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## ARTICLES

## EDITORIAL PREFACE

It is my pleasure to introduce to you, volume 22, N0 1, June 2017 of the Journal of Engineering Research (JER). This edition publishes contributions on advanced drying technology, bimodal transportation, welding technology, recycling of wastes materials and strength of materials. It also includes studies on formalisms, methodologies and simulation tools that are intended to support the new, broader interpretation of geo-informatics engineering, energy performance evaluation and environment.

JER is a referred, peer-reviewed and quarterly published international Journal with focus on basic and applied researches in engineering and its related disciplines. It publishes contributions on concepts, state of the art, all aspects of research, standards, implementations, running experiments, and industrial case studies as well as significant advances in basic and applied engineering, engineering technology and management. The Journal also encourages the submission of critical review articles covering the latest advances in engineering and related fields as well as scientific commentaries.

The Journal has a very dedicated Editorial Board constituted of exceptional academics and practitioners.

**Journal of Engineering Research hereby invites you, authors from Nigeria and all over the world to submit original research papers for possible publication.**

The manuscripts, which will be judged by qualified reviewers according to established criteria for technical merit, should represent completed original work embodying the results of extensive field, plant, laboratory or theoretical investigation, or new interpretations of existing problems. Materials must be considered to have significant permanent value.

In addition to technical acceptability, material should be presented clearly and concisely. Of particular importance is the description of the experimental procedures involved in the experiment (where applicable). It is very important that critical information about experimental conditions be included so that the work can be verified by other scientists and engineers.

More information about the *JER* guidelines for preparing and submitting papers may be obtained from: http://www.jer.unilag.edu . JER invites contributions from the entire international research community. The journal will continue to deliver up-to-date research to a wide range of engineering, engineering science, engineering technology and engineering management. The *JER* will assure that rap turnaround and publication of manuscripts will occur within two to four months after submission. It is our hope that this fine collection of articles will be a valuable resource for JER readers and will stimulate further research.

Thank you,

Yours truly,

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# Some Physico-Chemical and Adsorptive Reclamation Strategies of Spent Automobile Engine Lubricating Oil

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## Abstract
*This study aims to reclaim the base oil component of used lubricating oils for reuse. The base oil reclamation strategies were carried out in a three-stage process namely, physical, chemical and adsorptive processes. The physical processes adopted include sedimentation and natural settling by gravity, magnetization, and filtration for the removal of metallic and non-metallic related particles.The chemical process included acidification with $H_2SO_4$, alkalinization with NaOH, solvent extraction and hydro-treatment. The adsorption process used a combination of bentonite powder and silica gel / activated carbon adsorbent in specific proportions.Comparison of lubricating properties of all the samples indicated that sample 6, which passed through the adsorption process in addition gave the best conditions for the base oil reclamation process.Of all the lubricating properties investigated, only the flash point was not significantly reclaimed in comparison with others. The infra-red spectroscopy of the samples was also performed and indicated that peak infra-red spectroscopy values occurred at approximately equal wave numbers of 1457.76, 2852.28 and 2921.01cm$^{-1}$.*

**Key words:** Acidification, Alkalinization, Filteration, Hydro-treatment, Wastes.

## 1.0 INTRODUCTION

Lubricants are base oils with added additives. Base oils are of fossil origin obtained as part of the heavy products of the petroleum refinery (Mohammed *et al*., 2013), while the additives are various grades of synthetic products (Jha, 2005). The Nigerian fossil fuel reserve has been said to be dwindling with time (Owolabi and Osiyemi, 2013). This is as a result of its wide usage and overdependence.The increase in new industries and volume of vehicles in recent times led to the corresponding increase in volume of used lubricating oil produced each year (Eman *et al*., 2012). Serious wastage has also been observed in the lube oil economy. Environmental Protection Agency (EPA) statistics show that each year in the United States of America, about 200 million gallons of spent oil is dumped as waste oil in the United States (USEPA, 1994). The global industrial sector alone generates more than 35 million tonnes of used lubricating oil annually (Norrby, 2003). In Nigeria alone, over 200 million litres per annum of used oil has been estimated (Bamiro and Osibanjo, 2004). Most often, these identified wastages lead to indiscriminate discharge of the used oil in the immediate terrestrial and aquatic environment (Bamiro and Osibanjo, 2004).Furthermore, there is the presence of heavy and toxic metals, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) in the spent automobile lubricating oil. These components are highly detrimental when released to the environment. A solution to the highlighted problems is the use of bio-sourced automobile engine (Owolabi *et al*. 2013) or re-cycling of the spent oil to further conserve our fossil fuel.

Re-cycling of the spent lubricating oil and needs for other use have created important research interest to process engineers, petroleum chemists, and oil waste managers in recent time.This sudden interest became necessary as a result of serious wastage observed in the lube oil economy in this era of “do not waste waste”. Millions of tonnes of spent oils are on the ground or in water (Bhaskar *et al*., 2004). According to claim

Mithilesh (2005), lubricating oil does not wear out during use. It is only the additive part, which gets depleted. The oil molecules are not degraded, the presence of contaminants numerous to mention makes it necessary for replacement in automobile engines. The high volume of waste oils can, therefore, be turned into valuable fuel or materials by re-refining and re-treatment processes. Their acceptance as a high quality lubricant has been gradual, largely because of the skepticism of the public that the product can be re-refined to its original condition.

In the past, major recycling processes in use include centrifugation system, acid-clay process, Philips re-fined oil process, fixed and clear bed sand filtration process to produce relatively clean oil (Umesi, 2017). These methods only incorporate physical separation of contaminants which may not give significant change in the colour of the spent oil.

Owolabi *et al*. (2013) used both acids and solvents to chemically treat the spent oil . The results obtained suggested that the oil recovered by both reagents exhibited better lubricating properties, comparable to fresh lubricants with the addition of specific additives.The acid treatment demonstrated improved colour and appearance recovery compared to solvents. Other studies (Hamad *et al*., 2005; Sherman *et al*., 1993; Dos Reis *et al*., 1988; Elbashir, 1998; Nimir *et al*., 1997; and Bendebane *et al*., 2010) have similarly extracted usable fractions of spent oil using solvents, such as alcohols, ketones, and other hydrocarbons.

Yu-Lung (2005) adequately carried out analysis and comparison of regenerative technologies of spent lubricating oil. However, solvents extraction process received much attention (Lai *et al*., 1989; El-Din *et al*., 1987; Reis *et al*., 1988; Chementator, 1996; Sherman, 1993; Elbashir, 1998; Saunders, 1996; Reis, 1991).

Shaaban and Salavani (1996) also reported the management of used lubricating oil by converting it to energy, such as combustion in boiler, direct burning in cement kiln etc. No method to the best of our knowledge (**Figure 1** for instance) has combined the trio of physical, chemical and adsorptive methods for the reclamation of the spent lubricating oil.

In this study, the spent oil reclamation processes involving physical methods (sedimentation, magnetization, filtration and centrifugation), chemical method (dehydration, acid treatment, alkaline treatment, solvent extraction and hydro-treating) and adsorption followed by re-additivation were adopted. This combined all the treatment processes to reclaim the spent oil. The solvents have also been selected to reflect differences in polarity and other solvatrochromic parameters and these are hexane, which is highly non-polar (with dielectric constant 1.88) and propan-2-ol that is highly polar (with dielectric constant 20.18; Sigma- aldrich, 2015).

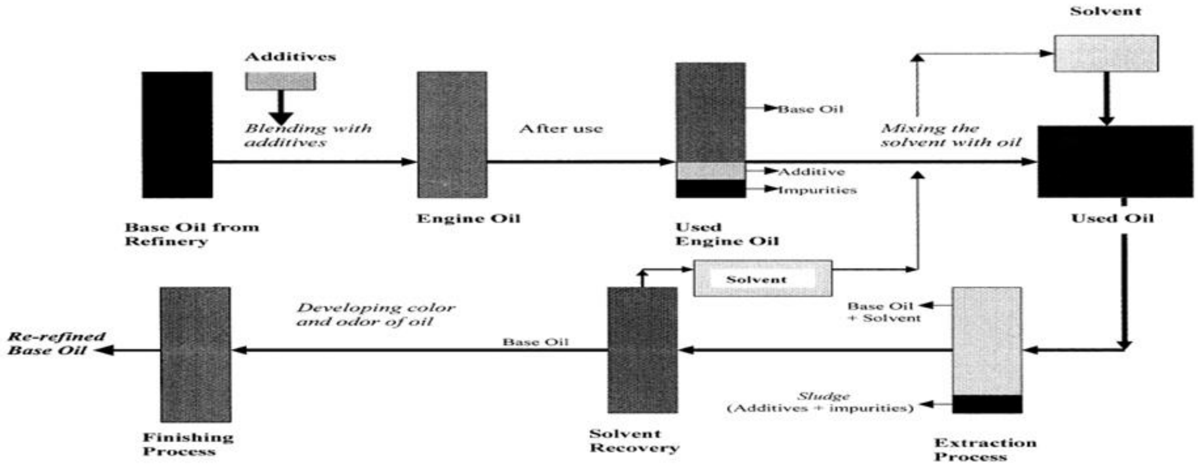


**Figure1: Schematic diagram representing the used lubricating oils cycle, through production, usage, and solvent extraction recycling** (Elbashir *et al*., 2002)

## 2.0 MATERIALS AND METHOD

### 2.1 Materials used

Samples of spent oil were obtained from a Mobil auto servicing station in the Lagos mainland region of Lagos State, Nigeria, after one of the regular routine maintenance of an automobile vehicle, which uses lubricating oil with the specification MOBIL SUPER 1000 XHP 20W-50. The used oil was stored in a 4-litre gallon to allow natural settling by gravitation to take place. Hexanes (highly non-polar) with an equal volume (50-50) of hexane /propan-2-ol (highly polar) were used. Other reagents used for the study include tetraoxosulphate (vi) acid ($H_2SO_4$), sodium hydroxide (NaOH), zinc metals, bentonite powder, silica gel and activated carbon. The methodology adopted in this study is illustrated in the sequence of event below.

Sequence of event: Magnetization → Acid–Base Treatment → Filtration → Solvent Extraction → Hydro-Treatment → Adsorption

### 2.2 Magnetization, Acid/Base Treatment and Filtration Process

Using the natural settling method, such as sand, metals left as sediments and later discarded while retaining the top layer. A magnet was placed in the filtered oil for about 24 hours to further remove fine metallic/ferrous metals particles that may be present. The filtered oil was placed in a large conical flask heated and stirred rigorously using a magnetic heater. Attached to the heater, was a stirrer operating at atmospheric pressure. This aspect is significant as it ensures the removal of water that is an essential component for rust formation in automobile engines (Owolabi *et al*., 2013). The de-hydrated oil was mixed with concentrated acid ($H_2SO_4$) in a beaker in ratio 4:1 of oil to acid while maintaining temperature at 60 $^oC$ with fixed stirring also . This aspect is also important to remove all degradation products in the spent oil and other asphatenic materials (Eman *et al*., 2012). During this step, insoluble sulphur containing compounds (sludge asphalt) were at the bottom of the beaker. To maintain a neutral oil reclamation process, equal concentration of (1 molar) NaOH was introduced, stirred and maintained at same temperature. Thereafter, the sludge formed was discarded.

### 2.3 Solvent Extraction

The neutralized and decanted oil was treated separately with hexane and hexane/Propan-2-ol in equal proportion at 60 $^0C$ for 30 minutes. After rigorous agitation, it was left at room temperature for 24 hours to allow further extraction. After this step, solvent-oil solution was separated from the remaining sludge by filtration. De-solventization was later carried out at the boiling point of each of the solvents.

### 2.4 Hydro-Treatment

Laboratory generated hydrogen gas ($H_2$) was used in the hydro-treatment of the remaining decanted oil. This was done by $H_2SO_4$ with Zn metals in a reaction glass apparatus with gas delivery tubes. This process improves the quality of the reclaimed oil and further decreases its evaporation in automobile engines during operations.

### 2.5 Adsorption

The adsorption process was done using a long fluorescent tube that served as a column containing treated mixture of bentonite powder and silica gel. The oil was allowed overnight to slowly pass through the column while contacting the adsorbent and thereafter at the bottom.

## 3.0 RESULTS AND DISCUSSION

**Tables 1 and 2** show the samples description/notations and results obtained for the various tests and methods employed in the reclamation process of the used automobile engine lubricating oil.

**Table 1 Sample Description and Notation**

| No. | Title | Sample No |
|---|---|---|
| 1 | Virgin lubricating oil | Sample 1 |
| 2 | Used lubricating oil | Sample 2 |
| 3 | Dehydrated used lubricating oil | Sample 3 |
| 4 | Treated oil after solvent extraction using solvent hexane | Sample 4 |
| 5 | Treated oil after solvent extraction using hexane / propan-2-ol blend | Sample 5 |
| 6 | Treated oil after solvent extraction and adsorption | Sample 6 |

The spent automobile engine lubricating oil is a complex mixture of recoverable base oil, polymeric additives, water, light hydrocarbons, metals and other carbonaceous particles (Mohammed *et al*., 2013).The technique introduced solvents with strong affinity for the base oil. Apart from the usual sedimentation, settling and filtration physical treatments, which already dominated the literature on lubricating oil reclamation processes, the effects of magnetization of the used oil was in addition carried out for the removal of very tiny metallic related items. This aspect was found to be effective as the analysis of the reclaimed oil especially in sample 6 showed presence of 0.075 mg/l of Pb compared to the others as shown in **Table 2**. The solvents consisting of hexane and blend of hexane with propan-2-ol for the extraction demonstrated some level of efficiency especially with respect to the viscosity of the reclaimed oil. Thus the solvent precipitates out some non-metallic material, which finally improved the viscosity. The reclaimed oil show reduced flash point, but the viscosity was found to improve. This will further assist effective lubrication. The flash point of the fresh oil is 240 $^0$C while that of the spent automobile engine lubricating oil is 135 $^0$C. Similar reduction in the values of viscosity has also been obtained by other authors such as Mohammed *et al*. (2013).They posited that the decrease in flash point of the spent oil could be as a result of the presence of light ends in the oils. In the combustion chamber where the oil undergoes combustion and oxidation at elevated temperatures, the oil breaks down into component parts including some light ends (Rincon, 2007). The results of the oil analysis in **Table 2** show that the specific gravity for the used oil is higher than that of the virgin and reclaimed oils. Udonne (2011) in their study reported that the specific gravity of contaminated oil could be lower or higher than that of its virgin oil. This depends on the nature or the degree of contamination. If the contamination was due to the fuel dilution, then its specific gravity will be lower. But if the contamination is due to water originating from fuel combustion in the engine and/ or accidental contamination by rain, its specific gravity will be higher than that of its virgin oil. The value of the pour point depends on whether wax removal has been done or not (Firas *et al*., 2006). The spent oil was found to contain high ash value. This shows the presence of metallic impurities in them. Samples 4-6 recorded slight decrease in the ash content after treatment as shown in **Table 2**.

The adsorption treatment of oil is based on the ability of an adsorbent to selectively extract resinous and sulphur containing compounds, unsaturated and polycyclic material and also organic residues of sulphuric acid and solvents from oils (Mohammed *et al*., 2013). Sample 6 treatments involve adsorption using a combination of adsorbents gave the most improved lubricating properties such as viscosity, flash point, and cloud point.

**Table 2: Analysis of the Samples**

| No. | Properties | Sample 1 | Sample 2 | Sample 3 | Sample 4 | Sample 5 | Sample 6 |
|---|---|---|---|---|---|---|---|
| 1 | Viscosity @ 40$^o$c | 171 | 177.3 | - | 177 | 175.1 | 174.8 |
| 2 | Moisture Content (%) | 0.21 | 4.1175 | 0.00 | 0.00 | 0.00 | 0.00 |
| 3 | Flash Point ($^O$C) | 240 | 135 | 140 | 146 | 150 | 152 |
| 4 | Pour Point ($^O$C) | -27 | < -7 | - | - | - | <-5 |
| 5 | Cloud Point ($^O$C) | < 0 | -5 | < 0 | < 0 | | < 0 |
| 6 | Specific gravity | 0.880 | 0.8889 | - | - | - | 0.7389 |
| 7 | % Ash | 0.75 | 0.98 | 0.98 | 0.91 | 0.885 | 0.885 |
| 8 | Ni (Mg/L) | 0.282 | 0.824 | - | - | - | Not detectable |
| 9 | Pb (Mg/L) | 1.220 | 8.411 | - | - | - | 0.075 |
| 10 | Mn (Mg/L) | 0.098 | 5.301 | - | - | - | 2.331 |
| 11 | Cr (Mg/L) | 0.804 | 1.302 | - | - | - | Not detectable |

The infra-red spectroscopy shows the presence of functional groups and other minor impurities present in samples of organic, inroganic or polymeric material. Scanning of the samples were done using infra red light for the observance of key functional groups. The observed spectroscopy of the virgin oil sample and the used /reclaimed oil sample are presented in **Figures 3** and **4** respectively. For the virgin oil sample (**Figure 3**), it was observed that transmittance peak values are at 721.72, 1007.20, 1032.90, 1053.90, 1376.33, 1457.75, 2362.55, 2852.28, and 2921.01 $cm^{-1}$. Those of the used and reclaimed oil sample (**Figure 4**) are at similar wave numbers. The implication is that the functional groups of virgin oil and the used/reclaimed oil samples are identical. In all, the two spectra confirm the presence of C-H bend at 2852.28, and 2921.01 $cm^{-1}$ , C-O-C stretch at, 1032.90 and 1053.90 $cm^{-1}$, C-O stretch at 1032.90 and 1053.90 $cm^{-1}$as well as C-H plane blend at 1376.33 $cm^{-1}$, C=C stretch at 1457.75 $cm^{-1}$, C-H aldehyde stretch at 2852.28 $cm^{-1}$ and C-H stretch at 2921.01 $cm^{-1}$.

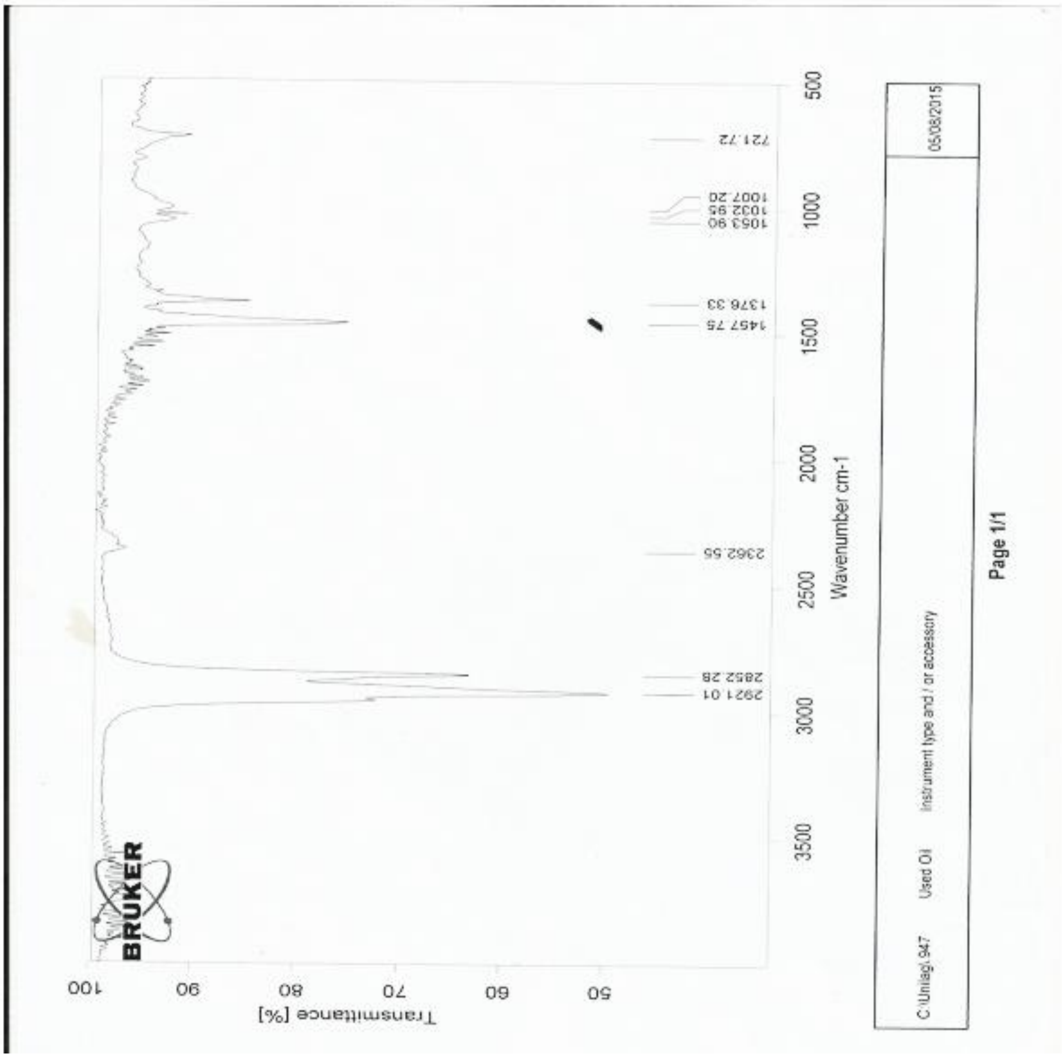


**Figure 3: Infra-Red Spectroscopy of the virgin oil**

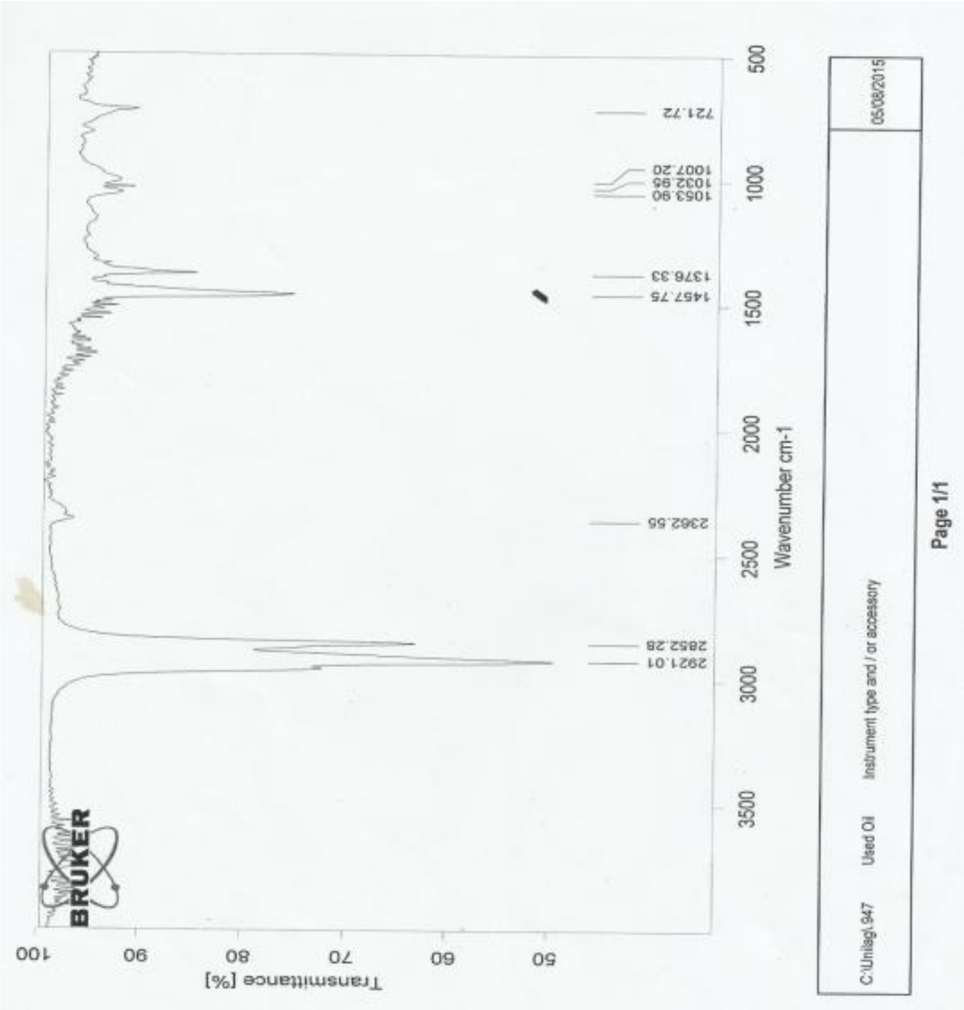

**Figure 4: Infra-Red Spectroscopy of the used oil**

## 4.0 CONCLUSION

The performance of highly non-polar solvents (Hexane) and its blend with highly polar solvents (propan - 2 -ol) has been studied. The use of these solvents for the extraction of the used oil coupled with adsorption using a combination of bentonite and silica gel has been found to be promising for the recycling of waste lubricating oil. physical processes such as sedimentation, settling, magnetization and filtration have also been found to be very significant pre-treatment processes that should be done in the reclamation of spent oil.

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