

# Refining of LUBRICATING OIL by different solvent methods

<sup>1</sup>Manish Mishra, <sup>2</sup>Minaxi B Lohani, <sup>3</sup>Ranvir Singh, <sup>4</sup>D. K. Awasthi, <sup>5</sup>Archana Dixit

<sup>1,2,3,5</sup>Assistant Professor, <sup>4</sup>Professor

<sup>1</sup>S.R. Group of Institution Lucknow U.P. India

<sup>2</sup>Integral University Lucknow U.P. India

<sup>3</sup>C.D.R.I. Lucknow U.P. India

<sup>4</sup>JNMPG College Lucknow U.P. India

<sup>5</sup>D.G.P. G College, Kanpur U.P

**Abstract-** Solvent treating is a widely used method of refining lubricating oils as well as a host of other refinery stocks. Since distillation (fractionation) separates petroleum products into groups only by their boiling-point ranges, impurities may remain. These include organic compounds containing sulfur, nitrogen, and oxygen; inorganic salts and dissolved metals; and soluble salts that were present in the crude feedstock. In addition, kerosene and distillates may have trace amounts of aromatics and naphthenes, and lubricating oil base-stocks may contain wax. Solvent refining processes including solvent extraction and solvent dewaxing usually remove these undesirables at intermediate refining stages or just before sending the product to storage. The refining of lubricating oils from waste lubricating oil was examined utilizing a novel blend of solvent extraction and activated alumina adsorbent. The activity of these solvent extraction blends {toluene, butanol and methanol (A)}, {toluene, butanol and ethanol (B)} and {toluene, butanol and isopropanol (C)} was evaluated experimentally, oil to solvent proportions from 1:1 to 1:3 were analyzed for mixture blend (C). The results confirm solvent mixture (A) gave good efficiency with the highest percent sludge removal. The maximum percent of sludge removal improves with the increase of solvent to oil ratios. The physical properties of the recycle oil were measured. The results show the change in the properties of recycling oil and have good efficiency.

**Keywords:** alumina adsorbent, solvent mixture, recycle oil, lubricating oils

## 1. INTRODUCTION

The most important petroleum fraction is Lubricating oil that is used in almost all vehicles and machines. Lube oils are used to decrease rubbing between surfaces in moving parts. After oxidation, most impurities are generated in base oil, during its application in internal combustion engine. This contamination contains unsaturation, phenolic compound, aldehyde, acidic compound, additive, metals, varnish, gums and other asphaltic compounds originating from the overlay of bearing surfaces and degradation of the base oil components. In spite of impurities, most of the base oil part in the waste oil is not exhausted. The chemical composition of the lubricating oil is usually preserved to a large amount because of the high stability of the heavy compounds contain in the base oil. Used lubricating oils which difficult to handle anthropogenic pollutant due to its toxicity and become undesirable for use. Its transfer strategies of the past, for example, arrive filling, street oiling, dump on the ground diminishes soil efficiency and makes the plants developed on the dirt to be unsatisfactory for food and forage. The recycling of waste oil may be an appropriate and cheap alternative to and burn incineration. Different recycling techniques have been proposed for refining of used lubricating oils. During refining, the chemical, physical and mechanical impurities are removed with the following processes: distillation, acidic refining, clay treatment and hydrogenation. These processes give different yield and product. Solvent extraction followed by adsorption is more effect processes for recycling of waste lubricating oils. It is aimed to conserving natural resources and recovering (rather than destroying) the lubricating oil. This is a mostly attractive cleaner technology. The solvent selected should have a maximum solubility for base oil and minimum for additives carbonaceous. The solvent is then recovered by distillation for recycle reason. The key commitment of this examination is to diminish the percent oil misfortunes utilizing suitable solvent extraction. Different parameters i.e. the proportion of solvent to oil, extraction condition and kind of solvents are also studied.

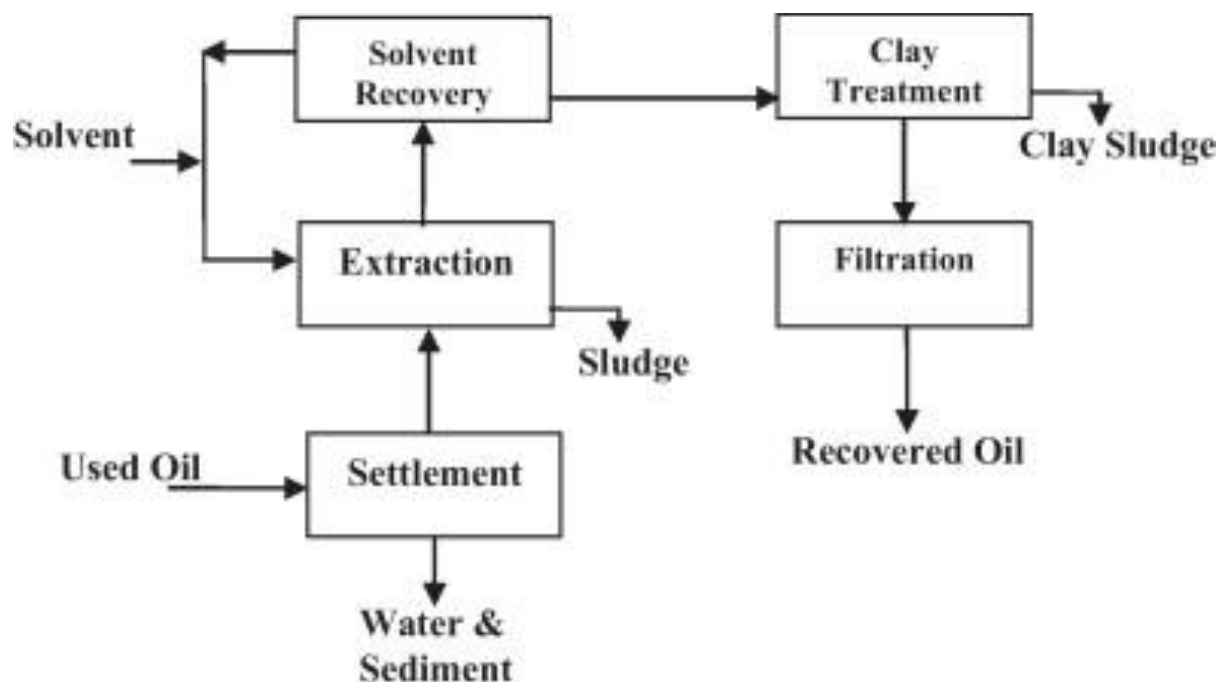
The process of transferring a substance from one solvent to another due to differences in solubility or distribution coefficient between the two immiscible (or slightly soluble) solvents is known as the solvent extraction process. The solvent extraction technique has been considered an effective separation method due to its ease, simplicity, speed, and broad scope. The solvent extraction process is a physical separation method that is used in all conventional lube plants.

The solvent extraction process produces high-quality lubricating oils characterized by good thermal and oxidation stability, light color, and a good additive response. The byproduct extract phase produced in the Solvent Extraction Unit is rich in aromatics and is used as a carbon black feedstock, rubber extender oils, and many other non-lube uses.

In solvent extraction, also known as Liquid-liquid extraction (LLE) or partitioning, a mixture of two components treats with a solvent that preferably dissolves one or more of the components in the mixture. The raffinate is the treated mixture and the desired product, while the solvent-rich phase is the extract. The solute is the component transferred from the raffinate to the extract, while the diluent is the component left behind in the raffinate. The solvent in the extract that leaves the extractor is usually collected and reused.

The feeds to the Solvent Extraction unit are vacuum distillate cuts such as spindle, light neutral, intermediate neutral, heavy neutrals, and bright stock which is produced from the propane deasphalting of vacuum residue.

These feeds are suitable for the production of LOBS (Lube Oil Base Stock). The finished lube oils are obtained by blending metallic soaps and additives along with the lube oil base stocks. More than half the lube oil supply today comes from these solvent processes.



The conventional method for improving the viscosity index of the oil is solvent extraction, which involves partially removing the aromatic hydrocarbons, which are high-viscosity and low-viscosity index components. The solvent extraction process also removes undesirable components such as compounds containing heteroatoms such as oxygen, nitrogen, and sulfur, present in vacuum distillates and residual stocks.

Many refineries also use the solvent extraction process also known as the solvent refining process to manufacture lubricants and petrochemical units used to recover propylene, benzene, toluene, and xylenes for further processing into polymers.

## Experimental

### *Solvents for Solvent Extraction Process*

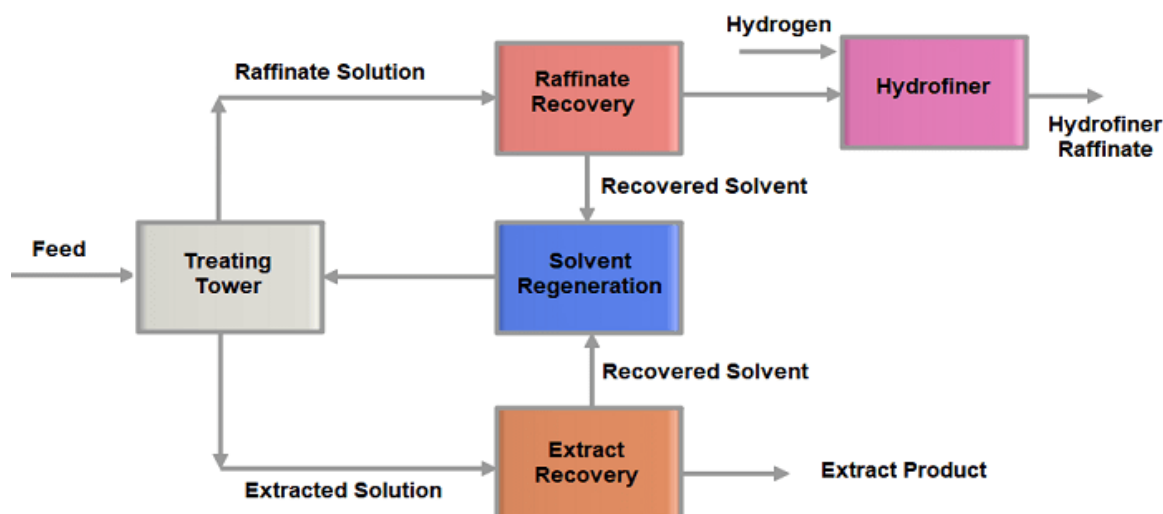
Solvents such as phenol, furfural, and nitromethyl pyrrolidone (NMP) are often utilized in refineries. These solvents have a strong affinity for aromatic hydrocarbons, which dissolve and generate a distinct layer or phase known as an extract. The processed feedstock, the pollutants present, and the finished product requirements all affect the selection of specific processes and chemical agents. Solvent needs to be available at a reasonable price, safe for the environment, and non-corrosive to construction materials.

Properties	Phenol	Furfural	Nitro-Methyl Pyrrolidone (NMP)
Molecular Formula	C <sub>6</sub> H <sub>6</sub> O	C <sub>5</sub> H <sub>4</sub> O <sub>2</sub>	C <sub>5</sub> H <sub>9</sub> NO
Specific Heat (at 130 °F/54 °C)	0.56	0.42	0.47
Boiling point (at 1 ATM)	359 °F/182 °C	323 °F/162 °C	399 °F/204 °C
(Flash Point)	(175 °F/80 °C)	(137 °F/58 °C)	(187 °F/86 °C)
Latent Heat BTU/Lb	206	194	187
Specific Gravity (at 20 °C)	1.07	1.16	1.03
Molecular Weight	94.1	96	99.1
Melting Point	105.6 °F/40 °C	-37 °F/-38 °C	-11.6 °F/-82 °C
Toxicity	High	Moderate	Low

**Properties of Solvents Used in Solvent Extraction Process**

### Description of Solvent Extraction Process

The Solvent Extraction Process flow chart is shown below.



**Block Diagram of Solvent Extraction Process**

- The lube feedstock and the solvent are contacted in a trayed column counter currently. There are several types of continuous treater tower designs used in conventional lube plants. These include trayed towers, packed towers, and rotating disk contactors. The treater tower internals are designed to promote contact and separation of the oil and the solvent phases
- The uprising stream is gradually lean with aromatics and rich with paraffins and other non-aromatics and finally emerges as the raffinate stream from the tower top. Not all of the Aromatics removal is desired from the feed. Therefore, the removal of aromatics is carefully selected based on the required adjustment of the viscosity and viscosity index of the final product.
- The Raffinate stream exits from the top of the tower and is routed to a solvent recovery section for the separation of solvent from this stream. The solvent is separated from the primary raffinate by vacuum flashing and steam stripping under the vacuum.
- The extract stream containing the bulk of the solvent exits the bottom of the extraction tower and is routed to the recovery section for the removal of solvent from this stream. The solvent is separated from the extract phase by multiple effect evaporation at various pressures followed by vacuum flashing and steam stripping under vacuum.
- The overhead vapors from steam, strippers are condensed and combined with solvent condensate from recovery sections and are distilled at low pressure to remove water from the solvent.
- The stripped solvent subsequently undergoes some regeneration to prepare the solvent phase for recycling. The loaded strip solution is then treated to remove the desired product before recycling. One of the essential components of this process is that liquid phases are recovered and recycled wherever possible. Recovery of liquid is significant both economically and environmentally.

### Material

lubricating oil was obtained and collected from EPRI (Egyptian petroleum institute) oil service station. All reagents (purchased from Merck Co., Aldrich, and Fluka chemical Co.) (Toluene, 1-butanol, ethanol, methanol, isopropanol and alumina).

### Procedure

The used oil is subjected to filtration before treatment. This was done using a funnel with a filter paper placed in it, and then a vacuum pump was connected to the filtering flask to which the funnel was fixed with the aid of a rubber stopper. 100 ml of used lubricating oil was mixed with a blend comprised of 100 ml of toluene, 100 ml of 1-butanol and 100 ml of methanol in a closed vessel. The whole mixture in a beaker was placed on a magnetic stirrer and stirred for one hour. Then it was allowed to stand for 24 h. The clear surface oily layer containing solvents and oil was transferred to a rotary evaporator in order to separate the solvents from the regenerated lubricating oil. The separated base oil was then mixed with activated alumina at a proportion of 1:5 alumina. The alumina was added to remove the dark color. The same method was employed in the Toluene, 1-butanol, and ethanol and also with Toluene, 1-butanol and isopropanol. The same method was working in the Toluene, 1-butanol, and isopropanol by solvent to oil ratio 1:2 and 1:3

### Results and discussion

Waste oil is a blend of combustion product such as water, fuel, road dust, wear metal and oxidation product which form complex and corrosive organic acids. The latent heat of vaporization is the amount of Vander Waals forces that hold liquid molecules together. An important experimental measurement of the solvent extraction re-refining process is normally represented by the amount of sludge removed from the used oil. This may be expressed as the percent sludge removal (PSR) which is the mass of sludge removed in gram/100 g of used oil.

The experimental results indicate that the more effect for sludge removal capability of solvent mixtures A, B and C as shown in the Table-1, Table-2 It is found that mixture A removed maximum sludge percent (52%) followed by mixture B (36.7%) and

mixture C removed lower percent (18.9%). these attribute to the solubility of the base stock oil in these solvent and their dielectric constant as shown in table-3. The raffinate percent decrease from solvent mixture A followed by solvent mixtures B and C as given in Table-1. The raffinate produced from solvent mixture A is yellow in color because of it free from sludge as shown in Table-1, Table-2

Table-1. Effect of different solvent mixtures on the refining of used oil.

Empty Cell	A	B	C
Raffinate, wt%	46	61.3	82.1
Sludge, wt%	51.6	34.4	17.9
Color, wt%	YELLOWISH	BLACK BROWN	BLACKGRYESH

Table 2. Effect of activated alumina on the raffinates.

Empty Cell	A	B	C
Raffinate, wt%	48	42.8	44
Sludge, wt%	52	57.2	56
Color, wt%	YELLOWISH	PALEYELLOW	LIGHTYELLOW

Table 3. Solubility and dielectric constant of the three solvent mixtures.

Solvent sample	Solubility (j/m3)	Dielectric constant
Toluene + butanol and methanol (A)	22.2	6.984
Toluene + butanol and ethanol (B)	21.2	6.973
Toluene + butanol and iso propanol (C)	21.1	6.962

This result is due to the solubility of solvent mixture A is higher 22.2 (g/m<sup>3</sup>)<sup>1/2</sup> as compared with that of solvent mixture B and C, (21.2 and 21.1 g/m<sup>3</sup>) respectively. Also, the dielectric constant of solvent mixture A is higher than the other solvent mixtures (B and C) as given in Table-3 These results indicate that as chain length of carbon atoms in the solvent and polarity decreases, its ability to eliminate sludge increase, although the solvent become more miscible in the oil as shown in Table-1, Table-2 and Table-3 It is clear that solvent mixture A has higher solubility and dielectric constant. So, has maximum efficiency for sludge removal. Methanol removes the heavy components more than the other two solvent mixtures because of its dielectric constant is higher.

#### 4. Study of solvent–oil ratio

The effect of the solvent–oil ratio on the percent of sludge removal for the solvent mixture at 25 °C was shown in Table-3 and Table-4 It is clear that as the solvent oil ratio increase, the maximum percent sludge removal increase and the raffinate oil decreased. This is because as the oil to solvent proportions increases the medium mutual solubility of the oil in the solvent increase. The more percent of sludge removal means good efficiency of re-refining oil, these process is cheaper than refining stages such as vacuum distillation and finishing stage by alumina adsorption or hydro finishing stage. It is found that the results for 1:3 solvent oil ratio of all inside the requirement of the base stock oil.

Table 4. Effect of solvent: oil ratio on the refining of used oil using solvent mixture C.

Solvent: Oil Ratio	1:1	1:2	1:3
RAFFINATE	80.1	71.1	54.6
SLUDGE	17.9	28.9	42.4
COLOR	BLACK BROWN	BLACK BROWN	BLACK BROWN

Table 5. Effect of activated alumina on the refining for raffinates.

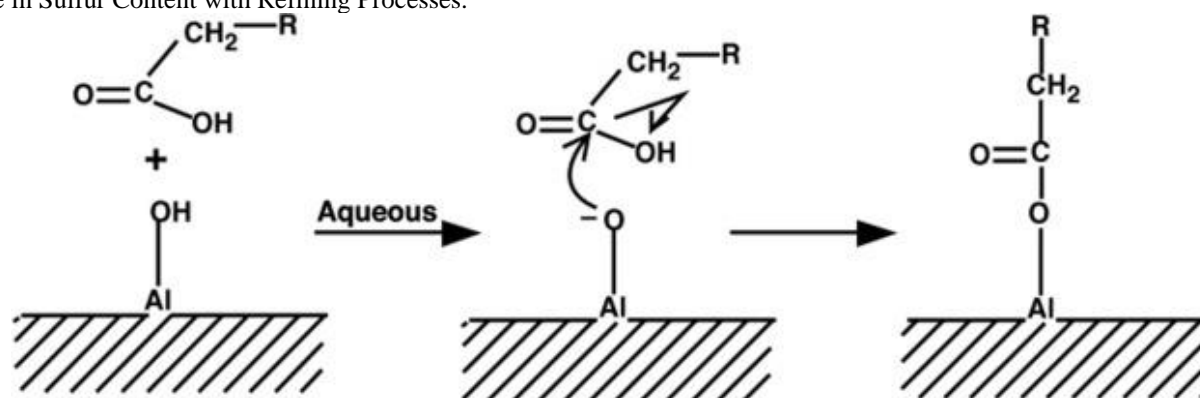
Empty Cell	C1:1	C1:2	C1:3
RAFFINATE	41.3	37.9	36.9
SLUDGE	58.7	62.1	63.1
COLOR	YELLOWISH	YELLOWISH	YELLOWISH

After alumina treatment for sludge removal as given in Table-4 and Table-5 it is clear that there is a decrease in the oil loss and increment in the sludge separation. This is attributed to that the adsorbent activity of raffinate oil depends on the ability of an adsorbent to selectively remove resinous, compounds containing sulfur, unsaturated, polycyclic aromatic materials.

### 5. Effect of alumina adsorption

The ion adsorption behavior of alumina ( $Al_2O_3$ ) arises from the acid–base surface hydroxyl groups. The protonation and deprotonation of these surface hydroxyl groups effect the oxide surface to develop an electrical charge promoting adsorption. The cation and anion exchange takes place at the acid ( $-OH$ ) and the base ( $-OH$ ) hydroxyl sites .

Change in Sulfur Content with Refining Processes.



**Mechanism** of the effect of hydroxyl groups of alumina surface and carboxylic acid of (organic group).

Although the activated alumina improved the color of the oil. The physical method of refining with the adsorbent is a surface phenomenon depending on the specific affinity between the adsorbent and the adsorbate dispersed in the spent engine oil. It can be seen that the properties of the treated oil with activated alumina has the best performance.

The treated oil with solvent extraction and activated alumina was analyzed according to the standard method in ASTM , IP for density, carbon residue, ash content, pour point, water content, sulfur content, viscosity and total acid number as shown in Table-5 and Table-6

Table 6. Physicochemical Properties of Used Oil and Refined Oil By Solvent Extraction And Alumina Treatment.

Experiment	Origin sample	A	B	C
Density@15.56	0.9116	0.8810	0.8847	0.8826
Specific gravity@15.56	0.9125	0.8818	0.8855	0.8834
Viscosity, cSt, @40 °C	107.48	51.66	76.02	83.67
@100 °C	12.93	8.48	12.1	9.98
V.I	115.1	139.55	155.76	98.4
Pour point, °C	0	3	3	0
Water content,ppm	2573.2	143.4	94.1	49.9
Ash content,wt%	1.05	0.0094	0.046	Nil
Carbon residue, wt%	1.12	Nil	0.01	Nil

Experiment	Origin sample	A	B	C
Total acid number, mg KOH/g	7.8	1.47	0.79	0.59
Sulfur content	0.82	0.74	0.67	0.66

Table 7. Physicochemical Properties For Refined Oil Using Different Solvent: Oil Ratio Using Solvent Mixture C and Fresh Co Operation Company Oil.

Experiment	1:1	1:2	1:3	Result of Fresh Cooperation Company Oil
Density@15.56	0.8826	0.8825	0.8816	0.8817
Specific gravity@15.56	0.8834	0.8834	0.8825	
Viscosity, cSt, @40 °C	83.67	74.14	72.08	52.34
@100 °C	9.98	11.80	11.59	7.41
V.I.	98.4	154.31	155.15	92
Pour point, °C	0	3	0	-3
Water content,ppm	49.9	86.6	3.7	-
Ash content,wt%	Nil	nil	Nil	0.003
Carbon residue, wt%	Nil	nil	Nil	-
Total acid number, mg KOH/g	0.59	0.15	0.06	0.067
Sulfur content	0.66	0.42	0.25	0.34

The results in Table-6 and Table -7 indicate the physical characteristics of used oil, refined oil by solvent extraction process and after activated alumina treatment. It is clear that the density of the used oil is higher than that for the treated oils. This is due to the presence of sludge and a higher percent of sulfur compounds. For used oil, the pour point is lower as compared with that of refined oil. The lube oil and the method of refining; especially it dewaxing has been done affected on pour point. All measured properties have been improved to reasonable values such as Water content, ash content, carbon residue, sulfur content and given in Table-6,Table-7. The value of Ash content shows the presence of metallic impurities which has been reduced by 89.5% in case of solvent mixture A in the raffinate oil, showing the removal salts. Acid value is also reduced as shown in the Table-6 Due to organic, inorganic acids, esters, phenolic compounds, lactones, and resins have been separated out suitably. The results also show that the viscosity gave higher viscosity improvements after the refining process. This is because of the possible conversion of possible impurities in the used oil. In observation of the interest of the oil to act as a coolant or heat transfer medium, it must be capable of maintaining adequate fluidity at high film temperature. The sulfur content is reduced from 0.82 wt% for used oil to 0.64, 0.67, 0.666 wt% for solvent mixture A, B, and C respectively as shown in Table-6 . It can be seen that the properties of the refined oil have the best performance.

**Conclusion** Solubility and dielectric constant parameters are good indicators of solvent behavior. Mixture solvent (A) has the maximum efficiency for sludge removal. The removal of sludge increases as the solvent: oil ratio increases . The physical properties of the refined have been enhanced to reasonable

#### REFERENCES :

1. Sadeek A. Sadeek, Hoda S. Ahmed, Ebaa A. ElShamy, Hussien A. El Sayed, Asma A. Abd, El. Rahman Egypt. J. Pet., 23 (2014), pp. 53-60 View PDFView articleView in Scopus
2. Houssien A. Kheireddine, Mahmoud M. El-halwag, Nimir O. Elbashir Clen Techn Environ Policy, 15 (2013), pp. 35-44



## CrossRefView in Scopus

3. T. Bhaskar, M.A. Uddin, A. Muto, Y. Sakata, Y. Omura, K. Kimura, Y. Kawakami Fuel, 83 (1) (2004), pp. 9-15 View PDFView articleView in Scopus
4. A. Kamal, F. Khan Effect of extraction and adsorption on refining of used lubricating oil Oil Gas Sci. Technol., 64 (2) (2009), pp. 191-197 CrossRefView in ScopusGoogle Scholar
5. N.M. Abdel-Jabbar, E.A.H. Al Zubaidy, M. Mehrvar Wast lubricating oil treatment by adsorption process using different adsorbents World Acad. Sci. Eng. Technol., 14 (2010), pp. 24-28 View in ScopusGoogle Scholar
6. H.A. Durrani, M.I. Panhwar, R.A. Kazi Re-refining of waste lubricating oil by solvent extraction Mehran Univ. Res. J. Eng. Teach., 30 (2) (2011), pp. 237-246 Google Scholar
7. A. Hamad, E. Al-zubaidy, M.E. Fayed Used lubricating oil recycling using hydrocarbon solvent J-Unviron. Manage., 74 (2005), pp. 153-159 View PDFView articleView in ScopusGoogle Scholar
8. J. Sauners Used oil refining revolution Lubricants World, 6 (9) (1996), pp. 20-24 Google Scholar
9. N.O. Elbasshir The Effect of Design Parameters on the Solvent Extraction Performance for Recycling of Used Oil M.Eng. Thesis Thesis University of Technology Malaysia (1998) Google Scholar
10. J.H. Sherman Removal Transition metals from motor oil using ion exchange resins Environ. Technol., 14 (11) (1993), pp. 1097-1100 CrossRefView in ScopusGoogle Scholar
11. M.I. Abdul\_Mutalib, N.O. Elbashir, M. Sahrif, R. Adnan, Practical use of the solubility parameters in determining effective solvent extraction parameters for recycling used lubricating oil, proceedings of RSCE98, Manila, Philippines, 1998, pp. 110-117. Google Scholar
12. J.L. Assuncao Filho, I.G.M. Mora, A.C.S. Ramos Braz. J. Chem. Eng., 27 (2010), p. 687
13. M. Jamshidnezhad J. Jpn. Pet. Inst., 51 (2008), p. 217 CrossRef
14. J. Burke, Solubility Parameters: theory and Application the American institute for conservation. The Book and Paper Group Annual, vol. 3. The Oukland Museum of California, Oukland, 1984. Google Scholar
15. ASTM, Annual Book of Standard Petroleum Products and Lubricants, section 5, Vol. (05.01-05.03), American Society for testing and Materials, Philadelphia, U.S.A., 2000. Google Scholar
16. IP, Standard Methods for Analysis and Testing of Petroleum And Related, Product, the Institute of Petroleum, London, U.K., 1999
17. Handbook of Petroleum Processing, 2<sup>nd</sup> Edition by Steven A. Treese, Peter R. Pujado, David S. J. Jones
18. Handbook Petroleum Refining by James G. Speight.
19. Springer Handbook of Petroleum Technology by Paul R. Robinson
20. Fundamentals of Petroleum and Petrochemical Engineering by Uttam Ray Chaudhuri.
21. Solvent Extraction Principles and Practice Second Edition, by Jan Rydberg, Michael Cox, Claude Musikas, and Gregory R. Choppin