

Re-Refining of Spent Lubricants: Single Step Percolation through Activated Adsorbents

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Abstract-This article describes a simple single step process for re-refining spent lubricants involving percolation through activated alumina, magnesite and sodium carbonate. Properties of recovered oil are comparable to that of the properties of commercial base oil. UV and FTIR examinations of the finished oil show minimized amounts of carcinogenic PAH whereas metal content removal is from 94 to nearly 100%. Adsorption through magnesite gives the highest yield about 95%.

Index Terms- adsorption, magnesite, metal content, , PAH, Used lubricating oil.

1 INTRODUCTION

Increase in industrial construction and vehicles have enlarged the production of waste oil. Used lubricating oil is a stable mixture of base oil, broken down additives, oxidation products, metals, C- particles, dirt, water and resins. Despite contamination, a major portion of waste oil may useable after a suitable treatment while improper dumping of the oil causes environmental pollution and loss of valuable resource.

Various methods have been used for recovery of base oil. Acid treatment for the removal of asphaltenic material is one of the oldest techniques. It involves prerefining steps of dehydration, filtration and light hydrocarbon stripping. Acid (sulfuric/ phosphoric/ arsenic) is mixed with the dewatered used oil to extract contaminants in the form of sludge. Finally, the oil is treated with clay for further purification and color improvement. Acidic sludge requires safe disposal [1]. Different grades of base oil have been recovered by distillation technique. Used oil is passed through a number of distillation steps (Atmospheric, vacuum, wiped film etc) after removal of suspended material. This technique is capital oriented and requires large investment [2],[3],[4]. Solvent extraction is a modern technology and being used widely nowadays. It generally involves elimination of water and light hydrocarbons by fractional distillation, sedimentation of additives and contaminants by solvent (butanol, propanol, methyl ethyl ketone etc.), centrifugation for sludge removal, distillation for solvent recovery and hydrogenation or clay treatment for color and odor reduction [5],[6]. In hydrotreatment process, color of used oil is improved by cracking and destroying undesired oxygen, nitrogen, sulfur and chlorine containing compounds at high temperature and pressure in the presence of hydrogen. Cracking of oil is usually a post distillation step, generally adopt to fractionate out the desired product. Clay adsorption step is sometimes used to enhance color and odor more. However, high capital investment makes it less attractive [7]. Use of inorganic and polymeric membranes involves series of centrifuging and high pressure filtering steps to remove metals and contaminants however color improvement is not significant [8]. Adsorption has been used as pre and post rerefining technique in conjunction with other techniques such as solvent extraction, distillation, acid treatment etc. [1],[9].

Present work aims at finding a simple method of rerefining which could eliminate tedious steps contaminants removal from waste oil. This work is based on only adsorption chromatographic technique followed by solvent recovery. In this regard, efficiency of different adsorbents to recover base oil was compared.

2 EXPERIMENTAL

2.1 Materials Used

Waste motor engine oil was collected from various city service stations and stored for several days to settle large suspended material. N-hexane was chosen as an eluent. Adsorbents used were alumina, sodium carbonate and local magnesite rock obtained from the deposit of Muslim Bagh situated in Balochistan, Pakistan. Former two adsorbents and eluent were supplied by E.Merck. Particle sizes of alumina, sodium carbonate and magnesite were 70-230, 140-270 and 100-230 mesh respectively obtained by sieve analysis.

2.2 Adsorption Process

Activated adsorbent was taken in a glass column for adsorption of used oil. Activation was carried out in an oven / furnace at particular temperature and duration (Table. 1). Adsorbent bed was soaked by n-hexane followed by used oil-eluent solution for adsorption. Oil to eluent ratio was 1:2. Adsorbent bed was washed by n-hexane after complete run of oil solution. Recovered oil and washings were collected in a flask. Solvent was separated from oil through vacuum distillation and traces of solvent were

removed by under vacuum drying. Recovered oil yield was calculated on the basis of initial mass of waste lubricating oil taken for adsorption.

2.3 Analysis of Used and Recovered Oil

Specific gravity, viscosities at 40 and 100 °C, Total Acid Number (TAN), Total Base Number (TBN), sulfated ash, Conradson carbon residue were determined by ASTM D 1480, D 445, D 974, D 2896, D 874 and D 189 respectively. Flash point was found by Cleveland Open Cup (D 92) and Color by Lovibond apparatus (D 1500).

Quantitative determination of metals was carried out through Atomic Emission Spectroscopy (ASTM D 6595). Comparison of oxidation / degradation products and polynuclear aromatics present in oils (before and after adsorption) was done through FTIR (ASTM E-2412-0) and UV spectroscopy (UV-1601 PC Double beam spectrophotometer).

3 RESULTS AND DISCUSSION

3.1 Selection of Adsorbent

Lubricating oils are the blend of base oil and additives. Degradation products are generated at engine temperature by full or partial pyrolysis of various compounds [10]. Alumina, magnesite and sodium carbonate have different polarity, were chosen to separate additives (remaining) and degradation products from base oil.

3.2 Alumina

Alumina consists of parallel layers of aluminum and oxygen ions having water under normal conditions. At high temperature, hydroxyl groups are generated having strong electrostatic field and alumina becomes polar. It is used to separate polar molecules from a mixture [11]. It has been used as guard bed prior to hydrotreatment for the removal of halides, trace phosphorous and residual sludge from dewatered and defueled distilled feed of used oil in re-refining [2]. It has also been used as catalytic support in mild hydrogenation of solvent extracted used oil [12]. After treatment of waste oil with acid, it was used as adsorbent to remove ash forming contaminants [1].

3.3 Sodium Carbonate

Sodium carbonate has lower polarity than alumina [13]. It has been used to precipitate metallic and polar compounds and neutralizing agent for acidic compounds in regeneration of used oil [14],[15]. Sludge separation of waste oil has also been done by using a mixture sodium carbonate, rosin, sodium silicate and aluminum sulfate [16]. Its pre re-refining ability was also checked with other bases in base oil extraction through liquid propane [17].

3.4 Magnesite

Magnesite is a mineral containing magnesium carbonate with small quantity of calcium, iron and silicone compounds [18]. It has proved its role in re-refining of solvent extracted used lubricating oil due to the development of porosity on activation at 400-600°C [9],[10].

In this study, separation of all contaminants from used oil in single step was attempted using activated magnesite-ferroan rock as adsorbent through adsorption chromatography. Major constituents of this rock are $(Mg,Fe)CO_3$ and calcite ($CaCO_3$) indicated by M and C respectively in its XRD pattern (Figure 1). Peaks of M are prominent around $2\theta = 33$ (2.749 \AA°), 36 (2.514 \AA°), 43 (2.107 \AA°), 47 (1.941 \AA°), 54 (1.705 \AA°) [19],[20] while peak of C can be seen around $2\theta = 29$ (3.033 \AA°) [21].

4 EFFECT OF ADSORPTION ON CHEMICAL AND PHYSICAL PROPERTIES OF OIL.

4.1 Specific Gravity (ASTM D-1480)

Specific gravity of lubricating oils lies in the range of 0.85-0.9 at 60 °F/ 60 °F (¹⁰). Contaminants in used oil include carbon, gummy resinous materials, aromatics and degradation products cause to increase specific gravity of oil. All three adsorbents improve specific gravity of used oil (Figure 2) resulting removal of such impurities during adsorption.

4.2 Color Index (ASTM D-1500)

Lubricating and base oils both are transparent and their color may vary with composition. Used oils are opaque and dark brown or black. Figure 2 shows that alumina and magnesite both have a good tendency to reduce used oil color up to a significant level. Sodium carbonate fails to remove coloring matter during adsorption.

4.3 Total Acid Number TAN (ASTM D-974)

Used oils have high TAN value due to the presence of some acidic natured compounds (phenols, acids, lactones, resins and esters etc.) generated by oxidation and degradation of base oil constituents and additives. Figure 2 indicates that alumina and magnesite remove completely such material from used oil while sodium carbonate is also capable to minimize a considerable level.

4.4 Total Base Number TBN (ASTM D-2896)

Role of alumina and magnesite in separating salts of weak acids and poly acidic bases from used lubricating oil is looking excellent than the role of sodium carbonate as adsorbent (Figure 2).

4.5 Sulfated Ash (ASTM D-874)

Metals found in used oil, which come from wear of metallic engine parts and decomposition of additives, form sulfated ash on reacting with sulfuric acid. Alumina and magnesite have similar capability to remove such metals completely from used oil during adsorption than the third adsorbent (Figure 2).

4.6 Carbon Residue (ASTM D-189)

This is the determination of carbon amount left after pyrolytic evaporation of oil. It indicates coke-forming tendency of oil due to carbon particles, polymers, fuel and aromatics present in used oil. Figure 2 is showing that all three adsorbents minimize carbon residue from used oil up to the acceptable limit [22].

4.7 Viscosity (ASTM D-445)

Measurement of internal resistance of fluid to flow is viscosity depending upon temperature. Viscosity Index Improvers are the polymeric gummy materials added to stabilize viscosity of lubricating oils at higher temperature. These materials may be present after a long run of lubricating oil in engine. Decrease in viscosity values at 40 and 100 °C show effective removal of these materials by all three adsorbents (Figure 3).

4.8 Flash Point (ASTM D-92)

Oxidation and leakage of fuel can bring in lighter compounds in used oil. Presence of these compounds lowers the flash point. All the three adsorbents improved flash point at different levels shown in Figure 3.

5 METAL ANALYSIS (ASTM D-6595)

Atomic Emission Spectroscopy is used for quantitative determination of metals in oil. Iron, chromium, copper may be added in oil due to engine parts wear [23]. Lead may incorporate from leakage of lead containing gasoline during piston blow out in engine. Degradation of lubricating oil additives (antioxidant, antiwear, antirust, antifoaming) may include copper, zinc, sodium, magnesium, calcium, phosphorous and silicone in oil during engine running [23] resulting gradual loss in lubricating ability. Table 2 indicates that alumina and magnesite have removed such metals nearly 100% while efficiency of sodium carbonate is also better which removes over 94% of these metals.

6 SPECTRAL ANALYSIS

6.1 UV Spectroscopy

During service, polynuclear aromatics (PNAs) are generated during combustion and mixed with crankcase oil having carcinogenic and toxic nature. About sixteen different types of PNAs consisting of 2-7 rings of aromatic hydrocarbon have been reported [24]. Characteristic wavelength of different PNAs in UV region is presented in Table 3.

Beer-Lambert's law states a direct relationship between absorbance and concentration of a substance present in a sample. UV spectrum of used oil is present at the highest level in Figure 6 proving the largest concentration of PNAs. Adsorbed oil by alumina is showing the least amount of PNAs due to the lowest absorbance level. Magnesite and sodium carbonate both perform satisfactorily role in separating PNAs from used oil. Role of magnesite looks better than sodium carbonate.

6.2 FTIR Spectroscopy (ASTM E-2412-0)

Lubricating oil contains a variety of additives for fulfilling requirement of a particular service. These additives may be antioxidant (aromatic amines), viscosity modifiers (poly methacrylate), dispersant (succinimide), detergents (calcium sulfonate) and antiwear (zinc dithiophosphate). They generate a number of carbonyl group containing compounds (aldehydes, esters, ketones and carboxylic acids) on their degradation / oxidation and mixing with deteriorated oil in engine atmosphere [25]. Such compounds can be identified by ASTM method E-2412-0 using Fourier Transform Infra Red Spectroscopy (FTIR). It is based on the fact that particular functional groups absorb energy in specific mid infra red region and permit their identification [26].

Aromatics, additives and oxidized compounds have been identified in 600- 1300 cm^{-1} and 1500-2000 cm^{-1} regions. Peaks of aromatics and additives overlap in these regions however aromatics are prominent in 650-784 cm^{-1} and 1510-1600 cm^{-1} ranges [26],[27],[28]. Carbonyl oxidation products are identified in 1500-1900 cm^{-1} region [29]. Bands at 1154, 1169 and 1731 cm^{-1} are referred to poly methacrylate; bands at 1231, 1708, 1773 cm^{-1} have been identified as succinimide. Stretching bands of zinc dithiophosphate are obtained at 655 and 975 cm^{-1} and calcium magnesium sulfonate is recognized at 1061, 1076 and 3500 cm^{-1} [26],[27],[28].

FTIR spectra of used (UO) and different recovered oils (ARO, MRO and SCRO) present in Figures 4. Reduction in

concentration of these compounds is the inverse function of % transmittance of IR. Significant reduction in concentration of aromatics at 1527.7, 1592.5 cm^{-1} and of carbonyl compounds at 1665.6, 1761.8, 1814.8, 1856.2 and 1882.9 cm^{-1} can be observed by spectra of all recovered oils. Poly methacrylate (1731 cm^{-1}) and dispersant (1773 cm^{-1}) are removed completely by alumina (ARO) and sodium carbonate (SCRO). However magnesite (MRO) also reduces the concentration of such compounds during chromatographic adsorption.

These FTIR spectra explain that all three adsorbents take part in reducing the concentration of additives, aromatics and oxidized compounds. Sodium carbonate and alumina have similar capacity and their performance is better than ability of magnesite. However, magnesite is also efficient to reduce concentration of these compounds.

7 CONCLUSION

Recent trends in rerefining involve removal of contaminants by filtration, centrifugation, solvent extraction and distillation [9],[10],[26],[30]. Most of the techniques use decolourization as the final step. This article gives a complete rerefining of used lubricating oil by single step including decolourization through adsorption chromatography without the generation of any hazardous by-product such as sludge.

This rerefining process produces encouraging results of recovered oil regarding properties of commercial base oils. All the three adsorbents bring a drastic change in specific gravity, sulfated ash, carbon residue, TAN and TBN, metal content of used oil which are comparable with the properties of base oil. Color is highly improved by using alumina and magnesite. Physical and chemical properties of sodium carbonate recovered oil are poorer than the oils obtained by the other two adsorbents. FTIR and UV spectral analyses show that all adsorbents have effectively reduced PNAs and degradation/oxidation products, however performance of sodium carbonate is better in removing degradation or oxidation products while its aromatics removal and metal reduction capability is the least.

Oil recovery through magnesite adsorption is 95% as compared to the yield through alumina (86%). Magnesite is locally available rock that may be preferred for rerefining of used lubricating oil over imported and expensive alumina.

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TABLE 1

Variables of adsorption

	Alumina	Sodium Carbonate	Magnesite
Particle size (mesh)	70-230	140-270	100-230
Adsorbent to oil ratio (w/w)	10:1	10:2	10:2.5
Activation temperature (°C)	105	105	500
Activation duration (min.)	30	30	120
Mass loss on activation (%)	2.15	1.14	12.6
Eluent	n-hexane	n-hexane	n-hexane

TABLE 2

Comparison of metals in used and recovered oils

Metals	Used Oil	Recovered Oil by column chromatography using		
		Alumina	Sodium Carbonate	Magnesite
	(UO)	(ARO)	(SCRO)	(MRO)
Pb	7	0	0	0
V	2	0	0	0
Fe	74	0	23	0
Cr	27	0	1	0
Cu	38	0	12	0
Al	23	0	3	0
Si	19	6	6	2
Zn	60	0	29	0
Na	32	1	96	3
Mg	565	0	80	0
Ca	2000	0	75	0
P	621	0	106	0
Total (mg/Kg)	7480	7	431	5
Reduction (%)		99.9064	94.2379	99.9331

TABLE 3

Aromatics	UV Absorptive Region (73, 85-86) nm
Mono Aromatics	215-270
Di Aromatics	226-230, 275, 285
Tri Aromatics	248, 255
Tetra Aromatics	265
Poly nuclear Aromatics	300-350

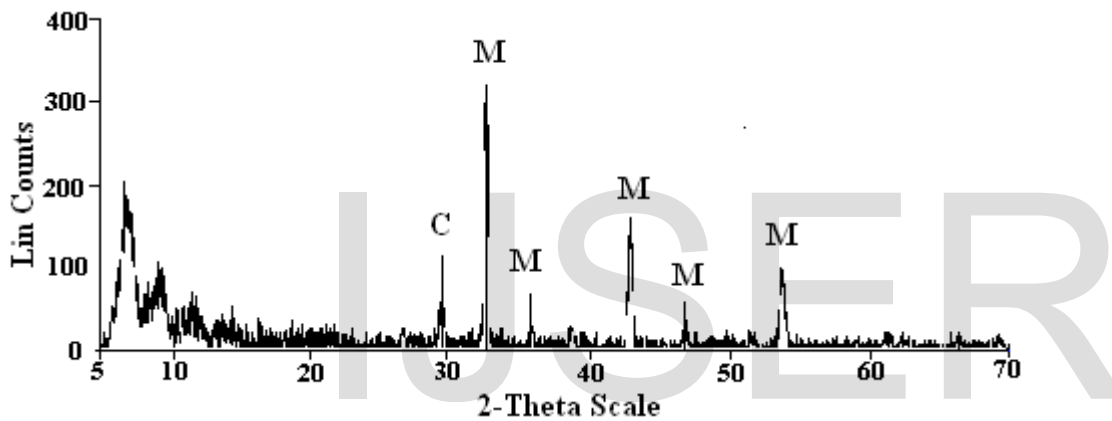


FIGURE 1: XRD of magnesite-ferroan rock (M: magnesite and C: calcite)

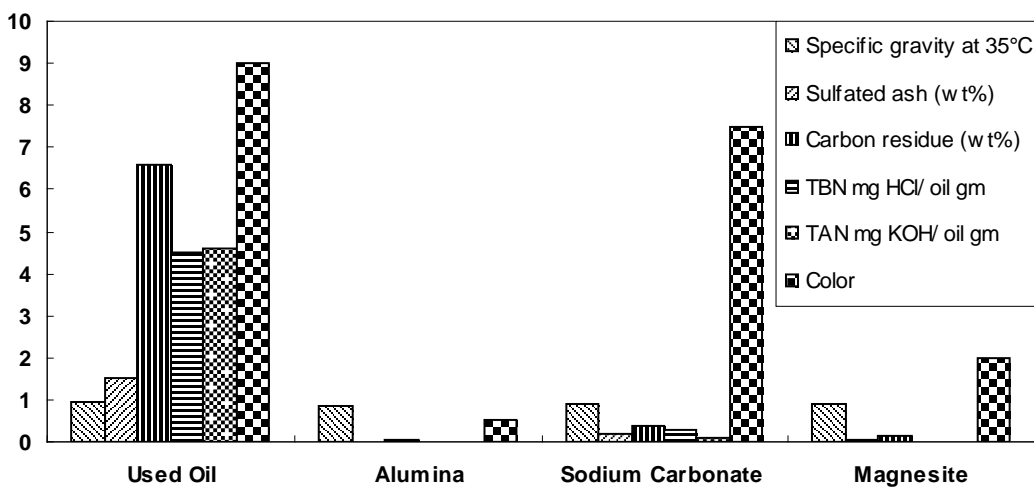


FIGURE 2: Comparison of properties of used and recovered oils obtained using adsorbents (alumina, sodium carbonate and magnesite)

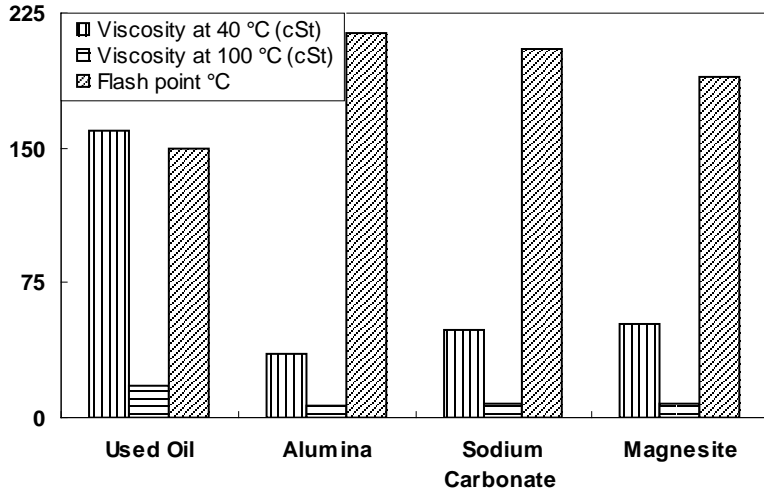


FIGURE 3: Comparison of viscosity and flash point of used oil with recovered oils obtained using adsorbents (alumina, sodium carbonate and magnesite)

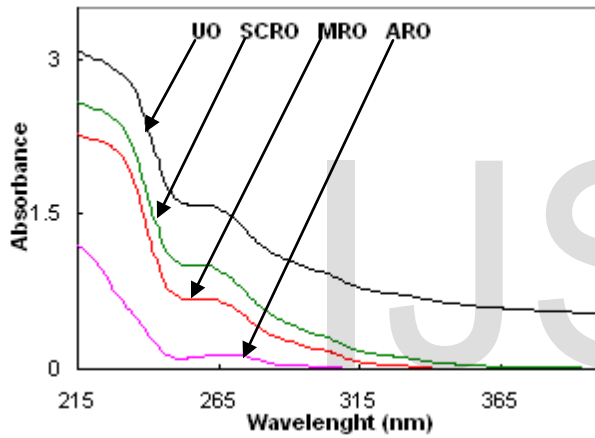


FIGURE 4: Comparison of used oil (UO) UV spectrum with spectra of recovered oils obtained using adsorbents sodium carbonate (SCRO), magnesite (MRO) and alumina (ARO).

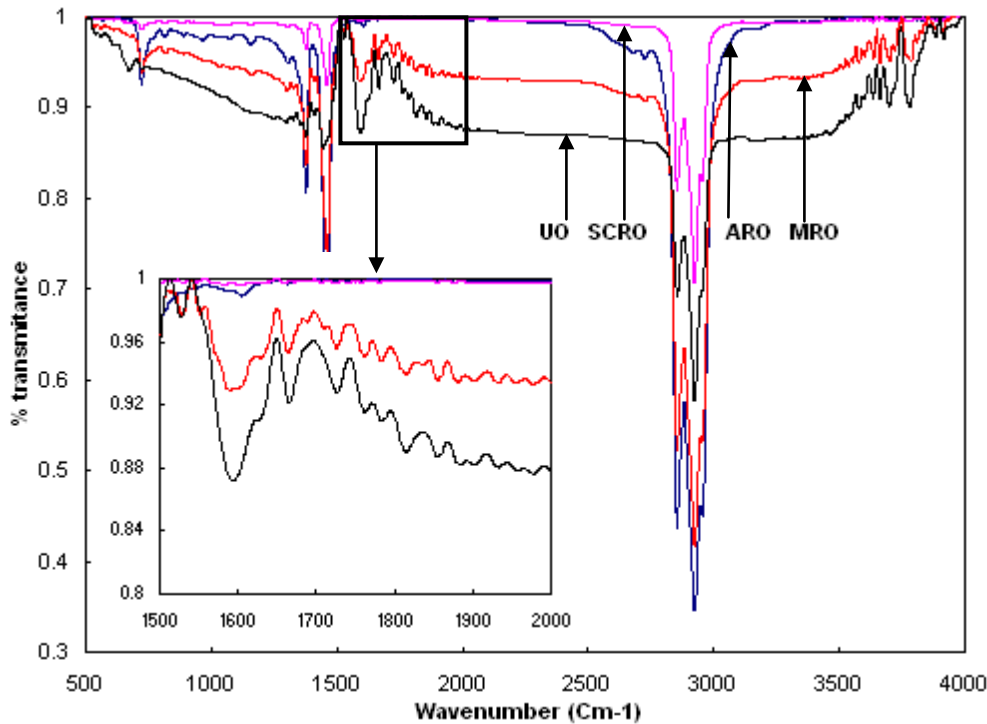


FIGURE 4: Comparison of used oil (UO) FTIR spectrum with spectra of recovered oils obtained using adsorbents sodium carbonate (SCRO), magnesite (MRO) and alumina (ARO).

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