CHARACTERIZATION OF SLUDGE FROM THE WASTEWATER-TREATMENT PLANT OF A REFINERY

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ABSTRACT

In this study, characterization of filtrated cake of sludge drying section from a petroleum refinery wastewater treatment plant in Melaka was carried out with the objective to analyze its chemical, physical and fuel characteristics. Proximate analysis, ultimate analysis and higher heating value (HHV) are very important in chemical and fuel characterization. Dielectric properties and density test were also carried out to determine it suitability as microwave thermal treatment candidate. The density was found higher compared to those reported in literature. According to proximate analysis, moisture content of sludge is very high (75.3 wt%) which would decrease the heating value. However, the higher heating value (HHV) of 20.5 MJ/kg of sludge in this study is higher than HHV in other petroleum sludge probably due to the hydrocarbon content in the sludge. It is also found that volatile matter is high at 58.6 wt% where it can be converted into valuable products via material decomposition. Relatively high content of oxygen element (39.7 wt%) contributed to the low value of HHV and possible highly oxygenated liquid product during pyrolysis. Metal content analysis revealed high content of Fe (1,850 ppm) and also significant amount of Al, Mg, Zn and Na which categorize the waste as schedule waste. The values of dielectric constant were found to follow the trend that of water because of its high moisture content at 1.24 to 20 GHz. However, the dielectric loss trend is opposite to the water at frequency below 5.0 GHz. It was found that the value of dielectric constants at frequency of 2.45 GHz, which is common in industrial processing, were 50.8 and 2.3 for wet sludge and dried sludge, respectively. While for dielectric loss, its values were 15.7 and 0.1, respectively. Hence, good penetration can be achieved by microwave energy during microwave thermal treatment process to allow material decomposition but the energy conversion will be occur fairly.

Keywords: *sludge, characterization, microwave, thermal treatment.*

INTRODUCTION

Large amounts of waste generated during the exploration, production, refining and distribution of petroleum [1]. There are many sources of these sludge including storage tank bottoms, oil-water separators, dissolved air floatation units, cleaning of processing equipment, biological sludge from waste water treatment units and oil spills in the oil fields, drilling sites and refineries [2]. It usually contains a significant amount of water, solid and oil, where there are many of toxic, mutagenic and carcinogenic components [3, 4, 5, 6]. The composition of sludge differs due to their origin and storage conditions. However, generally it is contain up to 10-30 wt% hydrocarbons, 5-20 wt% solids and the remainder is water [7]. In the past, petroleum sludge from storage tank bottom and biological sludge from wastewater treatment units will be disposed of by applying biological treatment such as land farming or composting [8] which is a well-proven method in the treatment of municipal sewage sludge. Nonetheless, even though the cost of land farming is low, it is strictly controlled due to the adverse impact on human health and the environment [9, 10]. Hence, in a few years ago, sludge drying plant was built as an alternative disposal method that allowed by Department of Environment Malaysia where sludge is dried before sent to Kualiti Alam as a certified schedule waste handling facility. In this study, characterization of petroleum sludge was carried out to analyze its chemical, physical and fuel characteristics. This is important for further research to improve the waste management method and to utilize this waste for better energy conversion.

MATERIALS AND METHODS

Material

In this study, petroleum sludge was taken from a Petronas Refinery wastewater treatment plant located in Melaka, Malaysia. Sludge was treated in a biological sludge storage tank before dewatered in drying plant. The sample is a black colored semi-solid cake as was taken from the sludge drying plant which is the effluent from biological sludge storage tank. The sample was placed in a cold room to preserve the originality of its characteristics.

Dielectric properties measurements

The dielectric properties of the sludge were measured at selected levels of moisture and at various temperatures to investigate the effect of moisture content and temperature on dielectric properties. The transmission characteristics were measured using PNA-L Network Analyzer (Agilent Technologies 85070N). Samples of the petroleum sludge were dried in a drying oven at temperature of 105^{o}C ±2 ^{o}C and taken out at different times to obtain moisture contents of 7.0%, 12.0%, 23.0%, 38.0% and 81.0%. Samples were also were placed in 50 mL ceramic crucibles and covered with the caps and heated in a drying oven until the temperature reached 28.0, 41.0, 63.0^{o}C and 84.0^{o}C. The samples were measured for its dielectric properties and temperature simultaneously using dielectric analyzer and digital thermometer, respectively.

Chemical analyses

The proximate analyses of sample were carried out using thermogravimetric analyzer (Mettler Toledo TGA/SDTA851^e). Purified nitrogen and compressed air were used as purge gas at temperature 30 to 600^{o}C and 600 to 900^{o}C, respectively. The flow rate of the purge was 20 mL min^{-1}. Runs were performed at heating rate 30^{o}C min^{-1} using a sample of approximately 10-15 mg. The percentage of mass loss calculated according Equation 1:

$$Weight\ loss\ (\%) = \left(\frac{m_i - m_a}{m_i}\right) x100 \qquad (1)$$

where m_i is the initial mass (g) and m_a is the actual mass (g).

Elemental analyses were carried out using CHNS/O analyzer. The lower heating value of sample was determined using Parr 1341 bomb calorimeter according to the ASTM D 2015. Approximately 1 g of sample was pelletized and burnt in an adiabatic oxygen bomb calorimeter. Heat of combustion for the sample can be calculated due to the following Equation 2 (Parr, 1979):

$$W = \frac{Hm + e_1 + e_2}{t} \qquad (2)$$

where W is energy equivalent of the calorimeter (cal/^{o}C), H is informal heat of combustion of the sample (cal/g), m is mass of the sample (g), t is net corrected temperature rise (^{o}C), e_1 is correction for heat of formation of nitric acid (cal) and e_2 is correction in cal for heat of combustion of fuse wire (cal).

Inorganic content

The inorganic content analysis of sludge was analyzed via acid digestion of the dried sludge according to US EPA method 3050B. The content was evaluated inductively coupled plasma using Optical Emission Spectrometer (Perkin Elmer Optima 3700 DV) according to Method 3050B.

Measurement of thermal conductivity

The thermal conductivity of sludge was measured using thermal analyzer (KD2, Decagon). Theoretically, this property can be calculated using the following Equation 3 [11]:

$$K = \frac{8LC^2}{C_p M d^2 P} \qquad (3)$$

where L is length (m), d is diameter (m), M is mass, C_p is specific heat, C is apparent heat capacity and P is experimental parameter.

Measurement of specific heat capacity

Differential scanning calorimeter (Mettler Toledo DSC823^e) was used to determine the specific heat of petroleum sludge at temperatures ranges from 30 to 60^{o}C.

Determination of apparent density

The apparent density analysis on the dried sample was performed using Micromeritics, Accupyc Helium Pycnometer.

RESULTS AND DISCUSSION

Chemical analyses

The sludge was analyzed by breaking it down into structural components (proximate analysis) and into chemical elements (ultimate analysis) as tabulated in Tables 1 and 2, respectively. The moisture and ash contents are important parameters affecting the heating value directly [12, 13]. The dried petroleum sludge has high heating value of 20.5 MJ/kg, slightly lower compared to the literature. This possibly due to the higher content of ash at more than twice compared to that of sludge reported in literature [8]. The lower heating value could also cause by the low fixed-carbon and high oxygen contents in the sample [14]. The difference in moisture contents values between samples in this study with those in literature might be related to the difference methods of sample filtration or treatment.

Table 1: Ultimate analysis of petroleum sludge (wt%)

	Moisture content	Volatile matter	Fixed carbon	Ash
Dried sludge	3.1	58.6	11.4	27.3
Wet sludge	75.3	9.9	8.1	6.7
Literature [8]	33.0	ND	ND	12.3
Coal [15]	4.8	8.3	43.6	8.3

Table 2: Proximate analysis of petroleum sludge (dry basis, wt%)

	C	H	N	S	O (by different)	HHV (MJ kg^{-1})
In this study	45.0	6.6	7.0	1.7	39.7	20.5
Literature [8]	59.9	10.0	0.1	2.1	27.8	22.4
Coal [15]	81.5	4.0	1.2	3.0	3.3	23-28

ND: Not determined

It can be observed that all these sludge have more oxygen and less carbon than coal. High content of oxygen (39.7 wt%) also contributed the lower high heating value and possible highly oxygenated liquid and solid products. Petroleum sludge also found contain relatively low sulfur compared to coal. However, nitrogen and ash content vary significantly among them. These components directly related to the NO_x emissions, corrosion and ash deposition. Therefore, environmental concern must be taken during treatment of these sludge. The large number of functional groups and low number of aromatic structure in wet sludge are expressed via the large amount of volatile matter in wet petroleum sludge [8]. Figure 1 shows the thermogravimetric analysis curve of dried and wet petroleum sludge. The heating of wet petroleum sludge shows that 75.3 wt% of water was removed at temperature below 200^{o}C. The decomposition of volatile matter (~70 wt%) in dried petroleum sludge started at 226^{o}C and its weight loss rate increased as the temperature increased until reached maximum value at 338^{o}C. At temperature 500^{o}C, its mass loss rate was low and the residue yield was about 27.5 wt%. Drying process took a long time due to its low heating rate which caused by the high apparent density of sludge as will be discussed later.

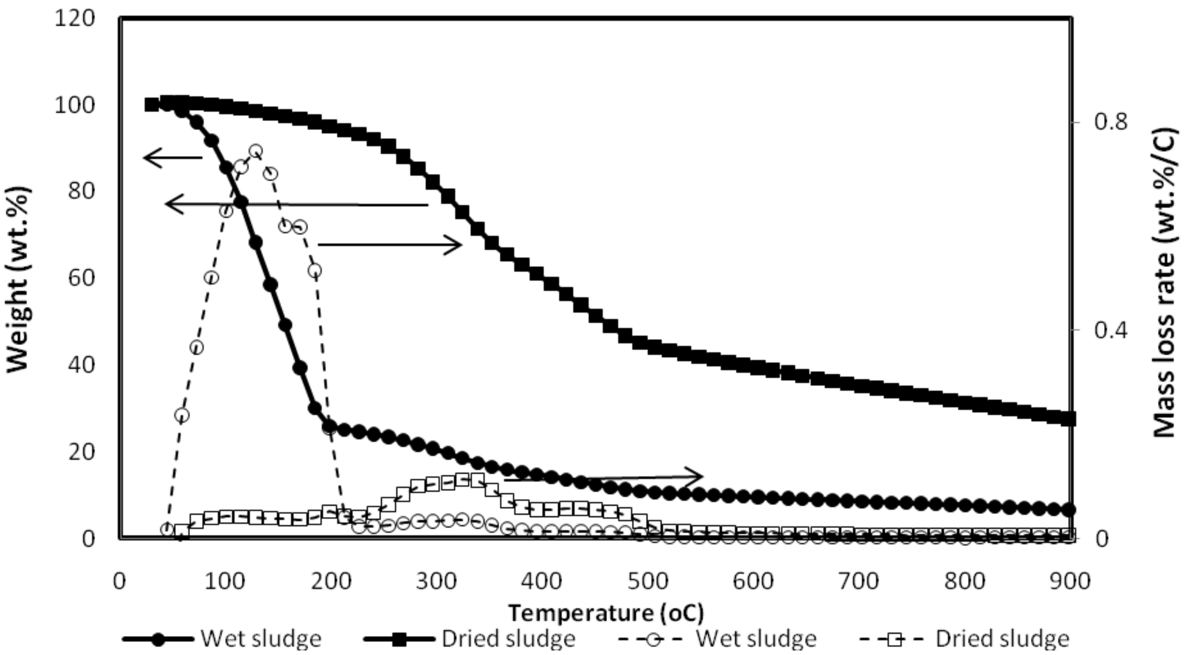

Figure 1: The thermal analysis profiles of the dried and wet petroleum sludge

Dielectric properties of petroleum sludge

The dielectric properties (dielectric constant (ε') and loss factor (ε'')) of sludge are important for predicting the behavior of materials when subjected to microwave electric fields in dielectric heating applications. It determines the interaction of that material with electric fields. Dielectric constant is measurement measure of a material ability to store electrical energy; while loss factor present its ability to convert electric field into heat [16].

The influence of dielectric properties on the heating of materials through energy absorption at microwave frequencies has been well known since many potential applications have been investigated [17]. The penetration depth, d_p described the depth into a sample where the microwave power has dropped to $1/e$ or 36.8% of its transmitted value [18]. It is a function of ε' and ε" as in Equation 4 [17]:

$$d_p = \frac{\lambda_o \sqrt{\varepsilon\prime}}{2\pi(\varepsilon\prime)^{0.5}} [\{1 + (\varepsilon''/\varepsilon')^2\}^{0.5} - 1]^{-0.5} \quad (4)$$

where λ_o is the free space microwave wavelength (for 2.45 GHz, λ_o= 12.237 cm). If the penetration depth is smaller than the thickness of the material, the absorption of microwave energy may be insufficient [19].

The dielectric properties of petroleum sludge are shown in Figure 2. The dielectric constant of wet petroleum sludge decreased as the frequency increased following the same trend with water. It might be due to the majority content of sludge is water (~80 wt%). However, the loss factor of wet sludge decreased exponentially from 100.0 to 16.4 at frequency less than 5 GHz and it remains constant for the subsequent frequency. At frequency of 2.45 GHz as applied on industrial and domestic microwaves, the dielectric constant of wet petroleum sludge was 50.8 which are near to the water (77.5) while for dried sludge only 2.3. Nonetheless, the value of loss factor for dried sludge was higher (15.7) than that of water (8.92). Still, the value of loss factor for dried sludge was the lowest at 0.1.

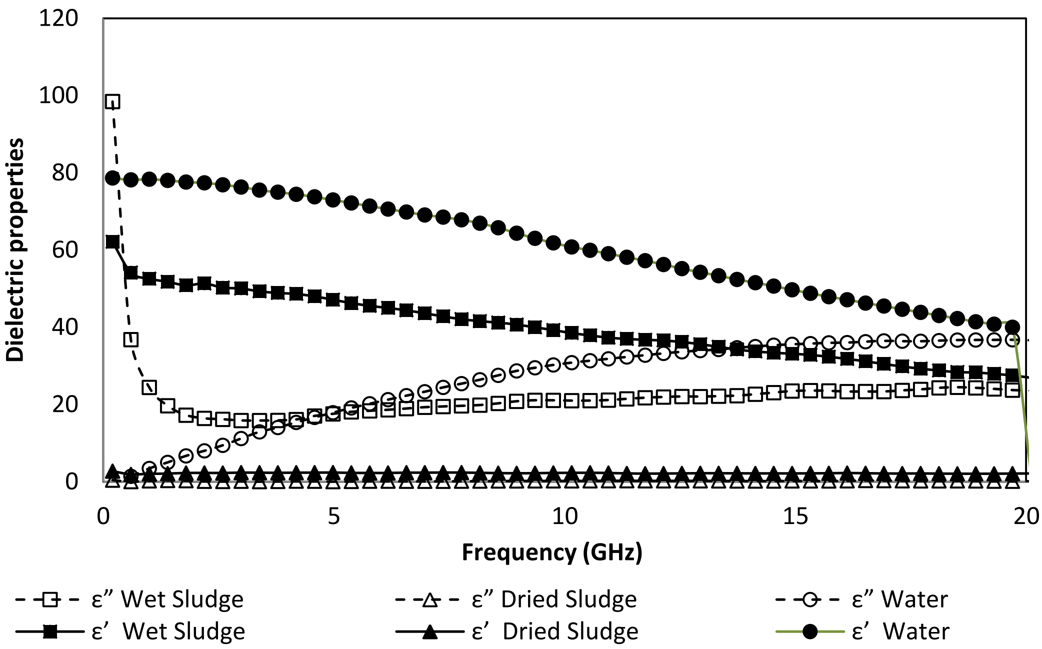

Figure 2: Dielectric properties of petroleum sludges compared to water.

Effect of moisture on dielectric properties

The relationship of moisture content and dielectric properties as can be observed in Figure 3 which shows that higher moisture leads to higher value of both the dielectric constant and loss factor. This strongly influenced by their permanent dipole moments. The dielectric constant and loss factor of the sludge increased from 2.3 to 5.8 and 0.1 to 15.7, respectively as the moisture content increased. Nonetheless, the penetration depth decreased from 80.8 to 1.3 cm as the water content lesser in the sludge. This probably because as the moisture content decreased, the microwave power can penetrate the sample better; resulting into increased penetration depth of microwaves [19]. The same decrease trend of penetration depth change found similar with those obtained from garlic but they were vary from 3 to 1.5 cm at moisture content range from 0 to 200 wt% at 2.45 GHz [19]. It also can be observed on penetration depth trend for bread with 0% salt at 25°C where the value of d_p decreased from approximately 10 to 2.5 cm as the moisture content increase.

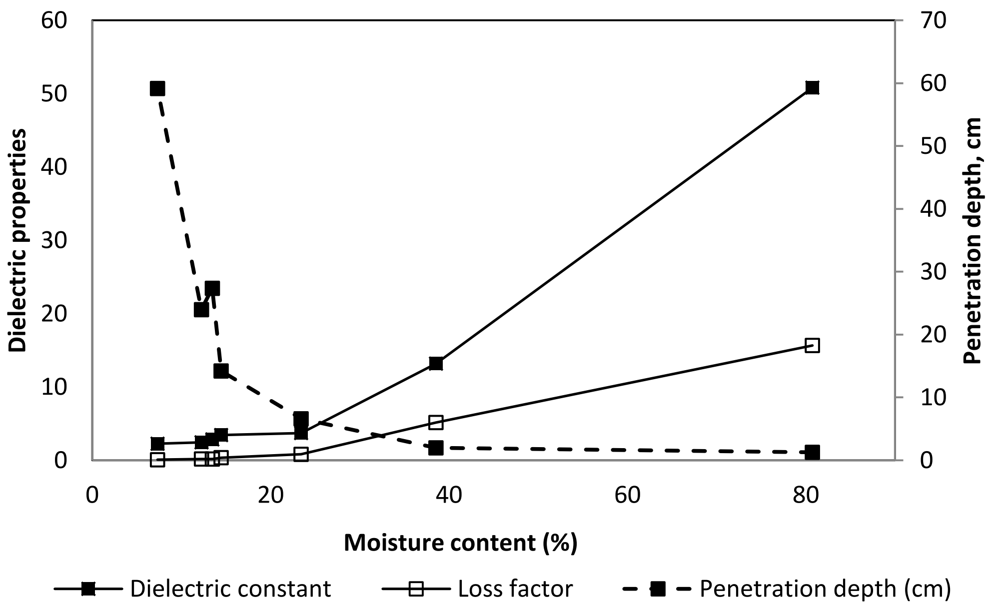

Figure 3: Variation of dielectric properties and its penetration depth at different moisture content.

Effect of temperature on dielectric properties

The effect of temperature on the dielectric properties and penetration depth of sludge is presented in Figure 4. As the temperature increased, the dielectric constant decreased linearly from 50.8 to 35.2, also its loss factor decreased marginally as well with temperature from 15.7 to 14.8. The penetration depth remains constant at approximately 1.3 cm. Even though the value of dielectric constant increased, penetration depth kept constant since it highly influenced by loss factor. Previous papers showed the high potential to treat the petroleum sludge via thermal treatment especially by applying pyrolysis method [5, 20, 21, 22]. From this process, sludge is able to be converted into others useful lower molecule organic compounds such as gases, oils and carbonaceous residues. This is due to the good dielectric properties and penetration depth of the petroleum sludge.

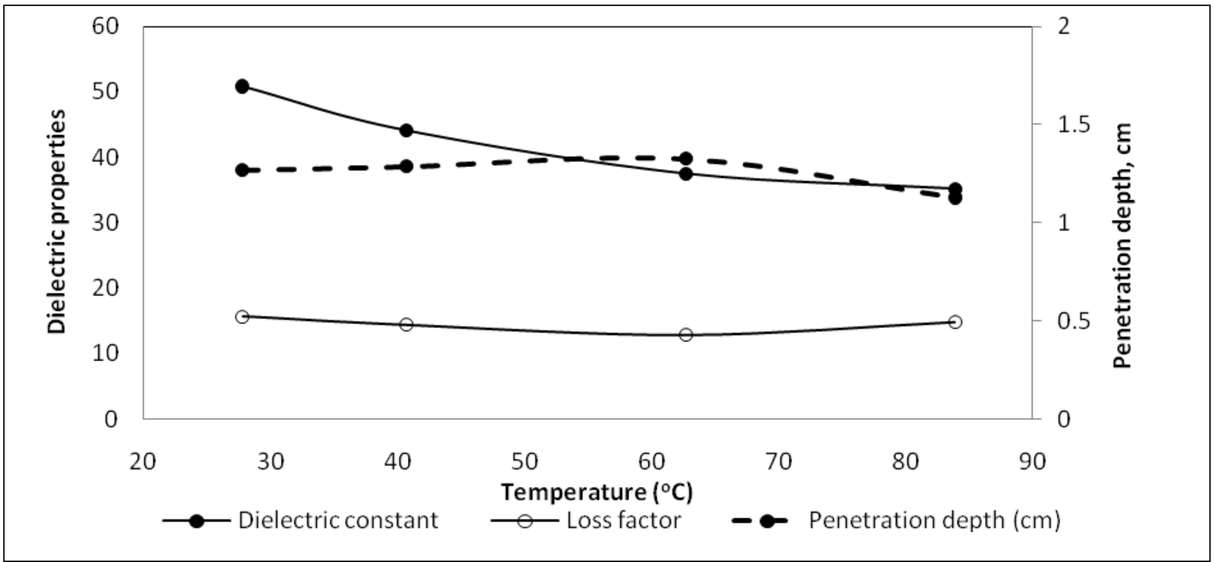

Figure 4: Variation of dielectric properties and its penetration depth at different temperature.

Inorganic matter

The main inorganic contents of the petroleum sludge are shown in Table 3. It is apparent that the content of heavy metals are lower compared than those reported by Karayildirim *et al*. [20]. It might be due to the different ways of wastewater treatment. However, the high content of Fe, Al, Mg, Na and Zn in this sludge in Table 3 might be among the main criteria for this waste to be classified as scheduled wastes from specific sources code S011 (waste oil or oily sludge from wastewater treatment plant of oily refinery or crude oil terminal).

Table 3: Main inorganic elements of the sludges (dry basis, mg/kg)

	Fe	Cu	Cr	Zn	Co	Ni	Ca	Mg	Na	K	Sn	Au	Al
In this study	1,850	9	ND	141	ND	ND	ND	250	222	ND	23	31	590
Literature[a]	43,826	590	427	4,206	26	631	17,775	6,038	2,958	83,487	NA	NA	NA

[a] Karayildirim *et al*., 2006
NA: Not available
ND: Not detected

Inorganic content information above is very important to determine the ability of sample to absorb microwave energy as some oxides compounds are able to increase maximum heating temperature. For example, Al_2O_3, C (charcoal), MgO and ZnO are able to increase maximum temperature up to 1900, 1000, 1300 and 1100^{o}C, respectively in less than 40 minutes [23]. However, all these compounds were categorized under three categories due to its heating rate achievement as which are hyperactive materials (Fe_3O_4 and charcoal), active (Fe_2O_3) and difficult to heat (MgO and ZnO).

Thermal Conductivity

Thermal conductivity is related to the heat transfer where temperature is transmitted through the raw material via conduction. Materials with high thermal conductivity are called as “conductors” while “insulators” are called for those with low thermal conductivity. Determination of thermal conductivity is important to evaluate the capability of material to transmit heat during heating process.

The thermal analysis in Figure 5 shows that the thermal conductivity of the sludge increased as the temperature increased. At temperature of 15.5^{o}C, the thermal conductivity of petroleum sludge (0.63 Wm^{-1o}C^{-1}) is near to the water value at room temperature (0.58 Wm^{-1o}C^{-1} [24]. This range of temperatures was chosen since sample was kept in a cold room before used and it takes a long time to achieve room temperature.

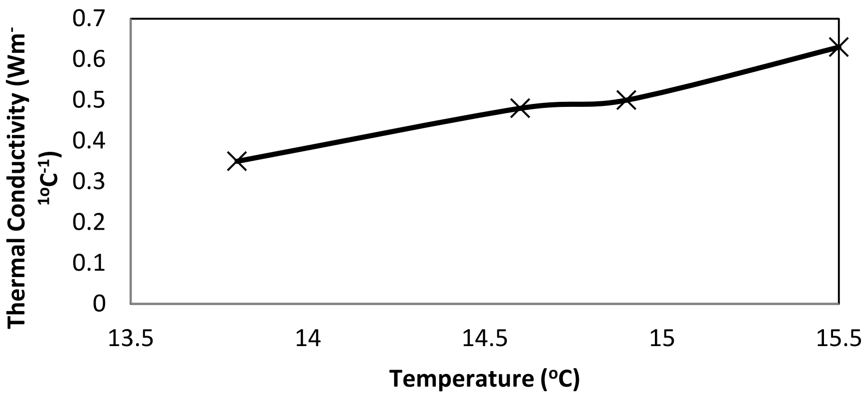

Figure5: Thermal conductivity of waste oil sludge at different temperature.

Specific heat is directly related to the thermal conductivity based on the Equation 3 above. Figure 6 shows the specific heat capacity data of petroleum sludge measured at temperature ranging from 30 to 60^{o}C. The values for C_p increased as the temperature increased except at temperature of 35 to 40^{o}C where the values were static as observed in Figure 6 below. The apparent density of dried petroleum sludge is 1.39 gcm^{-3} which is higher compared to deposited sludge from storage tank at 1.13 gcm^{-3} [25]. A higher apparent density is a good property of fuel source because of their high energy content per unit volume and slow burning rate [26].

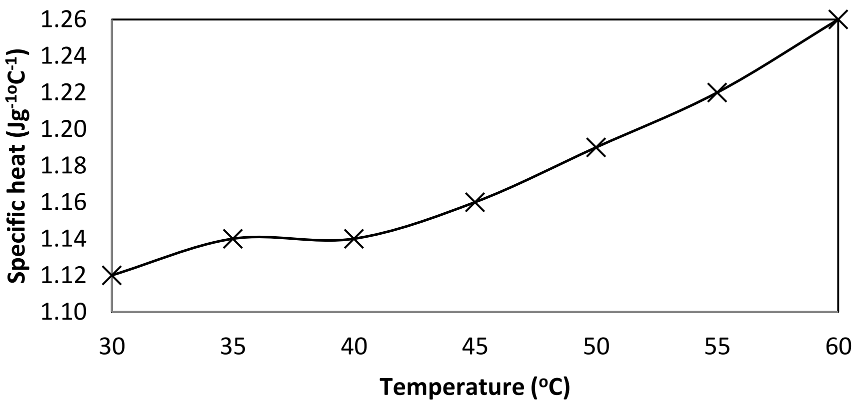

Figure 6: Specific heat of waste oil sludge at variation of temperature.

CONCLUSIONS

Large amounts of generated petroleum sludge present petroleum-based industries burden with the problem of these hazardous wastes. The sludge contains high amount of ferum at 1,850 ppm but still lower compared to the literature. Water was the majority compound in wet petroleum sludge with 75.3 wt% while volatile matter was dominant in dried sludge with 58.6 wt%. The results of characteristic analysis also found that the high heating value was 20.5 MJ/kg with carbon content of 45.0 wt%. Both dielectric constant and loss factor for wet sludge were higher compared to dried sludge where its values were 50.8 and 15.7 for wet sludge while 2.3 and 0.1 for dried sludge at 2.45 GHz. For thermal treatment purposes, petroleum sludge is expected to be a good sample candidate because of their high energy content per unit due to its higher apparent density compared to those reported in literature. At the same time, thermal conductivity and specific heat also found increased as the temperature increased.

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