

Effect of Extraction and Adsorption on Re-refining of Used Lubricating Oil

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Résumé — Effet de l'extraction et de l'adsorption sur le retraitement des huiles usagées — L'extraction par solvant suivie d'adsorption est considérée comme l'un des procédés les plus performants pour le recyclage des huiles usagées. Dans cet article, la performance de divers solvants pour la formation de boues a été étudiée. Le 1-butanol produit le plus de boues, suivi de la méthyle éthyle cétone (MEK), puis du 1-hexanol et du 2-butanol. La différence de formation des boues n'est que de 0,3 % entre le 1-butanol et le MEK. Cependant, en raison de son faible point d'ébullition et de son faible coût, le MEK a été préféré au 1-butanol. L'huile extraite est ensuite passée à travers une colonne de différents adsorbants. Une huile d'indice de couleur 2 (jaune), à 0,14 % de résidu de carbone, 0,02 % de cendres sulfatées et 216 °C de point d'éclair, a été obtenue avec 94 % de rendement.

Abstract — Effect of Extraction and Adsorption on Re-refining of Used Lubricating Oil — Solvent extraction followed by adsorption has been found to be one of the competitive processes for recycling of waste lubricating oil. In this paper, the performance of various solvents for sludge formation has been studied. 1-butanol produced maximum sludge followed by methyl ethyl ketone (MEK), 1-hexanol and 2-butanol. The difference in sludge formation between 1-butanol and MEK was only 0.3%. However due to low boiling point and low cost, MEK was preferred over 1-butanol. The extracted oil was then passed through a column of different adsorbents. An oil of colour index (yellow) 2, carbon residue 0.14%, sulphated ash 0.02% and flash point 216°C, was obtained with 94% yield.

INTRODUCTION

With increasing number of vehicles the volume of used lubricating oil produced each year is also increasing. The used oil contains water, salt, broken down additive components, varnish, gum and other materials. A small part of this finds its way to recovery process while the major portion is used in ways which are harmful for environment.

Recycle of used oil has been carried out by several methods. Concentrated sulphuric acid has been used to remove asphaltenic material. The product is then clay treated [1]. The sludge could be used as fuel which leads to the production of acidic gases. Use of acid could be avoided by treating used oil with natural polymers. The product is vacuum distilled then decolourized [2]. The recycled oil contains higher amount of metals.

Inorganic membrane has been used to extract the oil followed by adsorption which requires high pressure and specialized inorganic composite membrane [3]. Use of radiations has been reported [4]. Alkali (NaOH/KOH) with ammonium salt or ethylene glycol has been used to recover the oil [5-7].

Solvent extraction has been proposed as an alternate method [8, 9]. Solvent chosen should have maximum solubility for base oil and minimum for additives and carbonaceous matter. Super critical fluids propane and ethane have also been used as extracting solvents giving low yield 72-80% [10, 11]. Solvent could be recovered by distillation [12, 13]. Martins used a mixture of polar solvents in presence of potassium hydroxide [14]. Recently, used oil has been re-refined by thin film distillation under high vacuum followed by clay treatment or hydro treatment [15, 16].

The present work aims at finding a complete recycling process which could also be industrially feasible. The first part of the work is based on searching a cheap solvent which can reduce sludge concentration in used oil to a minimum level with higher recovery. The second part deals with adsorbent which can produce an oil having properties comparable with base oil.

1 EXPERIMENTAL

1.1 Materials Used

Used motor lubricating oil was stored for several days to allow large suspended particles to settle under gravity.

Solvents used for extraction were *n*-heptane, *n*-hexane, methyl iso butyl ketone (MIBK), MEK, 1-butanol, 2-butanol, benzene and 1-hexanol. The solvents were of analytical grade and supplied by E. Merck.

Adsorbents used were alumina and silica gel (column chromatography grade), supplied by E. Merck and local

magnesite rock. Sorbents (alumina and silica gel) of particle size 70-230 mesh were used. Magnesite in variable particle sizes 16-50, 50-100, 70-230 and 100-230 were tested.

1.2 Extraction Process

A mixture of solvent and used lubricating oil was shaken in a 100 ml separating funnel to ensure adequate mixing. Solvent to oil ratio was 3:1(v/v). The sludge was allowed to settle at a constant temperature of 35°C in a thermostatic bath. After 24 hours, solvent-oil solution was separated from sludge. The sludge was dispersed twice with the same solvent to extract any remaining oil. The sludge was then dried till constant weight at 105°C. The washing solvent was mixed with solvent-oil solution. The solvent was recovered by vacuum distillation. The yield of oil was calculated on the basis of initial mass of used oil taken.

To determine optimum conditions solvent-oil ratio, temperature and settling time were varied.

1.3 Decolourization/Adsorption

The extracted oil was decolourized by passing through adsorbent filled column. Types and particle size of adsorbent, adsorbent to oil ratio, types of solvent and solvent to oil ratio through column were varied.

The solvent-oil solution was distilled under vacuum and the recovered oil was dried in a vacuum dryer.

1.4 Analysis of Used, Extracted and Adsorbed Oil

Total Base Number (TBN), Total Acid Number (TAN), carbon residue, viscosities at 40 and 100°C were determined according to ASTM D 2896, D 974, D 189 and D 445 respectively. Colour was found using Lovibond (D 1500) and flash point by Cleveland Open Cup (D 92).

2 RESULTS AND DISCUSSION

2.1 Selection of Solvent

The solvents were selected according to Burrell's classification *i.e.* solvents with high capacity (alcohols), moderate capacity (ketones) and low capacity (hydrocarbons). Use of these solvents is based on their capacity to form hydrogen bond [17].

Results indicate that no sludge formation takes place when hydrocarbons and MIBK were used. 2-butanol formed two liquid phases at room temperature (35°C) after 24 hours settling. Efficiency for sludge removal capability of 1-butanol, MEK and 1-hexanol is 1st, 2nd and 3rd respectively Figure 1. This is in agreement with the findings of Onukwli *et al.* [18] and Alves dos Reis and Jeromino [19].

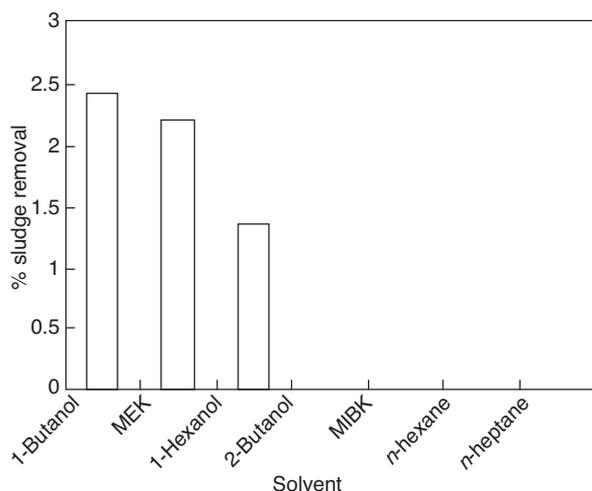


Figure 1

Sludge removal efficiency of solvents from used lubricating oil after 24 hour settling at room temperature (35°C) and solvent to oil ratio 3:1.

Used lubricating oil is a complex mixture of recoverable base oil, polymeric additives, water, light hydrocarbons, metals and carbonaceous particles. A good extraction-flocculation solvent should dissolve base oil and precipitate other substances to form sludge. 1-butanol, MEK and 1-hexanol behave as efficient extraction-flocculation solvents for used oil due to their good solubility parameters for base oil and good antisolvent effect for nonpolar or slightly polar polymeric additives, metals and carbonaceous particles.

On comparing properties of used and extracted oil (Table 1) it is clear that specific gravity, carbon residue and % yield decrease with increasing sludge formation capabilities

of solvents. The same trend is present in viscosity values at 40 and 100°C. Lowering of viscosity index (VI) value indicates that the solvents precipitate out the non-metallic polymeric VI improvers. 1-butanol has the best performance to remove these additives while MEK has the least. Sulphated ash value shows the presence of metallic impurities which is reduced by 45-55% in extracted oil. Total base number of oil extracted by 1-butanol and MEK is nil showing that complete removal of basic character constituents (amino compounds, salts of weak acids, basic salts of poly-acidic bases, and salts of heavy metals). Using 1-hexanol the base number is reduced by almost half present in used oil. Total acid number is also reduced significantly indicating that organic and inorganic acids, esters, phenolic compounds, lactones; resins etc. have been separated out satisfactorily. The used oil contains traces of fuel which lowers the flash point. The increased flash point is an indication that the extracted oil is free of fuel and solvent.

Due to low cost and low boiling point and ease of recovery, MEK was chosen for further study.

2.2 Effect of Settling Time

Amount of sludge removal increases by increasing settling time. Rate of settling was maximum during initial 12 hours. However it continued up to 24 hours. Impurities aggregate and form sludge which sediments out. Further increase in time has negligible effect on sludge settling (Fig. 2).

2.3 Sludge Formation as a Function of Temperature and Solvent / Oil Ratio

Amount of sludge removal increases by increasing solvent to oil ratio and by decreasing temperature as indicated in Figure 3. Sludge formation remains independent of solvent to oil

TABLE 1
Properties of used and solvent extracted oil at 35°C at solvent to oil ratio 3:1 after 24 hours settling

Property	Used oil	Extracted oil using		
		1-butanol	MEK	1-hexanol
Specific gravity at 35°C	0.887	0.884	0.885	0.886
Viscosity at 40°C (cst)	104.75	65.2	71.5	72.5
Viscosity at 100°C (cst)	13.94	8.72	9.59	9.67
Viscosity index	128	113.6	119	118.6
Sulphated ash (wt%)	0.9	0.4	0.4	0.49
Total base number (mg HCl/g oil)	4.64	Nil	Nil	2.41
Total acid number (mg KOH/g oil)	2.07	1.41	1.2	1.35
Carbon residue (wt%)	1.724	0.91	0.93	0.98
Colour (ASTM D 1500)	> 8	> 8	> 8	> 8
Flash point (°C)	190	214	220	212
Yield (%)	-	97.3	97.6	98.4

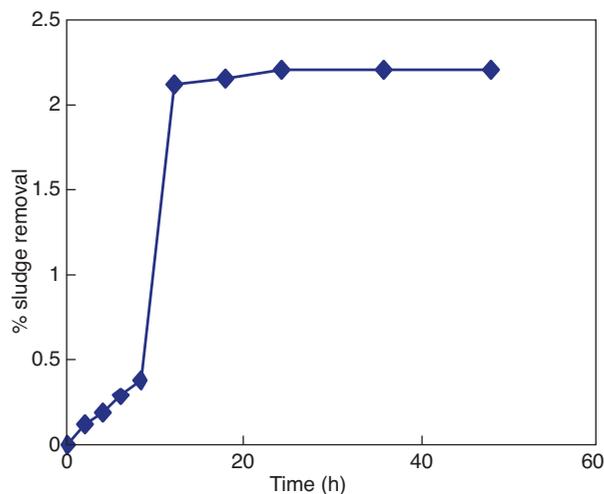


Figure 2
Effect of settling time on sludge removal by MEK at 35°C and solvent to oil ratio 3:1.

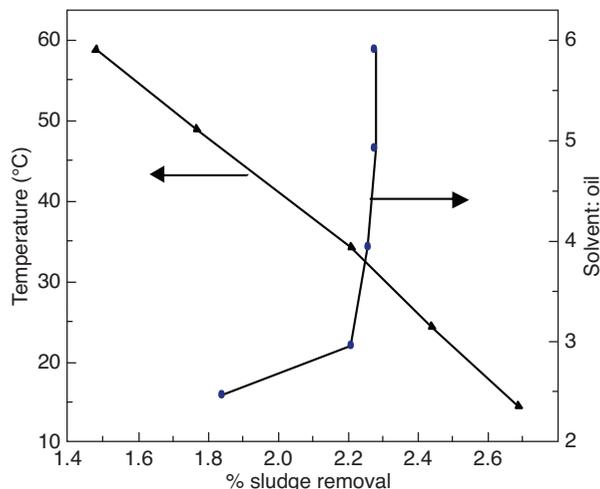


Figure 3
Sludge formation as a function of temperature and solvent to oil ratio after 24 hours settling.

ratio greater than 3:1 which continues to increase with decreasing temperature. The point of intersection of both trends shows that the optimum solvent to oil ratio and temperature are about 3.8 and 33°C respectively for sludge settling without centrifugation. However, critical clarifying ratio (CCR) for MEK has been reported as 2.6 at 35°C [19] with minimum oil remaining in sludge [20]. Perhaps the difference is due to free sedimentation instead of centrifugation.

At lower solvent to oil ratio, solvent becomes saturated by base oil resulting in reduced oil recovery while at higher solvent/oil ratio maximum oil could be extracted and oil free sludge is obtained. With increasing temperature, not only the oil yield but also the solubility of sludge in solvent goes on increasing which results in oil of poorer quality with reduced sludge formation. This coincides with the findings of Jesusa *et al.* [21] and Alves dos Reis and Jeromino (1988) respectively.

2.4 Decolourization/Adsorption

Column chromatography technique was used to decolourize the dark coloured MEK-extracted oil. In this regard, different variables such as, type and particle size of sorbent, activation temperature and duration, loss of sorbent mass on heating, type of eluting solvent and elution time were studied to obtain good quality oil with maximum yield.

2.5 Choice of Sorbent

Effect of two well known sorbents alumina and silica gel and possible use of indigenous magnesite rock for decolourization

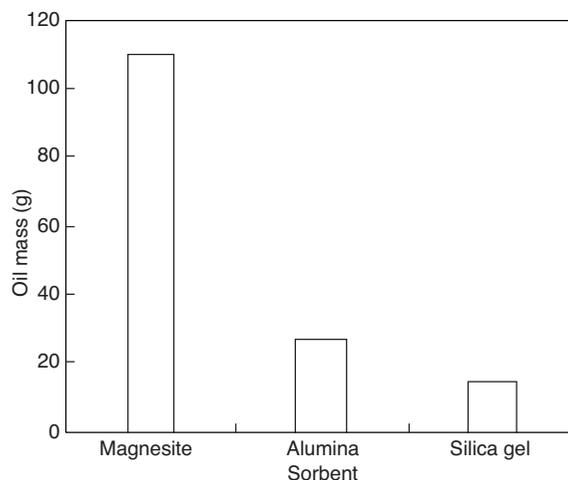


Figure 4
Mass of oil passed over 100 g of different sorbents. (Particle size 70-230, solvent/oil 3:1, elution time 1 h).

of extracted oil were studied. *n*-hexane was used as an eluting solvent. Alumina and silica gel both are porous materials with active surface which have ability to adsorb different colouring substances [22]. Magnesite rock attains similar property on heating to 500°C.

Figure 4 compares the decolourizing capability of these sorbents. Magnesite gave the best result, decolourizing the maximum amount of extracted oil to pale yellow (C.I. yellow 2). The column was then eluted with isopropanol, a highly polar solvent. Evaporation of the solvent under

vacuum gave a coloured, sticky and gummy material. A mixture of high molecular mass polymeric additives and resinous compounds which did not settle out completely during flocculation and sedimentation process was obtained.

Surface area of magnesite (100-150 m²/g) is smaller than the surface area of alumina (300-350 m²/g) and silica gel (750-800 m²/g). Alumina and silica gel are unable to absorb the resinous material and it soon starts to elute, while magnesite because of its bigger pore size can trap the colouring material. This results in decolourized product. However when the loading is increased to 110 g of oil / 100 g of sorbent the magnesite becomes saturated with colouring material.

Due to low cost, easy availability in all particle size and the best adsorbing performance, magnesite was chosen as sorbent for further study.

2.6 Comparison of Solvent

Elution was carried with three solvents of different polarities *n*-hexane (non-polar), benzene (less polar) and MEK (intermediate polar).

n-hexane can reduce colour to a very low level at lower loading of extracted oil. With increased loading its performance was still better than others. However it failed to decolourize when 100 g of extracted oil was introduced on 100 g of sorbent. MEK's performance remained constant over wide variation of extracted oil loading Figure 5.

Saturated hydrocarbons being less polar than other constituents of oil, will have less affinity for the stationary phase and elute first when hexane (polarity 0.0) is used. However on increasing amount of oil the stationary phase is overloaded and saturates together with other components

pass out partially absorbed thereby increasing the colour index. As a general rule, high polar solutes are held strongly with adsorbent which can be eluted by high polar solvent [23]. When the oil is eluted with benzene (polarity 0.32) the colour of resulting oil deepens without increase in yield. Using MEK (polarity 0.51) the colour further deepens and the yield slightly increases as some polar compounds are also eluted.

On comparing properties of extracted and recovered oil (Table 2) it is clear that column chromatography is a good technique for the removal of impurities from extracted oil which enhances desired properties for quality lubricating oil. *n*-hexane qualifies first with respect to specific gravity, viscosity index, sulphated ash, and carbon residue and colour index. Benzene and MEK also give satisfactory results.

Since *n*-hexane is a low cost and low boiling point solvent and also gives better result especially up to moderate loading so it was chosen as an eluting solvent for further study. The oil loading was restricted to 75 g per 100 g of sorbent.

2.7 Elution Time versus Sorbent Amount

In this study, magnesite was used as a sorbent for adsorption of extracted oil. On activation at 500°C for 1, 2 and 3 hours; % mass lost was 26.5 ± 1, 39.5 ± 1 and 49.5 ± 1 respectively. Evolution of water due to heating increases the surface area of magnesite which leads to the development of micro pores. The efficiency of magnesite as colour absorbing material increases accordingly.

Oil loading could also be increased by increasing residence time of eluting material. This effect is more prominent for solid activated for 3 hours Figure 6.

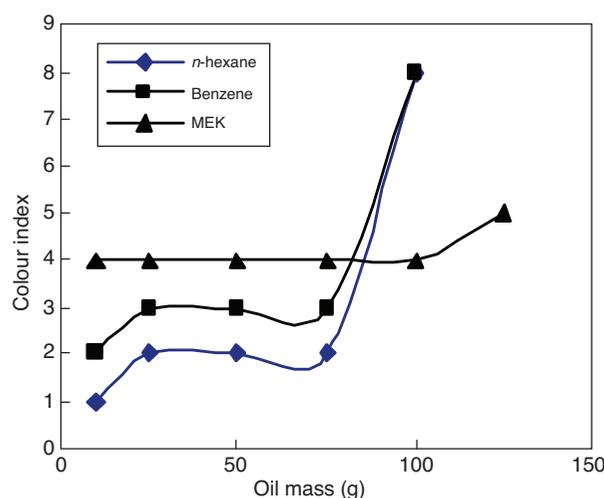


Figure 5

Mass of oil adsorbed using different solvents over 100 g of sorbent. (Particle size 50-100, solvent/oil 3:1, elution time 1 h).

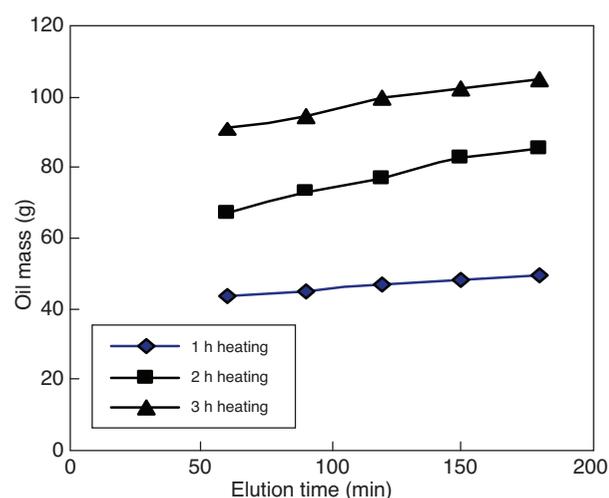


Figure 6

Mass of extracted oil passed over 100 g of magnesite (50-100 mesh).

TABLE 2
Properties of recovered oil by column chromatography using different solvents as mobile phase,
solvent to oil ratio is 3:1

Property	Extracted oil using MEK	Recovered oil by column chromatography using		
		<i>n</i> -hexane	Benzene	MEK
Specific gravity at 35°C	0.885	0.875	0.881	0.881
Viscosity at 40°C (cst)	71.5	67.55	67.02	66.85
Viscosity at 100°C (cst)	9.59	8.53	8.37	8.42
Viscosity index	119	104	101	104
Sulphated ash (wt%)	0.4	0.014	0.018	0.022
Total base number (mg HCl/g oil)	Nil	Nil	Nil	Nil
Total acid number (mg KOH/g oil)	1.2	Nil	Nil	Nil
Carbon residue (wt%)	0.93	0.14	0.142	0.146
Colour (ASTM D 1500)	>8	2	3	4
Flash point (°C)	220	216	216	218
Yield (%)	97.6	95	95	96

2.8 Effect of Particle Size

Particle size of a sorbent is an important factor of column chromatography. Four different particle sizes were tested. Smaller particle size gives larger surface area which favours larger amount of material to be adsorbed. Hence with larger particle size the loading of oil is very restricted due to voids and uneven packing. Figure 7 indicates that 100-230 mesh of magnesite gave the best result regarding maximum amount of oil recovered with colour index 2. Particle size smaller than 100-230 choked the column.

Experiments were repeated with industrial grade chemicals and reproducible results were obtained.

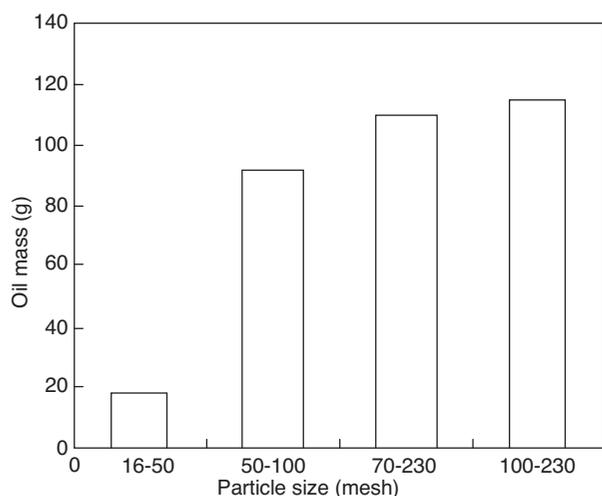


Figure 7

Mass of oil passed over 100 g of sorbent using different particle size.

(Mass lost 49.5±1%, solvent/oil 3:1, elution time 1 h).

CONCLUSION

The findings of this study can be used to recover quality base oil with 94% yield from used lubricating oil. The yield is higher than thin film distillation/clay treatment (70-80%) and KTI as well as Mohawk process (82%) [24, 25]. Some modifications of thin film has claimed 90-95% oil recovery. Moreover these processes are expensive and require skilled operations [24].

Solvent extraction of used oil can be carried out at ambient temperature with cheap and low boiling point solvent MEK. If the sludge is allowed to sediment out the solvent to oil ratio is 3.8 while mechanical centrifuge can reduce this ratio to 2.6 [19]. In the present study to eliminate the use of mechanical centrifuge the ratio has been maintained at 3.8 at which free sedimentation occurs. The sludge from this process can be mixed with asphalt without any problem. It is a better process than the traditional acid/clay treatment which produces an acidic sludge.

Pale yellow oil (colour index 2) is obtained by treating the extracted oil with magnesite, an indigenous cheap rock which is available in varying particle size. Gummy material and residual solvent associated with adsorbent both are incinerated during regeneration of adsorbent at 500°C. The adsorbent could be repeatedly regenerated with reproducible results.

Extraction by MEK followed by adsorption on magnesite using *n*-hexane gives the lowest colour index oil (C.I. 2). This system however uses two solvents and thus require two solvent recovery steps. If both extraction and elution are carried out by MEK it would reduce solvent recovery step to 1. However the oil produced has a colour index of 4.

The present work due to recoverable and cheap solvents and adsorbent could be industrially feasible. This motivates to evaluate costing of the process for future work.

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