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Low Sulfur Diesel Like Fuel Oil from Quick Remediation Process of Waste Oil Sludge

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***Abstract*—**Low sulfur diesel like fuel oil was produced from a quick remediation process of waste oil sludge (WOS). This quick process will reduce the volume of the WOS in petroleum refineries as well as oil fields by transferring the waste to more beneficial product. The practice includes mixing process of WOS with commercial diesel fuel. Different ratios of WOS to diesel fuel were prepared ranging 1:1 to 20:1 by mass. The mixture was continuously mixed for 10 minutes using a bench-type overhead stirrer, and followed by the filtration process to separate the soil waste from filtrate oil product. The quantity and the physical properties of the oil filtrate were measured. It was found that the addition of up to 15% WOS to diesel fuel was accepted without dramatic changes to the properties of diesel fuel. The amount of WOS was decreased by about 60% by mass. This means that about 60% of the mass of sludge was recovered as light fuel oil. The physical properties of the resulting fuel from 10% sludge mixing ratio showed that the specific gravity, ash content, carbon residue, asphaltene content, viscosity, diesel index, cetane number, and calorific value were affected slightly. The color was changed to light black. The sulfur content was increased also. This requires another process to reduce the sulfur content of resulting light fuel. A desulfurization process was achieved using adsorption techniques with activated biomaterial to reduce the sulfur content to acceptable limits. Adsorption process by $ZnCl_2$ activated date palm kernel powder was effective for improvement of the physical properties of diesel like fuel. The final sulfur content was increased to 0.185 wt%. This diesel like fuel can be used in all tractors, buses, tracks inside and outside the refineries. The solid remaining seems to be smooth and can be mixed with asphalt mixture for asphalting the roads or can be used with other materials as asphalt coating material for constructed buildings. Through this process, valuable fuel has been recovered, and the amount of waste material had decreased.

***Keywords*—**Oil sludge, diesel fuel, blending process, filtration process.

I. Introduction

WOS represent the heavy ends that separate from crude oil and present at the bottoms of storage vessels. WOS can accelerate corrosion, reduce storage capacity and disrupt operations. It typically comprises of three phases and multiple components of 20-90 wt.% water, 5-40 wt.% oil and about 5-35 wt.% solids [1]. Many authors developed various systems to separate the three phases for further reuse. This method can recover new fuels free of metals and water, which subsequently reduces emissions of major greenhouse gases such as CO_2, CH_4, and N_2O. The oily sludge is a water-in-oil emulsion, which is stabilized by fine solids [2].

Many works described the methods of recovering fuel oil from the oil sludge. The extraction process was used for removing fuel oil from oily wastes [3]. Refinery hydrocarbon was used as the extractive solvent. Waste solids are either used for fuel, or disposed of in a landfill. Iso-paraffinic mixture was used to extract hydrocarbons from different waste sludges [4]. The solvent-to-sludge mass ratio of 10 was used with an extracted temperature of 93 ºC and contact time of two hours. The extraction process was able to remove 99% of the hydrocarbons.

The resulting solids met the Environmental Protection Agency (EPA) standards for non-hazardous waste. It was concluded that the heavy metals were concentrated in the remaining solids, and this remaining solid was regarded as hazardous waste. Turpentine was used as a solvent in a Soxhlet extraction process [5]. The extraction process was able to recover 13% to 53% oil of the original sludge mass.

Several solvents were evaluated to extract fuel oil from oily sludge at room temperature [6]. Six solvents such as methyl ethyl ketone (MEK), LPG condensate (LPGC), heptane, hexane, iso-propanol, and iso-butanol were used to extract valuable fuel oil. The solvent-to-sludge mass ratios were ranging from one to six to determine the optimum ratio operated at room temperature. The solvent-to-sludge ratio of four was the optimum ratio. MEK had the highest performance for oil recovery. It was able to recover 39% as recovered fuel oil. The amount of asphaltenes in fuel oil was related to the concentration of fuel oil in the solvent phase during the extraction process. This finding concluded that the asphaltenes were extracted mainly by the fuel oil components, not the solvent [7]. The addition of a few drops of commercial oil-waster demulsifier increased the oil recovery to 45.4% using LPG condensate, and 39.4% using MEK [8]. The addition of KOH and oil demulsifier to the solvent during the solvent extraction process of oily sludge material was studied [9]. The KOH to solvent ration was ranging 1-10 g/kg in order to study the percentage increase in fuel oil recovery. The multiple solvent extraction process for fuel oil recovery from oil sludge was investigated [10].

Different extraction temperatures and different solvent to sludge ratios were applied to reduce the volume of waste sludge. The fuel oil recovery increased from 43.46% for the first extraction stage, increased to 54.2% for the second extraction stage and to 62.2% for the third stage. Hexane and xylene showed a high potential to extract the hydrocarbons from the accumulated sludge. This extraction process was able to extract 67.5% of the entire hydrocarbons. The authors applied gas chromatography to evaluate these hydrocarbons. The

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hydrocarbons were in the range of C_9 - C_{25} [11]. Gasoline and diesel oil usable fuels were obtained from waste engine oil by catalytic pyrolysis [12]. Distillation, cracking and pyrolysis processes were used. The pyrolysis products are used as alternative engine fuel. The yields of waste oil gasoline are increasing with increasing temperature and the amount of catalyst. The highest liquid product of 92.5% was obtained from the pyrolysis with 10% perlite catalyst. Pyrolysis process was also used to convert waste lube oil to diesel like fuel [13].

The emission characteristics of the resulted diesel like fuel were tested with four stroke single cylinder, direct injection, air-cooled or water-cooled diesel engine and compared with diesel fuel. The combustion and emission performance of blended recycle engine oil-diesel fuel was studied [14]. The waste lubricating oil was treated with acetic acid and then subjected to clay treatment. The resulted product was blended with diesel fuel. The physical properties of the blends were measured and tested by a diesel engine. The blends showed an increase in brake thermal efficiency and exhaust gas temperature with a decrease in brake specific fuel consumption and emission of NOx and HC compared with commercial diesel oil. The 5% by volume of waste plastic oil-diesel oil blend was investigated [15]. The physical properties of the blend were compared with diesel fuel. Total and specific fuel consumption was decreased while brake thermal efficiency was increased with the use of waste plastic oil/diesel blend.

Additional sludge is generated during the refining of crude oil. The heavy components deposit on the bottom of storage tanks and process equipment. Treatment process is required to recover the valuable oil from this sludge, and to reduce the volume of waste. Due to increasing environmental regulations, land filling was regarded as the less accepted and more expensive technique for disposal due to the problems associated with it. As a result, petroleum refineries and other oil services facilities have large accumulated volumes of this oil sludge waste in makeshift landfills or any other storage areas [16].

Liquid propane at moderate pressures in commercialized processes was evaluated to extract light hydrocarbons from the WOS [17]. Propane was recovered as a vapor by increasing the operating temperature and reducing the pressure of the raffinate. The light hydrocarbons stream was fed into the refinery, and the solids were disposed in a non-hazardous landfill. A pilot plant of a similar process was used to treat WOS from a petroleum refinery with multiple extraction processes [18]. It was found that the levels of aromatic hydrocarbons in the remaining solids were below the detection limits. Supercritical ethane and dichloromethane were also used to extract hydrocarbons from petroleum waste sludge using Soxhlet extraction technique [19]. Supercritical ethane was able to extract 16%-55% of the oil while supercritical dichloromethane was able to extract 50% oil from the petroleum waste. The recovered oil from the supercritical ethane was categorized mostly as saturated hydrocarbons, followed by aromatics, and has less than 5 mass percentage polar compounds.

II. Experimental Work

A. Materials

WOS was taken from local environmental company with the physical properties shown in Table I.

TABLE I
PROPERTIES OF WOS [7]

Property	Value
Water content, wt.%	4.1 %
Sediment and Ash, dry basis, wt.%	8.2%
Carbon residue, wt.%	9.5 %
Asphaltene content as heptane insoluble, wt.%	10.4 %
Organic material, dry basis, wt.%	91.2%
Specific gravity@15°C	0.905

The diesel fuel was taken from local petrol station. The properties of diesel fuel are shown in Table II.

TABLE II
PHYSICAL PROPERTIES OF DIESEL FUEL AND DIESEL LIKE FUEL OIL FROM 10% AND 15% WOS

Property	ASTM Method	Diesel fuel	10% added WOS	15% added WOS
Appearance	Visual	Clear	Gray	
Specific gravity @ 15°C	D-1298	0.8203	0.826	0.829
Carbon residue, wt.%	D-524	0.029	0.033	0.041
Ash content, wt.%	D-482	0.035	0.041	0.046
Asphaltene content, wt.%	D 3279	0.210	0.5504	0.572
Viscosity @40°C, cst	D-445	4.240	4.802	6.54
Sediment and water, vol.%	D-2709	Nil	0.2	Nil
Water content, vol.%	D-95	Nil	Nil	Nil
Aniline point, °C	D-611	73	70.75	67
Flash point, °C	D-93	83	86.2	89
Diesel Index	D-482	66.9+	62.86+	
Cetane index	D-976 & 4737	60.36	55.25	52
Calorific value, joule/g	D240 – 17	44,895	44,706	44,679
Sulfur content, wt.%	D-4294	0.155	0.284	0.43

B. Experimental Procedure

WOS was obtained from an environmental service company. It was stored at controlled room temperature between 22 °C and 24 °C and homogenized by stirring before performing any experiment. Since the characteristics and composition of the WOS are changing with every batch, sufficient quantity was obtained from a single batch for this work. The WOS was mixed with different amounts of diesel fuel (5-50% by mass) for 5 minutes using a variable speed bench-type overhead stirrer. The resulted mixture was filtered using a vacuum filter. The liquid fuel (diesel like fuel) was analyzed for different physical properties for comparison with original diesel fuel. The sulfur content of diesel like fuel was high. The adsorption desulfurization process was applied to reduce the sulfur content for the resulted fuel oil by mixing this fuel with $ZnCl_2$ activated date palm kernel powder as adsorbent material with contact time of 1 hour, room temperature, and 15% by mass of the date palm kernels powder activated with $ZnCl_2$ (DPK)$ZnCl_2$ as an adsorbent material. The activation process of the DPK powder with $ZnCl_2$ is as follows:

The DPK were collected, washed with tap water, then after with distilled water to be free from dirt and allowed to dry in an oven at 105 ºC for 24 hours; the dry product was then crushed and sieved to get fractions of less than 710 micrometers. This adsorbent was collected and kept in a closed jar. Zinc chloride was dissolved in water and added to the date palm kernels powder (DPKP) [20]. The solution concentration was adjusted to have a desired ratio of 2 :1 zinc chloride (as dry basis) to dry DPKP. Excess water was evaporated by heating using a hot plate followed by drying process using an oven at 120 ºC for 2 hours to remove the last traces of water. The impregnated DPKP was placed inside the furnace at 500 ºC for about three hours. After cooling the sample, the carbonized product was grinded into a fine powder in a mortar followed by washing thoroughly using distilled water. Next, 100 ml of diluted hydrochloric acid was added to the sample in a conical flask and the sample was left for one day. The samples were filtered and washed thoroughly with distilled water. The filtered water was tested for the presence of chloride ion using silver nitrate as an indicator. If chloride ion was still present, washing was continued until no chloride ions can be detected in the washing water. Finally, the sample was dried at 120 ºC for two hours, cooled, and stored in a closed container. The mixture was filtered and analyzed for different diesel oil properties. The process flow diagram of this work can be summarized in Fig. 1.

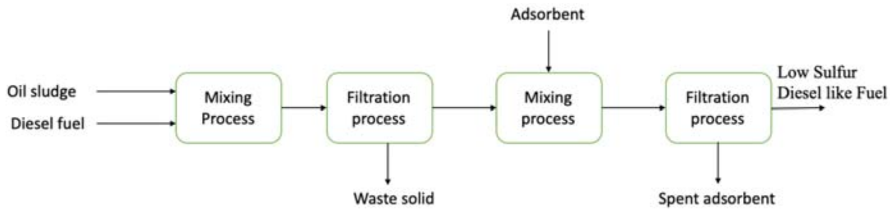

Fig. 1 Process flow diagram of low sulfur diesel like fuel from WOS

III. Result and Discussion

The mixing process of diesel fuel to WOS showed a recovery of fuel from WOS. The percentage recovery of diesel like fuel is shown in Fig. 2. This process was able to reduce the mass of WOS between 50-60%.

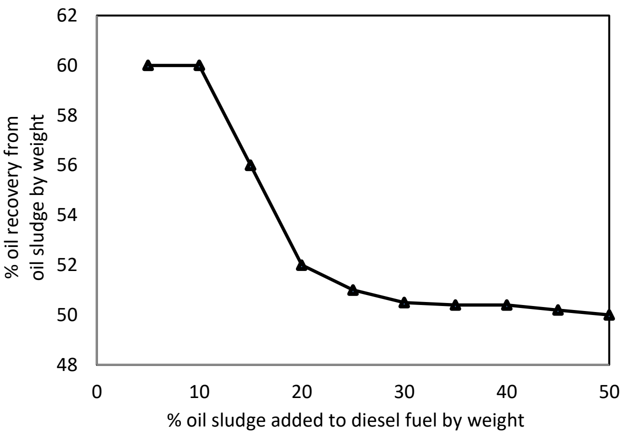

Fig. 2 % increase in the mass of sludge after diesel addition

The physical properties of the diesel like fuel from the addition of 5-50% WOS are shown in Figs. 3-7. Fig. 3 shows an increase in the specific gravity of the diesel like fuel from 0.8203 to 0.826 in the addition of 10% WOS and 0.829 in the addition of 15% WOS. This means that the specific gravity was increased by 1.1% with the addition of 15% WOS and 3.13% with the addition of 20% WOS. From the graph it is shown that there is a reasonable increase after 15% addition of WOS.

Fig. 4 shows a small increase in the kinematic viscosity of the diesel like fuel up to 15% and then reveals a sharp increase in viscosity which will affect the performance of the fuel pump to pump fuel to the diesel engine which may cause damage.

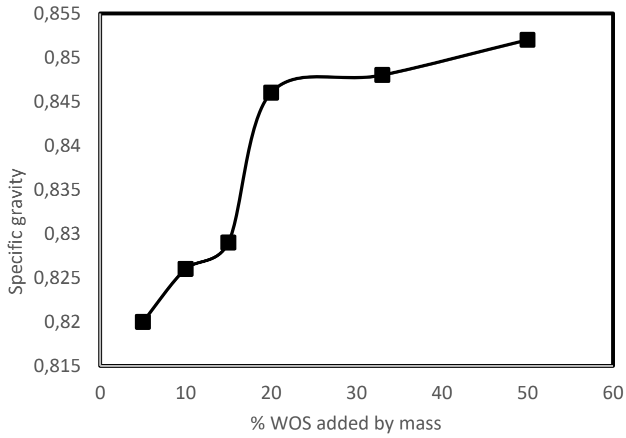

Fig. 3 Specific gravity of diesel like fuel with % addition of WOS

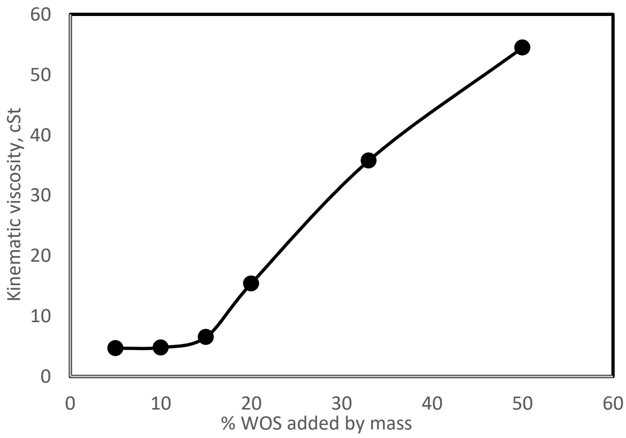

Fig. 4 Kinematic viscosity of diesel like fuel with percentage addition of WOS

The Conradson carbon residue, ash content and asphaltene content are shown in Fig. 5. From this figure, it is clearly shown that these properties are high for diesel like fuel and are increasing with the addition of WOS. The asphaltene content, ash content, and carbon residue remain at low values for 10% to 15% of oil sludge addition, and after these values there is sharp increase in these properties.

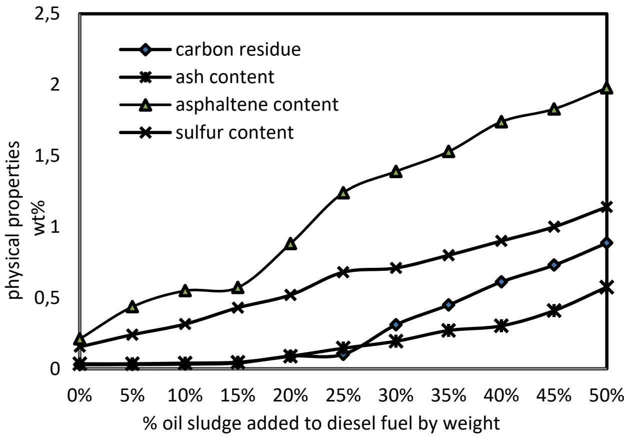

Fig. 5 Change of physical properties of resulted diesel fuel with amount added to oil sludge

Fig. 6 shows that the sulfur content of diesel like fuel increased sharply with the addition of WOS. The addition of 15% of WOS caused an increase in sulfur content from 0.155% to 0.435, i.e., an increase of 186%. Due to the limitations of sulfur content in fuel oil, the desulfurization process is required to reduce the amount of sulfur. The adsorption desulfurization process was performed using $ZnCl_2$ activated DPK powder as the adsorbent material with a contact time of 1 hour, room temperature, and 15% by mass DPK $ZnCl_2$. The ignition qualities of the diesel like fuel were plotted in Fig. 7. The diesel index and calculated cetane index were calculated from (1).

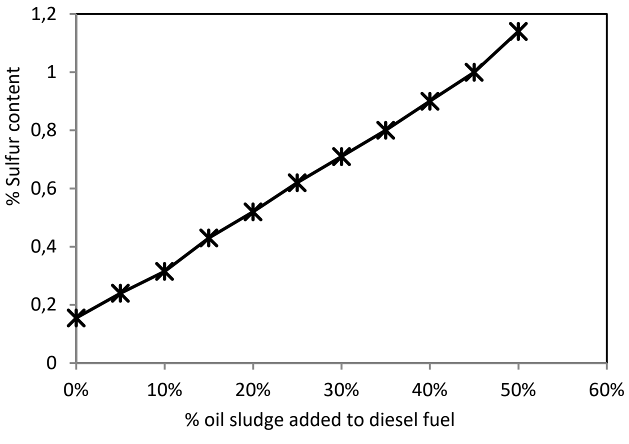

Fig. 6 Percentage of sulfur content with percentage of diesel added

$$\text{Diesel index} = \frac{\text{Aniline point (oF)x API gravity}}{100} \quad (1)$$

$$\text{Cetane index} = 0.72\ (\text{DI}) + 10 \quad (2)$$

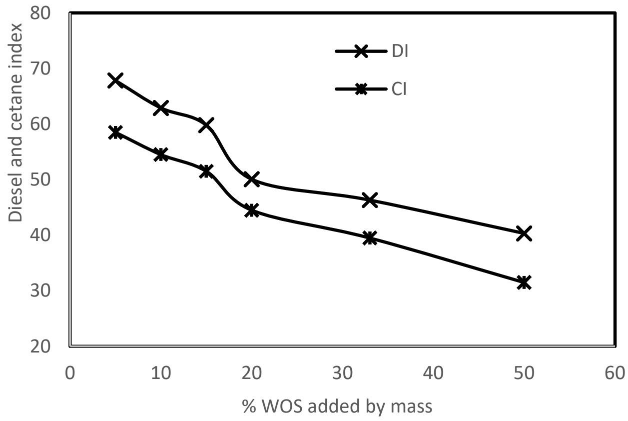

Fig. 7 Diesel and cetane index of diesel like fuel with percentage addition of WOS

The properties of the diesel like fuel with the addition of 10% and 15% WOS are shown in Table II. The calorific values of commercial diesel oil compared with the addition of 10% and 15% of WOS are shown in Fig. 8.

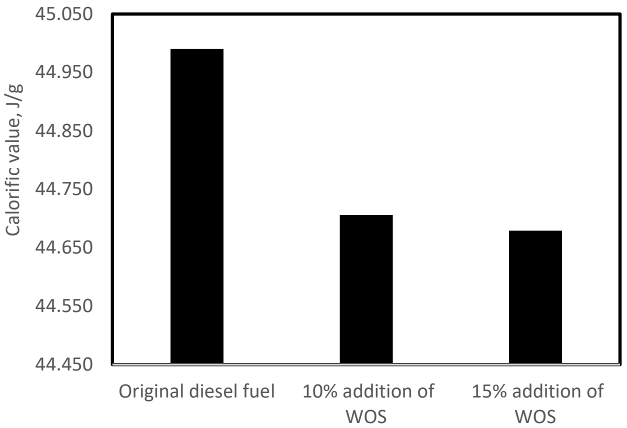

Fig. 8 Calorific value diesel like fuel with the addition of WOS

From Fig. 8, it is recommended to add 15% of WOS but with a quick and effective desulfurization process to reduce the amount of sulfur in diesel like fuel. The desulfurization process was performed and it was able to reduce the sulfur content from 0.43% to 0.183%. This means that there is 57.5% reduction of sulfur. The sulfur content was increased by 19% compared with the commercial diesel fuel. The comparison between the sulfur content of commercial fuel and the diesel like fuel before and after the desulfurization process is shown in Fig. 9. The physical properties and the metal content of the desulfurized diesel like fuel are shown in Table III. The ICP analysis according to ASTM D 5185 was used to measure the metal content of the resulted diesel like fuel after adding 15% of oil sludge. The metal content values are shown in Table IV.

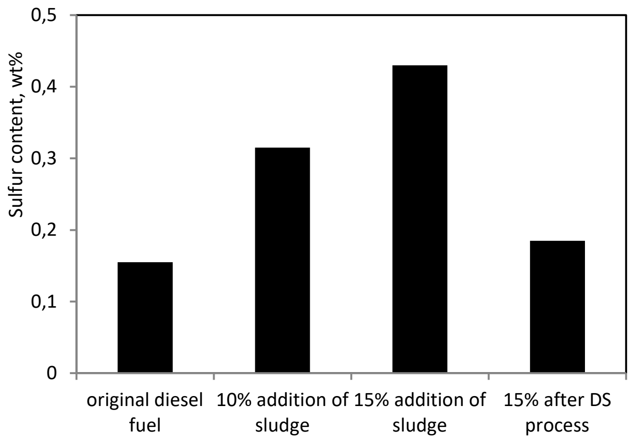

Fig. 9 Sulfur content of diesel fuel and final diesel fuel

TABLE III
PHYSICAL PROPERTIES OF DESULFURIZED DIESEL LIKE FUEL AFTER THE ADDITION OF 15% WOS

Property	ASTM Method	Diesel like fuel
Appearance	Visual	Clear
Specific gravity @ 15 ºC	D-1298	0.824
Carbon residue, wt.%	D-524	0.031
Ash content, wt.%	D-482	0.040
Asphaltene content, wt.%	D 3279	0.352
Viscosity @40 ºC, cst	D-445	4.82
Sediment and water, vol.%	D-2709	Nil
Water content, vol.%	D-95	Nil
Aniline point, ºC	D-611	70.5
Flash point, ºC	D-93	86
Diesel Index	D-482	63.915
Cetane index	D-976 & 4737	56.019
Calorific value, joule/g	D240 - 17	44,725
Sulfur content, wt.%	D-4294	0.183

TABLE IV
METAL CONTENT OF THE RESULTING DIESEL FUEL

Metal	Unit	Result
Aluminum (Al)	Mg/ kg	< 1.0
Barium (Ba)	Mg/ kg	< 1.0
Boron (B)	Mg/ kg	< 1.0
Calcium (Ca)	Mg/ kg	1.0
Chromium (Cr)	Mg/ kg	< 1.0
Copper (Cu)	Mg/ kg	< 1.0
Iron (Fe)	Mg/ kg	8.0
Lead (Pb)	Mg/ kg	< 1.0
Magnesium (Mg)	Mg/ kg	< 1.0
Manganese (Mn)	Mg/ kg	< 1.0
Molybdenum (Mo)	Mg/ kg	< 1.0
Nickel (Ni)	Mg/ kg	5.0
Phosphorous (P)	Mg/ kg	7.0
Potassium (K)	Mg/ kg	< 1.0
Sodium (Na)	Mg/ kg	2.0
Silicon (Si)	Mg/ kg	1.0
Silver (Ag)	Mg/ kg	< 1.0
Tin (Sn)	Mg/ kg	< 1.0
Titanium (Ti)	Mg/ kg	< 1.0
Vanadium (V)	Mg/ kg	1.0
Zinc (Zn)	Mg/ kg	1.0

It is shown that the iron and nickel contents are high. Other properties also showed a significant increase of sludge and it is believed that up to 15% of oil sludge addition can be accepted for different applications. So, it is recommended to add 15% by weight of oil sludge to the diesel fuel to get new fuel with accepted properties for specific applications in buses or trucks inside the petroleum refinery and oil field.

IV. CONCLUSION

The blending process of WOS with diesel fuel was studied and evaluated at different amount of diesel fuel. It was found that the blending and filtration processes were able to reduce the volume of waste sludge by recovering fuel oil. In addition, the composition of the resulted diesel fuel has higher sulfur content, so adsorption desulfurization was achieved to reduce the sulfur content to certain limit. The low sulfur diesel like fuel was evaluated by studying the physical properties of this product and comparing it with commercial diesel fuel. The diesel fuel can be regarded as a diluent and an extractant material to recover the fuel oil from WOS. It is necessary to optimize the quantity of diesel fuel so as to limit any changes in the physical properties and the ignition quality of the recovered diesel oil. It was found that the addition of 15% of sludge to the diesel fuel changed the properties of the commercial diesel fuel to certain limits. The sulfur content was high enough to reject it as diesel fuel according to the environmental restriction as fuel. Absorption desulfurization was applied to reduce the sulfur content but not to the required value. This low sulfur diesel like fuel can be used for trucks and buses inside the petroleum refineries and oil fields.

REFERENCES

[1] Elektorowicz M., and Habibi S., 2005. Sustainable waste management: recovery of fuels from petroleum sludge, Can. J. Civ. Eng. 32: 164–169
[2] Elektorowicz, M., Habibi, S., Chifrina, R., 2006, Effect of electrical potential on the electro-demulsification of oily sludge. Journal of Colloid and Interface Science, 295, 535-541
[3] Biceroglu, O., 1994. Rendering oily waste land treatable or usable. US Patent 5,288,391
[4] Trowbridge, T.D. and Holcombe, T.C., 1995, Refinery sludge 575 treatment/hazardous waste minimization via dehydration 576 and solvent extraction, Journal of the Air and Waste 577 Management Association, 45: 782–788
[5] Gazineu, M.H.P, de Araújo, A.A., Brandão, Y.B., Hazin, C.A., and Godoy, J.M., 2005, Radioactivity concentration in liquid and solid phases of scale and sludge generated in the petroleum industry, J of Environmental Radioactivity, 81: 47-54
[6] Abouelnasr, D.M. and Zubaidi, E. 2008, Treatment and Recovery of Oil-Based Sludge Using Solvent Extraction, In Proceedings of the Abu Dhabi International Petroleum Exhibition & Conference 2008
[7] Isam A.H. Zubaidi, Dana M. Abouelnasr, 2010, Fuel recovery from waste oily sludge using solvent extraction, Process Safety and Environmental Protection Journal, 88, 318–326.
[8] Abouelnasr, Dana M. and Zubaidi, Isam A.H., 2009, Fuel Recovery from Waste Oil Sludge Using Solvent Extraction Combined with a Demulsifier, Proceedings of the Fourth International Exergy, Energy and Environment Symposium, April 19-23, 2009, AUS, Sharjah, UAE.
[9] Isam Al Zubaidi, Effect of additives on Fuel Recovery from Oil Sludge Using Solvent Extraction Technique, World Heavy Oil Congress, Calgary 6-9 September, 2016
[10] Isam Al Zubaidi, 2018, Heavy Fuel Oil Recovery from Oil Sludge by Multiple Extraction Processes, Progress Petrochem Sci .1(4)
[11] Taiwo, E.A. and Otolorin, J.A., 2009, Oil recovery from petroleum 572 sludge by solvent extraction. Petroleum Science and 573 Technologies,

27: 836–844

[12] Mustafa Balat, 2008, Diesel-like Fuel Obtained by Catalytic Pyrolysis of Waste Engine Oil, Energy exploration and exploitation, Volume 26, Number 3, 197–208

[13] Venkata Ramesh Mamilla, Lakshmi Narayana Rao G, 2016, A review: Waste lubricating oil as an alternative fuel blended with diesel, International Journal of Advanced Scientific Research, Volume 1; Issue 1, 01-04

[14] B. Prabakaran, Zachu Thomas Zachariah, 2016, Production of Fuel from Waste Engine oil and Study of performance and emission characteristics in a Diesel engine, International Journal of Chem. Tech Research, Vol.9, No.05, 474-480

[15] Senthilkumar Tamilkolundu, Chandrasekar Murugesan, The Evaluation of blend of Waste Plastic Oil- Diesel fuel for use as alternate fuel for transportation, 2nd International Conference on Chemical, Ecology and Environmental Sciences (ICCEES'2012) Singapore April 28-29, 2012

[16] Kam, E.K.T., 2001. Assessment of sludge and tank bottoms treatment processes, Proceedings of the 8th International Petroleum Environmental Conference. Houston

[17] De Filippi R, Markiewicz J., 1991. Propane extraction treats refinery wastes to BDAT standards. Oil & Gas Journal, 89(36): 52-54

[18] Poche, L.R., Derby, R.E., and Wagner, D.R., 1991. Solvent extraction of refinery wastes rates EPA BDAT. Oil & Gas Journal, 89(1): 73-77

[19] Ávila-Chávez, M.A., Eustaquio-Rincón, R., Reza, J., and Trejo, A., 2007, Extraction of Hydrocarbons from Crude Oil Tank Bottom Sludges using Supercritical Ethane. Separation Science and Technology, 42: 2327-2345

[20] Yahia A.S. Alhamed, 'Preparation and characterization of activated carbon from dates' stone, The 6th Saudi Engineering Conference, KFUPM, Dhahran, December 2002