DEVELOPMENT OF LOCAL ADSORBENTS FOR SEPARATION OF SPENT LUBRICATING OIL USING AGRICULTURAL WASTES

By

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ABSTRACT

This study investigated the development of local adsorbents for the separation of waste lubricating oil from agricultural waste. The adsorbents were produced from agricultural wastes. The solvents were evaluated for the solubilization of spent lubricating oil. Adsorptive separation of spent lubricating oil was performed with a view to separate and characterizes various hydrocarbon fractions in the spent lubricating oil. The efficiency of the adsorbents developed was then evaluated.

Four adsorbents; egg shell, African star apple fruit shell, walnut shell and rice husk were locally prepared (they were purchased, sun dried, crushed and sieved using standard mesh to the sizes of ≥1.18mm and ≥6μm). The spent lubricating oil was collected from an oil service station in Osogbo, Osun State. Also solvents (N-hexane, 1-butanol and acetone) were selected to be used for the adsorption process. The oil and solvent were mixed separately for each of the solvent, and oil to solvent ratio of 1:5 and 1:10 were considered. Fix bed adsorption processes were performed and the performance of the four adsorbent were evaluated. The recovered compounds were determined by GC-MS analysis.

The results showed that, only n-hexane mixed perfectly with the spent lubricating oil, 1-butanol mixed partially and acetone was completely immiscible with the oil. From the results obtained from the GC-MS analysis, it was seen that, the amount of compounds recovered increases from oil to solvent ratio of 1:10 to 1:5. African star apple fruit shell adsorbent with oil to solvent ratio of 1:5 recovered 35 compounds when used in treating spent lubricating oil and recovered 29 compounds for oil to solvent ratio of 1:10. Walnut shell adsorbent recovered the second highest number of compounds which is 31 using oil to solvent ratio of 1:10. Egg shell
recovered 27 compounds with oil to solvent ratio of 1:5 while Rice husk could not separate the spent lubricating oil. From the results above, the African star apple fruit shell recovered highest number of compounds making its use as adsorbent more efficient.

The study concluded that African star apple fruit shell adsorbent is the most efficient adsorbent for the adsorptive separation of spent lubricating oil using n-hexane as the solvent.
CHAPTER ONE
INTRODUCTION

1.1 Background to the Study

A lubricant is a substance, usually organic, introduced to reduce friction between surfaces in mutual contact, which ultimately reduce the heat generated when the surfaces move. Other functions of the lubricating oil are; heating or cooling of surfaces when applied, transmitting forces, transporting foreign particles (Rafie et al., 2013). It is one of the most important liquids used in almost all vehicles and machines. Lubricating oil from petroleum consists essentially of complex mixtures of hydrocarbon molecules. It is mostly composed of isoalkanes having slightly longer branches and monocycloalkanes and monoaromatics which have several branches on the ring (Cutler, 2009).

Lubricating oils play a dual role of heat transfer and that of friction reduction. The main ingredient of lubricant oil is the base oil, which is either obtained from crude oil or synthesized. Base oil is mixed with additives to enhance its ability to act as a layer between contact surfaces. Therefore there are different grades of lubricating oil and each grade has its own quality and unique purpose, and this determines the types of additives to be added (Rafie et al., 2013)

Lubricating oil is made up of base oil or base stock between 71.5-96.2 wt% and 3.8-28.5% wt% of additives blended together according to its grade and specific duty. Additives are added to fulfill specific requirement for lubrication (Kajdas, 2000).

Various types of additives in typical lubricating oil composition is shown in Table 1.1
Lubricating oils undergo degradation and contamination during usage, which render them ineffective for further application. Lubricating oil goes through normal degradation and about 50% of it is consumed in the process. The rest of the oil picks up a number of contaminants from

**Table 1.1:** Composition of Typical Lubricating Oil

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAE 30 or 40 base oil stock</td>
<td>71.5-96.2</td>
</tr>
<tr>
<td>Additives</td>
<td></td>
</tr>
<tr>
<td>Metallic detergent</td>
<td>2.0-10.0</td>
</tr>
<tr>
<td>Ashless dispersant</td>
<td>1.0-9.0</td>
</tr>
<tr>
<td>Antioxidant/anti wear</td>
<td>0.1-2.0</td>
</tr>
<tr>
<td>Friction modifier</td>
<td>0.1-3.0</td>
</tr>
<tr>
<td>Pour point depressant</td>
<td>0.1-1.5</td>
</tr>
<tr>
<td>Antifoam</td>
<td>2-15ppm</td>
</tr>
</tbody>
</table>

Source: Kajdas, 2000
the working environment, such as, residual components of engine fuels, solids from wear processes along with corrosion products and dirt, soot, combustion products etc. (Rahman et al., 2008). The contamination contains unsaturation, aldehyde, phenolic compound, acidic compound, gums, additive, metals, varnish, and other asphaltic compounds originating from the overlay of bearing surfaces and degradation of the base oil components (Sadeek et al., 2014). Degradation involves changes in the lubricating oil molecular structure caused by cracking, isomerization and polymerization reactions prompted by high temperatures in the running engine. The overall effect of this degradation is the formation of low molecular weight compounds and oxidation products which include polymerized or condensed molecules known as sludge and gum. In spite of impurities, most of the base oil part in the waste oil is usually preserved to a large amount because of the high stability of the content of the base oil (Houssein et al., 2013). Used lubricating oil is an anthropogenic pollutant due to its toxicity, so it’s undesirable for use. When dumped in the ground, it diminishes soil efficiency and makes the plants that grow on it unsatisfactory for eating. The recycling of waste oil may be an appropriate and cheap alternative to incineration. Also, used lubricating oils are used in all core industrial sectors including; railways, marine, manufacturing and transport for lubrication (Bhaskar et al., 2004).

Also, the composition of typical waste lubricating oil is a stable dispersion of undergirded base oil and additives with high concentration of metals, varnish, gums and other asphaltic compounds coming from the overlay of bearing surfaces and degradation of the fresh lubricant components (Rafie et al., 2013). Chlorinated solvents may also be present in significant quantities as a result of the breakdown of additive packages and the addition of chlorine and bromine that act as lead scavengers in leaded gasoline. Polynuclear aromatic hydrocarbons (PAHs) are of particular concern due to their known carcinogenicity (Sadeek et al., 2014).
Therefore, recycling and re-refining of waste into virgin lubricating oil may be a suitable option for protecting the environment from hazardous waste. Another benefit associated with waste lubricating oil recycling is the economic gain due to increase in the percentage of base oil recoverable in waste lubricating oil than that from crude oil (Rafie et al., 2013).

Used lubricating oil is one of the abundant liquid wastes in the world that needs to be further treated. In some developing countries and Nigeria in particular, about 20 million gallons of spent-engine oil [SEO] are recovered yearly from mechanic workshops and disposed casually into the environment (Agarry and Ogunleye, 2012). There are basically three ways to deal with the waste oil: (a) dumping the waste oil on land, garbage heap and sewerage system, (b) regeneration of base-oil from waste oil and (c) extracting the heat value of waste oil through combustion processes (Nwinyi et al., 2014).

Used lubricating oil is a pollutant of great concern, with large volumes polluting the aquatic and terrestrial ecosystems (Yan and Qui, 2010). It consists of 80-90% huge quantities of long-chain saturated hydrocarbons. It also has a liquid combination of low to high molecular weight (C15-C18) aliphatic and aromatic hydrocarbon, chlorodibenzofurans, polychlorinated biphenyls, additives and disintegrated product (Koma et al., 2003). These compounds are toxic, carcinogenic and tetratogenic to human beings. However, owing to the rareness of knowledge about the severe environmental impact of the spent oil on the environment, artisans arbitrarily dispose-off the waste oil into sewers, water drains, open vacant plots and farmlands (Nwinyi et al., 2014). This constitutes an important cause of soil contamination in Nigeria. Chemical impurities in the spent engine oil contribute significantly to chronic hazards because they could get dissolved in soil surface and groundwater (Blodgette, 2001). The health hazards associated with human when exposed to spent oil include but not limited to: anemia, tremor with
consequent deaths (Nwinyi et al., 2014). Its wide-spread and long term effects on the coastal wetlands include reduction in photosynthesis in plants, transpiration and death of the biota depending on the volume of spill. Santas et al. (1999) reported enlarged kidney, liver, spleen weights, protein oxidation and lipid peroxidation as side effects of exposure to spent engine oil in areas exposed to or at spilled sites. The impact of spent engine-oil on soils range from depletion of nutrients especially nitrogen and phosphorus to degradation of soil physical properties and inhibition of microbial activities (Amadi and Debari. 1992; Osaigbovo et al. 2013).

If managed properly, waste oil can be a very valuable resource. It has varying refined fractions of petroleum and its recovery possibilities are extremely high. Average crude oils have 3-8% base oil, where as lube crudes typically have 12-16% base oil. This compares with 65-75% recoverable base-oil content in used automotive oils, which if burnt or dumped would mean the loss of a valuable natural resource (Nwinyi et al., 2014). The recycled oils produced with solvent refining or hydroprocessing can be used as lubricating base oils in modern engines. The most important methods for the recycling of used lubricating oils are re-refining and reclamation (Bachelder, 2005). Out of these two options the modern method is re-refining. During re-refining the properties of the oils are changed stepwise (Lukic et al., 2006).

Some major recycling processes in use include; settling centrifuge system, acid-clay process, Philips re-fined oil process, fixed bed sand filtration process to produce relatively clean