International Journal of Advanced Chemistry, 4 (2) (2016) 22-26

SPC

International Journal of Advanced Chemistry

Website: www.sciencepubco.com/index.php/IJAC
doi: 10.14419/ijac.v4i2.6880
Research paper

Quantitative analysis of fat, oil and grease in valikamam area, Sri Lanka and conversion of waste oil into grease

Kugamoorthy Velauthamurty [1]*, Dilki Manisha Kurukulasuriya [1]

[1] *Department of Chemistry, University of Jaffna, Sri Lanka*
**Corresponding author E-mail: kvelauthamurty@yahoo.co.uk*

Abstract

Groundwater is the main source of freshwater. Groundwater denotes to all the water occupying the voids, pores and fissures within geological formations, which originated from atmospheric precipitation either directly by rainfall infiltration or indirectly from rivers, lakes or canals. Groundwater pollution is a serious problem because many people depend on groundwater for their drinking water. Waste oil along with heavy metals is one of the major contaminant species makes water harmful. A one drop of heavy fuel oil is enough to contaminate a million gallons of freshwater. Waste oil is generated through dumping, land spreading, incineration, road oiling, industrial chemical spills, extensive use of pesticides, herbicides and fertilizers etc. For this study water samples were collected from forty of wells representing the Valikamam area. Then the water samples were analyzed for Fat, Oil and Grease using liquid-liquid extraction with hexane and gravimetric determination. The results shows only four wells exceed the 10 mg/L while thirty six wells were potable. Waste oil disposal is a big threat these days around the world. Hence this paper gives a brief review about recycling waste oil by converting it into commercially important lubricating grease. Once the grease characterization is done for the grease obtained from waste oil, we can bring it up to the commercial stage on the other hand giving a better solution for the depletion of waste oil.

Keywords: *Ground Water; Waste Oil; Recycling; Conversion; Grease; Heavy Fuel Oil.*

1. Introduction

Industrialization has opened up a new era in agriculture, trade, transport and all other economic activities while proving the quality of man power. Rapid industrialization is a must in order to increase the national income of the country, to reduce the pressure of increasing population, to utilize the resources and so on. Most of industrial activities rely on various types of oils for their proper functioning.

Lubricants are widely used in manufacturing industries, power stations, automobiles, marine engines etc. Lubricants perform in the roles such as keep moving a part, reduce friction, transfer heat, transmit power, carry away contaminants and debris, protest against wear, prevent corrosion, seal for gases, prevent rust, and prevent internal combustion of engines in automotives. (Howard, 1998)

For automotive purpose people use engine oils, brake fluids, hydraulic fluids, gearbox fluids, automatic transmission fluid. For tractors Universal Tractor Transmission Oil (UTTO) and Super Tractor Oil Universal (STOU) are in use. For the other motors 2-stroke engine oils, personal lubricants are in use. For industries air compressor oils, food grade lubricants, gas compressor oils, gear oils, bearing and circulating system oils, refrigerator compressor oils, steam and gas turbine oils are being used. Gas turbine engine oil and piston engine oil are used for the aviation. (Howard, 1998)

Thus a huge range of oil types is being used widely and currently with the beginning of the industrial revolution.

After these lubricants are being used for a number of applications, the negative side that we all have to accept is either intentionally or accidentally we all are responsible for piling up tons of dump oil to our precious nature. Even if we apply good lubricant initially, after passing through heavy machinery, it will enrich with many hazardous constituents as most of industries get waste oil as a byproduct.

Directly or indirectly a large quantity of waste oil is cumulating in our ecosystem daily. When these lubricants reach into the soil, it will deposit along with organic compounds like biphenyl, petrochemicals, and phenolic compounds and heavy metals like chromium, copper, lead, manganese, nickel, and zinc. A heavy metal refers to a metallic element which has a relatively high density and is toxic or poisonous even at low concentration. If any by chance this hazardous waste oil is mixed up with ground water source either by deposition, sedimentation, penetration through fissure or flowing with water, the consequences will be unimaginable. (Clesceri, 1998)

When the soil and ground water get polluted in agricultural area, the heavy metals that absorbed by plants and algae ultimately accumulate in their tissues. Animals that graze on those contaminated plants and drink polluted water, as well as marine lives that breed in heavy metal polluted water also aggregate such metal in their tissues and milk. The European union informs a standard of 0.3 mg/g for mercury. Sweden initially introduced a limit of 0.5 mg/g but discovered that most of the fish from the Baltic and inland lakes already exceeded this, so were forced to increase the limit to 1.0 mg/g. They advised the public not to eat more than two fish meals per week. (Clesceri, 1998)

At last humans who exposed to heavy metals by consuming contaminated plants and animals will experience various biochemical disorders such as gastrointestinal disorders, diarrhea, tremor, stomatitis, hemoglobinuria, ataxia, paralysis, vomiting, convulsion, depression, pneumonia, dysfunction in kidneys, joints, reproductive system, cardiovascular system, damage in central nervous system and neurotoxic, carcinogenic, mutagenic disorders. Our group mainly tried to figure out that minimizing this oil contamination problem. Instead of discarding waste oil directly into the environment we collect waste oil and recycle it producing lubricating grease. (Reuter, 1998)

Grease is a semi solid lubricant. It generally consists of soap emulsified with mineral or oil. The function of grease is to remain it contact with and lubricate moving surfaces without leaking out under the force of gravity, centrifugal action or being squeezed out under the pressure. The properties of grease are based on the amount and type of thickener used. Currently many researches were conducted to explore alternative sources for grease production due to increasing of crude oil prices in the world market and the depletion of source. So the success of this research will not only reduce the oil pollution but also produce grease at low cost.

Main components of lubricating grease are base oil (70-95%), thickener (3-30%) and additives (0.1-10%). Here the waste oil we are going to use act as the base oil once it removes all the heavy metal ions. Making grease is similar to making soap. Both products rely on a chemical reaction to take place between oil, fat or fatty acids (base oil) and alkali base material (thickener) to form soap like materials. Grease uses a variety of metal hydroxide alkaline to make and define grease type. For instance aluminum hydroxide makes aluminum grease, lithium hydroxide makes lithium grease and calcium hydroxide makes calcium grease.

Chemical reaction used in here known as “saponification reaction”. Fats and oils are composed of triglycerides. Three fatty acid molecules attached to a glycerol molecule. In waste oil, some of the glycerides have broken down so that the fatty acids are separated from the glycerol molecule and these are called free fatty acids. These free fatty acids tend to react with alkali catalyst and thus reduce the speed of the trans-esterification reaction.

Greases are manufactured in variety of consistencies using the number rating system of National Lubricating Grease Institute (NLGI). There are so many tests that run to characterize the quality of grease. Some grease tests are cone penetration test, moisture content test, density test, viscosity, Dropping point test, Copper corrosion test, oxidation stability test along the colour, appearance, soap thickeners, additives, plumbability, slumpability, operating temperature and water resistance. Once the grease formation is done it should be tested for all these parameters in order to produce commercial grease.

Among a wide range of waste lubricants, we selected waste Heavy Fuel Oil (HFO) to produce grease. HFO is an important resource and a petroleum base product. It is a black liquid oil with higher viscous, specific gravity and heavier molecular composition. It is a residue deriving from crude oil refining. Heavy fuel oils are used in medium to large industrial plants, furnaces, marine applications (ships, locomotives) domestic heaters and power stations in combustion equipment such as boilers, furnaces and diesel engines. HFO burnt in a furnace or boiler is for generation of heat or used in an engine for the generation of power. And also, to meet the needs of the electricity production in industries, manufacturing and power stations. Reasons for wide range of using HFO are: less consumption, less cost, low maintenance cost, complete combustion, improved efficiency of boilers, ovens and engines, fully customizable applications, safety and performance and high functionality.

2. Materials and methods

2.1. Sampling plan

Water samples were collected from wells around Chunnakam power plant area according to a systematic sampling plan. Wells for sampling were selected along eight directions namely North (N), Northeast (NE), East (E), Southeast (SE), South (S), Southwest (SW), West (W), and Northwest (NW). Along each direction, wells were selected on or near the grid points of 200 meter interval up to 1 km. Hence 40 wells were selected as we mentioned in our previous work. (Velauthamurty.K, 2016)

2.2. Collection of water samples

Grab sampling method was used to collect the water samples. Approximately 1500 ml water samples was collected into glass bottles and each sample was preserved with 5 ml of 1: 1 HCl. Water samples were collected from the surface and bottom of the dug wells. In the case of tube well only one sample is collected. Ruttner water sampler was used for the water sample collection in our analysis. Samples were collected by direct pumping in tube wells. (Velauthamurty.K, 2016) forty water samples were collected during the period of January 2016 to March 2016.

2.3. Determination of fat, oil, grease in ground water

All forty samples were subjected into liquid-liquid extraction with hexane and gravimetric determination which is an effective analytical method to detect fat, oil, and grease in water. Experiments were conducted in the inorganic laboratory in Department of Chemistry, University of Jaffna.

2.4. Analytical procedure used for determination of FOG

Initially all the samples were acidified by HCl (pH=2) samples were sequentially extracted three times using hexane, shaken vigorously for ten minutes per extraction. The ratio of solvent to sample should be no less than 1:20. The solvent extracts are drop wisely passed through a drying funnel containing anhydrous sodium sulfate. Distillation was done to acquire hydrocarbon residue. It was put into oven and set temperature as 70 °C then put into desiccator for cooling. Determination of the residue was done by analytical electronic balance. (Vogel Arthur, 1961 and Olumuyiwa, 2012)

3. Results and discussion

FOG content was calculated using following equation.

FOG content in mg/L = (weight of FOG / 300 ml) * 10^6

FOG content of water samples that we collected in 2016 is compared with the FOG content of water samples which collected in same locations in 2015. (Velauthamurty.K, 2016)

Table 1: FOG Content 2015 vs. 2016 Variation of FOG Content in Ground Water from 2015 to 2016.

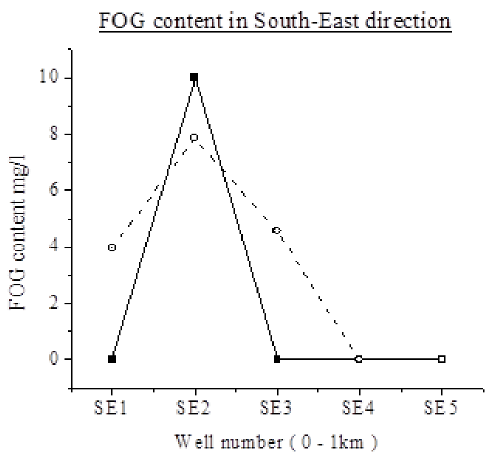
No	Sample Number	Final results of Fat, Oil, Grease in mg/l 2015	2016
1	N1	Not detected	2.33
2	N2	7.26	6.82
3	N3	4.62	4.57
4	N4	Not detected	Not detected
5	N5	Not detected	2.56
6	NE1	10.56	10.56
7	NE2	Not detected	Not detected
8	NE3	12.54	Not detected
9	NE4	1.65	Not detected

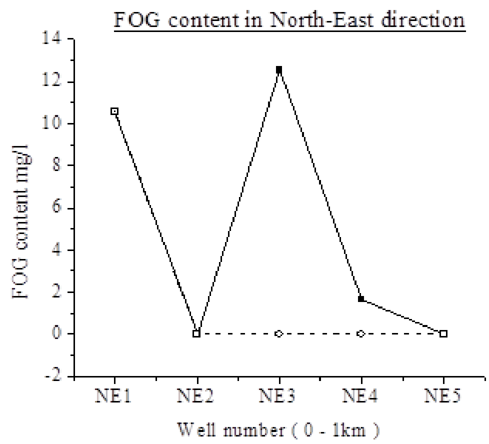
10	NE5	Not detected	Not detected
11	E1	Not detected	3.78
12	E2	5.28	74.8
13	E3	10.56	9.8
14	E4	Not detected	Not detected
15	E5	Not detected	5.68
16	SE1	Not detected	3.96
17	SE2	9.99	7.85
18	SE3	Not detected	4.55
19	SE4	Not detected	Not detected
20	SE5	Not detected	Not detected
21	S1	Not detected	2.88
22	S2	4.95	6.92
23	S3	8.58	4.56
24	S4	Not detected	8.47
25	S5	Not detected	Not detected
26	SW1	3.96	4.56
27	SW2	3.96	3.63
28	SW3	Not detected	4.24
29	SW4	Not detected	Not detected
30	SW5	Not detected	Not detected
31	W1	3.33	4.95
32	W2	13.53	7.53
33	W3	Not detected	3.41
34	W4	Not detected	6.97
35	W5	Not detected	3.95
36	NW1	9.24	10.56
37	NW2	8.25	10.89
38	NW3	1.65	Not detected
39	NW4	Not detected	Not detected
40	NW5	Not detected	12.54

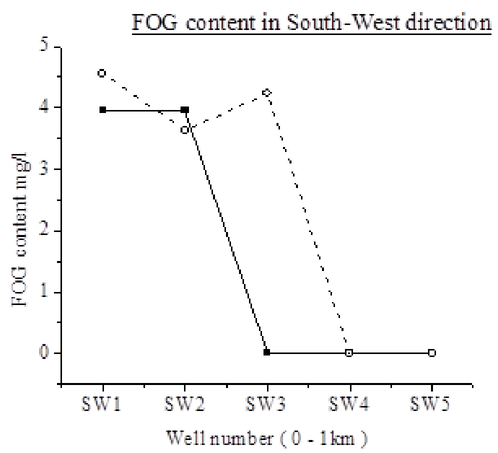
Variation of FOG content in ground water from 2015 to 2016

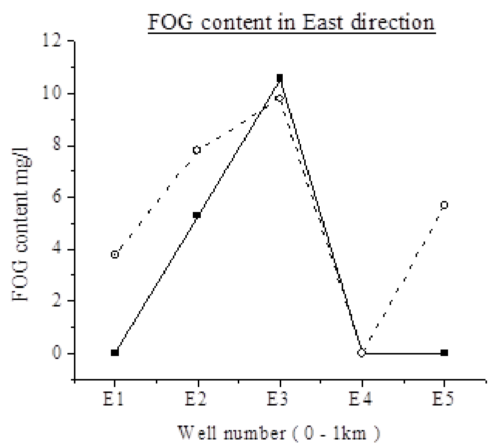
———— - FOG content in 2015

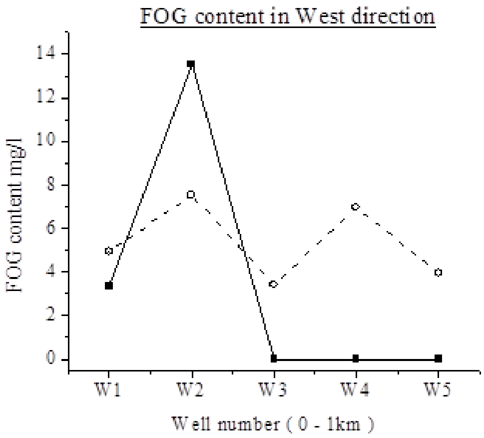
-------- - FOG content in 2016

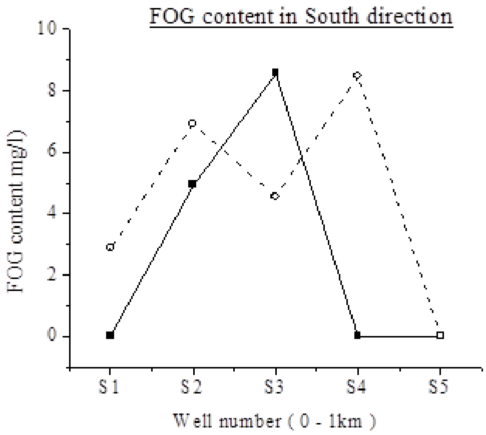


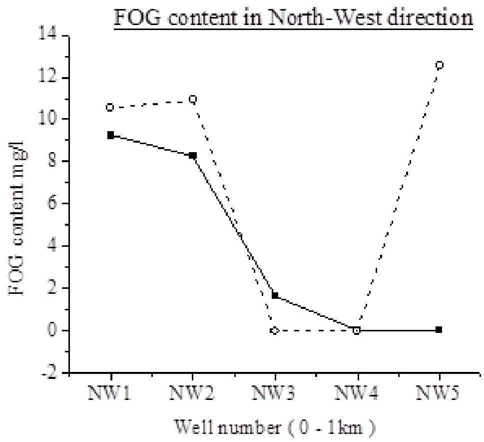


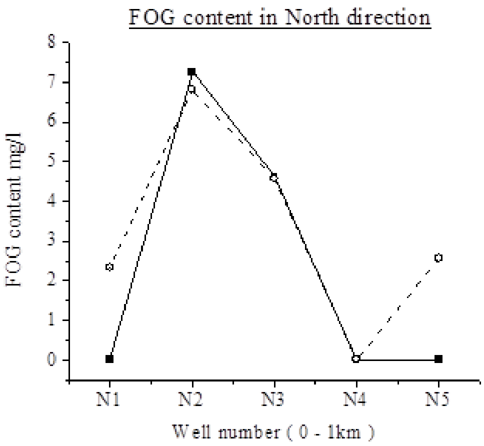












According to the results in 2016, only four wells exceeded the 10 mg/l and three of them were taking from NW direction wells. Twenty three samples were in the range of 2-10 mg/l, while thirteen wells revealed without FOG. When compare with data from 2015, FOG value has been rapidly increased in the S4, SW3, NW5 wells in high amount, while NE3 well unrevealed any FOG. So the risk of consuming well water in NE3 directed well has been totally removed by 2016. (Velauthamurty.K, 2016)

The variation of FOG is due to several factors like population density, closeness to the power station, agricultural activities, cultivated lands, abandoned wells, microbial activity, weather, salinity and geological conditions like slope, soil type, pores, fissures, minerals.

Valikamam is an intensive agricultural area with a dense population. Ground water here is always exposed to continuous supply of agrochemicals, alcoholic beverages, fertilizers, pesticide, weedicide, glyphosate (Round up, chelates, heavy metals), oil hydrocarbons, lubricants which gradually create a toxic environment. As a result of flowing of heavy metals and FOG it will sustain in our food chain, food web system and end up with a big havoc.

Abandoned wells contain high number of microbes as it is not used by humans regularly. Hence many secretions excluded by fungi, bacteria, Cyanobacteria and algae will also deteriorate the well water system.

It is advisable to held awareness programs for farmers, students, villagers about ground water pollution. Frequent usage is also a good habit to renew and refresh the well water system. And also introducing environment friendly natural organic fertilizers is also much appreciable. (Irwin, 1997 and Adewuyi, 2012)

3.1. Conversion of waste HFO into lubricating grease

The waste HFO was collected from some power plant in the middle of Jaffna peninsula. 100 ml of waste HFO was added into a beaker and heated to reach 120°C to remove the remaining water and volatile particles. This oil was allowed to cool down to room temperature. 2 ml of acetic acid was added and stirred at 100 r.p.m. 0.1 ml of $H_2O_2$was added in order to oxidise lead into lead (ll). This reaction continued for 30 minutes. (Daniel Solomon et.al, 2010)

Then the system was allowed to sedimentation for five hours. Next the oil layer on the top of the sludge was separated. This separated oil can use as the base oil and it is metal free. 65 ml of this base oil is mixed with 35 ml of cooking oil, 5 g of NaOH and 2 g of $Ca(OH)_2$ which were made as a aqueous solution by adding 10 ml of water. All the reagents were mixed vigorously.

The temperature was increased to 150°C. From this point saponification started. Then gradually temperature was increased into 225°C.Finally it was allowed to cool to room temperature while stirring. (Sangar.S, 2016) After cooling the grease was formed as appeared in the Fig.1.

Fig. 1: Produced Grease In Lab.

3.2. Discussion

Waste HFO is comprised of heavy metals like chromium, copper, lead, manganese, nickel, zinc. Even it has a high-energy value. The combustion is also not favorable as it can cause air pollution. So, recycling process will be more advisable.

Acetic acid is the chemical treatment that is used in our procedure to demetallize the waste HFO. It has a potential to precipitate all the present heavy metals as its acetates. They are $Pb(CH_3COO)_2$, $Cr_3(OH)_2(CH_3COO)_2$, $Cu(CH_3COO)_2$, $Zn(CH_3COO)_2$, $Mn(CH_3COO)_2$, $Ni(CH_3COO)_2$ sludge in the bottom layer contains the heavy metal precipitates. After the separating of the base oil from the acetic acid treatment we can conduct furthermore tests to analyze the bottom sludge layer containing heavy metal precipitates. But it is worthy to analyze this sludge part after the different amount of acetic acid treatment and optimize the amount of acetic acid which precipitate high amount of heavy metals. Further we suggested to conduct these chemical tests to conduct for water after mixing up with sludge.

Pb – Lead is precipitated as the chromate with K_2CrO_4 in medium buffered with acetic acid and ammonium acetate. The precipitate is washed with water, dissolved in dilute HCl, treated with KI solution and liberated I_2 titrate with a standard solution of $Na_2S_2O_3$.

$Pb(C_2H_3O_2)_2 + K_2CrO_4$ ----------> $PbCrO_4 + 2KC_2H_3O_2$

$PbCrO_4 + 2HCl$ -----------> H2

$CrO_4 + PbCl_2$

$H_2CrO_4 + 6KI + 12HCl$ ------------> $2CrCl_3 + 6KCl + 3I_2 + 8H_2O$

Cu – Copper can be analyzed by electrolytic determination in the presence of sulphuric acid.

Cathode - $Cu^{2+} + 2e$ -------> Cu Anode - 2, OH^- -------> $\frac{1}{2} O_2 + H_2O + 2e$

$2H^+ + 2e$ --------> H_2

Ni – Nickel is precipitated by the addition of an alcoholic solution of dimethylglyoxime (H.Dmg) to a hot slightly acidic solution of the nickel compound and then adding a slight excess of NH_3 solution. The precipitate is washed and weighed as nickel dimethylglyoxime after drying at 100°C-120°C.

Ni^{2+} + 2HDmg ---------->Ni (Dmg) $_2$ + H_2SO_4

Cr – Chromic salts are oxidized into dichromates by boiling with excess of persulfate solution in the presence of a little $AgNO_3$. The excess of persulfate remaining after the oxidation is complete ic destroyed by boiling the solution for a short time. The dichromate content of the resultant solution is determined by the addition of excess of standard ferrous solution and titration of the excess of latter with standard 0.1N $K_2Cr_2O_7$. (Daniel Solomon et.al, 2010 and Sangar.S, 2016)

4. Conclusion

In the case of grease production, acetic acid treatment is more beneficial for the demetallization process as its' less cost, mild condition, easiness to handle, availability, efficient precipitation of heavy metals. Only minute amount requires to demetallize a considerable amount of waste HFO. If there is an intention to bring it upto commercial stage more grease tests and quality parameters have to be carried out in future.

Among the several ground water quality parameters, Fat Oil Grease takes a significant place as it carries a bulk of heavy metals along with it. In order to minimize the FOG content we have to confine a wide range of oil hydrocarbons used fertilizers, mineral oil, soap, detergents, chemical sprays, petroleum products, waste oil etc. Once groundwater becomes contaminated it is really difficult and expensive to clean up and reinstate it.

Acknowledgement

KV like to thank Head/Department of Chemistry for granting permission to conduct this research work and Mr.A.Thabesan (Technical officer, Department of Chemistry, University of Jaffna, Sri Lanka) for all the technical assistance during the research in the Department of Chemistry, University of Jaffna, Sri Lanka.

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