

RECYCLING OF USED LUBRICATION OIL BY SOLVENT EXTRACTION - A GUIDELINE FOR SINGLE SOLVENT DESIGN

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ABSTRACT

Solvent extraction has been known as one of the potential techniques for recycling used lubricating oil. The technique has received considerable attention due to the advantages that it offers practically from environmental and economic points of view. Different organic solvents have been used to flocculate the deteriorated additives and impurities which presence in the form of fine suspension in the used lubricating oil prior to recovering the oil. This work attempts to study the performance of three types of solvents i.e. 2-Propanol, Butanol and MEK, in the extraction process for recovering used lubricating oil. Temperature and the weight ratio of solvent to oil were used as the key operating parameters in the study. The relation between these parameters and the performance of the individual solvents (describes in the form of percent sludge removal and percent oil losses) was investigated to see if some form of general and useful guidelines can be developed especially for predicting best operating region for a specific single solvent. The guideline developed is useful at the early stage of design where it is important to select proper solvent and to determine the best operating condition for such solvent.

INTRODUCTION

Used lubricating oil has been re-refined using several techniques such as chemical treatment i.e. acid/clay re-refining (Vaughn, 1975), physical treatment i.e. distillation and thin film evaporation (Brinkman, 1991), and solvent extraction (Reis, 1991). Solvent extraction, initially introduced as a replacement for the acid clay treatment process due to environmental problem, has received considerable attention in recent years (Saunders, 1996). There are several reasons for this namely, (a) it overcome the problems associated with acid sludge produced from the conventional re-refining by chemical treatment (Reis, 1991), (b) it eliminates the problem of having to deal with fouling and high control cost in distillation and evaporation for the physical treatment (Whisman, et al., 1978) and (c) the recent development which discovered that the cost factor for solvent extraction re-refinery plant was found to be one third of the cost of physical re-refinery (Chementator, 1996).

Previously, a large number of solvents in a pure or mixture form have been studied for the removal of additives and contaminants from used oil prior to its recovery. The criteria of selecting the best solvent for this process can be based on the ability to achieve high sludge removal with minimum volume of solvent used. This criteria have been measured using different methods such as percentage of oil recovery, i.e. percent of base oil recovered after the re-refining treatment, ash content and percentage of sludge removal (Vaughn (1975); El-Din et al. (1987); Reis and Jernimo (1988)). However, it is unfortunate that only few studies have been conducted to explore the general trend on the action of different solvents in segregating certain types of used oil components. Most of the focused has been directed towards specific solvent. With the above in mind, the objective of this study was set to investigate and to assess the impact of different type of solvents used in the solvent extraction process for recycling used lubricating oil. The idea of the study is to gain further

understanding with regards to the effect of the different type of solvents used as well as, the operating parameters namely, the temperature of the process, and the solvent to oil ratio.

EXPERIMENTAL

Sample.

In this study, only used crankcase lubricating oil was used as test samples. The samples were collected from different local garages and service station in Malaysia and mix in a single container. As the used lubricating oil samples were obtained from many locations, it was assumed that it can represent a typical feed stock to a re-refinery plant for recycling used crankcase lubricating oil. The used lubricating oil mixture was kept in a closed drum of 20 liters and the contents were homogenised prior to any testing.

Solvents.

Commercial grades solvents which consist of 1-Butanol, 2-Propanol and MEK were used in this study. The reason is that these solvents have been used in most of previous study where some understanding have been developed. However, a more systematic approach is adapted to achieve the objective of the study.

Solvent Extraction Process.

The used oil sample is mixed with the solvent in a test tube for 20 minutes under continuous stirring (stirring speed set at 275-300 r.p.m.). This is to ensure perfect mixing and at the same time preventing any losses of oil to the test tube wall. Various solvent to oil weight ratios were studied and at different extraction temperatures. The temperature was controlled with the help of a thermostat bath. The mixture was then left for 24 hours to settle under gravity. The following parameters were studied from the experiment;

i) Workable Solvent to Oil Ratio by Color Change.

The investigation of the clarity of used oil after mixing with the solvent was used to determine the range of workable solvent to oil ratio and the acceptable operating temperatures.

ii) Percent Sludge Removal (P.S.R.).

The percent sludge removal represents the quantity of dry sludge (additives and impurities) removed from the used oil after mixing with solvent according to the experiment above. The additional steps involved, consist of removing the sludge from the bottom of the settling flask after the settling period has lapsed into a weighted glass tube. This product is termed as wet sludge with a weight of W_1 . The following washing process was then used to remove the interstitial oil content as much as possible in order to determine the amount of oil losses with the sludge (Percent oil loss is also used as the parameter to describe performance). First, the separated sludge is redispersed by adding 7.0 cm³ of n-hexane followed by 28.0 cm³ of 2-propanol which immediately produces large flakes. After 12 hrs of gravity settling, the liquid is discarded using vacuum filtration and the bottom sludge cake (washed sludge) was collected. The washed sludge is then placed into an oven for 15 minutes at 100 °C for drying purposes. The hot dry sludge is then cooled to room temperature and weighted (W_2). The percentage of sludge removal can then be calculated as follows;

$$P.S.R. = \frac{W_2}{W} \%$$

where W is the mass of used oil in the solvent/oil mixture.

iii) Percentage of Oil Losses.

The oil loss represents the amount of oil that did not dissolve in the solvent but rather settles with the sludge. Percent oil losses (P.O.L.) is defined as the amount of oil in sludge phase per 100 grams of used oil. This factor was calculated from the same washing process stated above and calculated as follows ;

$$P.O.L. = \frac{W_1 - W_2}{W} \%$$

RESULTS AND DISCUSSION

Colour Investigation Result.

In this study, the effective solvent to oil ratio is defined as the proportion of solvent to oil that can destabilise fine micro particles (additives, and contaminants) in the used lubricating oil sample and allowing them to form large flakes which are able to settle under gravity action after a specified period of time. In actual fact, this can be distinguished from the colour changes of the analysed sample after the settling period has lapsed, i.e. from black to dark brown. The minimum solvent-oil ratio (M.R.) is thus defined as the minimum oil to solvent ratio that can cause this colour changes to occur. Note that due to the nature of the experiment, the value for the solvent to oil ratio is given in the form of approximation i.e. range, rather than a specific value. Another important point to note, which is located beyond the M.R., is the critical clarifying ratio (C.C.R.). At this point, a suppressant solution was observed containing two phases, namely the base oil and solvent phase (liquid layer) which presence on top of the sludge and base oil phase (solid layer). It was also observed that increasing the solvent to oil ratio beyond the C.C.R. point causes the particles to re-enter the liquid layer in the form of suspension. This leads to lower settling efficiency due to smaller particle size. Finally the last point to note is the limit of the solvent to oil ratio (L.R.) which is defined as the point beyond which the amount of settling sludge will not be affected by any increase in the solvent amount. This is due to the inhibition to flocculation causes by presence of excess solvent in the mixture thus producing fine flakes which is difficult to settle. As with M.R., the other two points are also given in approximation values, i.e. range.

General Observation on Colour Investigation Test.

From the colour investigation test, the solvent to oil ratio, whereby the flocculation of fine particles started to take place in the used oil sample, was found to varied at any given temperature. Table 1 shows the estimated range for M.R., C.C.R. and L.R. for the three solvents used. For alcohols i.e. 2-propanol and 1-butanol, the flocculation of the sludge particles was found to start at lower ratios than MEK. This was easily observed from the results of the test whereby it was difficult to obtain satisfactory result with MEK in comparison to the two alcohols. As temperature increases, the values for M.R., C.C.R. and L.R. also increase, for all the solvents under study. This observation help to minimise trial runs needed in order to select the appropriate solvent to oil ratios and the extraction temperature for the later test i.e. determination of the percent sludge recovery (P.S.R) and the percent oil losses (P.O.L.), as it closes down the range of these parameters.

Effect of Solvent to Oil Ratio on Percent Sludge Removal (P.S.R) and Percent Oil Losses (P.O.L).

As shown in Figure 1, an increase in the solvent to oil ratio led to an increase of P.S.R. but a decrease in P.O.L. In order to explain the results, consider the following aspects; (1) The increase of the solvent to oil ratio increases the differences between the solubility parameter of the liquid media where the non polar or slightly polar macromolecules are dissolved, i.e. the solution of base oil with some additives and solvent, and the solubility parameter of those macro molecules, (2) The viscosity and specific gravity of the oil decrease as the solvent to oil ratio increases thus increasing the speed at which the settling of particles take place, (3) Increasing the solvent to oil ratio, however, decreases the settleable matter concentration resulting in slower flocculation and a decrease in the speed of the settling process. Factors 1 and 2 explained the relation obtained on the percent sludge removal against solvent to oil ratio plot from the M.R. point to the C.C.R. point (see Figure 2). Similarly, factor 3 accounts for the curvature shape of the plot between the C.C.R. point to the L.R. point. Below the observed optimum solvent to oil ratio (located below the C.C.R. point), factor 1 and 2 are more dominant. Above the optimum ratio, i.e. the L.R. point, factor 3 prevails.

Determination of The Critical Clarifying Ratio from the Percent Sludge Removal Curve.

The major concern in this study is to evaluate the region which gives an optimum sludge removal from the used oil sample. This optimum value does not necessarily correspond to maximum P.S.R. because an increase of the solvent to oil ratio beyond the optimum point can still possibly lead to increase in P.S.R. The optimum solvent to oil ratio, considered here, is the critical clarifying ratio (C.C.R.) which was defined as in the colour investigation test. Figure 2 shows an example of the percent sludge removal (P.S.R.) curve, which is a plot of the percent sludge removal as a function of solvent-oil weight ratio, for a system which utilises 1-butanol as the solvent. It was found that all the percent sludge removal (P.S.R.) curves showed an almost linear relation up to the C.C.R. point. However, the relation shows a diminishing gain from C.C.R. to L.R. point inspite of increasing the solvent to oil ratio. The following geometrical technique was applied to determine the C.C.R. point from the percent sludge removal curve. As shown in Figure 2, a straight line representing the slope for the initial part of the P.S.R. curve is drawn and extended to intersect the line representing the maximum limit of the P.S.R. curve. The intersection point between the two lines is then projected vertically down until it touches the P.S.R. curve and this is defined as the C.C.R. The respective values for the point can be obtained from the x and y axis value (0.05 is added to define the region of C.C.R. for the solvent at specified temperature). Table 2, shows the region of C.C.R. for the solvents at three temperatures (25°C, room temperature, i.e. 28°C and 50 °C).

Effect of The Extraction Temperature on The Percent Sludge Removal and The Percent Oil Losses.

Also Figure 1, shows the effect of temperature on the percent sludge removal (P.S.R.) and the percent oil losses (P.O.L.), for 2-propanol. The results for the other two solvents i.e. MEK and I-butanol was found to be similar in trend. The P.S.R. and the P.O.L. was found to decrease with decreasing in temperature of the extraction process. In order to increase performance of the process, the P.S.R. needs to be increased and at the same time reducing P.O.L. However, varying the temperature will not help much in improving the performance as the effect on both (P.S.R. and P.O.L.) is similar. However, by looking at the problem from a different angle such as the cost between having a higher P.S.R. (higher recovery oil quality which reduces the cost of subsequent physical treatment such as vacuum distillation, clay adsorption or hydrofinishing (Saunders, 1996) and at the same time high P.O.L (higher oil losses in sludge which required additional extraction stage or a

counter current one (Lai, 1989)), can assist the decision making with regards to the selection of operating temperature for the process.

Effect of Solvent Type

The three different solvents used exhibit different performances with regard to the amount of sludge produced from the used oil and the amount of oil losses in the sludge phase. For example, from the first experimental work, it was clearly observed that 1-butanol and 2-propanol produce clear solution with a sludge layer settling at the bottom of the glass tube, at lower solvent to oil ratios than MEK (see Table 1). The following section attempts to discuss their effect with respect to the P.S.R. and the P.O.L. curves. Figure 3 shows the performance of the three solvents using the P.S.R. curves at room temperature. The results, as presented in the figure, show that 1-butanol produces the highest percent sludge removal, followed by 2-propanol and MEK. On the other hand, Figure 4 which display the results obtained for P.O.L. curves demonstrate that MEK produces the lowest oil losses followed by 2-propanol and 1-butanol at each of the specified temperatures. The above observations can be explained according to the following reasons; (1) The segregation of fine particles especially polymers in additive package is dependent on the polarity of the solvent used (Reis and Jernimo, 1988). The alcoholic solvents have a hydroxyl group (OH), which provides an electrostatic media that encourage fine particle to agglomerate into large flakes. (2) The solubility of MEK in base oil is generally higher than that of alcoholic solvents (Jordan and Mc Donald, 1973). Higher solubility in the base oil refers to higher miscibility of the solvent in base oil, which obviously decrease the amount of oil losses in the sludge. However, higher miscibility of solvent in oil does not necessary means an increased in the P.S.R., although it could give a good indication to the P.O.L. (3) The immiscibility of the solvent in additives and carbeneous particles is another factor that can increased the P.S.R. (antisolvency effect of the solvent in polymers and carbeneous particles). The absolute difference between the solubility parameters of solvent (δ_1) and polymer in oil additives i.e. polyisobutylene (δ_2), is an effective method to measure the antisolvency property. According to Reis and Jernimo (1988), the larger the differences between the two solubility parameter, the better the P.S.R. would be. The performance of the solvents used for this work agrees with this theory since 1-butanol was found to produce the best result and the highest differences between the two solubility parameter, i.e. $7.86 (\text{J/cm}^3)^{1/2}$, followed by 2-propanol $(0.78 (\text{J/cm}^3)^{1/2})$ and MEK $(0.67 (\text{J/cm}^3)^{1/2})$.

CONCLUSION

The followings are the main conclusion of this study. (1) The preliminary selection for efficient solvent to oil ratio and the extraction temperature can be guided using the colour investigation test. It was found that there were strong agreement between the suggested values of C.C.R. as shown in Table 1 and the one determined from the percent sludge removal (P.S.R.) curve in Table 2. (2) The two extraction performance indicators i.e. percent sludge removal and percent oil losses have to be taken into consideration prior to the selection of the extraction parameters i.e. solvent type, solvent to oil ratio and extraction temperature. (3) Alcohols i.e. 1-butanol and 2-propanol produce the best extraction performance with regard to sludge removal, while ketone, i.e. MEK, posses the best performance with regard to oil losses. Research to find a new single or composite solvents can be guided using the adapted approach.

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Table 1. The Range of Minimum Solvent -Oil Ratio (M.R.), Critical Clarifying Ratio (C.C.R.) and Limit Solvent-Oil Ratio (L.R.) point, for Three Solvents at Three Temperatures.

Solvent	Temperature in °C	M.R.	C.C.R.	L.R.
2-Propanol	25	0.9-1.1	1.4 - 1.5	5.00
	Room Temp. (28)	1.1- 1.2	1.6 - 1.7	5.50
	50	1.5-1.70	2 - 2.2	6.00
1-Butanol	25	0.8-0.9	1.0 - 1.2	4.50
	Room Temp. (28)	1.1-1.2	1.3- 1.5	5.00
	50	1.5-1.7	1.70-1.8	6.00
MEK	25	2.7 - 2.8	3.0 - 3.2	6.50
	Room Temp. (28)	2.5 - 3	3.2-3.3	7.00
	50	3.8 - 3.9	4.0 - 4.2	8.00

Table 2. The Range Critical Clarifying Ratio Determined from The Percent Sludge Removal Curves, for a Used Oil Sample Treated by Three Solvents at Three Temperatures.

Solvent	25 °C	Room Temp. (28 °C)	50 °C
2-Propanol	1.30 - 1.4	1.35 - 1.45	1.70 - 1.80
1-Butanol	0.95-1.05	1.20 - 1.30	1.60-1.70
MEK	2.30 - 2.40	2.50 - 2.60	3.1 - 3.20

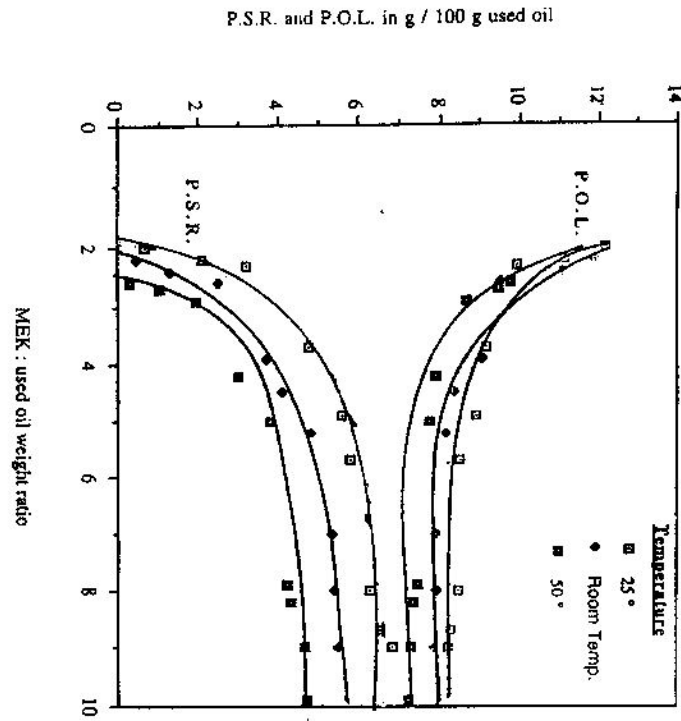


Figure 1.

Percent Sludge Removal and Percent Oil Losses Curves, for a System of MEK, Used Oil at Three Temperatures.

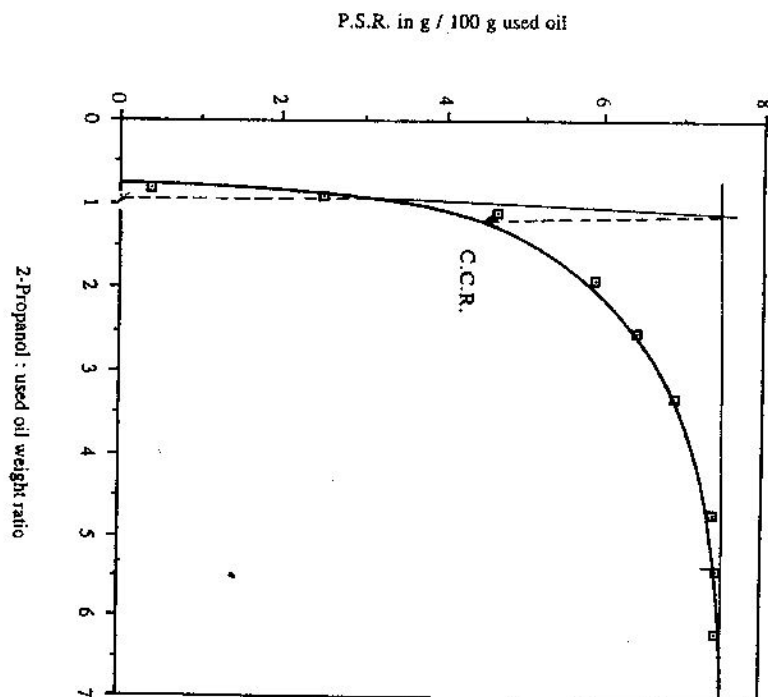


Figure 2.

Percent Sludge Removal Curve for a System of 2-propanol, Used Oil at 25 °C, and the Geometrical Method Applied For Determination of Critical Clarifying Ratio (C.C.R.).

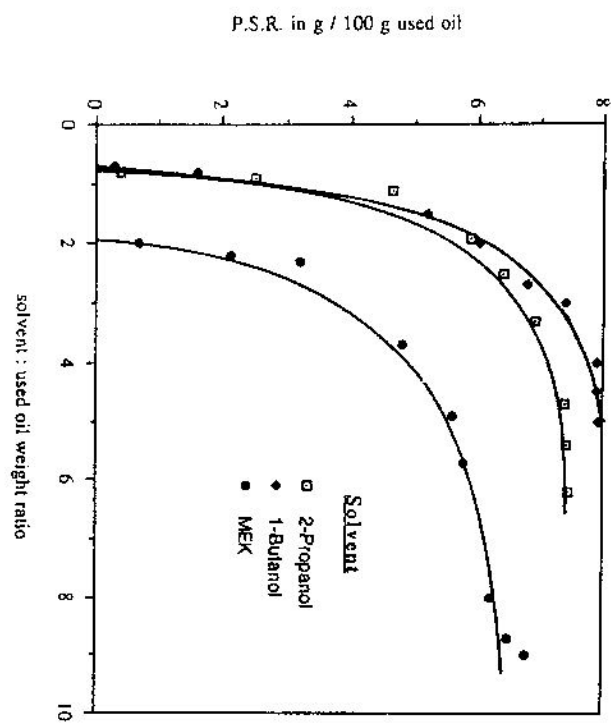


Figure 3.
Percent Sludge Removal Curves For The Three Solvent 2-Propanol, MEK
and 1-Butanol at 25 °C.

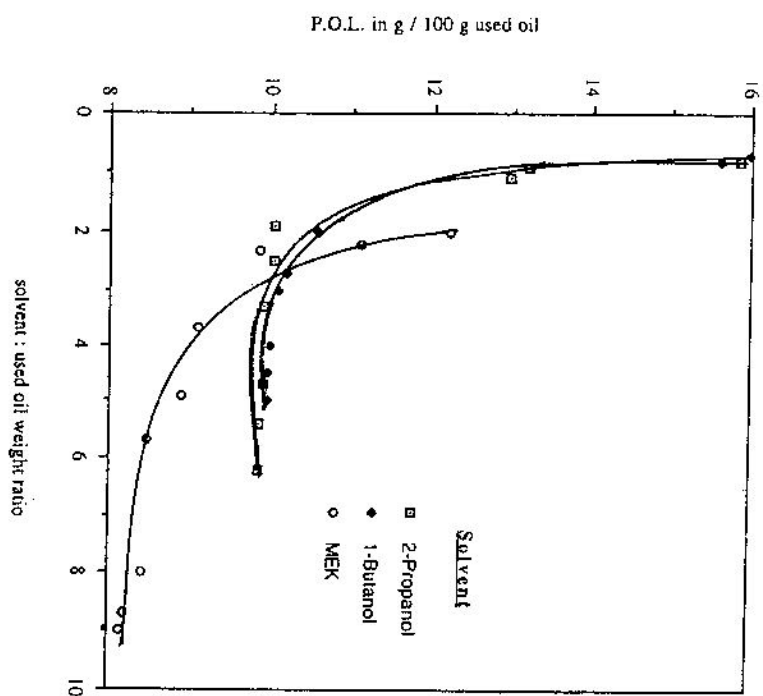


Figure 4.
Percent Oil Losses Curves for The Three Solvents 2-Propanol, MEK
and 1-Butanol at 25 °C.