Modeling Of Asphaltic Sludge Generation from Spent Engine Oil

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***Abstract* - Spent engine oil is a prime source of environmental pollution. It causes soil and groundwater contamination when disposed in sewers. There is therefore need to recycle the oil in order to reduce its negative effects on the environment. Spent engine oil can be treated to produce asphaltic sludge and regenerate base oil. The sludge produced can be used as a resin for black printing ink and the base oil can be refined for further use in lubrication. The spent engine oil was first treated with sulphuric acid at different temperatures to produce resinous sludge. To study the effect of acid volume and temperature on sludge weight, univariable models were developed and the coefficients determined using the least square technique. Two models were developed to determine the effect of acid volume on sludge yield and the quadratic model was found to be more accurate based on the error functions calculated. First order, quadratic, cubic and fourth order models were tested to study temperature effect on sludge weight and fourth order model was found to best fit the experimental data. The optimum temperature was found to be 52°C and the sludge weight begins to decrease when this temperature is exceeded.**

***Keywords* - Spent engine oil, base oil, acid, soil, groundwater, contamination, resin, sludge, lubrication, temperature, volume and model**

I. INTRODUCTION

Over the years, more than 70% of used engine oil (commonly referred to as condemned or spent oil) is most often disposed as waste in Nigeria after lubrication. Lubricating oil goes through normal degradation and about 50% of it is consumed in the process, the rest of the oil picks up number of contaminants from the working environment such as residual components of engine fuels, solids from wear processes along with corrosion products and dirt, soot, combustion products etc. (Kajdas, 2000). Waste engine oil is a hazardous pollutant that requires responsible management. This waste lubricating oil has higher values of ash, carbon residue, asphaltenic materials, metals, water, and other dirty materials; which are built during the course of lubrication inside the engine. (Abdel- Jabbar et al., 2010) Waste engine oil may cause damage to the environment when dumped into the ground or into water streams including sewers. This may result in groundwater and soil contamination. However, it has been found to be a potential raw material for producing sludge used as binder in black ink production and the base oil regenerated from the desludging process can be refined for use in lubrication. Its utilization in this area will minimize its wastage and the negative effects on the environment. Used engine oil contains resin, organic acids and polymers (Domo Spiff, 2009). These substances can be precipitated as varnish and asphaltic resin known as sludge. This can be achieved by treating the oil with concentrated sulphuric acid, sodium hydroxide and other additives to yield crude base oil and sludge as byproduct. The sludge produced contains polymeric materials such as asphaltenes, carboids, carbenes and petroleum resins which are responsible for the black colour of engine oil.

Engine Oil Degradation

During the use of engine oil in lubrication, it deteriorates by two main processes. These include oxidation and thermal degradation. These processes generate a lot of impurities in the lubricating oil, during its application in internal combustion engines. These impurities contain unsaturates, aldehydes, phenolic compounds, alcohols, acidic compounds and non-stable hydrocarbons. Moreover, the viscosity increases by production of an asphaltic sludge, which a metallic scrapings act as catalysts at the high operating temperature and oxygen vicinity (Bridjanian and Sattarin, 2006; Rahman et al., 2008) Oil oxidation is similar to the usual oxidation reaction, such as rusting. It brings about the permanent chemical modification to the base oil molecules.

II. MATERIAL AND METHODS

Spent engine oil with an average SG of 0.925 (about 21.5 °API) was obtained from an automobile workshop in Owerri metropolis. 150ml of used engine oil was mixed with 30ml of 2.0 molar H2SO4 in a beaker. The mixture was placed in an oven set at a temperature of 60°C and carefully stirred for about 30 mins for even distribution. Two distinct layers were observed: a mobile oil layer, on top of a dense bottom layer (the resinous sludge). The oil layer was afterwards decanted, leaving behind the sludge. The PH of the layers was then measured and recorded. The procedure was repeated at different acid volume (25ml, 40ml, 50ml, 70ml, 80ml, 90ml and 100ml). In order to determine temperature effect, the desludging process was carried out using same volume of acid but at different temperatures(30°C, 35°C, 40°C, 45°C, 50°C, 55°C etc.).

III. RESULT AND DISCUSSION

There were two principal studies carried out, they include the effects of acid volume and temperature on the yield of sludge. These effects were studied using linear, quadratic, cubic and 4th order polynomial models. Error functions were used to determine the model that best fit the experimental data obtained. The effect of acid volume was determined at a constant temperature of 50°C. Temperature effect was determined by keeping the volume of acid constant at 30ml. As shown in Table 1, the produced sludge has a lower PH due to the presence of acidic contaminants in the used engine oil. It can be seen from Table 2 and Fig 1 that on increasing the acid volume, there was an increase in sludge weight. This simply implies that for a larger yield of sludge, more acid is required. Also it can be inferred that about 0.3-0.5 ml of the acid is required to produce 1g of sludge. This range arose due to improper mixing, residence time variation in the batch and systemic errors encountered in the weighing balance.

Table 1 Property of Produced Sludge and Oil

Property	Used Engine Oil	Produced Sludge	Regenerated Oil
PH	2.5	2.0	3.0
Kinematic Viscosity @ 30°C (cSt)	157	198	138
SG @ 30°C	0.925	0.945	0.8707
Flash Point(°C)	158	-	180
Pour Point	-5	-	-7

Table 2 Quantities of Sludge and Oil Produced at Varying Acid Volume

Volume of Acid(ml)	Weight of Sludge(g)	Weight of Regenerated Oil (g)	Acid volume required per g of Sludge Produced (ml/g)
25.00	52.43	90.58	0.477
30.00	68.12	58.00	0.440
40.00	105.61	80.77	0.379
50.00	139.10	60.80	0.359
60.00	172.38	10.82	0.348
70.00	205.76	5.76	0.340
80.00	243.26	3.12	0.329
90.00	276.64	2.43	0.325
100.00	311.83	1.17	0.321

A look at Fig.3.1 shows that the graph is defined by a straight line equation. However, to find the model that best fit the data, linear and quadratic models were tested using the standard error of estimate (SEE), sum square errors and coefficient of determination (R2) calculated using these equations:

$$SEE = \sqrt{\left[\frac{\sum_{i=1}^{N}(Wexp - Wmodel)2}{N-2}\right]}$$

$$R^2 = \frac{\sum_{i=1}^{N}(Wexp-Wavg)2}{\sum_{i=1}^{N}[(Wexp-Wavg)2+(Wexp-Wmodel)2]}$$

$$SSE = \sum_{i=1}^{N}(Wexp - Wmodel)\ 2$$

Where Ymodel and Yexp are the weights of sludge calculated by model and obtained from experiment respectively. Yavg is the mean calculated weight and N is the number of data points. From the SEE values calculated for the two models, the quadratic model has a SEE of 1.19825249 which is lower than that of linear 1st order model (1.207298285). Thus, the quadratic model is more accurate and best fit the experimental data obtained.

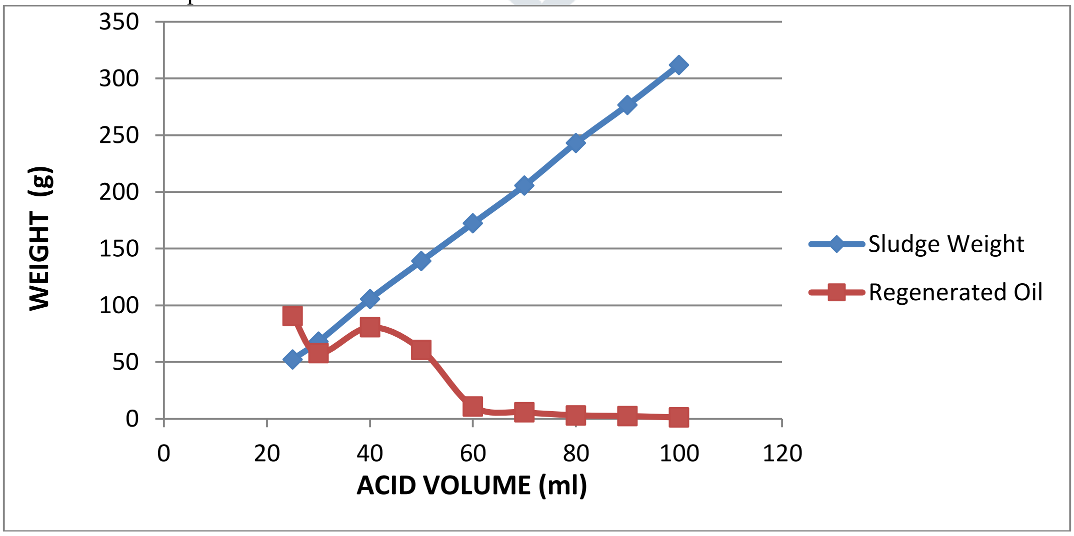

Fig 1 Variation of Sludge and Oil Weight with Acid Volume

Table 3 Comparison of Models

V	W_{prdt1}	W_{prdt2}	W_{exp}	$(W_{prdt1}-W_{exp})^2$	$(W_{prdt2}-W_{exp})^2$
25	52.0846	52.3013	52.43	0.11930116	0.01656369
30	69.3716	69.4738	68.12	1.56650256	1.83277444
40	103.9456	103.8638	105.61	2.77022736	3.04921444
50	138.5196	138.3138	139.10	0.33686416	0.61811044
60	173.0936	172.8238	172.38	0.50922496	0.19695844
70	207.6676	207.3938	205.76	3.63893776	2.66930244
80	242.2416	242.0238	243.26	1.03713856	1.52819044
90	276.8156	276.7138	276.64	0.03083536	0.00544644
100	311.3896	311.4638	311.83	0.19395216	0.13410244
			$\sum (W_{exp} - W_{model})^2$	10.202984	10.0506632

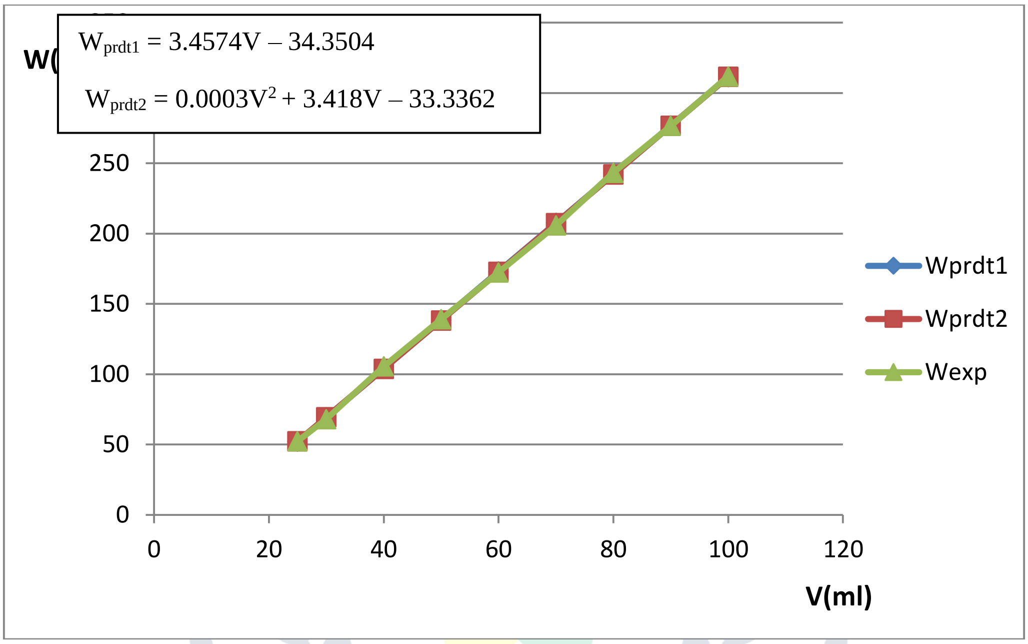

Fig 2 Comparison of Models

Table 4 Error Functions for Volume Effect Models

Error Functions	First Order	Quadratic
SSE	10.202984	10.0506632
SEE	1.207298285	1.19825249

The weight of sludge produced with a given volume of acid varies with temperature as shown in Table 4 and Fig 2. It was also observed that as the temperature rose from 30°C to 50°C, the sludge weight increased appreciably from 55.12g to 66.81g. As the temperature was increased further above 50°C, the sludge weight began to fall. This drop in the amount of sludge may be due to the conversion of most of the hydrocarbons by sulphonation reaction of the acid and the thermal cracking of the sludge formed. From the R^2, SSE and SEE values calculated for the three temperature effect models, 4th order polynomial was found to have the lowest SSE and SEE; highest R^2. Thus, the 4th order polynomial fits the data obtained.

Table 5 Temperature Effect on Sludge Weight

T(°C)	W_{exp}	W_{quad}	W_{cubic}	W_{4th}	$(W_{qaud}-W_{exp})^2$	$(W_{cubic}-W_{exp})^2$	$(W_{4th}-W_{exp})^2$
30	55.12	56.4062	54.3066	54.3194	1.65431044	0.66161956	0.64096036
35	58.05	59.4416	59.8638	59.8477	1.93655056	3.28987044	3.23172529
40	63.40	61.7108	63.2541	63.2375	2.85339664	0.02128681	0.02640625
45	65.62	63.2140	64.8277	64.8224	5.78883600	0.62773929	0.63616576
50	66.81	63.9510	64.9349	64.9408	8.17388100	3.51600001	3.49390864
55	62.43	63.9220	63.9257	63.9357	2.22606400	2.23711849	2.26713249
60	61.08	63.1268	62.1505	62.1549	4.18939024	1.14597025	1.15541001
65	60.12	61.5656	59.9594	59.9510	2.08975936	0.02579236	0.02856100
70	58.20	59.2382	57.7028	57.6815	1.07785924	0.24720784	0.26884225

75	56.14	56.1448	55.7306	55.7082	2.304E-05	0.16760836	0.18645124
80	54.05	52.2852	54.3933	54.3982	3.11451904	0.11785489	0.12124324

Temperature Effect Models

$Y_{quad} = -0.015322T^2 + 1.603T + 22.106$

$Y_{cubic} = 0.00046695T^3 - 0.092368T^2 + 5.6328T - 44.1539$

$Y_{4th} = 3.1702E\text{-}07T^4 + 0.0003972T^3 - 0.086813T^2 + 5.4436T - 41.8381$

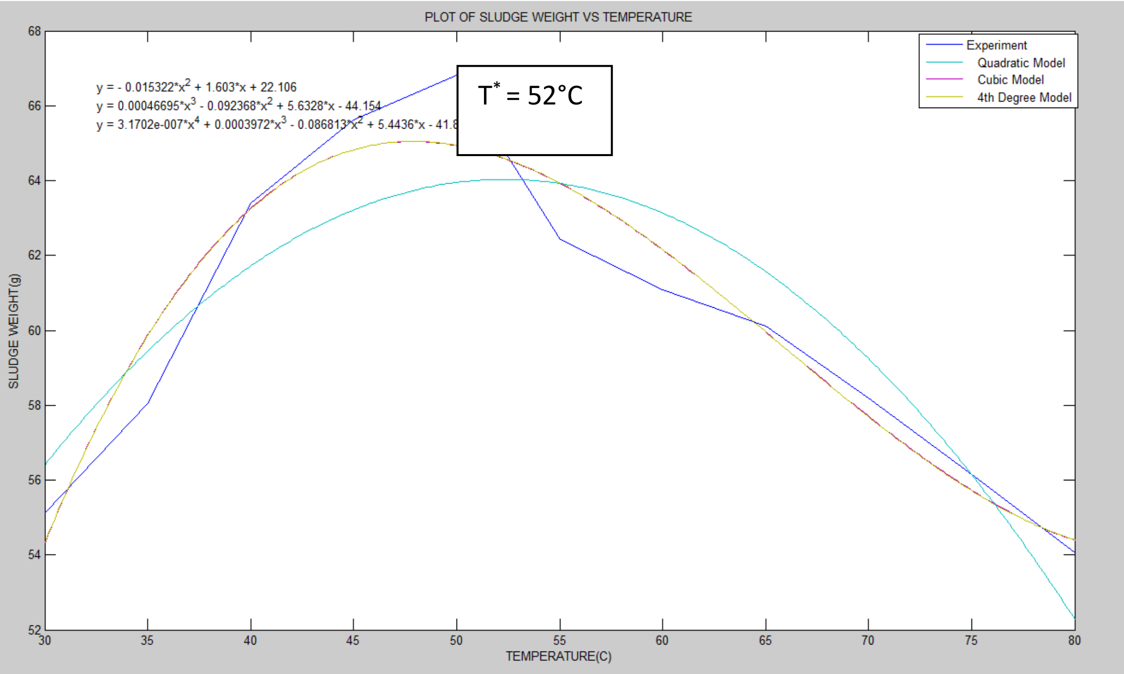

Fig. 3 Effect of temperature variation on sludge weight

Table 6 Error Functions of Temperature Effect Models

Model	SEE	SSE	R^2
Quadratic	3.67828773	33.1045896	0.8429389
Cubic	1.33978537	12.0580683	0.93644576
4th Order	1.33964517	12.0568065	0.93645197

IV. CONCLUSION

Spent engine oil is treated to remove most of the oxidation and degradation products and consequently produce the resinous sludge as a binder for black ink. This was achieved with sulphuric acid which proved to be very efficient because of its poly-functional nature. The amount of sludge produced is dependent on the volume of the acid. Model 2 is the best for predicting the effect of acid volume. The desludging process is temperature dependent and as a result, the yield of sludge was lowered at temperatures above 52°C. Therefore the optimum temperature for the production of sludge is 52°C. The 4th order polynomial model is the best for determining the effect of temperature on sludge weight. Therefore, the desludging should be carried out at temperatures below 52°C to avoid the reduction in the weight of the sludge produced.

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