Original Research Article

Optimization of base oil regeneration from spent engine oil via solvent extraction

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ABSTRACT

Regeneration of base oil from spent engine oil (SEO) has been studied and the parameters involved were optimized using Response Surface Methodology. A mathematical model was obtained for the dependent variables, base oil yield (Y_1) and ash content (Y_2) while effects of solvent to oil ratio and time were determined. From the analysis of variance, the quadratic model generated for the dependent variables, Y_1 and Y_2 are significant with f-values of 3764.26 and 161.84, respectively. This simply implies that the predicted values generated by the model equations are in good correlation with the experimental values for both responses, the adequacy of the model was further depicted by the 'lack of fit' which are not significant. Also, the coefficients of determination (R^2) of 0.9996 and 0.9914 for Y_1 and Y_2 which are very close to unity show that the regression model explains the experimental data by 99.96% and 99.14%, respectively. Increase in solvent to oil ratio gave an increment in the base oil yield and reduced the ash content, but increase in reaction time had little or no effect on the yield and increased the ash content which is not desirable. The optimum conditions obtained are; solvent to oil ratio of 5:1, and 30 min reaction time at ambient temperature. The level of contaminants in the SEO was determined by its kinematic viscosity, viscosity index, ash content, heavy metal content, pour point and specific gravity. The method revealed an environmentally friendly way of managing engine spent oil.

Keywords: Optimization, Base oil, Regeneration, Spent engine oil, Extraction

1. INTRODUCTION

Engine oil is applicable in an environment operating with high temperature that exposed it to thermal oxidation and other impurities that degrade the oil. This makes engine oil in the early century, to be used within a short period of time [1]. Thus, additives are compounded with the lubricant (base oil) to prolong the service life in that environment due to these challenges. Nevertheless the additives have duration of usage after which the oil becomes so degraded majorly by thermal degradation (oxidation) [2]. The oil is then removed and replaced with fresh one. Oxidation increases the viscosity of the oil to due to sludge, thereby the oil losses its lubrication quality. Previous studies [3-5] revealed that SEO contains a lot of contaminants like salt, broken down additives, gum, hydrocarbons, heavy metals, polychlorinated biphenyls (PCBs), halogen compounds that are poisonous to aquatic life, human beings and its environs. Also, carcinogenic compounds like polycyclic aromatic hydrocarbons (PAHs) are present in the used oil [6,7] which are generated from the combustion process and fuel [8].

Due to the high level of contaminants and the negative effects to plants, aquatic and human lives, several ways have been developed to manage SEO among which is re-refining to regenerate base oil [9]. Recycling or re-refining of SEO have been studied by several authors and from their findings, this method of re-refining greatly depend on the nature of the oil base stock and the level of contaminants in the oil [10].

Solvent extraction is one of the most economical and environmentally friendly methods for SEO treatment [7]. It creates room for solvent re-use and the sludge obtained is acid free unlike that of acid treated SEO. The sludge can be useful for the production of ink [11], cement kilns [12]. In this work, the following process variables were studied: Solvent to oil ratio and reaction time to determine the optimal process variables via Response Surface Methology.

Response surface methodology (RSM) is a mathematical and statistical method used to develop model, to analyze problems whereby the dependent variables (response) is influenced by the independent variables chosen for the analysis [13,14]. It can also be used to determine optimal conditions for a process [15]. Centre composite design (CCD) which is a kind of RSM can be used to generate a matrix for process variables study [16]. This optimization technique requires less experimental runs with detailed explanation of interaction between variables unlike the conventional Uni-factorial technique.

The purpose of this study was to develop a regression model collaborating the response (base oil yield and ash content) to the process variables (solvent to oil ratio and time), to determine the optimum conditions and the effects of the linear, interactive and quadratic model terms.

2. MATERIAL AND METHODS

2.1 Material Collection

SEO was collected from a gasoline engine vehicle (after 20 days of commercial usage) that uses 20W50 (Total), 2-propanol, 1-butanol and Butanone are the solvents used which are Merck products with 99.95% purity.

2.2 Methodology

Pre-treatment of the oil was carried out to remove light hydrocarbons like gasoline and water. The oil was kept to settle for some days by gravity. The top layer of the oil was collected by decantation followed by filtration using a Buchner funnel. The filtrate was dehydrated for 20 min at 200^{o}C and left to cool to ambient temperature before further treatment.

Pre-treated SEO (spent 20W50) was placed in a conical flask with composite solvent. 30 mL was the initial quantity of the oil used. The sample was mixed with composite mixture of solvent (26% 2-propanol, 35% 1-butanol, and 39% butanone) at the ratio of 3:1. The mixture was stirred vigorously with a magnetic stirrer for 30 min at ambient temperature [17]. The process was repeated using the design matrix in Table 1 generated by the CCD.

The quality of the base oil generated at optimum conditions base and SEO were determined via the following properties: Viscosity, viscosity index, pour point, specific gravity, and heavy metal content.

Viscometer was used to determine the viscosity of the used and the treated oil. Petroleum ether was used to wash the viscometer tube before use. The viscometer tube was charged with the sample into the viscosity bath. It was left to attain the desired temperature (40^oC and 100^oC). The sample was then drown up with a vacuum pump above the upper meniscus. The time it took for the oil to flow from the upper meniscus to the lower meniscus was recorded. The kinematic viscosity was calculated by multiplying the efflux time by a constant (from viscometer constant Table) which is traced by the serial number on the viscometer tube used. This method follows ASTM D445.

Viscosity index (V_I) was determined from kinematic viscosity of the oil at 40^oC and 100^oC. Equation 1 was used to calculate V_I .

$$V_I = \left(\frac{L-U}{L-H}\right) \times 100 \qquad 1$$

Where U is the kinematic viscosity at 40^oC of the oil whose V_I is unknown, L and H are obtained from the viscosity index standard Table using the kinematic viscosity at 100^oC of the oil whose V_I is unknown to trace the corresponding L and H. If not found, linear interpolation was done to determine the value (ASTM, 1998).

Ash content of the untreated and treated oil was determined in order to evaluate the inorganic residue left after combustion. 2 mL of oil was placed in a crucible and charged into a furnace at 200^oC, below the operating temperature with intent to gradually increase to the operating temperature which is 500^oC. At the operating temperature, the oil was left to ash for 30 min and thereafter, was left to cool to room temperature and weighed.

34 mL of oil was poured into a pour point tube and covered with a cock attacked to a thermometer. The whole content was placed in a pour point refrigerator. The temperature which the oil begins to solidify or resist flow was recorded as the pour point of the oil. The method follows ASTM D121.

Empty Pycometer bottle was dried, cooled and then weighed as W_1. Pure water was poured into the bottle and weighed as W_2. The bottle was emptied, oven dried, cooled, filled with the sample and weighed as W_3. Equation 2 was used to calculate the oil's specific gravity.

$$\text{specific gravity} = \frac{W_3 - W_1}{W_2 - W_1} \qquad 2$$

Heavy metal content of lead (Pb) and chromium (Cr) was determined by Atomic absorption spectrophotometer (AAS).

2.3 Experimental Design

Design expert software version 8.0.6 (trial version) was used for the regression analysis to validate the developed model equation with the experimental data, its statistical significance and to generate the optimal conditions. The process variables that were studied are: solvent to oil ratio and reaction time, with base oil yield and ash content as the responses. Table 1 shows the design matrix for the study. Central Composite Design (CCD) which is the most popular response surface design comprises of 2^n for the factorial runs (±1), 2n for axial runs (±α) and the centre point runs (0) which is used to determine the experimental error [13] and n represents the number of variables in study.

Table 1. The Response Surface Methodology (RSM) design matrix and data obtained from the solvent extraction experiment on spent 20W50

Run	Levels		Sol:oil, A	Time, B (min)	Yield, Y_1 (%)	Ash content, Y_2 (%)
1	-	-	3:1	30	22.00	0.40
2	+	-	5:1	30	36.00	0.20
3	-	+	3:1	40	21.67	0.50
4	+	+	5:1	40	34.00	0.30
5	-A	0	2.59:1	35	18.33	0.60
6	+A	0	5.41:1	35	37.00	0.30
7	0	-A	4:1	27.93	30.00	0.20
8	0	+A	4:1	42.07	28.33	0.30
9	0	0	4:1	35	28.00	0.27
10	0	0	4:1	35	28.00	0.30
11	0	0	4:1	35	28.33	0.28
12	0	0	4:1	35	28.33	0.30
13	0	0	4:1	35	28.00	0.30

3. RESULTS AND DISCUSSION

Model comparison was made with design expert software (Trial version 8.0.6) between linear and quadratic model using Response Surface Methodology and quadratic model appeared to be the best for the extraction process on spent 20W50 with coefficient of determination closer to one and more significant factors. Thus, the experimental data was found fitted with the quadratic model equation. The analysis of variance in Tables 2 and 3 show the adequacy of the quadratic model which is statistically significant with F-values of 3764.26 for Y_1 (base oil yield) and 161.84 for Y_2 (ash content). 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, if the term did not have any influence on the response is shown by the p-values. The terms that are not significant are eliminated from the model equation because they have no influence the response.

Table 2. Analysis of variance (ANOVA) for response surface quadratic model on base oil yield from Spent 20W50 (Y_1)

Source	Sum of squares	Degree of freedom (DF)	Mean square	F value	P-value prob>F	Comment
Model	353.55	5	70.71	3764.26	<0.0001	Significant
A-sol:oil	347.60	1	347.60	18504.71	<0.0001	Significant
B-time	2.75	1	2.75	146.48	<0.0001	Significant
AB	0.70	1	0.70	37.12	0.0005	Significant
A^2	0.38	1	0.38	20.08	0.0029	Significant
B^2	1.86	1	1.86	99.03	<0.0001	Significant
Residual	0.13	7	0.019			
Lack of fit	8.112E-004	3	2.704E-004	8.277E-003	0.9988	Not significant
Pure error	0.13	4	0.033	-	-	-
Cor. total	353.68	12	-	-	-	-

Table 3. Analysis of variance (ANOVA) for response surface quadratic model on ash content yield for treated 20W50 (Y_2)

Source	Sum of squares	Degree of freedom (DF)	Mean square	F value	*P*-value Prob>F	Comment
Model	0.15	5	0.030	161.84	<0.0001	Significant
A-sol:oil	0.085	1	0.085	456.41	<0.0001	Significant
B-time	0.015	1	0.015	78.31	<0.0001	Significant
AB	0.000	1	0.000	0.000	1.000	Not significant
A^2	0.045	1	0.045	239.27	<0.0001	Significant
B^2	2.783E-003	1	2.783E-003	14.95	0.0062	Significant
Residual	1.303E-003	7	1.861E-004	-	-	-
Lack of fit	5.025E-004	3	1.675E-004	0.84	0.5396	Not significant
Pure error	8.000E-004	4	2.000E-004	-	-	-
Cor total	0.15	12	-	-	-	-

The ANOVA results for base oil yield (Y_1) in Table 2 show that the following model terms are significant: A, B, AB, A^2, B^2 because the p-value less than 0.05 implies that the term is significant. For the ash content (Y_2), A, B, A^2, and B^2 are the model terms that are significant whereas AB is not significant. The quadratic term A^2 and interactive term AB for Y_1 are less significant than others with p-values of 0.0029 and 0.0005, respectively which is also revealed in their corresponding F-values. Among all the model terms, it can be observed from their F-values that A has the highest influence in the regression model for Y_1 response likewise in the solvent extraction process. This was applicable for Y_2 in Table 3. But AB interaction for Y_2 is the only term that is not significant. Thus it was eliminated from the model equation because it does not have any influence on the response Y_2. Below is the multi-regression model equations in coded and actual factors, generated by the design expert based in the experimental data obtained.

Final equation in terms of coded factors for the dependent variable Y_1:

$$Y_1 = 28.13 + 6.59A - 0.59B - 0.42AB - 0.23A^2 + 0.52B^2 \quad (3)$$

Final equation in terms of experimental factors for the dependent variable Y_1

$$Y_1 = 15.79371 + 11.37717 \times \text{sol:oil ratio} - 1.23124 \times \text{time} - 0.0835 \times \text{sol:oilratio} \times \text{time} - 0.23288 \times (\text{sol:oil ratio})^2 + 0.020685 \times (\text{time})^2 \quad (4)$$

Final equation in terms of coded factors for the dependent variable Y_2:

$$Y_2 = 0.29 - 0.1A + 0.043B + 0.00AB + 0.08A^2 - 0.02B^2 \quad (5)$$

Equation 5 reduced to:

$$Y_2 = 0.29 - 0.1A + 0.043 + 0.08A^2 - 0.02B^2 \quad (6)$$

Final equation in terms of experimental factors for the dependent variable Y_2:

$$Y_2 = 0.70339 - 0.74303 \times \text{sol:oil ratio} + 0.064536 \times \text{time} + 4.44089E-17 \times \text{sol:oil ratio} \times \text{time} + 0.08 \times (\text{sol:oil ratio})^2 - 8.0000E-4 \times (\text{time})^2 \quad (7)$$

Equation 7 reduced to:

$$Y_2 = 0.70339 - 0.74303 \times \text{sol:oil ratio} + 0.064536 \times \text{time} + 0.08 \times (\text{sol:oil ratio})^2 - 8.0000E-4 \times (\text{time})^2 \qquad 8$$

The negative and positive coefficient indicates the synergistic and antagonistic effects respectively [13]. The positive and negative sign with the independent variables in the regression model equations shows synergistic and antagonistic effects respectively which implies that increase in the synergistic variable increases the ash content (R_2) whereas increase in the antagonistic variables reduces R_2 which is favourable [13]. For that of R_1, increase in the synergistic variables, increase the base oil yield (R_1) which is desirable whereas increase in the antagonistic variables reduces R_1.

The developed models were used for the optimization of the solvent extraction process [14]. The 'lack of fit' value for Y_1 and Y_2 which are 0.9988 and 0.5396, respectively are not significant (which is a desirable condition). 'Lack of fit' means that there are no outliers points which are depicted in Figure 1 and 2. It also signifies that there is a minimal difference between the predicted values which are generated by the model equation, and the experimental data. This reflects the adequacy of the regression model.

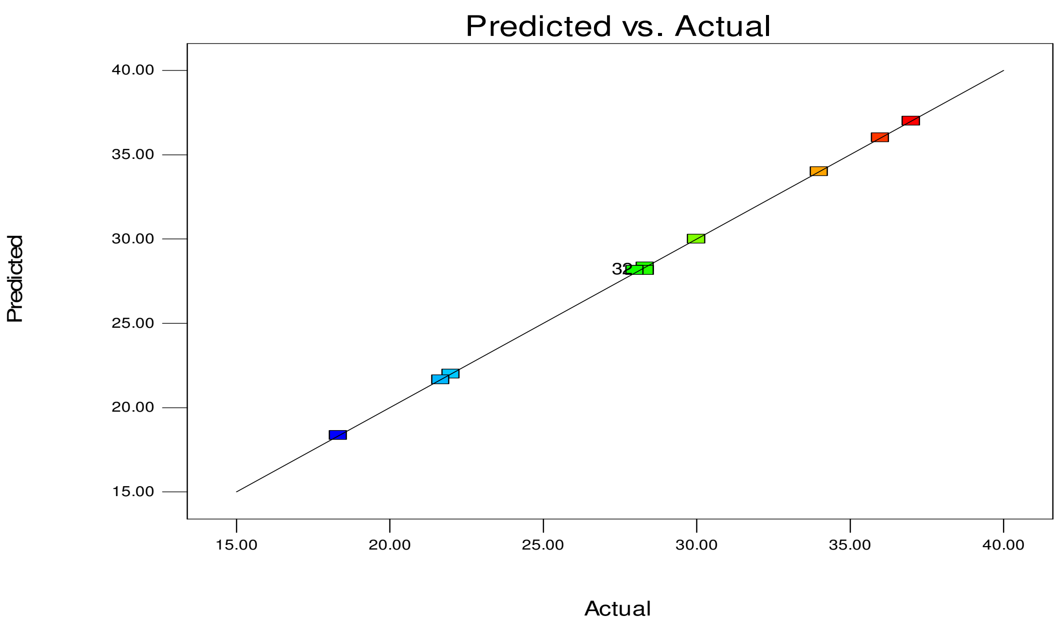

Fig. 1. Plot of predicted yield against the actual yield for Y_1

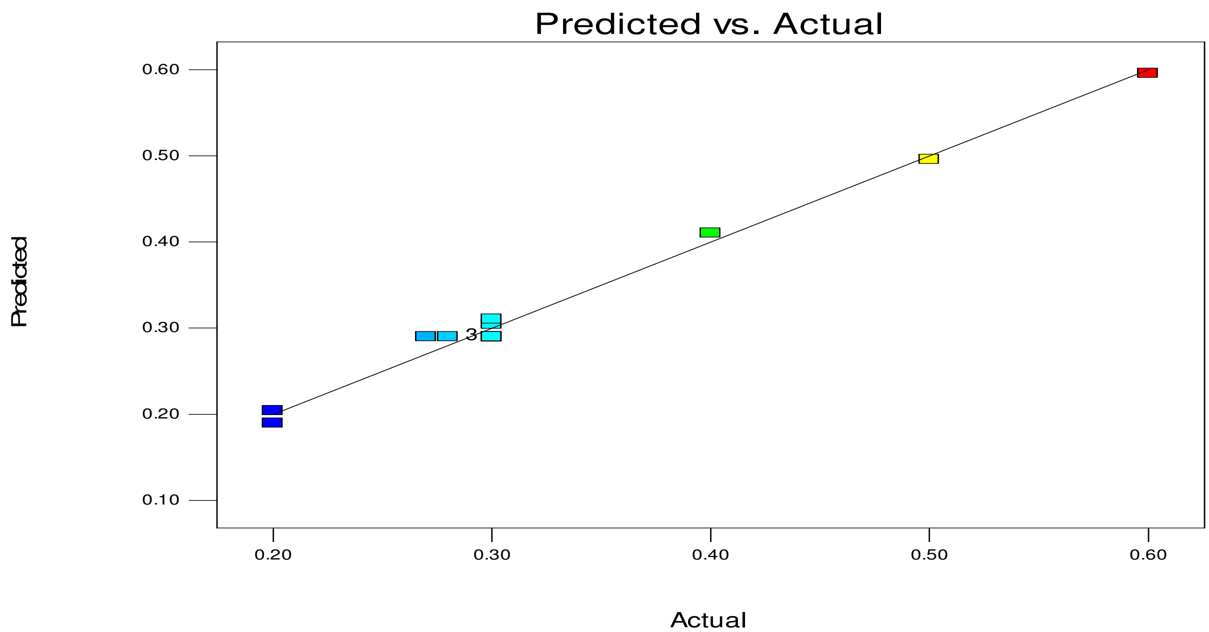

Fig. 2. Plot of predicted value against the actual value for Y_2

The adequacy of the model was further established by the coefficient of determination (R^2) and the agreement between the predicted R^2 and adjusted R^2 are shown in Table 4. The R^2 of 0.9996 for Y_1 and 0.9914 for Y_2 which is very close to one show that the regression model explains the experimental data by 99.96% and 99.14% respectively, which depicts the level of correlation between the predicted and the experimental response.

Table 4. R^2 statistics for the regression models

Response	R^2	Adj- R^2	Pred.- R^2	Adeq. prec	Std. dev.	Mean	C.V.%	PRESS
Y_1	0.9996	0.9994	0.9994	200.234	0.14	28.31	0.48	0.21
Y_2	0.9914	0.9853	0.9682	43.818	0.014	0.33	4.17	4.82E-3

Adj: adjusted, Pred: predicted, Adeq Prec: Adequate Precision, C.V.: coefficient of variation, PRESS: Predicted Residual Sum of Square

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) is not more than 0.02 which implies that they are in a reasonable agreement [16].

3.1 Three Dimensional Surface Plot.

This plot gives the graphical representation of how the process variables affected the model response. From Figure 3, increase in solvent to oil ratio increased Y_1 regenerated from spent 20W50 and this is in conformity with the results of the findings of Sterpu *et al*. [4], Kamal and Khan [5], Durrani *et al*. [17]. But increase in time could not favour the yield which could be as a result of equilibrium of extraction attained by the solvents at a short period of time due to short distance travel created by vigorous agitation between molecules of the base oil and solvents [18]. The ash content was used to determine the best quality of the oil because earlier studies [4,17] indicated that increase in solvent to oil ratio increases the solvency power and its quality; though after a particular ratio further increment leads to dissolution of contaminants in the solvent phase which was confirmed in this research work. Thus, in Figure 4, it can be observed that increase in solvent to oil ratio reduced the ash content but increase in time increased the ash content of the oil.

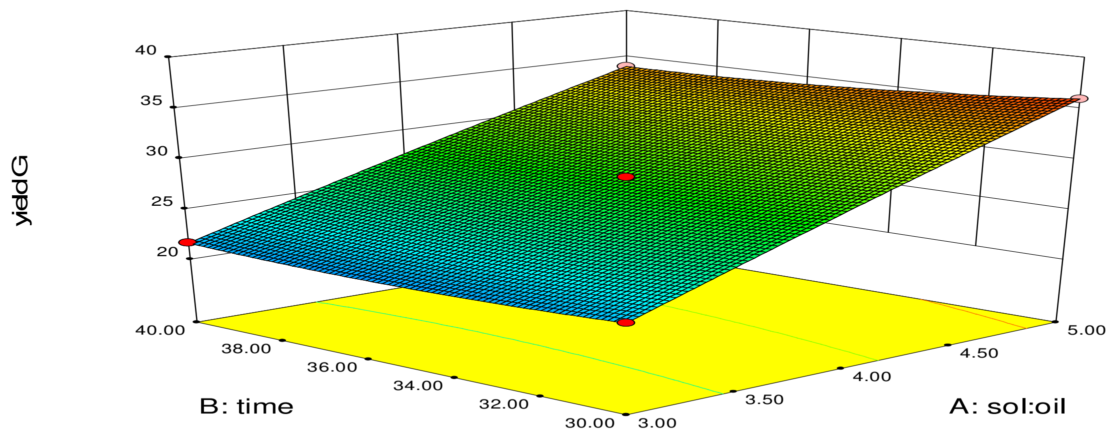

Fig. 3. Three dimensional response surface plot for Y_1 from spent 20W50 (effects of solvent to oil ratio and time, at ambient temperature)

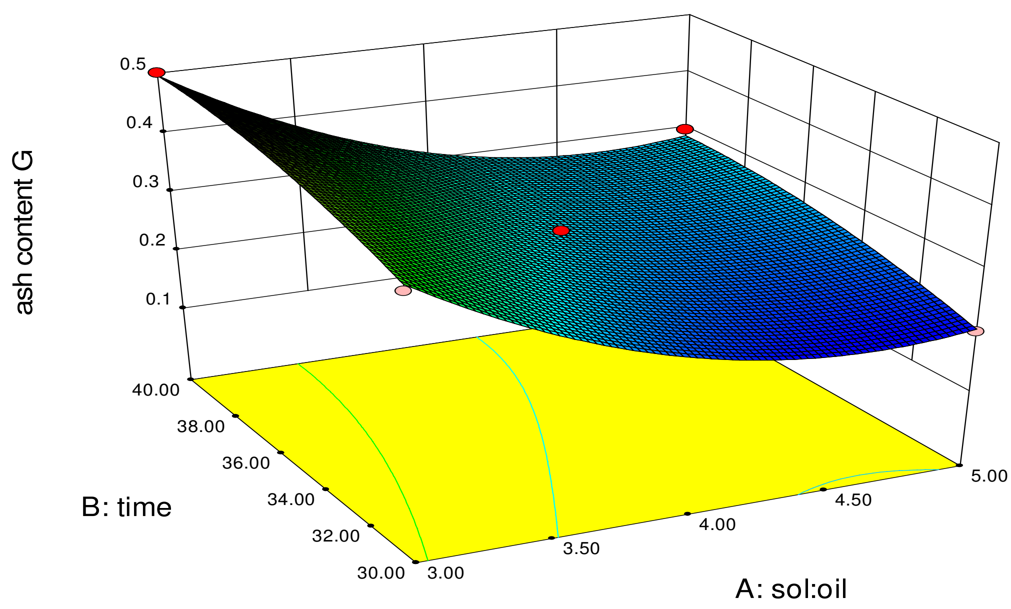

Fig. 4. Three dimensional response surface plot for Y_2 (effects of solvent to oil ratio and time, at ambient temperature).

Numerical optimization was used to determine the experimental data that gave the optimal conditions. Only one solution was generated with 0.968 as the desirability which is very close to one. The following are the optimum conditions predicted; solvent to oil ratio of 5:1 and time at 30 min which gave 36.01% for Y_1 and 0.20 for Y_2. The optimum conditions predicted are the same with that of the experimental data. Thus the predicted optimum conditions were not validated by repeating the experiment.

Viscosity which is the most important property of lubricating oil because of its area of application was determined for the sample produced with the optimum conditions. From the results shown in Table 5, the property was greatly improved in comparison with the untreated SEO which is reflected in other properties. Similar results were obtained in previous studies [5,10,19].

Table 5. Characteristics of regenerated base oil and spent 20W50.

Sample	Kinematic viscosity (mm^2/s)		Viscosity index	Pour point	Ash content (%)	Specific gravity	Heavy metals (ppm) X 10^{-2}	
	$40^{O}C$	$100^{O}C$					Pb	Cr
Spent 20w50	146.65	16.96	-	-15	0.90	0.902	37.73	7.55
Regenerated base oil	80.08	8.75	75	-14	0.20	0.895	30.99	4.53

Viscosity index is a property that shows how oil changes its viscosity with respect to change in temperature [20]. The viscosity index for the treated oil can be seen to be 75 which is very close to the range (80 to110) of high VI oil. It falls within the medium class which is between the range of 35 to 80. Thus, the fluid is expected to have a very small change in viscosity with change in temperature.

Pour point which indicates flow characteristics at low temperature, that depicts the minimum temperature at which the oil will flow without disturbance when it is cooled under a service condition [21], can be seen in Table 5 to have increased after treatment. This property is of great importance when oil is under reasonable cold condition and it differs depending in the source of the lube oil, base oil and the principal technique of refining mostly if the removal of wax has been done [22].

Ash content determines the level of contaminants especially ash forming materials in lubricating oil and that of treated oil reduced to 0.2% which is an improvement compare to that of Sterpu *et al*. [4].

Recycling of spent oil to generate base oil is very essential because previous reports [17,21] indicate that only 0.5 gallons of lubricating oil is contained in 42 gallons of crude oil whereas one gallon (3.8 kg) of SEO can regenerate 2.3 kg of lubricating oil.

4. CONCLUSION

A type of RSM called Central Composite Design (CCD) was used to optimize the process parameters for the regeneration of base oil from spent 20W50. From the analysis, the predicted and experimental values are all most the same which depicts that the mathematical models are in good agreement with the experimental data. The process parameters that were studied are time and solvent to oil ratio which were statistically processed by RSM. Solvent to oil ratio had a synergistic effects on the base oil yield and ash content than time. Time had less or no effect on the yield whereas its increment increased the ash content of the oil which is not desirable. The low yield obtained in this research work could be as a result of the high level of contaminants present in the untreated engine oil. The characterization results reviewed that the level of contaminants in the untreated engine oil was greatly reduced by solvent extraction with raffinate (sludge) that can be useful without causing any harm. The solvents can be recovered and reused which makes the process economically viable. More base oil can be generated via recycling of SEO than from crude oil.

COMPETING INTERESTS

"Authors declared that no competing interests exist."

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