment)

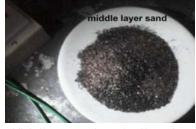


Fig. 9: Artificially contaminated soil (Before treatment)

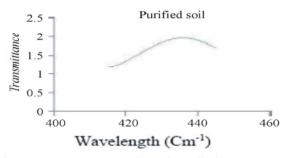


Fig. 10: FTIR Spectra of engine oil in coarse sand (After treatment)



Fig. 11: Artificially contaminated soil (After treatment)

After the shouldering combustion process, FTIR spectrum of the purified sand particle was recorded and is given in Fig 10. It is evident from the Fig 10 is that the spectrum did not have any remarkable peak in the entire region i.e. within 4000 cm⁻¹ – 600 cm⁻¹, but the peak from 420 cm⁻¹ – 440 cm⁻¹ is the indication of presence of silica in soil.

Absence of any peaks in the IR region indicates that the sample do not have any organic molecules. The resulting spectrum represents the molecular absorption and transmission of only the molecular fingerprint corresponding to the silica (SiO₂) particles a major constituent of soil.

CONCLUSION

A prototype shouldering combustion unit used for removing petroleum hydrocarbons found on the contaminated soil has been designed and fabricated using coal stove, heating coil, mini air compressor and the thermocouple measurement system. prototype designed and fabricated for treating the engine oil contaminated soil, during the combustion process the contaminants were escaped in the form of volatile products in 2-3 hours at the operating temperature of the fabricated device at 650°C. During shouldering process, it was observed that the temperatures achieved in the middle region of the sample were highest and decreased towards the top of the

sample. Photographic examination of the treated soil and from the FTIR results, it is concluded that the shouldering combustion reduces significantly the amount of hydrocarbon contaminants present in the soil. This result shows that shouldering combustion is a promising remediation technique for contaminated soil by petroleum hydrocarbons.

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