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Refining and Characterization of Car Engine Used / Unused Lubricating Oil

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Abstract

Present research work deals with refining of car engine used lubricating oil into base oil by solvent extraction using hexane and ethyl acetate. The extracted oil was further diluted by making various solvents to extract oil ratios, to determine the physiochemical parameters such as acid values, viscosity, specific gravity and refractive index. Percent sludge removal (PSR) and percent oil loss (POL) was calculated for determining the performance of the extraction process and quality of re-refined oil. Fourier Transform InfraRed (FTIR) analysis has also been done to study the changes in used and unused car engine lubricating oil.

Key Words: Refining, Used engine lubricating oil, Physiochemical parameters, Percent sludge removal, Percent oil loss

1. Introduction

Engine performs the most important and central operating mechanism, so in order to protect the engine of a car from breakdown and maintain its performance, they needs to be lubricated [1]. Lubricating oil consist of different number of carbon and hydrogen (20 to 70 carbon atoms per molecule) with highly complex arrangement of straight chains, side chains and five to six membered ring structures, not only serve as friction reducer and wearer by providing thin liquid film between moving surfaces but also use to reduce heat, protect from corrosion and keeps equipment clean [2-3]. They are usually divided into three broad groupings i.e., Paraffinic, Naphthenic and Aromatic. But there is no prominent division exists between these various groupings as many lubricating oil molecules are a combination of the different types of hydrocarbons. As petroleum products are composed of hydrocarbons [2] in which the most important petroleum fraction is lubricating oil that is used in almost all vehicles and machines [4].

Refining which is the most important recycling technology is a process in which substances are purified by removing the non-essential elements from the substance to produce desirable substance. Refining of used lubricant oil extract out all types of pollutants and impurities from used oil to gives valuable products [5].

Used lubricant oil is one of the major cause of environmental pollution as they are hardly biodegradable so hazardous for natural system and it becomes unsuitable for further use due to contaminant's accumulation and chemical changes. The main contaminants are combustion products (water. soot and carbon, lead, and fuel), abrasives (road dust and wear metals) and chemical products (oxidation products and depleted additive remnants) [4].

Number of methods are available for refining like, dehydration, acid treatment [6-7], adsorption [8] and hydro treating [9]. But refining by solvent extraction can produce valuable products or base oil. It is an efficient process because it removes the hazardous components and protect our environment from pollution [10]. Chemical treatment generates acid slug and environmental problems therefore, solvent extraction is adopted frequently for refining of used lubricating oil [5].

Solvent extraction process is mainly inexpensive and carried out for removing sludge, heavy metals and polar organic complexes from the used lubricating oil [11]. The main function of using solvent extraction is to extract the oil and separate the particulate matters, sludge and additives by mixing with solvent which is then recovered by distillation [12]. Several researchers have been carried out to refine the lubricating oil through solvent extraction [13-16].

Refining of used lubricant oil through solvent extraction by using composite solvent such as 2-propanol, 1-butanol and butanone in different proportions with several solvent to oil ratio was investigated by Durrani et al. 12]. Osman et al [4] also studied the extraction by solvent blends {toluene, butanol and ethanol}, {toluene, butanol and ethanol} and {toluene, butanol and isopropanol} and the results interpreted in terms of percent sludge removal (PSR).

The present work based on the refining of used car engine lubricating oil through solvent extraction. For this purpose two organic solvents i.e., hexane and ethyl acetate were used and influence of solvent to oil ratio on PSR and POL was studied. The percent sludge removal (PSR) is an important parameter which shows the quality of re-refined oil. Higher value of percent sludge removal means good quality of re-refined oil. The percent oil loss (POL) is also another important parameter. The lower value of percent oil losses reveals high yield in the extraction process. These two parameters PSR and POL are depends on the solvent type, solvent to oil ratio and temperature of extraction. As the solvent to oil ratio and extraction temperature raised to higher value, PSR was also increased but POL decreased. The better solvents for extraction is the one which has low solubility difference or have high miscibility in oil and gives low percent oil losses. Physical parameters such as density, viscosity, refractive index and acid value have been determined to support the results. FTIR spectroscopy was also used to study the effect of contaminants on functional groups of lubricating car engine oil. In FTIR spectroscopy variations in the oil can be obtained by subtracting the spectrum of the additives and base oil from the spectrum of the used oil sample. These variations in oil cause by additive depletion, buildup of degraded by-products, and contamination. FTIR can also be used to detect the oil aging which is mainly due to oxidation, nitration and sulfation [17].

2. Experimental

The used car engine lubricating oil was collected from various service stations and mixed in a large container to homogenize the sample and kept for 60 min for settlement. Hexane and ethyl acetate of Labscan, 99 % pure were used for the experimental work. Solutions of solvent (hexane or ethyl acetate with water) to use lubricating oil such as 3:1, 5:1, 7:1 and 9:1 were prepared by taking known volume of solvents (hexane or ethyl acetate with water) and used lubricating oil as shown in Table 1.

Table 1: Composition of Solvent to Lubricating Oil and Solvent to Extracted Oil Ratio

Volume of Solvents			
Solvent: Lubricating Oil Ratio (ml/ml)	**Volume of Hexane or Ethyl acetate, (ml)**	**Volume of Aqueous Phase, (ml)**	**Volume of Used Lubricating Oil, (ml)**
3:1	75	75	50
5:1	125	125	50
7:1	175	175	50
9:1	225	225	50

After Extraction		
Solvent: Extracted Oil Ratio (vol/vol)	**Volume of Hexane or Ethyl acetate, (ml)**	**Volume of Extracted Oil, (mL)**
1:1	6	6
2:1	12	6
3:1	18	6
4:1	24	6
5:1	30	6

For this the mixture of solvents (hexane and water) and used lubricating oil was taken in 500mL separating funnel and continuously shaken for 30 min to allow sufficient mixing.

The mixture was allowed to settle at room temperature. After 24 hrs, two layers were formed in which upper layer contain lubricating oil extract in solvent and lower layer contain sludge. The both layers were then separated. Similar procedure was adopted for ethyl acetate as a solvent for extraction. The sludge was mixed again with hexane or ethyl acetate for removing any remaining oil in sludge. The solvent was then separated by vacuum distillation.

Further ratios of solvent to extracted oil such as 1:1, 2:1, 3:1, 4:1 and 5:1 (v/v) were prepared by taking known volume of solvent (hexane or ethyl acetate) and extracted oil as shown in Table1.

The physical parameters of these ratios were also determined like acid value, specific gravity and refractive index to support the results. Acid value (AV) is obtained by taking 10.0 g of oil sample in 25 ml of neutral alcohol then placed in water bath for 10 min and then titrated with standardized 0.1N KOH-ethanolic solution by using phenolphthalein as indicator. AV value represents the number of mg of KOH require to neutralize free fatty acids which are present in 1 ml of oil sample as showed in the formula (18).

$$\text{Acid value} = \frac{56.1 \times N \times V}{\text{Wt of oil sample taken}} \quad (1)$$

Where N is the Normality of KOH solution, V is the volume of KOH(ml) used, 56.1 is the Equivalent weight of KOH. The specific gravities of solvents and solutions were measured at different temperatures with the help of relative density bottle having a capacity of $10cm^3$. Temperature was kept constant by keeping all solutions in a thermostatic water bath for about 10 to 15 min. A weighing balance of Shimadzu, AUW220 was used to measure the weight and refractometer of A KRUSS OPTRONIC were used to measure the refractive index. An Ostwald viscometer (Pyrex made in England, Techiconomial constant 0.05 Cs/s, Capillary 445) was used to measure the viscosities of solvents to extracted lubricating oils. The reproducibility of the results was checked by repeating the measurement three times. FTIR spectrum studies of car engine used/unused lubricating oil were carried out by using FTIR spectroscopy. FTIR spectrometer (Shimadzu, IR Prestige-21, Japan) was used for this purpose by using KBr disk technique. All the samples were oven dried before analysis to avoid the interference of moisture. Samples were prepared by grinding the finely powdered analytical grade KBr and spectra were recorded from 4000 to 400 cm^{-1} at the resolution of $8cm^{-1.}$

3. Results and Discussion

In the present study car engine used lubricating oil was refined and characterized into base oil by solvent extraction using two solvents i.e., hexane and ethyl acetate. To study the changes, FTIR analysis for used and unused car engine lubricating oil has also been done. The extraction process was carried out by making different solvent to oil ratios at room temperature and effective solvent to oil ratios was evaluated. The extracted oil was further diluted by making various solvent to extract oil ratios with the same solvent to determine the physiochemical parameters such as acid value, viscosity, specific gravity and refractive index. The obtained results shows that the acid value (2.8611) specific gravity (0.9317g/cm3) and refractive index (1.49741) of car engine used lubricating oil is greater than the unused lubricating oil (acid value = 1.9635, specific gravity = 0.9317g/cm3, refractive index = 1.46793). Because after using for prolong time lubricating oil become contaminated with saturated compounds, paraffinic sludge, aromatics compounds, metallic fragments, oxidative products, carbon residue, toxic metals and degradation of additives. These contaminants change the physical properties of lubricating oil. FTIR spectrum (Fig.1) also confirmed that for unused lubricating oil low intensities were observed in the peaks as compare to used lubricating oil. Fuel peak at 800cm-1 was observed for unused lubricating oil which was not seen for used lubricating oil.

The effectiveness of extraction process was determined by calculating Percent sludge removal (PSR) and percent oil loss (POL). Percent sludge removal (PSR) [19] and percent oil loses (POL)[12] were calculated by using the formula.

$$PSR = \frac{w(dry\ oil)}{w(oil)} \times 100 \quad (2)$$

$$POL = \frac{w(wet\ oil) - w\ (dry\ oil)}{(w(oil))} \times 100 \quad (3)$$

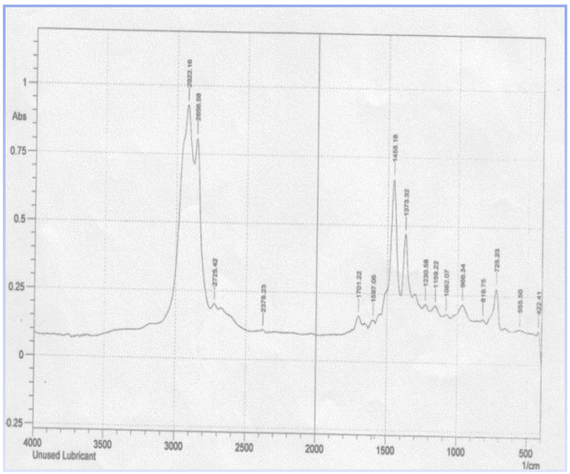
Where w(wet oil)is the weight of wet oil, w(dry oil) is the weight of dry oil and w(oil) is the weight of oil taken. For the sludge was weighed as wet oil ($W_{(oil)}$) then washed with hexane or ethyl acetate and dried in furnace till constant weight to give weighed of dry oil ($W_{(dry\ oil)}$).

Table 2: Physical Properties of Solvent to Lubricating Oil Ratios

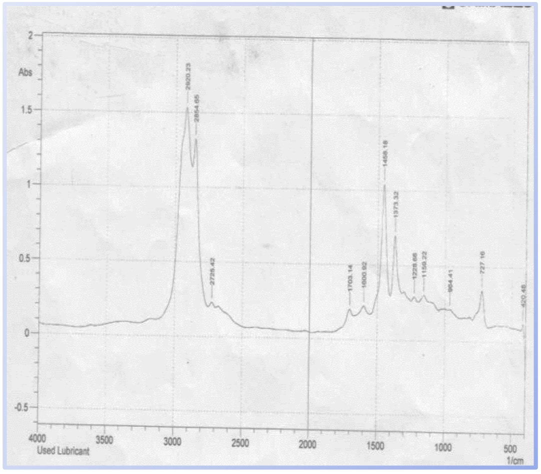
Solvent = Hexane			
Solvent: Lubricating Oil Ratio (vol/vol)	**Acid value**	**Specific Gravity**	**Refractive Index**
3:1	2.1318	1.2372	1.43205
5:1	2.1318	1.2038	1.42432

7:1	2.1318	1.1473	1.40469
9:1	2.0765	1.1305	1.39800
Solvent = Ethyl Acetate			
3:1	2.4684	0.9436	1.43369
5:1	2.5245	0.9439	1.40463
7:1	2.6367	0.9442	1.39481
9:1	2.6928	0.9449	1.39053

Results summarized in Table 2, indicate that in solvent (hexane) to used lubricating oil ratios i.e. 3:1, 5:1, 7:1 and 9:1, constant values were observed for acid value due to the nonpolar nature of n-hexane which solubilizes non polar substances while in ethyl acetate acid value was increased due to solubility of free fatty acids this result also confirmed by FTIR spectrum (Fig 1.) as peaks were observed in 2854, 2920 cm^{-1} which is mainly for CH_2 Stretching (symmetric and asymmetric) and 1458 cm^{-1} is for CH_2 bending. The peaks in the range of 1,660-1,800 cm^{-1} represented the oxidation product formation (17) and absorption bands in the region of 1000-800 cm^{-1} are the characteristic of CH out of plane bending or wagging vibrations of hydrogen atoms attached to unsaturated carbons. Table 2 also represented that in hexane to used lubricating oil ratios i.e. 3:1, 5:1, 7:1 and 9:1, decreased in values of specific gravity and refractive index showed the presence of saturated compounds as well as paraffin compounds [20]. In Ethyl acetate to used lubricating oil ratios i.e. 3:1, 5:1, 7:1 and 9:1, increased in specific gravity was observed showed less saturated compounds at high solvent to oil ratios.



(a)



(b)

Fig. 1: FTIR spectrum of Car engine (a) unused and (b) used Lubricating Oil

Density of hexane is low as compared to ethyl acetate which also effect on solvent to used lubricating oil ratios. Peaks at 1703 and 1701 cm^{-1} for used and unused lubricating oil is due to degradation products of oil which was higher in used lubricating oil than unused oil. These degradation products contain carbonyl group i.e., lactones, esters and carboxylic acids.

Percent sludge removal (PSR) for car engine used lubricating oil is tabulated in Table 3. It was observed that when both hexane or ethyl acetate is used as a solvent the PSR increased with the increase in solvent volume from 3:1, 5;1, 7:1 and 9:1. The increased in percent sludge removal value is due to the decrease in viscosity and specific gravity, which indicates that the increase in settling speed of particles in sludge [13].

Table 3: Effect of Solvent to Lubricating Oil Ratios on Percent Sludge Removal

Solvent: Lubricating Oil Ratio (vol/vol)	Weight of oil, (g)	Weight of dry oil, (g)	PSR, (%)
Solvent = Hexane			
3:1	44.878	36.947	82.33
5:1	44.818	39.468	88.06
7:1	44.585	41.168	92.34
9:1	44.519	42.074	94.51
Solvent = Ethyl Acetate			
3:1	43.079	10.735	24.92
5:1	43.414	11.410	26.28

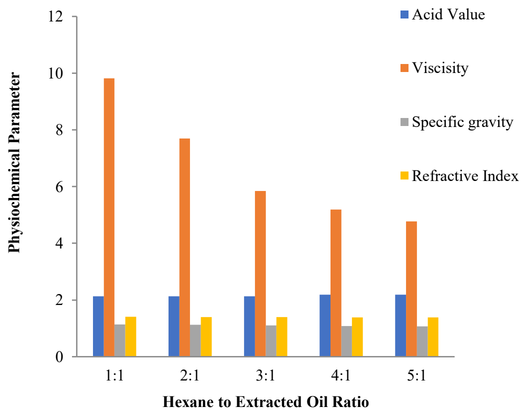
7:1	43.086	11.965	27.75
9:1	44.414	12.462	28.06

Table 4: Effect of Solvent to Lubricating Oil Ratio on Percent Oil Losses

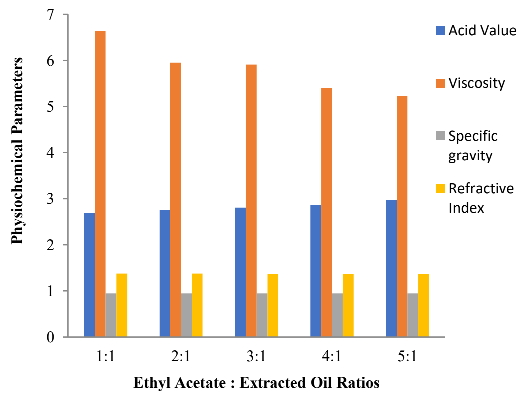
Solvent :Lubricating Oil Ratio (vol/vol)	Weight of oil, (g)	Weight of wet oil, (g)	Weight of dry oil, (g)	POL (%)
Solvent = Hexane				
3:1	44.878	54.943	36.947	40.10
5:1	44.818	59.031	39.468	43.65
7:1	44.585	61.619	41.168	45.87
9:1	44.519	63.78	42.074	48.76
Solvent = Ethyl Acetate				
3:1	43.079	12.025	10.735	2.99
5:1	43.414	13.395	11.41	4.57
7:1	43.086	15.439	11.965	8.06
9:1	44.414	17.636	11.205	14.47

The effect of hexane and ethyl acetate to lubricating oil ratios on POL was also investigated in different solvent to oil ratios such as 3:1, 5:1, 7:1 and 9:1 and shown in Table 4. It was observed that in hexane or ethyl acetate, as the solvent to oil ratio increased, the POL also increased because as the volume of solvent increased, it decrease the medium mutual solubility of oil in solvent which raised the oil losses in sludge phase. The increase in oil losses in sludge phase indicates the lower yield in the process of extraction High yield in the extraction process can be obtained by designing counter current extraction system or by increasing the number of extraction stages [21].

When extracted oils were further diluted by forming hexane: extracted lubricating oil ratios or ethyl acetate: extracted lubricating oil ratios i.e. 1:1, 2:1, 3:1, 4:1 and 5:1 acid value was decreased because of the presence of unsaturated fatty acids in oil as shown in Fig. 2.



(a)



(b)

Fig. 2: Plot of Physiochemical Parameters Versus Solvent (a) hexane (b) ethyl acetate To Extracted Car Oil Ratio

Similarly, decrease in viscosity and specific gravity showed the presence of light fuel contaminants and oxidative products. FTIR spectra (Fig. 1) also confirmed that chances of base oil are more than fuel, as in used lubricating oil no peak was found at 800cm^{-1}. These saturated and aromatic compounds due to the presence of paraffin materials also cause the reduction in refractive index [20, 22].

Peaks for light paraffins were observed in FTIR for unused and used lubricating oil as 1458, 1373 and 725 or 727 cm^{-1} for C-C alkenes, alkanes and alkyl halides respectively. By comparison, it was observed that in hexane high values of PSR and POL were obtained, while in ethyl acetate low values of PSR and POL were attained. As hexane is less polar as compared to ethyl acetate which is able to more interact with light paraffins. So it can be used frequently to extract oil and grease fraction from waste oil, soil and water because it cannot be easily deprotonated. Presence of peaks at 1701 and 1703 cm^{-1} for unused and used lubricating oil also confirmed that lubricating oil having carbonyl group. While ethyl acetate is also commonly used in extractions due to its low cost and low toxicity.

4. Conclusion

Current research work was based on the refining of lubricating used car engine oil, through solvent extraction. Hexane and ethyl acetate were used as a solvent which separate the impurities in the form of sludge in different solvent to oil ratios i.e. 3:1, 5:1, 7:1 and 9:1. In hexane, it was observed that as the solvent to oil ratio increased, high values of percent sludge removal (PSR) and percent oil losses (POL) were obtained. In ethyl acetate it was noticed that with the increase of solvent to oil ratio, low values of percent sludge removal (PSR) and percent oil losses (POL) were obtained as compared to the hexane. FTIR data also supports the observed results.

5. Acknowledgments

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