Potential for Re-refining of Used Lubricating Oils for Re-use Using Zinc Dialkyl Dithiosulphate as an Additive

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Abstract

Used lubricating oils generated from automotive and process industries pose environmental hazards if not properly managed. In this study, the potential to re-refine used lubricants for reuse was investigated. Used oil collected from a local garage was dehydrated at 240°C and varying pressure of 4-12bars under vacuum distillation. Solvent extraction was employed using Methyl Ethyl Ketone (MEK) as a solvent with varying ratios from 2:1 to 6:1 at a mixing temperature of 60°C. MEK and oils mixture underwent atmospheric distillation at 80 °C to allow separation of oils and MEK. During the re-refining process, the amount of water removed, ash content, sulphur content, viscosity, specific gravity, flash point and pour point were measured. Optimum oil yield of 94 (wt %) was achieved at a solvent to oil-ratio of 6:1. Re-refining of used oils resulted in a 73% reduction in sulphur content, 76% reduction in ash content and 64% water removal. The re-refined oil's viscosity of 90 cP, flash point of 160 °C, the specific gravity of 0.91 and pour point of -12°C. The re-refined used oils properties were almost similar to those of virgin oil using a combination of vacuum distillation and solvent extraction with an additive for maximum performance. Re-refined oils employing zinc dialkyl

dithiosulphate as an additive exhibited physicochemical characteristics similar to virgin lubricating oils and can be adopted for re-use.

Keywords: Re-refining, used oils, zinc dialkyl dithiosulphate, waste management

1. Introduction

Used lubricating oils are generated daily by the automotive and processing industries and these have the potential to cause water and soil pollution. Lubricating oils or lubricants are used to reduce friction between engine moving parts, protect against wear and tear, remove contaminants in the engine, cleaning, anti-corrosion and cooling agent (Abro et al., 2013). Used lubricating oils mostly contain water, solids particulates, fuel fractions, dust, carbon, sludge, oxidised oil products as well as some additives (Udonne and Bakare, 2013; Srivastava, 2014; Innamullah et al., 2015). The need for lubricating oils on a daily basis results in the accumulation of waste lubricating oils posing an environmental threat. Figure 1 shows the main sources of used oils which include process oils, hydraulic oils and automotive lubricants.

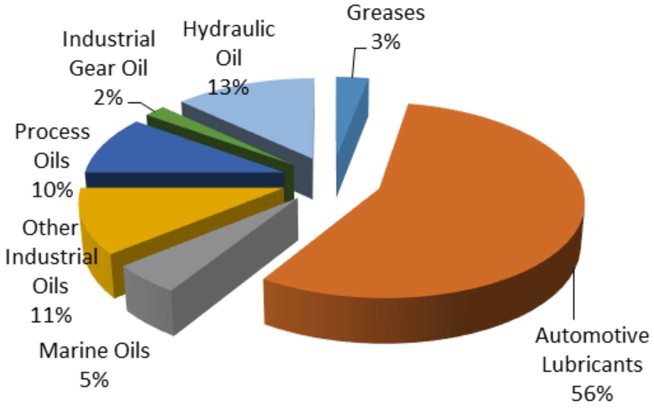

Figure 1.Sources of waste lubricating oils (Diphare et al., 2013)

In the event that lubricating oils find themselves in water bodies, there is potential for destruction of the marine life (Abro et al., 2005). This creates a need for the re-refining of used lubricating oils in a bid to promote sustainability. The re-refining of lubricating oils involves the following processes: collection, separation, dehydration, stripping, vacuum distillation, oils recovery, treatment, filtration and additives addition (Srivastava, 2014). Figure 2 shows the various processes and products of refining used oils.

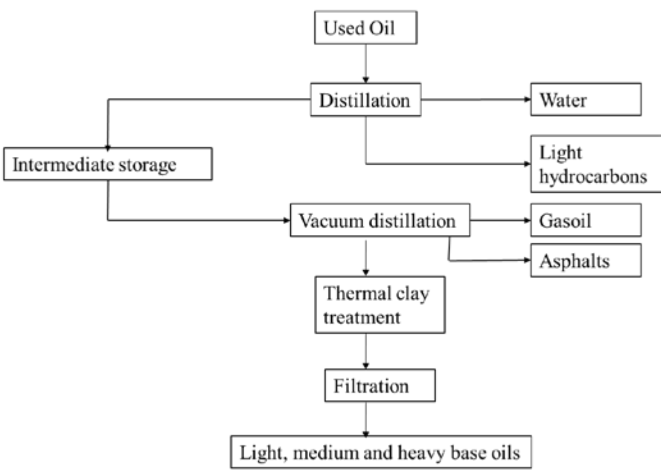

Figure 2.Used oil re-refining processes

Additives are used in used oil re-refining in order to act as antioxidants, act as anti-wear agents, corrosion inhibitors, friction modifiers, to act as antifoam agents as well as to act as viscosity index improvers (Merai, 2015). Additives such as zinc dialkyl dithiosulphate have been reported to improve the quality and performance of lubricating oils (Kannan et al., 2014). Zinc dialkyl dithiosulphate is also readily available and a low-cost additive. This study focused on the potential of re-refining used oils for re-use in a bid to properly manage the used oils waste using zinc dialkyl dithiosulphate as an additive due to its high-performance additive characteristics.

2. Materials and methods

2.1 Materials

Used lubricating oils were collected from a Total garage in Southerton, Harare, Zimbabwe. An organic solvent, Methyl Ethyl Ketone (MEK) from Sunfirm Distributors, Harare, Zimbabwe was used as the solvent during the re-refining process. A Toption lab scale vacuum distiller was used during the dehydration process. Zinc dialkyl dithiosulphate was obtained from Sunfirm Distributors, Harare, Zimbabwe and was used as an additive to the re-refined oils. A CS-800 sulphur analyser from Eltra, Germany was used for the sulphur content determination. A Mettler Toledo hygrometer was used for viscosity measurements and a Pensky Martens flash point apparatus was used for the oil composition determination. A PEC instruments viscometer was used for the oils viscosity measurements.

2.2 Methods

The used lubricating oils' physicochemical parameters were measured to ascertain their quality and these included the pour point, flash point, ash content, water content, sulphur content, viscosity and specific gravity. These were then compared to the physicochemical characteristics of virgin lubricating oils and of re-refined lubricating oils. The various methodologies followed are described in detail in the subsequent sections.

Dehydration of lubricating oils: Used oils were collected and heated to a temperature of 120 °C to remove water (Kannan et al., 2014). The amount of water removed was measured as the difference in weight of the oils after heating. The dehydration of the oils was carried out using the vacuum distillation field under negative pressure of 4-12 bars at a temperature of 240 °C (Peng et al., 2016).

Solvent extraction of oils: Methyl Ethyl Ketone (MEK) was used as the selective solvent to recover the lubricating oils through vacuum distillation due to its low boiling point and low cost. The solvent to oil ratios of 2:1; 3:1; 4:1; 5:1 and 6:1 were investigated at a mixing temperature of 60 °C. The solvent-oil mixture was allowed to settle for 4 hours, this allowed the aromatic compounds and the degraded additives to settle as a residue at the bottom whilst the solvent and oil mixture layer formed at the top. The solvent-oil mixture was then subjected to atmospheric distillation.

Atmospheric distillation of solvent-oil mixture: Atmospheric distillation was carried out at 80 °C which is the boiling point of MEK. MEK vapour produced was condensed and re-used in the process with fresh MEK whilst the re-refined lubricating oil was collected as a liquid. Zinc dialkyl dithiosulphate was added as an additive to improve the quality of the lubricating oil in the ratio 200 grams of the salt to 1L of the oil as this is the recommended ratio for optimum additive function (Kannan et al., 2014).

Ash content measurement: The ash content of the oils was determined as a percentage (%) in accordance with the American Standard Testing Methods (ASTM) D 2974-87.

Sulphur content measurement: The sulphur content was determined as a percentage using CS-800 sulphur analyser for the various solvent-oil mixtures during atmospheric distillation.

Specific gravity measurement: The specific gravity of the oil samples was measured using a digital hydrometer of Thermo-Hygro at 15 °C in accordance with ASTM D941-55 methodology.

Flash point measurement: The flash point was determined using the open cup flash point apparatus in accordance to ASTM D97 methodology. 10 mL of the oil was placed in a beaker and fitted with a thermometer and allowed to burn on a Bunsen burner. A source of flame was brought at 10 minutes interval to determine the temperature at which a flash appeared on the surface of the sample.

Viscosity measurement: Viscosity was measured in centipoises (cP) for the oil samples, using a viscometer in accordance to the ASTM D445 methodology at 40 °C.

Pour point measurement: Pour point of the oil samples was analysed using an ASTM D97 methodology whereby 20 mL samples were put in a test tube and allowed to cool. The temperature at which the oils crystallised and stopped to flow was recorded as the pour point.

3. Results and discussion

3.1 Characteristics of the used lubricating oils

The used lubricating oils collected for this study had a high ash content of 48.1% which indicated a high level of impurities that were in the used oils hence the need for re-refining and addition of additives like zinc dialkyl dithiosulphate to improve the quality of the re-refined used lubricating oils. In addition to the ash content, the high pour point of -28.1 °C as well as the high water content of 22.3% confirmed the high level of impurities in the used lubricating oils. The summary of the used lubricating oils characteristics is given in Table 1.

Table 1.Characteristics of the used lubricating oils

Parameter	Value
Pour point (°C)	-28.1±0.15
Flash point (°C)	100.3±1.53
Ash content (wt %)	48.1±0.15
Water content (wt %)	22.3±0.21
Sulphur content (wt %)	21.1±0.31
Viscosity (cp) at 40 °C	110.3±0.20
Specific gravity at 15 °C	0.92±0.01

3.2 Dehydration of used lubricating oils

The used lubricating oils had a water content of 22.3%, the presence of water in lubricating oil has a potential of decreasing the quality and lifespan of the oils. Too much water in the re-refined lubricating oils will result in increased equipment corrosion, additives precipitation, fluid oxidation, viscosity variation as well as reduced lubricity of the oils (Peng et al., 2016). The amount of water removed from the lubricating oils decreased by around 64% with the increase in pressure (Figure 3).

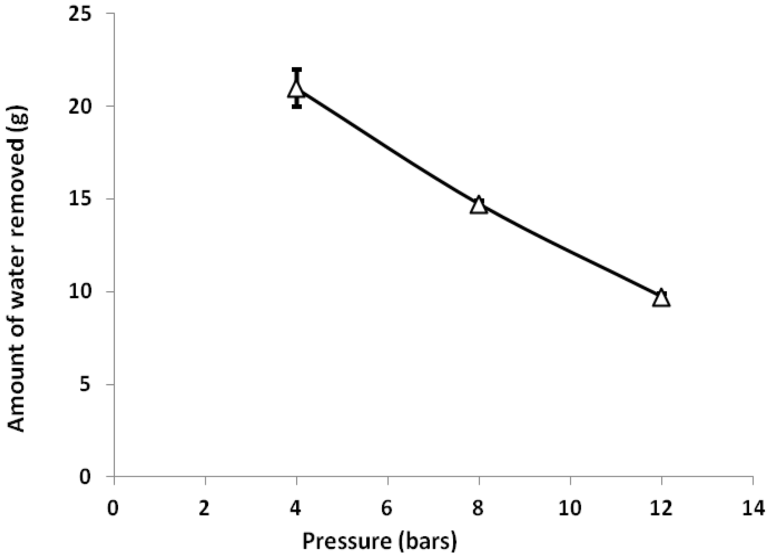

Figure 3.Amount of water removed from the used oils at different pressures

The recommended amount of water in the re-refined lubricating oils is 20 (0.002%) parts per million (ppm). The final amount of water in the re-refined lubricating oils in this study was 7% which is a considerable amount for using re-refined lubricating oils. Further dehydration of the used lubricating oils was recommended to ensure the water content values are within the accepted 0.002%.

3.3 Determination of optimum solvent to oil ratio

As the solvent to used lubricating oils ratio increased from 2:1 to 6:1, the amount of re-refined oil recovered increased by almost 10% (Figure 4).

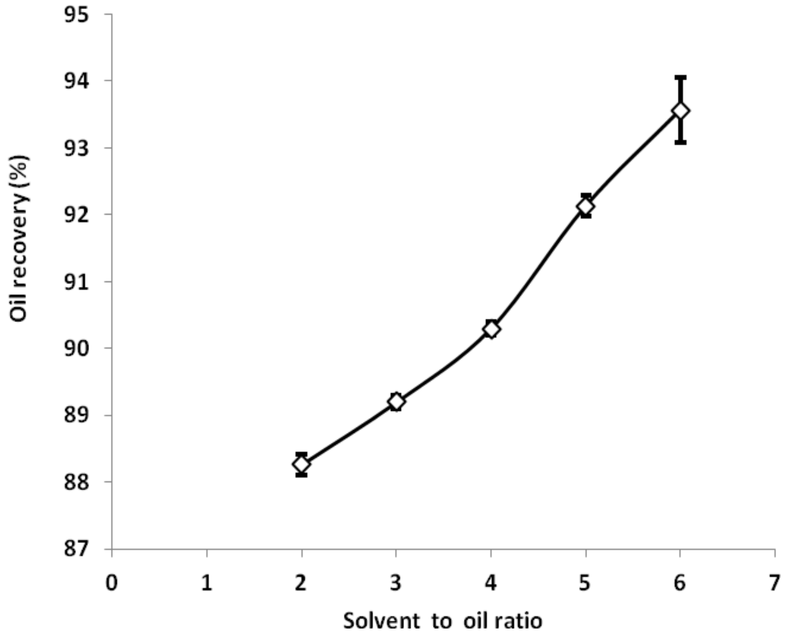

Figure 4.Effect of solvent to oil ratio on oil recovery

Increasing the solvent ratio has been reported to increase the amount of sludge removed during the re-refining of the lubricating oils increasing the quality and quantity of the lubricating oils recovered (Kamal and Khan, 2009).

3.4 Effect of solvent to oil ratio on ash reduction

As the solvent ratio increased from 2:1 to 6:1, the ash content in the refined used lubricating oils decreased by 76% (Figure 5).

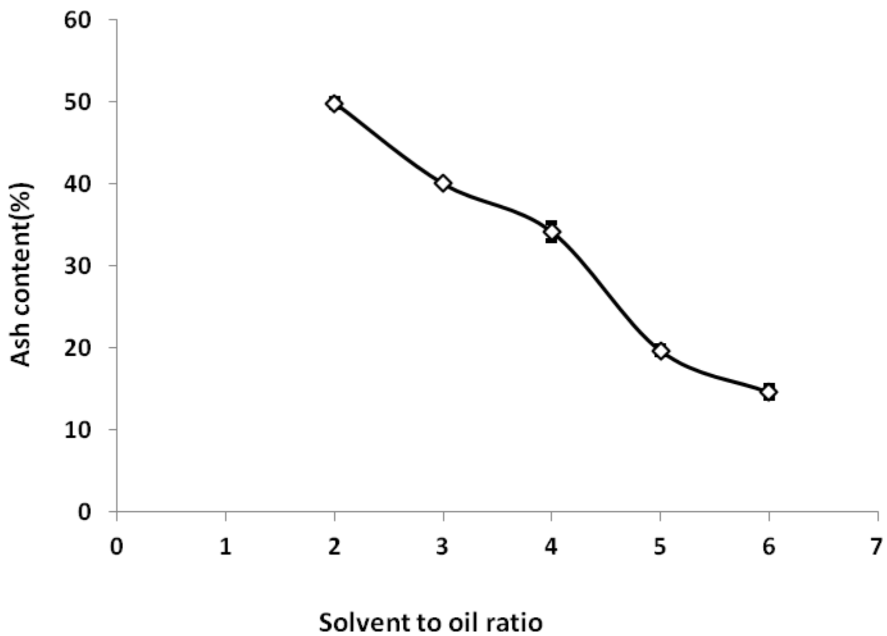

Figure 5.Effect of solvent to oil ratio on ash content reduction

The reduction of ash content in the re-refined lubricating oils correlates with the increase in the quality of the re-refined used oils as the amount of the solvent that was used for purification increased.

3.5 Effect on sulphur reduction

As the solvent ratio increased from 2:1 to 6:1, the sulphur content in the refined used lubricating oils decreased by 73% (Figure 6).

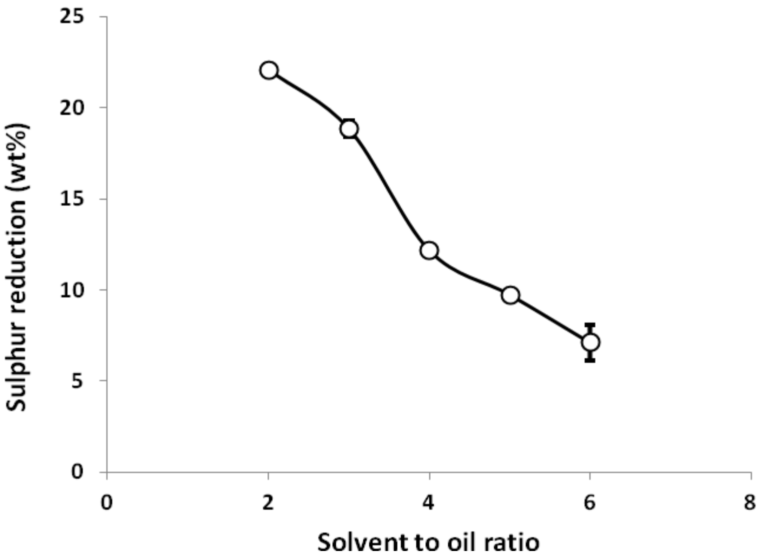

Figure 6.Effect solvent to oil ratio on sulphur content reduction

The reduction in ash content correlates with the increase in the quality of the re-refined used oils as the amount of solvent that was used for purification increased. Sulphur removal is important since it has the potential to corrode the engine during usage, if left uncontrolled.

3.6 Effect of re-refining on used lubricating oils physicochemical characteristics

3.6.1 Flash point

The flash point refers to the lowest temperature at which vapours of the oil will burn if ignited (Rincon, 2005). The flash point of virgin lube oil was 180.2 °C; the used lubricating oils had a flash point of 100.3 °C and the re-refined oil 160.1 °C (Table 2).

Table 2.Flash point values for the different oils

Type of oil	Flash point (°C)
Virgin oil	180.2±0.15
Used lubricating oil	100.3±1.53
Re-refined oil	160.1±0.20

The flash point of the virgin oil was slightly higher than that of the re-refined lubricating oils by 10%. The higher flash point for the re-refined oil in comparison to the used lubricating oils was an indication of evaporation of light components from the lubricating oils during the refining process (Rincon, 2005). However, they were within an acceptable range for usability. The flash point results obtained in this study were almost similar to results reported by Abro et al. (2013) who got flash points of around 130-150 °C upon treatment of used engine oil using a composite treatment method.

3.6.2 Viscosity

Viscosity refers to the resistance of flow of a material and can be used to determine the level of contaminants in the lubricating oils (Abro et al., 2013). In this study, the viscosity of fresh lubricating oil was 80.2 cP whilst that of used lubricating oil was 110.3 cP, which showed a huge presence of contaminations in used lubricating oils (Table 3).

Table 3.Viscosity values comparison

Type of oil	Viscosity (cP)
Virgin oil	80.2±0.15
Used lubricating oil	110.3±0.20
Re-refined oil	90.3±0.21

The viscosity of the re-refined used lubricating oils compared to that of virgin lubricating oil within 8% (Table 3). The reduction in viscosity of the re-refined lubricating oils was attributed to the removal of aromatic contents that are normally responsible for the high viscosity value during the re-refining process. The viscosity values obtained in this study related to the values reported by Udonne and Bakare (2013) who got values between 84 cP and 88 cP when used oils were treated using various methodologies including distillation, acid clay treatment and acid treatment.

3.6.3 Specific gravity

Specific gravity refers to the density of a material in relation to that of water. The specific gravity of the re-refined oil which was 0.91 was almost the same as that of the virgin oil with a value of 0.90 (Table 4).

Table 4.Specific gravity values comparison

Type of oil	Specific gravity
Virgin oil	0.91±0.01
Used lubricating oil	0.92±0.01
Re-refined oil	0.90±0.01

This was a clear indication that the re-refined lubricating oils could be reused since their lubricity was also enhanced through the re-refining resulting in the decrease in viscosity. Kannan et al. (2014) reported the same results when they observed a specific density of 0.87 for refined lubricating oils in comparison to a value of 0.91 in the virgin oil. This is an indication that re-refining of used oils using distillation with zinc dialkyl dithiosulphate as an additive achieves results with used oil that are comparable to virgin lubricating oils.

3.6.4 Pour point

This refers to the temperature at which a liquid becomes a semi-solid and loses its flow characteristics and a low pour point is always an indication of low-level impurities in the re-refined lubricating oils (Abro et al., 2013). The pour point of fresh oil was −10.3 °C, refined lubricating oil was −12.3 °C and the used lubricating oil was −28.1 °C (Table 5).

Table 5.Pour point values for the various oils

Type of oil	Pour point (°C)
Virgin oil	-10.3±2.1
Used lubricating oil	-28.1±0.15
Re-refined oil	-12.3±0.15

The re-refined used oil’s pour point was within 16% of the virgin oil pour point value. The decrease in pour point in the re-refined used oil was due to the degradations of additives, which were present in fresh oil as pour point depressants. Pour points of oils are usually determined by the viscosity, high viscosity results in high pour points (Hamawand et al., 2013).

A summary of properties of re-refined lubrication oils in comparison to the virgin oil and used lubricating oil is shown in Table 6.

Table 6.Summary of the various oils physicochemical properties

Parameter	Virgin oil	Used lubricating oil	Re-refined oil
Flash point (°C)	180.2±0.15	100.3±1.53	160.1±0.20
Viscosity (cP)	80.2±0.15	110.3±0.20	90.3±0.21
Specific gravity	0.91±0.01	0.92±0.01	0.90±0.01
Pour point (°C)	-10.3±2.1	-28.1±0.15	-12.3±0.15

4. Conclusion

Re-refining of used lubricating oils is essential for used oils management and recycling. Re-refined used lubricating oils exhibit almost the same characteristics of virgin oil in terms of the physicochemical parameters such as viscosity, pour point, specific gravity and flash point. This is achievable through vacuum distillation and solvent extraction with MEK with zinc dialkyl dithiosulphate being employed as an additive. Though re-refining used lubricants proved to be feasible at laboratory scale, the economic viability of the re-refining process needs to be investigated for scale up.

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