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# REGENERATION OF USED ENGINE LUBRICATION OIL BY SOLVENT EXTRACTION. THE SOLVENT INFLUENCE ON OIL RATIO

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## ABSTRACT

*Huge amounts of used lubricating oils from automotive sources are disposed of as a harmful waste into the environment. For this reason, means to recover and reuse these wastes need to be found. Problems arising from acid treatment include environmental problems associated with the disposal of acid sludge and spent earth, low product yield (45–65%) and incomplete removal of metals.*

*The processes of re-refining of used lubricating oils depend greatly on the nature of the oil base stock and on the nature and amount of contaminants in the lubricant resulting from operations. The study was carried out on a sample of 15W40 type of used oil collected from one automobile. The re-refining process of used oil consists of dehydration, solvent extraction, solvent stripping and vacuum distillation. This study aims to investigate a process of solvent extraction of an alcohol–ketone mixture as a pre-treatment step followed by vacuum distillation at 5 mmHg. The primary step was conducted before the solvent extraction that involves dehydration to remove the water and fuel contaminants from the used oil by vacuum distillation. The solvent extraction and vacuum distillation steps were used to remove higher molecular weight contaminants. The investigated solvent to oil ratios was 2, 3, 4, 5 and 6. The solvent composition is 25% 2-propanol, 50% 1-butanol and 25% butanone or methyl ethyl ketone (MEK). The percentage of oil recovery for the solvent to oil ratio of 6:1 is further improved, but for the ratio values higher than 6:1, the operation was considered economically not feasible. Finally, the re-refined oil properties were compared to the commercial virgin lubricating oil properties.*

KEYWORDS: regeneration used oil, solvent extraction, vacuum distillation, ash content

## 1. Introduction

Large and increasing amounts of lubricating oil are produced each year that, after use, are considered a hazardous waste because of their high content of pollutants (thermal degradation products from the base oil and additives and combustion products from the fuel and lubricant). Nevertheless, the used oil still contains a large proportion of valuable base oil that may be used to formulate new lubricants if undesirable pollutants are separated from the oil by an appropriate recycling procedure [1]. Thus, not only environmental but also economical reasons justify the waste oil regeneration process.

The principal obstacle of regeneration process is that cleaning used motor oil by filtering or centrifuging does not ensure that the products of aging, contained in fine particles (0.5–5.0 µm), are not totally removed.

Those contaminants can form sludge and promote the formation of varnish, carbon deposits, and other deposits on engine parts, thus shortening their service life.

Clarification of oil during cleaning to remove mechanical impurities and water is a necessary operation in the technology of reprocessing collected oil, although this requires special conditions and materials and improved equipment. [2].

### *Used Oil Recovery Processes*

There are a large number of physical and chemical processes for reclamation, re-refining and reprocessing of used lubricating oil [3-5]. The earliest process known was the acid–clay treatment process. This treatment involves mixing the used oil with 93 to 98% sulfuric acid. The sulfuric acid acts as an extraction medium for the removal of asphaltenes, unsaturates, dirt, additives, color bodies and other impurities from the used oil. The acid treated oil will be then mixed with clay and filtered to remove mercaptans and other contaminants and to improve oil color. 30-42% of acid sludge can be combusted, whereas the remaining portion is called combustion residual. Problems arising from acid treatment include environmental problems associated with the disposal of acid sludge and spent earth, low product yield (45–65%) and incomplete removal of metals, especially lead. An alternate process using dehydration, distillation and hydro finishing consists in passing feed oil through a flash furnace and a tower to separate water and gasoline fractions. The oil is then heated up to 360–370$^{o}$C and passed to vacuum fractionators operating at 400$^{o}$C and 34 mBar. The column separates the oil into light and heavy oil products [6]. The main problems encountered in vacuum distillation processes are plugging of the lines, fractionators and furnace tubes due to formation of a resinous material that fouls the equipment. All modern technologies have included a physical or chemical pre-treatment step in order to avoid or eliminate these problems. Some authors [3, 7] describe a method of treating the dehydrated used oil with a mixture of one part 2-propanol, two parts 1-butanol and one part MEK. The solvent to oil ratio was 3 to 1 by volume. By this treatment the alcohol – ketone mixture will reduce coking and fouling problems during distillation.

## 2. Experimental results

The experimental procedure of solvent extraction process is presented schematically in Fig.1.

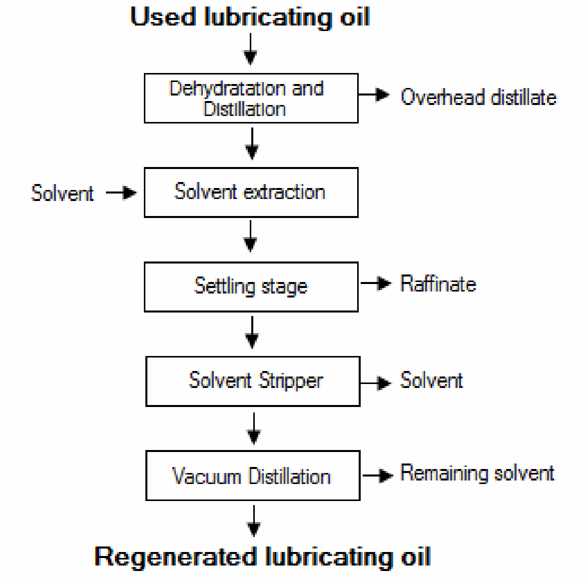

***Fig. 1.*** *Detail of the solvent extraction process*

### *2.1. Dehydratation*

The dehydration of used lubricating oil was performed in a simple batch vacuum distillation (Fig. 2) to eliminate water and light hydrocarbons (gasoline). In this process used lubricating oil is firstly filtrated to remove debris and other solid particles.

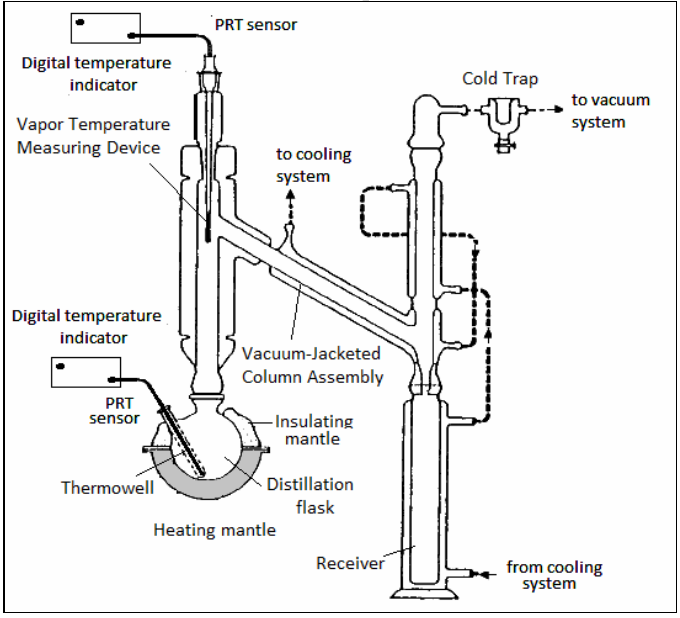

***Fig. 2.*** *Vacuum distillation apparatus*

Water and gasoline fractions were separated under vacuum at 5 mmHg and 210°C (atmospheric equivalent temperature).

Distillation was carried out until no further distillate was produced.

The dehydrated used oil was collected and then used for the next step of solvent extraction.

## 2.2. Solvent Extraction

The dehydrated used oil was prepared in amount of 100 ml for each experiment. The solvent composition was fixed to one part 2-propanol, two parts 1-butanol and one part MEK (25% 2-propanol, 50% 1-butanol and 25% MEK) as reported by some authors [7]. The main solvent properties are presented in Table.1.

***Table 1.** The main solvent properties*

| Test | 2-propanol | 1-butanol | MEK |
|---|---|---|---|
| Formula | $C_3H_7OH$ | $C_4H_9OH$ | $C_4H_8O$ |
| Molecular weight, g/mol | 60.1 | 74.12 | 72.11 |
| Density, g/cm$^3$, at 20°C | 0.786 | 0.81 | 0.8050 |
| Viscosity, cP at 20°C | 2.46 | 3 | 0.43 |
| Refractive index, $n_d^{20}$ | 1.3776 | 1.399 | 1.3788 |
| Boiling point, °C | 82 | 118 | 80 |
| Pour point, °C | -89 | -90 | -86 |
| Solubility in water g/l | miscible | 63.2 | 275 |

According to Table 1, there are three solvents in the oil with large differences in boiling point temperature of two of the solvents, i.e., 2-propanol (82°C) and MEK (80°C), compared to the third solvent 1-butanol (118°C). Thus, all atmospheric distillation experiments failed to recover all the solvent amounts at temperature below 250°C, which is the degradation temperature of the oil, while 2-propanol and MEK were successfully recovered at 200 °C.

The investigated solvents to oil ratios were 2, 3, 4, 5 and 6. Solvent to oil ratio less than 2 produced viscous mixture during separation. For a solvent to oil ratio higher than 6 to 1, the operation is considered economically not feasible. According to these considerations, the solvent amounts added were 200, 300, 400, 500 and 600ml. Adequate mixing of the solvent–oil mixture was obtained by stirring for 30 minutes at 2.5 rot/s. The mixture was allowed to settle for 24 hours in order to separate the extract phase (solvents and base oil components dissolved) from the raffinate phase (contaminants or sludge). Separation of the two phases was carried out in 1 liter separating funnels. The extract phase was red to brown in color and of low viscosity, while the raffinate phase was black and semisolid. This procedure was repeated in all experiments for every solvent to oil ratio.

The extract phase was subjected to simple batch atmospheric distillation to recover the solvent from the oil by heating up to 200°C.

## 2.3. Vacuum distillation

The vacuum distillation operation is done to recover the remaining 1-butanol from the amount of used oil after the solvent extraction process.

The vacuum distillation experiments were carried out according to ASTM D 1160 - 03 by the vacuum distillation apparatus described in Fig.2. The operation conditions of the vacuum distillation process of the treated oil were at 5mm Hg and 190°C to minimize cracking and to maximize yield.

After each experiment, the vacuum distillation apparatus was washed with *n*-hexane solvent in order to remove any contaminants that accumulated in the column, condenser and vacuum lines. The *n*-hexane washed the contaminants and accumulated them at the bottom of the still pot where they can be removed. After washing, all connections and joints were re-lubricated, and prepared for the next experiment.

### *Vacuum distillation apparatus*

The vacuum distillation apparatus, shown schematically in Fig. 2, consists of the components described below:

- *distillation Flask*, of 500ml capacity, made of borosilicate glass and having a heating mantle with insulating top;
- *vacuum-Jacketed Column Assembly*, of borosilicate glass, consisting of a distilling head and an associated condenser section. The head shall be enclosed in a completely silvered glass vacuum jacket with a permanent vacuum of less than $10^{-7}$ mm Hg. A vertical glass slide window along the column is available to observe the liquid and vapor behavior in the column. The attached condenser section shall be enclosed in water jackets as illustrated in Fig. 2;
- *vapor Temperature Measuring Device* and associated signal conditioning and processing instruments for the measurement of the vapor temperature. The system must produce readings with an accuracy of ±0.5°C over the range 0 to 400°C. The

location of the vapor temperature sensor is extremely critical. The vapor temperature measuring device shall be centered in the upper portion of the distillation column with the top of the sensing tip 3±1mm below the spillover point.

The vapor temperature measuring device shall be mounted through a compression ring type seal mounted on the top of the glass temperature sensor/vacuum adapter or fused into a ground taper joint matched to the distillation column. The boiler temperature measuring device may be either a thermocouple or PRT.

- *receiver* of borosilicate glass;
- *vacuum Gage*, capable of measuring absolute pressures with an accuracy of 0.01kPa in the range below 1kPa absolute and with an accuracy of 1% above this pressure;
- *cold trap* mounted between the top of the condenser and the vacuum source to recover the light boiling components in the distillate that are not condensed in the condenser section.

## 3. Results and discussions

Used lubricating oil was analyzed to investigate density, cinematic viscosity, flash point and ash content.

The analysis and tests used for analyzing the oil samples to evaluate their properties were done according to the standard methods as shown in Table 2.

***Table 2.*** *Used lubricating oil properties*

| Test | Method | Apparatus | Value |
|---|---|---|---|
| Density, (g/cm$^3$) at 20$^o$C | ASTM D 7042 | Anton Paar SVM 3000 | 0.896 |
| Viscosity, (cSt) at 20$^o$C | ASTM D 7042 | Anton Paar SVM 3000 | 89 |
| Ash content, % wt. | ASTM D 482-03 | - | 2.39 |
| Flash point, $^o$C | ISO 2592 | Marcusson open cup | 184 |

Flash point of the used oil showed evidence of gasoline dilution, which has to be removed by distillation during the dehydratation process.

The best dehydration results are obtained at lower vacuum pressure and even though there is a wide range in boiling point between water, gasoline and the base oil cut. Also lower vacuum pressure is preferred to ensure that the temperature will not rise above 250$^o$C, which is the oil degradation temperature. The final dehydration temperature depends on the amount of water and gasoline fractions in the used oil. The concentration of light hydrocarbons after this treatment was expected to be negligible. Both types of compounds are undesirable for the formulation of new lubricants. Elimination of water was also necessary because it may modify the solubility parameter of base oil components in solvent.

The amounts of water and gasoline separated in all dehydratation experiments were small due to low fuel dilution.

The results for mass balance for the optimum solvent to oil ratio experiments are tabulated in Table 3 while the tests percentage of oil recovery and of ash content are presented in Table 4. The properties of produced solvent treated oil, i.e., oil recovery, solvent recovery and ash reduction in relation to solvent to oil ratio are shown in Fig. 3.

***Table 3.*** *Measurements of mass balance for optimum solvent to oil ratio experiments*

| **Solvent to oil ratio** | **Oil feed** | **Solvent** | **Extract** | **Raffinate** | **Extract** | | |
|---|---|---|---|---|---|---|---|
| | | | | | **Oil** | **Solvent** | **Loss** |
| | [mL] | | | | | | |
| 2:1 | 100 | 200 | 265.4 | 34.6 | 78.3 | 185.2 | 2 |
| 3:1 | 100 | 300 | 373.9 | 26.1 | 86.4 | 285.7 | 1.8 |
| 4:1 | 100 | 400 | 478.8 | 21.2 | 92.3 | 384.9 | 1.6 |
| 5:1 | 100 | 500 | 587.8 | 12.2 | 95.5 | 490.8 | 1.5 |
| 6:1 | 100 | 600 | 690.7 | 9.3 | 96.1 | 593 | 1.6 |

***Table 4.*** *Test analysis of the optimum solvents to oil ratio experiments*

| **Solvent to oil ratio** | 2:1 | 3:1 | 4:1 | 5:1 | 6:1 |
|---|---|---|---|---|---|
| **Oil recovery** (vol %) | 78.3 | 86.4 | 92.3 | 95.5 | 96.1 |
| **Ash content** (wt%) | 1.91 | 1.45 | 1.23 | 1.42 | 1.87 |

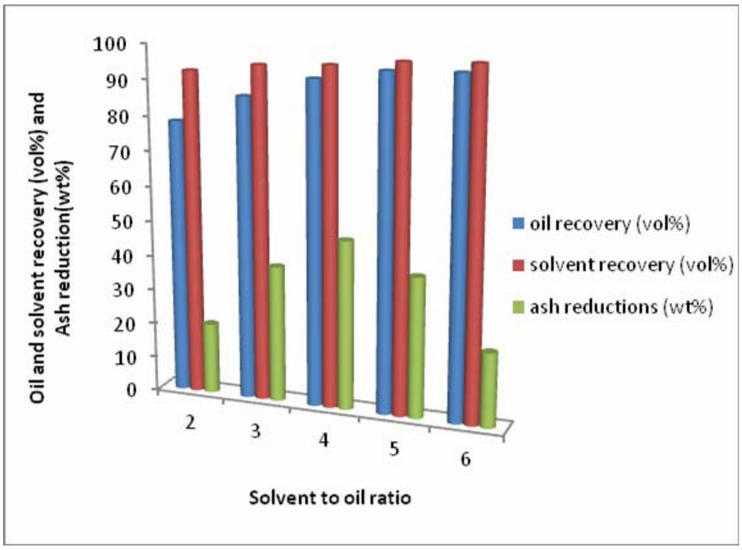

***Fig. 3.*** *The percentage of oil recovery, solvent recovery and ash reduction vs. solvent to oil ratio*

The results of the investigation, Table 4 and Fig. 3 indicate that the maximum ash reduction is achieved for solvent to oil ratio of 4:1. The oil recovery and ash reduction for the same ratio are better than the ones obtained for solvent to oil ratio of 3:1 and 2:1.

This indicates that by increasing the solvent amount, the solvency power is improved. The percentage of oil recovery for the solvent to oil ratio of 6:1 is further improved, but this solvent to oil ratio produces an ash reduction lower than that obtained for the solvent to oil ratio of 4:1 and 5:1 as shown in Fig. 3. Ratios above 3:1 were not considered economically feasible by industry, but considering that the solvent can be recovered and reused, the ratio of 4:1 was considered to be the better solvent to oil ratio for the treatment of used lubricating oil.

A comparison between virgin oil and solvent treated oil (at solvent to oil ratio of 4:1) is presented in Table 5 which shows that the solvent treated oil is more pure than virgin oil as indicated by the lower ash content and the same density value.

***Table 5.*** *Comparison between virgin oil and solvent treated oil properties*

| **Test** | **Method** | **Virgin oil** | **Solvent treated oil** |
|---|---|---|---|
| Density, (g/cm$^3$) at 20$^o$C | ASTM D 7042 | 0.890 | 0.890 |
| Viscosity, (cSt) at 20$^o$C | ASTM D 7042 | 117.5 | 98.4 |
| Ash content % wt. | ASTM D 482-03 | 1.3 | 1.23 |
| Flash point, $^o$C | ISO 2592 | 225 | 212 |

The solvent extraction process can be followed by clay treatment or hydrotreatment to improve color and odor of regenerated oil.

## 4. Conclusion

Four process stages were studied, namely: dehydration, solvent extraction, solvent stripping, and vacuum distillation. The study was carried out on a sample of 15W40 of type used oil collected from one automobile.

All gasoline and water fractions were separated using vacuum distillation at 5 mm Hg and 210$^o$C for the dehydration process. Solvent to oil ratio of 4 to 1 with solvent composition of 25% 2-propanol, 50% 1-butanol and 25% MEK was found to be the optimum composition for solvent extraction. Solvent stripping was conducted by two stages: atmospheric distillation to recover 2-propanol and MEK solvents and vacuum distillation at 5mm Hg to remove the remaining 1-butanol.

Extraction reduces the contaminants (inorganic materials) to low level, i.e. 49% ash reduction, such that no further operational problems were encountered on vacuum distillation.

The best oil recovery and ash reduction by extraction were obtained using optimum evaluated solvent to oil ratio of 4 to 1 with solvent composition of 25% 2-propanol, 50% 1-butanol and 25% MEK were 49% ash reduction and 92% oil recovery. That means that solvent to oil ratio larger than 4:1 will lead to dissolution of some contaminants in the solvent phase especially the ash forming material, which was considered to be undesirable.

As a result of the above mentioned facts, the solvent to oil ratio of 4:1 was considered to be the best solvent to oil ratio used for treatment of used lubricating oil.

Finally, it should be pointed out that these results can be very useful for the design of the continuous extraction process to recycle waste oil at industrial scale.

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