Nigerian Research Journal of Engineering and Environmental Sciences 2(2) 2017 pp. 375-382

Nigerian Research Journal of Engineering and Environmental Sciences
Journal homepage: www.rjees.com

Original Research Article

OPTIMIZATION OF SOLVENT EXTRACTION IN USED LUBRICATING OIL RE-REFINING USING RESPONSE SURFACE METHODOLOGY

***Osemwengie, S.O., Ossai, J.E. and Otokpen, O.R.**

Department of Chemical Engineering, Faculty of Engineering, University of Benin, Benin City, Nigeria
*saint.osemwengie@uniben.edu

ARTICLE INFORMATION

Article history:
Received 06 November, 2017
Revised 04 December, 2017
Accepted 05 December, 2017
Available online 29 December, 2017

Keywords:
Used lubricating oil
Solvent extraction
Box-Behnken design
Response surface methodology
Optimization

ABSTRACT

Response surface methodology was used to optimize the process parameters and response factors in the refining of used lubricating oil using solvent extraction process. The solvent used for the treatment process was 1-butanol. The response variables optimized were base oil yield and total acid number. It was established that using 1-butanol as the solvent for the extraction process, the optimal response was a yield of 66% and a total acid number of 1.4 mg KOH/g oil. The optimum process parameters were determined to be at 253 rpm mixing speed, 3:1 solvent to oil ratio and 30 °C extraction temperature. A mathematical model was obtained for the response variables, percentage oil yield (Y_1) and acid number (Y_2). From the analysis of variance, the quadratic model generated for the response variables were significant with f-values of 80.89 and 557.28, respectively. The properties of the extracted oil at the optimum process conditions was compared with the used lubricating oil and it was inferred that the use of solvent extraction helped improve the properties of the base oil by separating it from its contaminants.

1. INTRODUCTION

Large quantities of used lubricating oil are generated globally. As at 1996, Nigeria accounted for about 364,166,000 litres of used lubricating oil annually (Isah et al., 2013). With the large amount of lubricating oils used, the disposal of lubricating oils has now become a major problem. If discharged into the land, water or even burnt as a low-grade fuel, it can cause serious pollution problems because of the release harmful pollutants into the environment (Isah et al., 2013). Some of these pollutants include salt, broken down additive components, varnish, gum and other materials (Durrani et al.,

2011; Kamal and Khan, 2009; Ogbeide, 2010). Other impurities found in the used lubricating oil include unsaturates, aldehydes, phenolic compounds, alcohols, acidic compounds and non-stable products of hydrocarbons, generated by oxidation or thermal degradation during its application in internal combustion engine. Many nations are now addressing the problem of environmental pollution posed by waste or used lubricating oils in their countries (Cutler, 2009).

The conventional methods of recycling waste lubricating oil either requires a high cost technology such as vacuum distillation or the use of toxic chemicals such as sulphuric acid (Ihsan et al., 2013). These methods also produce contaminating by-products which have high sulphur levels. Solvent extraction is one of the most economical and environmentally friendly methods for used lubricating oil treatment (Thrash, 1991). It creates room for solvent re-use and the sludge obtained is acid free unlike that of acid treated used lubricating oil. The use of this method has increased tremendously in the developed countries, in some countries meeting up to 50% of the country's need for lubricating oil (Thrash, 1991).

Response surface methodology based on statistically designed experiments has been found to be very useful in optimising multivariable processes. It is employed for multiple regression analysis of quantitative data obtained from statistically designed experiments (Montgomery, 2005). Hence, the aim of this study was to optimise the effect of mixing speed, solvent to oil ratio and extraction temperature on the re-refining of used lubricating oil. The extraction performance indicator evaluated for the re-refining process were percentage oil yield (POY) and total acid number. A three variable Box-Behnken design was adopted to design the extraction experiments.

2. MATERIALS AND METHODS

2.1. Material Collection and Preparation of Samples

The test samples of used lubricating oil were collected from FAGCOOP oil service station in the University of Benin. The used lubricating oil was collected from used oil dumps of cars during servicing operation and was treated with 1-butanol of analytical grade.

2.2. Methods

A sample of used lubricating oil (300 ml) was pretreated by allowing to settle in a large tank for 48 hours to remove solid contaminants after which it was poured into a beaker for dehydration, it was dehydrated at about 140^{o}C in a fume chamber for 1 hour using a heating mantle to remove water and light ends from it. The temperature was controlled by using a thermometer. The pretreated lubricating oil was mixed by agitating on a magnetic stirrer at a varying speed of 50 – 350 rpm and temperatures of 30, 45 and 60^{o}C, with 1-butanol at different solvent to oil ratio (3:1, 5:1 and 7:1). The lubricating oil and solvent mixture was left to settle in the separation beaker for 72 hours. The treated oil was separated from the sludge and the solvent was recovered from the oil by distillation at 118^{o}C which is the boiling point for 1-butanol, to reuse it again. The process was repeated using the design matrix in Table 1 generated by the Box-Behnken design. ASTM standard methods were used to determine the various properties of the base oil.

2.3. Extraction Performance Indicator

The extraction performance indicator evaluated for the re-refining process were percentage oil yield (POY) and total acid number.

2.3.1. Percentage oil yield (POY)

The percentage oil yield was calculated as the ratio of the weight of lubricating oil extracted to the weight of the used oil sample.

$$\text{POY} = \frac{\text{W1}}{\text{W}} \quad (1)$$

Where w_1 is weight of the extracted lubricating oil and w is weight of the used lubricating oil.

2.3.2. Total acid number (TAN)

About 10 grammes of the oil were weighed into a 250 ml conical flask. Ethanol (50 ml) was weighed into another conical flask to which a phenolphthalein indicator was added (2 drops) and heated to 40 ^{o}C using a heating mantle while the temperature was controlled using a thermometer. The alcohol was neutralized with a 0.5 normal potassium hydroxide (KOH) solution. The neutralized alcohol was added to the oil and heated. The mixture was stirred to ensure complete extraction of the acid by the alcohol. Thereafter, 2 drops of phenolphthalein solution was added and the mixture was allowed to cool for some time and then titrated with 0.5 N potassium hydroxide solution.

The total acid number was calculated from:

$$\text{TAN} = \frac{(56.1 * NV)}{W} \quad (2)$$

Where N is the normality of KOH solution, V is the volume of KOH solution used and W is the grammes of oil used.

In order to determine the extent of re-refining, the quality of the base oil generated at optimum conditions were evaluated by determining the following properties: Viscosity, viscosity index, flashpoint, specific gravity and heavy metal content.

2.4. Experimental Design

Box-Behnken experimental design was employed to optimize base lubricating oil extraction from its contaminant. A three-level-three-factor design was applied, which generated 17 experimental runs. This included 6 factorial points, 6 axial points and 5 centre points to provide information concerning the interior of the experimental region, making it possible to evaluate the curvature effect. Selected extraction process factors for the oil separation from contaminants were solvent oil ratio (SOR), extraction temperature (^{o}C), and mixing speed (rpm). The coded and actual variable levels are displayed in Table 1. The Design Expert® 7.0.0 (Stat-ease, Inc. Minneapolis, USA), a statistical software was used to develop the experimental design using the Box-Behnken Design.

Table 1: Coded and actual levels of the factors for three factor Box-Behnken Design

Variables	Symbol	Coded and actual levels		
		-1	0	+1
Mixing speed (rpm)	X_1	50	200	350
Extraction temperature (^{o}C)	X_2	30	45	60
Solvent oil ratio (SOR)	X_3	3	5	7

3. RESULTS AND DISCUSSION

3.1. Statistical Modeling

Comparison with Design Expert version 7 was made between linear and quadratic models using Box-Behnken design in Response Surface Methodology and quadratic model was found to be the best for the extraction process. A similar observation was also recorded by Ani et al. (2015). The model was developed to represent the two responses evaluated; percentage oil yield (Y_1) and total acid number (Y_2), as a function of mixing speed (X_1), extraction temperature (X_2), and solvent oil ratio (X_3).

$$Y_1 = +73.4592 - 0.000617x_1 - 0.37028x_2 + 0.10833x_3 + 1.556\text{E}-05x_1x_2 - 0.00049x_1x_3 + 0.013833x_2x_3 + 1.183\text{E}-05{x_1}^2 + 3.37222\text{E}-03{x_2}^2 - 0.14219{x_3}^2 \quad (3)$$

$$Y_2 = +2.378411 - 0.004072x_1 - 0.01115x_2 - 0.147333x_3 + 2.67\text{E}-05x_1x_2 + 3.441667\text{E}-04 - 0.00095x_2x_3 + 2.837\text{E}-06{x_1}^2 + 1.34778\text{E}-04{x_2}^2 + 0.015019{x_3}^2 \quad (4)$$

Equations 3 and 4 are the model equations used to estimate the responses percentage oil yield and total acid number respectively. The analysis of variance results presented in Tables 2 and 3 show the adequacy of the quadratic models which were statistically significant with F-values of 80.89 for Y_1 (extracted oil yield) and 557.28 for Y_2 (total acid number). The effects of the model terms in the dependent variables are reviewed by their F-values and the probability of getting an F-value of that magnitude.

Table 2: Analysis of variance (ANOVA) for response surface quadratic model on extracted oil yield

Source	Sum of Squares	df	Mean Square	F Value	p-value
Model	27.02615	9	3.0029054	80.886341	< 0.0001
X_1-mixing speed	2.322013	1	2.3220125	62.545791	< 0.0001
X_2-temperature	0.05445	1	0.05445	1.4666667	0.2652
X_3-SOR	19.93961	1	19.939613	537.09394	< 0.0001
X_1 X_2	0.0049	1	0.0049	0.1319865	0.7271
X_1 X_3	0.087025	1	0.087025	2.3441077	0.1696
X_2 X_3	0.6889	1	0.6889	18.556229	0.0035
X_1^2	0.29848	1	0.2984803	8.0398724	0.0252
X_2^2	2.424007	1	2.4240066	65.293107	< 0.0001
X_3^2	1.362007	1	1.3620066	36.687046	0.0005
Residual	0.259875	7	0.037125		
Lack of Fit	0.091875	3	0.030625	0.7291667	0.5860
Pure Error	0.168	4	0.042		
Cor Total	27.28602	16			

The 'lack of fit' value for Y_1 and Y_2 which are 0.5860 and 0.0576, respectively are not significant which is desirable. The adequacy of the model was further established by the coefficient of determination (R^2).

Table 3: Analysis of variance (ANOVA) for response surface quadratic model on total acid number

Source	Sum of Squares	df	Mean Square	F Value	p-value
Model	0.131443	9	0.0146048	557.28442	< 0.0001
X_1-mixing	7.81E-05	1	7.813E-05	2.9810575	0.1279
X_2-temperature	0.004418	1	0.004418	168.57999	< 0.0001
X_3-SOR	0.026796	1	0.0267961	1022.4741	< 0.0001
$X_1 X_2$	0.0144	1	0.0144	549.46852	< 0.0001
$X_1 X_3$	0.042642	1	0.0426423	1627.1232	< 0.0001
$X_2 X_3$	0.003249	1	0.003249	123.97383	< 0.0001
X_1^2	0.017018	1	0.017018	649.36585	< 0.0001
X_2^2	0.003872	1	0.003872	147.74688	< 0.0001
X_3^2	0.015196	1	0.0151958	579.83479	< 0.0001
Residual	0.000183	7	2.621E-05		
Lack of Fit	0.00015	3	5.008E-05	6.0341365	0.0576
Pure Error	3.32E-05	4	8.3E-06		
Cor Total	0.131627	16			

Table 4: R^2 statistics for the regression model

Response	R^2	Adj R^2	Pred R^2	Adeq. Pre	Std. Dev.	Mean	C.V%	PRESS
Y1	0.9904	0.9782	0.9465	29.59683	0.192	64.1847	0.30019	1.7325
Y2	0.9986	0.9968	0.9813	82.07437	0.005	1.53005	0.33458	0.00245

Adj: adjusted; pred: predicted; adeq pre: adequate precision; C.V: coefficient of variation; PRESS: predicted residual sum of square.

The R^2 values for Y_1 and Y_2 (0.9947 and 0.9986 respectively) are very close to one meaning that the regression models were a good fit for the experimental data. The difference between Adj-R^2 (which is the measure of the amount of variation about the mean explained by the model) and Pred. -R^2 (measure of how good the model predicts a response value) (Ani et al, 2015), is not more than 0.04 which implies that they are in reasonable agreement. The coefficient of variation C.V = 0.3 for both responses is low, indicating high precision and good reliability of the experimental values (Ani et al, 2015). The low value of standard deviation recorded indicates that the responses are close to the mean which further depicts the validity of the model. The PRESS is used to assess the model predictive ability. The low value of PRESS indicates that the model can predict future responses effectively (Ani et al, 2015).

3.2. Response Surface Plots

Response surface plots were generated from the statistical models to examine the interactions between the independent variables and to determine the optimum levels of the variables. The plots show how mixing speed, extraction temperature and solvent oil ratio affect the percentage oil yield and total acid number of the extracted base oil.

Figure 1 shows the percentage oil yield as a function of solvent oil ratio and temperature. At constant temperature, increase in solvent oil ratio results in a decrease in extracted oil yield. The negative effect of solvent to oil ratio on yield at constant temperature could be attributed to increase in sludge formation as the solvent oil ratio increases (Kamal and Khan, 2009). Also at constant solvent to oil

ratio, increase in temperature initially decreases base oil yield up to 45°C beyond which further temperature increase results in increase in base oil yield. According to Hussein et al. (2014), at higher temperatures (beyond 45°C), solubility of base oil component in the organic solvent increased with temperature resulting in an increase in base oil yield. At lower temperature range, there is an increase in sludge formation resulting in a decrease in oil yield (Kamal and Khan, 2009).

Figure 2 shows the percentage oil yield as a function of solvent oil ratio and mixing speed. At any value of mixing speed, increase in solvent oil ratio results in a decrease in the base oil yield. This trend observed could be as a result of increase in sludge formation as the solvent oil ratio increases (Kamal and Khan, 2009). The quality of the base oil yield is a function of the sludge within it. At higher solvent to oil ratio the quality increases due to an increase in sludge formation resulting in lesser oil yield but with higher sludge removal (Araromi et al., 2016). This result obtained is also in conformity with the findings of sterpu et al (2012) and Durrani et al (2011). Also at low solvent to oil ratio (3:1), increase in mixing speed results only in a minimal increase in base oil yield. This could be as a result of equilibrium of extraction attained by the solvent at lower mixing speed due to the short distance travel created by the agitation between the molecules of the base oil and the solvent (Durrani et al., 2011).

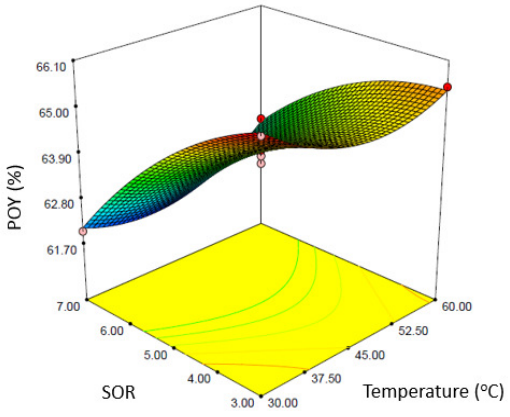

Figure 1: Response surface plot showing the effect of solvent oil ratio and temperature POY.

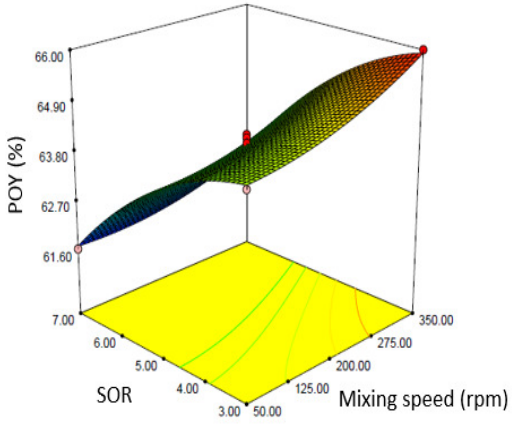

Figure 2: Response surface plot showing the effect of solvent oil ratio and mixing speed on POY.

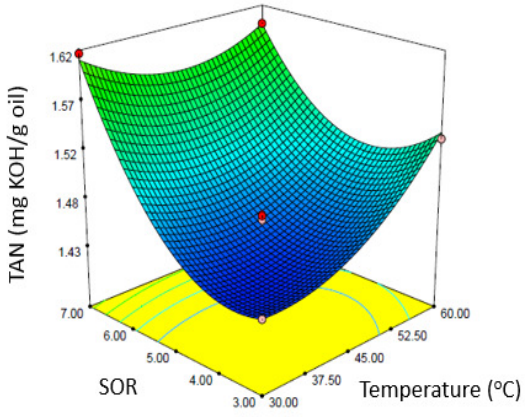

Figure 3: Response surface plot showing the effect of solvent oil ratio and temperature on TAN

Figure 3 shows the total acid number as a function of solvent oil ratio and temperature. At low solvent to oil ratio, increase in temperature has a negative effect on the acid number of the base oil. At higher temperatures, viscosity and specific gravity increases, thus increasing the rate of settling of the acid compounds along with the base oil on the solvent (Katiyar and Husain, 2010). However, at a high solvent to oil ratio, increase in temperature does not significantly affect the level of acid component within the base oil which remains high. At a low temperature, increase in solvent to oil ratio resulted in an increase in the acid number of the base oil. A similar trend was also observed at high temperature. Overall the effect of low temperature and solvent to oil ratio was found to be synergistic on the acid number while a high temperature and solvent to oil ratio had an antagonistic effect on total acid number of the base oil.

The optimal condition for this process using 1-butanol as solvent for extraction was established by solving the regression equation (Equations 3 and 4) using the Design-Expert software. The conditions were: mixing speed (X_1) = 252.85 rpm, temperature (X_2) = 30.41 ^oC and SOR (X_3) = 3.13. At this condition, the responses obtained were 66% oil yield and 1.4 mg KOH/g oil. The response values obtained were validated by carrying out the experiment under the optimal conditions for the extraction process. The mean of the results obtained from three replications was close to that predicted by the model thus showing validity. This result was similar to those obtained by Hussein et al. (2015). At this processing conditions, the extracted lubricating oil obtained was characterized and its properties were compared with those of the used lubricating oil as shown in Table 5.

Table 5: Physical properties of used and refined lubricating oil.

Property	Used Oil	Re-refined Oil
Specific Gravity @ 35^{o}C	0.920	0.882
Viscosity @ 40^{o}C (cst)	106.96	140.60
Viscosity @ 100^{o}C (cst)	12.32	15.32
Viscosity index	111	112
Total acid number (mg KOH/g oil)	2.52	0.42
Total base number (mg HCl/g oil)	4.26	0.06
Flashpoint (^{o}C)	193	215
Metal Content (ppm)		
Lead	980	1.46
Copper	25.21	4.17
Iron	50	< 0.005

The result of the analysis showed that the specific gravity of the used oil was reduced in the refined oil. This shows that contaminants from combustion, thermal cracking and other sources has been removed (Udonne, 2011). The result of the viscosity test showed that the refining process had recovered most of the viscosity of the oil lost due to contamination during usage. Viscosity decrease can be caused by dilution with light fuels (Udonne, 2011). Total acid number is reduced significantly for the extracted base oil. This indicates that organic and inorganic acids, esters, phenolic compounds, lactones, resins etc. have been separated out satisfactorily (Kamal and Khan, 2009). Result of the test showed that the flashpoint has been greatly improved indicating the absence of light ends in the oil. The metal content of the re-refined lubricating oil sample has been greatly reduced. The metal deposits in the used lubricating oil have been effectively separated out with the sludge from the base oil by the solvent extraction.

4. CONCLUSION

The results of this work have revealed that 1-butanol is able to extract base lubricating oil from its contaminants. The optimal condition for this process using butanol as solvent for extraction was established as: mixing speed (X_1) = 252.85 rpm, temperature (X_2) = 30.41 ^oC and SOR (X_3) = 3.13. The optimum response was recorded at 66% oil yield and 1.4 mg KOH/g oil. The low yield obtained in this research work could be as a result of the high level of contaminants present in the used lubricating oil. From characterization, the refined oil was shown to have improved and better properties than the used oil.

5. ACKNOWLEDGMENT

The authors wish to acknowledge the assistance and contributions of the laboratory staff of Department of Chemical Engineering, University of Benin, Benin City toward the success of this work.

6. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

REFERENCES

Ani, I.J., Okafor, J.O., Olutoye, M.A. and Akpan, U.G. (2015). Optimization of Base Oil Regeneration from Spent Engine Oil via Solvent Extraction. *Advances in Research*, 4(6), pp. 403-411.

Araromi, D.O., Aremu, M.O. and Gbolahan, O.O. (2016). Application of Solvent Extraction Process for Revivification of Used Lubricating Engine Oil. *American chemical science journal,* 10(4), pp. 1-7.

Cutler E.T. (2009). Conserve Lube Oil: Re-refine. *Hydrocarbon processing,* 265, March.

Durrani, H.A., Panhwar, M.I. and Kazi RA., (2011). Re-Refining of Waste Lubricating Oil by Solvent Extraction. *Mehran University Residential Journal of Engineering Technology*, 30(2), pp 237-243.

Hussein, M., Amer, A.A. and Gaberah, A.S. (2014). Used Lubricating Oils Re-Refining by Solvent Extraction. *American Journal of Environmental Engineering and Science*, 1(3), pp. 44-50.

Ihsan, H., Talal, Y., and Rafat, S. (2013). Recycling of Waste Engine Oils Using a New Washing Agent. *Energies*, pp. 1023-1049.

Isah, A.G., Abdulkadir, M., Onifade, K.R., Musa, U., Garba, M.U., Bawa, A.A. and Sani, Y. Regeneration of Used Engine Oil. *World Congress on Education,* pp. 565-568.

Kamal A., Khan F., (2009). Effect of Solvent Extraction and Adsorption on Re-refining of Used Lubricating Oil. *Oil & Gas Science and Technology*, 64(2), pp. 191-197.

Katiyar, V. and Husain S., (2010). Recycling of Used Lubricating Oil using 1-butanol. *International Journal of Chemical Science,* 8(3), pp. 1999-2012.

Montgomery, D.C. (2005). Design and Analysis of Experiments: *Response surface method and designs*. New Jersey, John Wiley and Sons, Inc.

Ogbeide, S.O. (2010). An Investigation to the recycle of spent engine oil. *Journal of engineering science and technology review*, 3 (1), pp 32-35.

Sterpu, A.E., Dumitru, A.I. and Popa, M.F. Regeneration of Used Engine Lubricating Oil by Solvent Extraction. *Journal of Ovidius University Annuals Chemistry*, 2012, 23(2), pp. 149-154.

Thrash, L.A. (1991). Annual Refinning Survey. *Oil and Gas Journal*, p. 84.

Udonne, J. D. (2011). A comparative study of recycling of used lubrication Oils using distillation, acid and activated charcoal with clay methods. *Journal of Petroleum and Gas Engineering*, 2(2), pp. 12-19.