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Re-refining of used oil using multi-component solvents

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Abstract
Engine oil is used to lubricate moving parts, reduce friction and to protect engine from knocks. They also help to suspend solids, particulate matter, metal particles, notably iron and steel as well as other compounds like burnt carbon, ash and water. Re-refining of engine oil involves the separation of water and suspended particles, other compounds and sludge from used oil. It also involves an improvement on the colour and removal of any associated contaminants that infiltrated into the engine oil during use. This study concerns itself with the application of multi-component solvents in the treatment of used engine oil with a view to restoring it to re-useable state and original state or its equivalent. The used engine oil was blended with different solvents as samples A, B and C. The solvent to oil ratios were varied and identified as sample D and E. Given samples were treated with alumina and silica gel identified as sample F. The various samples were analyzed. The ash content, fire point, pour point, viscosity, specific gravity, density colour and colour reduction were determined. The ash content decreased from 0.56 to as low as 0.37 and closer to the ash content of the original oil (Mobil special) of 0.27. The fire point improved to 330 from 280 and moved closer to the fire point of Mobil special, which is 322. The pour point improved to -30 as against -29 of Mobil special from the original value of -24. The specific gravity moved from 0.888 to 0.8807 which is quite close to Mobil special's 0.8805. Density decreased from 0.8841 to 0.8751 which is quite close to Mobil special's 0.8759. The colour of the samples indicated optical change from black to yellow. The ranges approximates to the standard properties of engine oils although with slight deviation from the reference Mobil special except for viscosity which has been altered by the blended solvents.

Keywords: engine oil, used engine oil, re-refining, recycling, multi-component solvents

Introduction

Engine oil, motor oil or engine lubricant is any of the various substances comprising base oils enhanced with additives, particularly anti-wear additives, plus detergents, dispersants and, for multi-grade oils, viscosity-index improvers. In addition to that, almost all engine oils contain corrosion (rust) and oxidation inhibitors. Engine oils are used to lubricate moving parts, to reduce friction and to protect engines from knocks. Also to help suspend solids, particulate matter, metal particles, notably iron and steel as well as other liquids and compounds like water, burnt carbon and ash among others. Re-refining of used engine oil involves the separation of water and suspended particles, other compounds and sludge from used oil. It also involves an improvement on the colour and removal of any associated contaminants that infiltrated into the engine oil during use. This study concerns itself with application of multi-component solvents in the treatment of used oil with a view to restoring it to a re-useable state and in the process, avoid the traditional practice of disposing it on land and water bodies where they can constitute a major source of pollution.

It is common knowledge that the growing need to enhance movement and increase efficiency of equipment has resulted in a global dependence on engine powered vehicles and equipment including cars, lorries, trucks, harvesters, tractors etc that run on engine. These vehicles and equipment rely on engine oil for lubrication of engine components not only for performance or efficiency but also for sustainability. The used oils from these vehicles and equipment which are periodically changed are disposed on the rivers, seas, lakes and other surface water bodies as well as on land where they constitute harm to aquatic and terrestrial life of organisms and man. One gallon of oil constitutes hazard to any water or land organism on which it is disposed: the more the disposal, the more the damage on land and water including, fauna and flora.

Unfortunately, this will continue without recycling. The reason is not farfetched: automobile engines need engine oil for protection from wear and tear.

Hence, lubricating oils are used to lubricate moving parts, to reduce friction and in the process protect the engine from knock while enabling it to perform optimally. The lubricant equally helps to suspend solids, particulate matter, metal particles notably iron and steel as well as liquids and compounds like water, burnt carbon and ash among others.

The recycling of the used engine oil involves the separation of the water and suspended solid particles and compounds from the used oil. Recycling also involves an improvement on the colour of the used oil and removal of any associated contaminants that infiltrated into the oil either through the engine or the environment.

Appropriate processes are employed to restore the used oil to re-useable base oil that will not only spare the environment of the harm resulting from disposal of used engine oil but will conserve resources and save cost.

Problem Statement/Justification

The global need to enhance movement and increase efficiency of equipment has resulted in a growing dependence on engine-powered vehicles and equipment including cars, lorries, trucks, motorcycles, boats, tractors, harvesters etc, that run on engine. These vehicles and equipment rely on engine oil for lubrication of moving parts and to achieve efficient performance of engines. The used oils from these vehicles and equipment which are periodically changed are disposed in the rivers, seas, lakes and other water bodies as well as on land where they constitute harm to aquatic and terrestrial organisms and man. One gallon of oil constitutes a hazard to any water or land organism on which it is disposed.

The more the disposal, the more the damage on water and land, as well as fauna and flora. Unfortunately, this will continue and go unabated for as long as engine oil is not recycled. The reason is not farfetched: the innumerable number of vehicles and other engine-powered equipment will continue to require engine oil to lubricate moving parts, reduce friction to avoid engine knock and to perform optimally. The lubricants are known to also help to suspend solids, particulate matter, metal particles as well as liquids and other compounds that infiltrate the oil during use. Hence, the chemical properties of used oil constitute an environmental concern. Most petroleum base stocks are considered toxic to the environment. Hence, over 40% of the pollution in America's waterways is from used motor oil and used oil is considered the largest source of pollution in US habour and water ways at 385million gallons per year mostly from improper disposal. By far, the greatest cause of pollution in the ocean comes from drains and urban street runoffs, much of which is from improper disposal of engine oil.

Aim/Objective(s) of the Study

The principal objectives of this work are:

1. To treat or re-refine used lubricating oil, and restore it to its original state or equivalent, where it can be re-used.
2. To investigate recycling possibilities and potential use of multi- solvents in refining used lubricating oil.

Literature Review

Engine Oil

Engine oil, motor oil or engine lubricant is any of the various substances comprising base oils enhanced with additives, particularly anti-wear additives, plus detergents, dispersants, and for multi-grade oils, viscosity index improvers. In addition to that, almost all engine oils contain corrosion (rust) and oxidation inhibitors.

Engine oil is used for the lubrication of internal combustion engines. The main function of motor oil is to reduce friction and wear on moving parts, and to clean the engine from sludge, which is the function of dispersants and varnish (detergents). It also neutralizes acids that originate from fuel and from oxidation of the lubricants. It improves scaling of the piston rings, and cools the engine by carrying heat away from moving parts. (www.en.m.wikipedia.org)

Used Engine Oil

According to Chiakwelu (2018), Nigeria is relatively an emerging industrial nation with dilapidated automobiles roaming the nooks and crannies of the country, together with outdated industrial machines which are generating thousands of litres, if not millions of waste oil and lubricants. Lubricants are common elements in the daily lives of Nigerians, as they are essential to enable motor engines and industrial equipment to operate. Chiakwelu expressed concern that there is no environmentally safe and sound strategy to dispose the generated spent oil that end up carelessly discharged into the surrounding. (www.environment.gov.au)

Used engine oil according to Australian Department of the Environment and Energy, is a valuable resource. Australians are good at recycling used oil, with about 250 million litres of used oil recycled during the 2007-2008 financial year. Not all used oil is disposed of appropriately. Local governments in Australia help to conserve a valuable resource and protect the environment by encouraging Australians to recycle their used engine oil.

Materials Present in Used Oil

To recycle used oil, processors and refiners remove water, insolubles, dirt, heavy metals, nitrogen, chlorine and oxygenated compounds from oil drained from automobiles or other machines.

The resulting product is known as re-refined or treated oil. Re-refining simply reconditions oil into new, high quality lubricating oil (www.archive.epa.gov).

Environmental Effects

Due to its chemical properties, worldwide dispersion and effects on the environment, used motor oil is considered a serious environmental problem. Most current motor oil contains petroleum base stocks which are toxic to the environment and difficult to dispose of after use. Over 40% of the pollution to America's water ways is from used motor oil. Used oil is considered the largest source of oil pollution in US harbour and water ways at 385 million gallons per year, mostly from improper disposal. By far, the greatest cause of motor oil pollution in the oceans comes from drains and urban street runoffs, much of which is from improper disposal of engine oil (www.en.m.wild.org).

According to the US Environmental Protection Agency (EPA), films of oil on the surface of the water prevent the replenishment of dissolved oxygen, impair photosynthetic processes and block sunlight. Motor oil has detrimental effects on plants that depend on healthy soil to grow. They affect plants by contaminating water supply, contaminating soil and poisoning the plants. Hence, they reduce land productivity and negatively affect agricultural activities and output.

Motor oil poured onto the ground or into strom drains, or tossed into trashcans can contaminate and pollute the soil, groundwater, streams and rivers (www.calvecycle.ca.gov).

Recycling of Used Oil

Lubricating oil keep engines running smoothly. It does not wear out, but gets dirty after a while, and has to be properly disposed of or recycled i.e. cleaned and used again, to keep it from contaminating the environment. According to the US Environmental Protection Agency, two hundred million gallons of used oil are improperly disposed of each year. Used oil can be treated and fully re-used as fuel oil, with one gallon of used oil providing one gallon of fuel oil (www.mobiloil.com).

Recycling used oil is becoming the preferred way of handling used oil to protect the environment and conserve natural resources (www.archive.epa.edu, www.calvecycle.ca.gov). With higher intensity processing, used oil can be re-refined into lubricants at about 60% yield; one gallon of used oil provides about 2.5 quarts of lubricating base oil (www.mobiloil.com), or new high quality lubricating oil according to the US Environmental Protection Agency, as against 42 gallons of crude oil (www.archive.epa.edu).

Pre-Treatment of Used Oil

Pre-treatment of used oil is basically concerned with de-watering of the oil. This involves the removal of any excess water in the oil. This is achieved by pouring the oil into a settling tank, thereby enabling the oil settle, and separating by the process of decantation.

Processes involved in re-refining used oil

Used oil based on its nature, can undergo a number of refining processes or stages or recycling, and may include the following processes:

1. Filtration- Filtering the oil to remove any solid or particulate matter present in the oil.
2. Demineralization- This is the process of removing inorganic materials and certain additives in the oil.
3. Propane de-asphalting- This is a process for removing the heavier bituminous fractions.
4. Distillation- Distillation physically separates the components of lubricating oil using their boiling point range.
5. Solvent extraction- Solvent extraction allows the oil to dissolve, enabling removal of undesirable compounds.
6. Hydro-finishing- This is a process that helps to improve physical properties of the refined base oil. (www.environment.gov.au).

Benefits of recycling oil

Against the thinking of many, used oil does not wear out in the process of usage. It only gets dirty or contaminated. As a result, treating it helps to recover a valuable resource that otherwise could have been wasted. When oil is treated, it can be reused. Hence, it is kept from polluting the soil and water. Besides, the recovery of natural resource has economic advantage. It is cheaper to recycle than to produce base oil as more energy and resources is required to produce a gallon of base oil from a base stock of crude oil than from used oil.

Methodology

Material

Used engine (lubricating) oil was obtained from Mobil Oil Service Station in Enugu Metropolis. All reagents used were duly purchased and includes: toluene, 1- butanol, isopropanol, methanol, ethanol, silica gel and alumina. They were used without further treatment or purification.

Procedure

The used engine oil was subjected to filtration before treatment. This was done with a filter paper placed on a funnel standing on a filtration flask and a vacuum pump connected to the flask. A 100ml of the used oil was mixed with a blend of solvents comprising of 100ml each of toluene, 1-butanol and isopropanol in a closed vessel. The mixture in a beaker was placed on a magnetic stirrer and stirred for one hour. Then, it was allowed to stand for 24hours. The clear surface comprised of oil and solvents was transferred into a beaker and heated on a water bath set at 60ºC in order to remove the oil from the regenerated oil. The regenerated oil was passed through a column filled with activated alumina and silica gel separately using n-hexane as eluting solvent, to remove the dark colour. The same procedure was employed in toluene, methanol and 1-butanol and also toluene, 1-butanol and ethanol, but using only alumina. The oil to solvent ratios was varied to obtain an optimum condition. After each experiment, the percentage of raffinate, sludge and colour was calculated.

The oil gotten and the used engine oil was analyzed for density, specific gravity, viscosity, pour point, ash content, fire point and percentage colour removal accordingly.

Percentage colour removal

A portion (1ml) of the oil was mixed with 10ml of n-hexane and the absorbance was read on a UV/VIS spectrophotometer Model 752 using n-hexane as blank.

Density

A 50ml pycnometer was filled with the oil and the lid was gently covered. The sides of the pycnometer was cleaned and allowed to stand for 5 minutes, thereafter the weight was noted. The same procedure was performed using distilled water and density and specific gravity were calculated thus:

Ash content

A portion (2g) of the sample was carefully measured into a crucible and placed in a muffle furnace set at 600ºC and allowed to char. The crucible was removed when the colour of the residue was grey or white and transferred into a dessicator and allowed to cool. The weight was noted and ash content calculated thus:

Viscosity

The u-tube viscometer was used. The tube was cleaned with chromic acid cleaning solution and rinsed with water. A portion (10ml) of sample was added to the tube and using function, the water level was drawn above the upper mark. The liquid level was allowed to fall and the process was timed with a stop watch. The timer was stopped when the meniscus passes the lower mark. The same process was performed with the oil and the time required for the sample to pass the meniscus was noted and viscosity calculated thus:

Fire point

A given quantity of the oil was carefully measured into a crucible and a thermometer dipped into the oil. The crucible was ignited below and the temperature at which it caught flame was noted as the fire point.

Pour point

A portion (50g) of the sample was carefully measured into a beaker and a thermometer inserted into it. The beaker was placed on top of an ice bath and allowed to stand. The temperature at which the flow of the oil ceases was recorded as pour point.

Results and Discussions

Table 1: Effect of different solvent mixtures on the refining of used engine oil

Parameters	A	B	C
Raffinate (Vol %)	62.5	65.0	90
Sludge (Vol %)	37.5	35.0	10

Table 2: Effect of different parameters on refining used engine oil

Parameter	A	B	C	D	E	F	G	H
Ash content %	0.385	0.200	0.282	0.646	0.385	0.580	0.189	0.560
Fire point (ºC)	>360	>360	>360	>348	>330	>280	>322	>280
Pour point (ºC)	-18.4	-21.0	-30	-21.0	-21.0	-24	-29	-24
Viscosity (CPs)	5231.9 8	3549.3 7	4747.6 5	5292.5 8	7057.4 2	4765.8 0	14105.0 0	7116.6 2
Specific gravity	0.8765	0.8858	0.7912	0.8798	0.8817	0.7943	0.8805	0.8888
Density (g/cm3)	0.8719	0.8808	0.7870	0.8751	0.8770	0.7901	0.8759	0.8841
% colour reduction	7.51	15.93	47.54	7.93	4.57	2.46	98.50	

Note
A = Toluene + Butanol + methanol B= Toluene + Butanol + Ethanol C = Toluene + Butanol + isopropanol D = 1:1 oil and solvent E = 1:2 oil and solvent F = Silica G = Mobil special H = used engine oil % = Percentage ^{0}C = degrees centigrade CPs = centipoises per seconds g/cm^3 = gram per centimeter

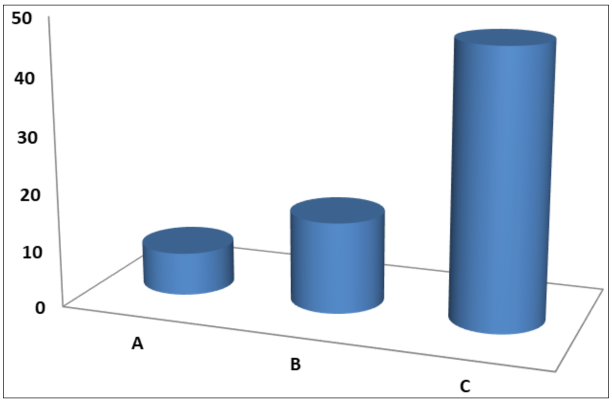

Fig 1: Studge removal by different muti componants (Samples)

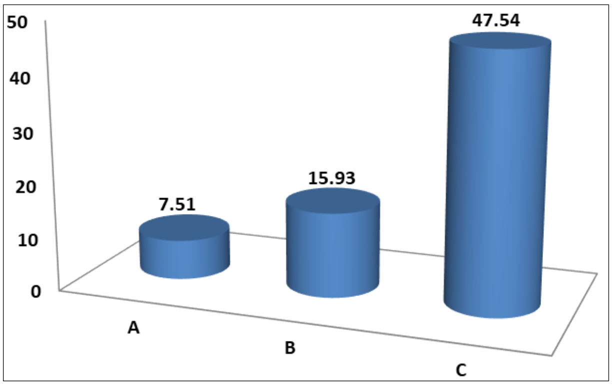

Fig 2: Percentage colour reduction by sample

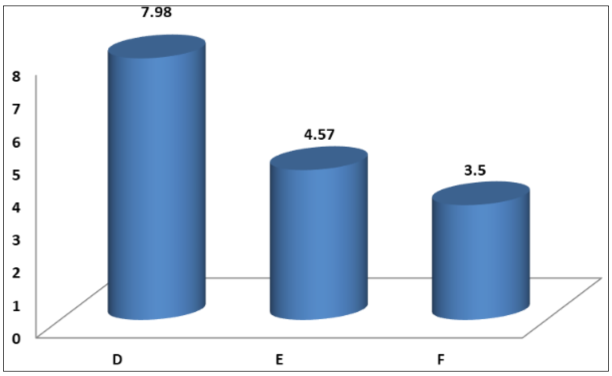

Fig 3: Percentage colour reduction by sample

Used engine oil according to Osman *et al* (2017), is a blend of combustion products.

Such as water, Fuel, dust, wear metals and oxidation products which form complex and corrosive organic acids. Lubes oil 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 engines. This contamination contains instauration, phenolic compound, aldehyde, acidic compound, additives, metals, varnish, gums and other asphaltic compounds originating from the overlay of bearing surfaces and degradation base oil components. These impurities can be removed by distillation, acidic refining, clay treatment and hydrogenation. However solvent extraction followed by adsorption is considered more effective (www.sciencedirect.com accessed on November 13, 2019).

The re-refining process is measurable by the amount of sludge removed from the oil by solvent extraction. This is presented in Table I above: the effect of different solvent mixtures on the refining (removal of sludge) of the used oil.

The results of the experiment showed that sample A removed the maximum amount of sludge (37.5%), followed by sample B (35.5%) and sample C removed the minimum sludge (10.0%). This might be due to the solubility of the oil in the solvent mixtures and their dielectric constant. A negative trend was observed for the colour removal with C having the highest colour removal followed by B and A. The reason behind this trend is not certain. Further verification may be necessary but chances of pursing that was limited in this work.

It was also observed that the density and specific gravity of the used engine oil were higher than the treated one. The lower density and specific gravity of the treated oil might be due to the removal of the sludge.

The results of the ash content showed that the treated samples had ash contents lower than the used engine oil, except for samples D and F. This reduction in ash content might be due to the removal of sludge which led to the removal of metallic impurities, the very high ash contents of samples D and F, might be due to the further purifications with silica gel and alumina and/or solvents used for the purification which may have added some metallic impurities or the deposition of foreign materials.

The slight deviation in viscosity of the treated samples in comparison with the used engine oil might be due to the treatment with solvents and further heating of the samples to remove the solvents.

The results of the fire point showed that the treated samples had higher fire point than the used engine oil. This might be due to the removal of sludge as impurities lower the boiling point, hence the fire point. There is no significant difference in the pour point of the used engine oil and the treated samples.

Further, the results show that the recycled oil tended towards the standard (Mobil special) qualities in varying ways - while oil from blend A gave the most viscous oil of the three blends, (5,231.98cPs), as earlier stated showing a movement closer to the standard, A sample also gave the best specific gravity (0.8765) which is also close in range to the standard (Mobil special).

Blend B gave the best ash content (0.200%) and closest density to the standard (0.8808g/cm^3) while blend C gave the best colour reduction (47.54%) and pour point (-30^{0}C). However, the best colour reduction indicates need for improvement towards the standard (8.50%).

The fire point for all three blends were not significantly different, but was higher than normal or standard, an indication that further refining may be necessary.

However, an increase in the ratio of oil to solvent blend (1:2) gave an oil of improved quality in terms of fire point (330^{0}C), viscosity (7057.42cPs), specific gravity (0.8817) and density (0.8770g/cm^3). It also has a high ash content and low percentage colour reduction (4.95%).

This could be as a result of an increase in solvent quantity used. Blend E's viscosity is an improvement from that of A to just about half of the standard viscosity result. This trend suggests the possibility of an improvement in viscosity and possible quality of oil by altering ratio of solvent to oil blend. Also blend B gave a good ash content result as blend C had the best percentage colour reduction. This suggests that the best blend of solvents could include parts of B & C to possibly further improve the ash content and percentage colour reduction. The implication of this is that increased solvent to oil ratio has the tendency of improving the quality of the used oil. Further increasing the ratio is necessary but wasn't done due to certain limitations that the research work faced

Discussion of the comparative properties as manifest in the results

Viscosity

One of the most important properties of engine oil which helps it in maintaining a lubricating film between moving parts is it's viscosity. This refers to a measure of it's resistance to flow. Viscosity of a fuel liquid can ensure this resistance if it is reasonably high although not so high as to impede flow of the fluid. The viscosity hovered around the viscosity of the used engine oil of 7116.6 with sample E having 7057.4. Apparently, the blended solvents further decreased the viscosity which indicates a clear departure from Mobil special's 14105.0. This is expected. Blowing with viscosity-enhancers may be necessary to further improve the viscosity.

Pour Point

In the case of engine oil, flow should commence at low temperatures given that flow is required to inhibit metal to metal contact in moving parts of an engine. This property is determined by the pour point which describes the lowest temperature at which the engine oil flows at specified laboratory conditions. A good rule of thumb is that the pour point of lubricating oil should be at least 10°C below the lowest anticipated ambient temperature. This will ensure dependable lubrication and better equipment reliability in the long run (http//www.bcl.co.za- accessed on November 29th, 2019).

Pour point is also defined as the temperature at which the oil looses it's flow characteristic. At this point, the oil becomes too viscous and looses flow ability. It has many implications especially within engines, as it can be used to determine what temperature ranges the oil can be used in. It will also give a good indication of the temperature of which the oil will become too viscous that it will prevent the engine from starting (Liam, 2019). Pour point of engine oils range from 32°C to below -57°C (90°F to below -70°F) (Http//www.Britainica.com accessed November 29th, 2019).

The pour point ranges of the treated oil fall within standard oil ranges with sample C showing best result of -30°C compared to Mobil special pour point of -29°C.

Ash Content

According to Rashid *et al* (2013), when the lubricating oil is completely burnt, the remaining solid is called ash and it shows the oil purity. Sample A relatively has a comparatively good ash content of 0.37 having moved from original ash content of 0.56 of the used oil and improved as it tends towards Mobil special's 0.27 ash content.

Flash Point (Fire point)

Given the makeup of engine oil which is largely comprised of hydrocarbons which are flammable, in order words, they can ignite and burn, the fire point measures the lowest temperature at which the vapours released by the engine oil can ignite and burn. This property of oil should be high to avoid oil readily igniting. Sample E indicates a relatively good fire point of 330 which is an improvement from the 280 of the original used oil and a clear moment towards Mobil special's fire point of 322.

Specific Gravity

The specific gravity of the reference engine oil (Mobil special) is 0.8805 whereas that of the used engine oil is 0.8888. The treated engine oil showed varying specific gravities ranging from 0.7912 of sample B to 0.8817 of sample E which is the closest to Mobil special. The specific gravity is affected by the nature and type of contaminant and could be higher or lower than that of the fresh engine oil.

Density

Density is a key property of a fluid and is given by the ratio of its specific mass to a known volume (**e** = M/V). The water, reference standard, has a density of 1,000kg/m^3 by definition. These of oils vary between 700kg/m^3 and 950k/m^3. That is why most oils float in water.

They are less dense than its high density fluids can help in order to control contamination. In this case, the longer period of floatation in the liquid, facilitates the removal of particles through filtration or other mechanisms aiding the process of cleaning the assembly (Pedor, 2018). The range of density falls within acceptable ranges with sample D (0.8798) closest to Mobil special (0.8803).

Conclusion

Based on the experimental work undertaken, it is found that the various blends of solvents, effectively removed contaminants from the used oil. Same applies to the variation in the oil/solvent ratios which shows significant enhancement in the quality of the used engine oil which in essence improved to qualities equivalent and comparable to the original engine oil stock from fresh oil. The re-refining of the original engine oil with multi-component solvents proved to be a very good method of processing in view of the significant alteration in the quality of the used oil at an instant. A combination of the blends and further variation in oil to solvent ratios promise best results that may be devoid of with Mobil special variations but the drawback was the cost of solvents which limited the options exploited. Varying the blends and increasing the solvent to oil ratio remains a focus in further studies to perfect the quality of the re-refined stock.

Recommendations

On the basis of the experiments carried out, it is obvious that multiple solvents are more effective than a single solvent in engine oil refining provided that the aim of the refining is to restore the used engine oil to original quality or its equivalent with comparable properties. Hence, the use of multi-component solvents is not only desirable but recommended.

On the basis of this work, a combination of solvent blends is ideally an indentified approach towards achieving increasingly improved quality of refining oil. This is also recommended.

Similarly, increase in solvent to oil ratio has a proven effect on solubility and impacts on quality. This is equally a measure that can be recommended. A blend of fresh oil with re-refined oil may be applicable in enhancing quality of the re-refined oil and in saving cost.

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