IJCPE
Iraqi Journal of Chemical and Petroleum Engineering
Iraqi Journal of Chemical and Petroleum Engineering
Vol.8 No.3 (September 2007) 31-35
ISSN: 1997-4884
University of Baghdad
College of Engineering

Quality Improvement of Spent Lubricating Oil

Abdul-Halim A.-K. Mohammed*, Dhia El-Din M. Kassim, and Huda M. Hassan***

Chemical Engineering Department - College of Engineering - University of Baghdad – Iraq

** *Ministry of Technology – Chemistry Research Center - Iraq* *

Abstract

The acidity of spent lubricant was treated using sodium hydroxide solution. The effect of three variables on the treatment have been studied . These are mixing time ranging from 5-35 minutes, NaOH to lubricant weight ratio ranging from 0.25-1.25 and weight percentage of NaOH ranging from 2-6 % .

The experimental design of Box-Wilson method is adopted to find a useful relationship between the three controllable variables and the lowering in the acidity of the spent lubricant. Then the effective variables and interactions are identified using the statistical analysis(F-test) of three variable fractional design. The mathematical model is well represented by a second order polynomial.

By the analysis of the experimental results, the best treatment conditions which achieved an acceptable acidity of the spent lubricant are 20 minutes mixing time , 1 weight ratio of NaOH to spent lubricant and 4.5 weight percentage of NaOH. At these condition the acidity of the lubricant decreases from 0.62 to 0.0602 mg KOH/g oil.

Keywords: lubricating oil.

Introduction

A lubricant is a result of the blending between base stocks and additives. Base stock of lubricants are all derived from mineral or synthetic origin (1)

Mineral oils produced from crude oil are the largest classes of lubricants in common use (2).Physical properties,such as viscosity, viscosity-temperature-pressure characteristics and performance, depend largely on the relative distribution of paraffinic, aromatic and alicyclic (naphthenic) components.

Mineral oils gave excellent service in the older jet engines, but, as performances were gradually icreased, troubles were experienced due to coking , high evaporation loss, thermal degradation and inadequate load-carrying capacity (3). For new design jet engines mineral oils do not work satisfactory therefore synthetic lubricants replace the mineral oils.

Synthetic lubricants may cover a range of chemicals. Several types of seynthetic lubricants at various times have been considered as possible base oil for jet engine. There are several types of synthetic lubricants: aliphatic esters, phosphate esters, silicate esters, polyglycols and silicones.

The fresh jet engine oils are generally synthetic lubricants of the type aliphatic esters and always after a peroid of time of using will be rejected. There is no concrete evidence about spent oil and its time needed for rejection of a lubricant.

Lubricating oil deteriorates during use in several different ways, and with this deterioration comes a risk of damage to the lubricated system (4).The early deterioration of lubricant properties, which can be caused by product breakdown or build up of contaminants can be caused ingress or wear of mashine surfaces, leading to deterioration in performance and eventual failure(5).The deterioration of oil in use is affected by many factors and these factors are(6): Breackdown due to shear, Evaporation, Oxidative and thermal effect, Contamination by solids and Contamination by water.Studies by Denever Research Institute under Air

Force contract included the effect of different decomposition products ande trace amounts of various materials on lead corrosion, the development of analytical methods to separate degradation products, the effect of various oil additives on storage stability and a program to develop an accelerated storage test.A major contribution of these studies was the concluison that dibasic acid esters undergo decomposition by means of a mechanism which involves a peroxide intermediate. Bohner, Frederickson and Schimdt considered two basic deterioration mechanisms, oxidation and hydrolysis. In consideration of the oxidation dibasic acid esters, the work of Murphy and Ravner was cited showing that the end products of diester oxidation are primarily the dibasic acid and the alcohol with trace amounts of aldehydes, ketones, carbon dioxide and water formed. There is evidence that a peroxide or hydroperoxide intermediate is formed which on cleavage yields the acid half-ester and alcohol and, ultimately, the dibasic acid(7).

This work deals with the investigation of the possibility of spent synthetic oil (type 210 A) improvement.

Experimental Work

Raw material

The yellow colour spent gas turbine lubricant 210A was used in this investigation. Table 1 shows the properties of the fresh and the spent oils.

Table 1. Physical properties of fresh and spent oils

Characteristics	Fresh oil 210 A	Spent oil
Appearance	Yellow	Yellow
Specific gravity	0.84-0.87	0.8561
Kinematic viscosity, Cs		
At 100 C	3.0-3.3	3.4
At 40 C	11.0-14.0	15.7
At – 40 C	<2500	-
At – 45 C	<11000	-
Viscosity index	104.07-132.40	18.6
Acid number,mg KOH / g	<0.1	0.63
oil	>180	171
Flash point, C	<-75	-
Pour point, C	<500	nil
Water cntent,ppm		

Solutions of 2.0, 2.8, 4.0, 5.2 and 6.0 weight percent NaOH are prepared. The spent lubricant is weighed and mixed with solutions of NaOH in the desired concentrations and the desired weight ratios of NaOH/ spent lubricant, then mixed by using the electric mixer of 600 RPM for the desired period of time. The mixer is placed in a separated funnel to separate the NaOH solution from the treated lubricant. The treated lubricant washed by 1 liter of distilled water to separate the NaOH solution that remains in the lubricant, then the acidity of the treated lubricant is determined.

Acid value determination

Acid value was determined by dissolving 10-15 g of the lubricant sample in 100 ml solvent(blank), which consists of 50 % toluene,49.5 % isopropanol and 0.5 % distilled water. Then, the mixture was titrated with 0.08-0.1 N alcoholic KOH which prepared by dissolving 3 g of KOH in 500 ml isopropanol. In the titration , phenolphthalein indicator is used by adding 3-5 drops to the mixture (the lubricant and the solvent).In the titration process, the volume of KOH required to neutralize the mixture is measured. Then the acid value is calculated by the following formula:

$$\text{Acid value (mg KOH / g oil)} = \{(A - B) * N * 56.1\} / W \qquad (1)$$

Where, A = ml of KOH solution required for titration the lubricant, B = ml of KOH solution required for titration the blank, N = the normality of KOH, and W = the weight of the lubricant sample.

Application of Box-Wilson method for the lubricant acidity treatment

Acidity treatment is studied for the spent lubricant by using alkali solution of NAOH. The effects of mixing time, NaOH solution / lubricant weight ratio and NaOH concentration are investigated and analyzed by using the experimental design. Box-Wilson central composite design (9) is adopted to find a useful relationship between the three controllable variables and the observed response (the lowering in the acidity of the spent lubricant).

For the purpose of this design the following three variables X_1 , X_2 and X_3. Where X_1 = mixing time between 5 and 35 min, X_2 = NaOH solution /lubricant weight ratio between o.25 and 1.25, and X_3 = NaOH concentration between 2 and 6 % weight. To find the number of experiments that are needed for Box-Wilson design, the following equation is applied.

$$N = 2^P + 2(P) + 1 \qquad (2)$$

Where, N = the number of the of the experiments, and P = the number of the variables. In the above equation, 2^P represent the factorial points, the 2 * P are the axial points, and 1 is the center point.

In this investigation the number of experiments calculated by equation 2 was 15. To set up the relationship between the coded level, x_j, (where j = 1, 2, 3) and the corresponding real process variables, equation 3 is applied.

$$x_{coded} = \frac{[x_{actual} - x_{center}]}{\left[\dfrac{x_{center} - x_{minimum}}{\sqrt{P}}\right]} \qquad (3)$$

Then,

$$x_{1\,coded} = \frac{x_{1\,actual} - 20}{(20-5)/\sqrt{3}} = \frac{x_{1\,actual} - 20}{8.66} \qquad (4)$$

$$X_{2\,coded} = \frac{X_{2\,actual} - 0.75}{(0.75-0.25)/\sqrt{3}} = \frac{X_{2\,actual} - 0.75}{0.2887} \quad (5)$$

$$X_{3\,coded} = \frac{X_{3\,actual} - 0.04}{(0.04-0.02)/\sqrt{3}} = \frac{X_{3\,actual} - 0.04}{0.03464} \quad (6)$$

Table 2 shows The experiments that applied for the spent lubricant, which are conducted according to Box-Wilson method and experimental response represented by the lowering in the acidity of the spent lubricant (y).

Table 2. The acidity of Box-Wilson method experiments for the spent lubricant

No	Coded variables			Real variables			y
	X_1	X_2	X_3	X_1	X_2	X_3	
1	1	1	1	28.66	1.04	0.052	0.061823
2	-1	1	1	11.34	1:04	0.052	0.078177
3	1	-1	1	28.66	0.46	0.052	0.16849
4	-1	-1	1	11.34	0.46	0.052	0.18484
5	1	1	-1	28.66	1.04	0.028	0.136823
6	-1	1	-1	11.34	1.04	0.028	0.153177
7	1	-1	-1	28.66	0.46	0.028	0.261820
8	-1	-1	-1	11.34	0.46	0.028	0.278177
9	1.732	0	0	35.00	0.75	0.04	0.129167
10	0	1.732	0	20.00	1.25	0.04	0.076670
11	0	0	1.732	20.00	0.75	0.06	0.036670
12	-	0	0	5.00	0.75	0.04	0.320000
13	1.732	-1.732	0	20.00	0.25	0.04	0.281667
14	0	0	-1.732	20.00	0.75	0.02	0.191670
15	0	0	0	20.00	0.75	0.04	0.113330

A second – order polynomial will be employed in the range of the independent variables. For three variables, the general form of second – order polynomial is written as follows:

$$\eta = B_0+B_1X_1+B_2X_2+B_3X_3+B_4X_1^2+B_5X_2^2+B_6X_2^2 +B_6X_3^2+B_7X_1X_2+B_8X_1X_3+B_9X_2X_3+B_9X_2X_3 +B_{10}X_1X_2X_3 \quad (7)$$

η= true value of the mathematical model response. As in the statistica progrm there is some insignificant interactions for the second order polynomial equation of the acidity of spent lubricant. After using the statistica program on the above mentioned table these insignificant interactions will be cancelled and the new form of the spent lubricant second order polynomial became as in equation 8.

$$Y= B_0+ B_1 X_1 + B_2 X_2 + B_3 X_3 +B_4X_1^2+B_5X_2^2+B_6X_3^2 \quad (8)$$

For postulating the best form of the two models, the coded data of the table 2 will be first fitted to equation 8, so that the regression analysis of central composite design can applied to the approximating model. By this analysis each term for the fitted polynomial can be checked for significant.

Using the coded data of central composite design given in table 2 the coefficient of equation 8 can be determined simply from the statistica program, and the second order polynomial for the treating of the acidity of the spent lubricant with its coefficients become as shown in equation 9.

$$Y=0.786276-0.022186X_1-0.567792X_2-2.79432X_3 +0.000473X_1^2+0.243885X_2^2- 10.7934X_3^2 \quad (9)$$

The correlation coefficient was 0.9625 while the estimated standard deviation of y was 0.087944.

From this mathematical model, a graphical figures of the acidity of the spent lubricants versus each variable can be costructed within the variables ranges used in forming the model. Such figures describe the effect of each variable on the acidity at different values of the other variables to show the interaction between them

Results and Discussion

The effect of mixing time

Equation 9 shows that there is no interaction between the mixing time and the other two variable , therefore it can be studied separately.

Plotting the acidity against the mixing time at five different weight ratio of NaOH / spent lubricant gave a parallel curves as seen in Fig. 1 and also the acidity against mixing time at five different weight percentage of NaOH gave parallel curves as seen in Fig. 2. Fig. 1 shows clearly that within 13 minutes the acidity reached 0.26-0.08 mg KOH /g oil depending upon the weight ratio of NaOH / expired lubricant. At 1 weight ratio of NaOH/expired lubricant the increment in acidity decreasing after 13 minutes become lower, and then becomes very small after 20 minutes. Fig.1 shows that the acidity within 20 minutes reaches 0.25-0.05 mg KOH/g depending upon the weight ratio of the NaOH/ spent lubricant.

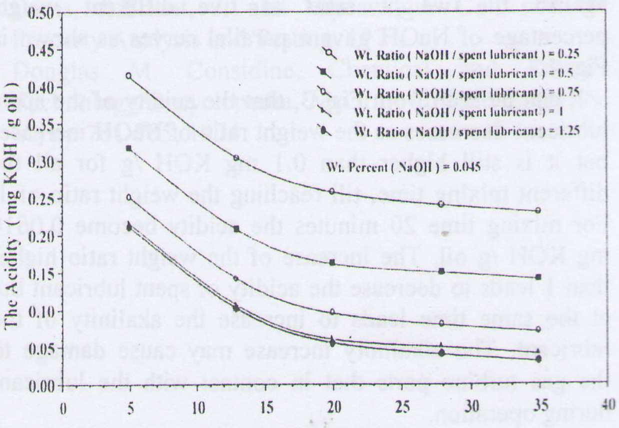

Fig.1 The effect of the mixing time on the acidity of the spent lubricant at different wt. ratio NaOH/spent lubricant

The analysis of Figs. 1 and 2 indicates that the best mixing time for treating the spent lubricant is about 20 minutes.

The small increments in the acidity decreasing after 13 minutes may be due to the consumption of all the NaOH solution for neutralization and there is no more reaction can occurred between the lubricant and the NaOH solution.

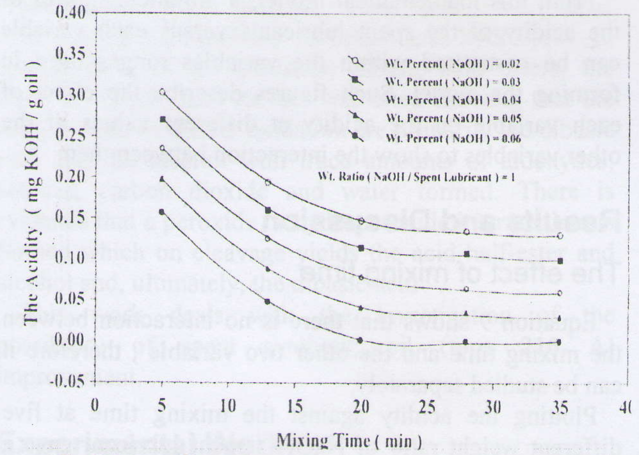

Fig.2 The effect of the mixing time on the acidity of the spent lubricant at different wt. percent NaOH

The effect of weight ratio of NaOH/ lubricant

For the spent lubricant , the weight ratio can be studied separately, since according to equation 9 there is no interaction of weight ratio of NaOH / lubricant with other two variables.

Plotting the acidity of the spent lubricant against the weight ratio of NaOH / lubricant at five different mixing time gave approximately a parallel curves as shown in Fig. 3, also plotting the acidity of the spent lubricant against the weight ratio at five different weight percentage of NaOH gave a parallel curves as shown in Fig. 4.

It can be seen from Fig. 3, that the acidity of the spent lubricant decreases as the weight ratio of NaOH increases but it is still higher than 0.1 mg KOH /g for all the different mixing time, till reaching the weight ratio of 1. For mixing time 20 minutes the acidity become 0.0618 mg KOH /g oil. The increase of the weight ratio higher than 1 leads to decrease the acidity of spent lubricant but at the same time leads to increase the akalinity of the lubricant. The alkalinity increase may cause damage to the gas turbine parts that in contact with the lubricant during operation.

Fig. 4 shows that the weight ratio of NaOH / lubricant increasing at different weight percentage of NaOH decreases the acidity, but the acidity of the expired lubricant still more than 0.13 mg KOH/g oil for the weight percentage of NaOH in the range of 0.02-0.04. At 0.055 weight percentage of NaOH and 1 weght ratio of NaOH/ lubricant, the acidity decreases to 0.0618 mg KOH g oil.

The results presented in Figs 3 and 4 for spent lubricant indicate that the best weight ratio of NaOH / lubricant is 1.At this weight ratio, the acidity of spent lubricant decreases from 0.63 to less than 0.1 mg KOH /g oil for weight percentage of NaOH of 0.04-0.06 and at 20 minutes mixing time.

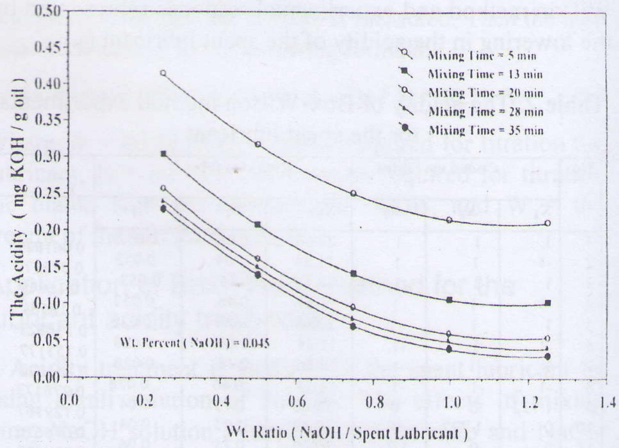

Fig. 3 The effect of the wt. ratio NaOH/spent lubricant on the acidity of the spent lubricant at different mixing time

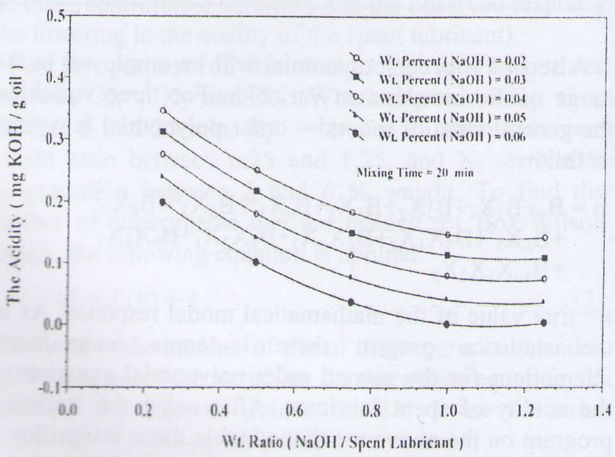

Fig. 4 The effect of the wt. ratio NaOH/oil on the acidity of the spent lubricant at different wt. percent NaOH

The effect of NaOH weight percentage

From equation 9 for spent lubricant, it can be seen that the NaOH weight percentage has no interaction with the other two variables, therefore it can be studied separately.

Plotting the acidity of the spent lubricant against the NaOH weight percentage at five different mixing time gave a parallel curves as shown in Fig. 5. Also plotting the acidity of the spent lubricant against the weight percentage of NaOH at five different weight ratio of

NaOH /lubricant gave a parallel curves as shown in Fig. 6.

Fig. 5 shows that the acidity decreases by increasing the weight percentage of NaOH. For mixing time 5-13 minutes the acidity still more than 0.1 mg KOH g oil for 0.05-0.06 weight percentage of NaOH and mixing time 20-35 minutes.

This is may be due to that 5-13 minutes is not enough to finish the reaction between the acid compounds and the NaOH solution, therefore the acidity still high.

It can be seen from Fig. 6 that the increasing of the weight percentage of NaOH for a given weight ratio of NaOH /spent lubricant decreases the acidity as a result of increasing the NaOH amount that neutalize the acid compounds.

The analysis of Fig. 6 indicates, that the recommended weight percentage of NaOH is about 4.5 for the spent lubricant.

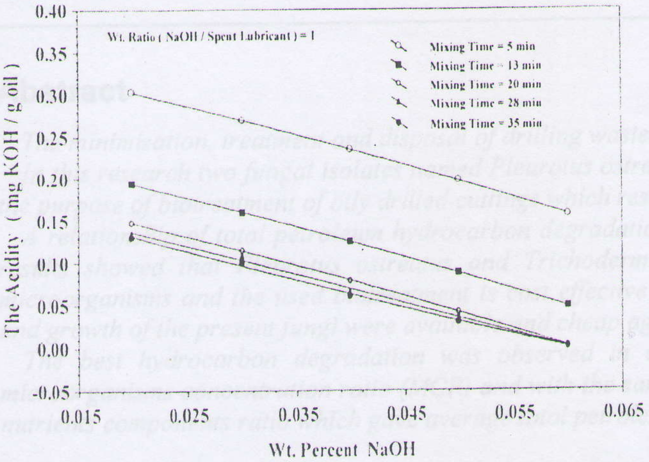

Fig. 5 The effect of the wt. percent NaOH on the acidity of the spent lubricant at different mixing time

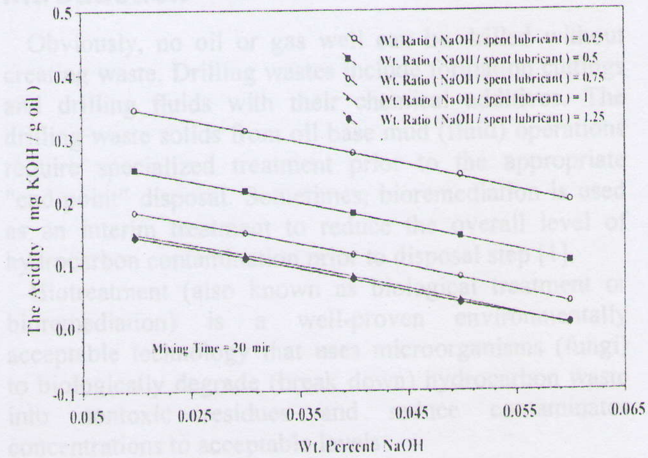

Fig. 6 The effect of the wt. percent NaOH on the acidity of the spent lubricant at different wt. ratio NaOH/spent lubricant

Conclusions

1. The acidity of the spent lubricant was treated and the three variables that effect the treatment were studied. The three variables range for Box-Wilson design that affect the acidity treatment was 5-35 minutes mixing time, 0.25-1.25 weight ratio of NaOH /treated lubricant and 2-6 % weight percentage of NaOH.
2. A quantitative relationship between the acidity of the spent lubricant and the three studied variables is well represented by second order polynomial equations.
3. The best condition for treating the acidity of the spent lubricant were 20 minutes mixing time, 1 weight ratio of NaOH /spent lubricant and 4.5 % weight of NaOH. At these conditions the acidity of the spent lubricnt decreases from 0.62 to 0.0602 mg KOH / g oil.

References

1. http://www.fluitec.com/education2.html,Internet, 2001.
2. Paul D.Hobson, Industrail Lubrication Practice, First Ed.,1955.
3. Elliott, J. S and Edwards, E. D., J. Inst. Petrol., 47, No. 446, p. 39, Feb.,1961.
4. Institute of Petroleum, Method for Abalysis and Testing, Part 1, Vol. 1, 1981.
5. http:/ www.TSC (UK) Limited, Lubricant Analysis, Internet, 2001.
6. Lansdown A. R., Lubrication, First Ed.,Pergamon Press, 1982.
7. Guderson R. C and Hart A. W., Synthetic Lubricant, First Ed.,Reinhold Publishing Corp., N. Y., 1962.
8. Denis, J.,Briant, J. and Hipeaux, J. C., Lubricant Property Analysis and Testing, 1977.
9. Douglas M. Considine, Chemical and Process Technology Encyclopedia, McGraw-Hill Company, N. Y., pp.701-705, 1974.