P068 - ANALYSIS OF ACID OPTIONS IN THE PURIFICATION OF SPENT MOTOR ENGINE OIL USING ACIDIFIED CLAY

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ABSTRACT

This study focuses on the purification of spent Shell Helix lubricating oil to promote environmental sustainability and economic viability. The purification process involves the use of acidified clay treatment, utilizing three different acid options: mineral sulfuric acid, organic acetic acid, and organic citric acid (a novel washing agent). Various physiochemical properties of the clay mineral, spent lubricating oil, purified oil, and fresh lubricating oil were examined. These properties included the kinematic viscosities at 40°C and 100°C, pour point, flash point, and metal content determined through Atomic Absorption Spectrometry (AAS). The clay mineral's surface area was notably enhanced from 53.308 m^2/g to 89.513 m^2/g after acidification, which facilitated the purification process. The results demonstrated that certain properties of the spent lubricating oil, such as kinematic viscosities, pour point, and flash point reduced due to the presence of contaminants from prior use, while metal content increased. However, the acidified clay treatment successfully purified the spent oil, bringing its physiochemical properties closer to those of the fresh oil sample after treatment. The extent of purification, however, varied depending on the type of acid used. This research underscores the potential for sustainable management of spent lubricating oils through acidified clay treatment.

KEYWORDS

Spent oil, purification, shell helix, acidified clay, kinematic viscosity

1.0 INTRODUCTION

Engine oil, a crucial component derived from crude oil, plays a multifaceted role in the functioning of internal combustion engines. Apart from lubrication, it also contributes to cleaning, corrosion prevention, sealing improvement, and engine cooling by dissipating heat (*1*). Lubricating oils, being a vital fraction of crude oil, find application in diverse engines and machinery, from automobiles to industrial equipment (*1*). These oils serve the purpose of reducing friction and wear in moving parts within combustion engines and various machines (*2*).

The disposal of used lubricating oils is an environmental and economic concern. Impurities introduced during use, such as dirt, metal debris, water, or chemicals, render the oil less effective over time. Disposing of used oil inappropriately, whether in drains or rivers, can lead to serious pollution issues, releasing harmful substances into the environment (*3*). Therefore, sustainable disposal methods, like purification, have gained importance in addressing the environmental challenges arising from the indiscriminate disposal of used engine oil (*4*). Recycling and re-refining of used engine oil can offer environmental benefits by reducing pollution and conserving resources (*5*). While re-refining is well-established in developed countries, it is yet to gain widespread traction in certain developing nations (*6*).

The ever-growing demand for fossil fuels, particularly in the transportation sector, highlights the need for recycling plants to mitigate the environmental hazards associated with improper disposal of spent oil (*7*). In this study, the purification of spent Shell Helix engine oils was conducted using acidified clay with three acid options as washing agents. The extent of purification using different acids was assessed, and the physicochemical properties of the purified Shell Helix oils were compared to fresh oil samples to determine the most effective washing agent.

2.0 MATERIALS AND METHODS

2.1 Materials

The materials used for this research work were all sourced locally, they include the used (Shell Helix 20W-50) Crankcase oil from Honda civic 2008 model, Clay from the back of Talba market in Minna, Niger State, At a depth of about 30cm, Conventional laboratory reagents from Panlac Chemicals along Keteren Gwari Road, Minna Niger State. Apparatus and Equiptments from Technology Incubation Centre David Mark Road, Minna Niger State

2.2 Methods

2.2.1 Sampling of clay

Clay sample was collected at the back of building material market along Talba farm in Minna Niger State, North Central Nigeria as-mined in lump form, crushed to suitable sizes and then sun dried (*8*). The Characterization of the clay was then carried out using Brunauer–Emmett–Teller (BET) analysis.

2.2.2 Used Oil Sampling Process

Spent engine oil (Shell Helix 20W-50) was used as the test sample, about 4 litres of used engine oil was collected from a Honda civic 2008 model in a plastic gallon after 2 months and 2 weeks of using the car over a distance of 3500 km using the Drain Stream Method as reported by (*3*). The equivalent fresh engine oil was purchased from Total filling station at Federal housing authority Lugbe FCT Abuja.

2.2.3 Preparation of The Clay Sample

A 200g sample of Untreated clay was crushed and combined with 500cm3 of distilled water to create a suspension. Impurities like solid materials, stones and other particles settled at the bottom of the container and were separated by carefully decanting off the clay particles at the top of the container. The remaining mixture was then placed in a Binatone oven (specifically the Binatone TTO 5001 laboratory oven) to remove moisture using a temperature of 1050c for a duration of 6 hours. Once dried, the clay was grounded into a powder form and sieved through a very fine mesh of 74µm. (*9*).

2.2.4 Acidification of clay

A round bottom flask with a capacity of 1000cm3 was used to mix thoroughly 200g of clay particles with a size of 74µm with 400cm3 of 1M H2SO4. The resulting mixture was heated on a magnetically stirred hot plate at a temperature of 2000C for a duration of 3 hours (*9*). Afterwards, the clay was washed carefully with distilled water to further remove precipitates, stones and impurities until a neutral pH was reached as indicated by a PH indicator. The clay was then filtered and baked for about 6 hours at 200 ºC to remove water and stored in dry place so that it can be used later in the purification process. The obtained dry and clean clay is called activated clay because it is active chemically and electrostatically as reported by (*10*).

2.2.5 Pre-treatment of Used/Spent lubricating oil

To eliminate contaminants like sand, metal chips and micro impurities from the used lubricating oil, a filtration process was carried out. The filtration process involved the use of a Buckner funnel and filter paper. The filter paper was fitted into the Buckner funnel and the used oil was then filtered by passing it through the set-up. The resulting lubricating oil was allowed to settle for 24hours after which it was preheated at 450 C for 30 minutes to degrade some additives and reduce the workload of the acid (*11*).

2.2.6 Treatment of Spent Lubricating Oil using Acid Technique

Three separate beakers were used to accurately measure three samples of pre-treated engine oil each measuring $300cm^3$. Then $30cm^3$ of each acid was poured separately into a $50cm^3$ beaker. The regulator hot plate was switched on and the $300cm^3$ of used engine oil in the beaker was placed on top. The used engine oil was then heated for about 5 minutes until temperature of 450C was attained; after which each acid was gently poured into the three separate beakers. The first beaker 1M H_2SO_4, Second beaker 1M CH_3COOH and third beaker 1M $C_6H_8O_7$. and the whole mixture was stirred continuously for 10 minutes.

At the end of the acid treatment step, the acid treated oils were allowed to settle for 24 hours to form sediments at the bottom of the beakers. After which the acidic-oil mixtures were properly decanted into separate 500 ml beakers using mesh clothes while the residue (acidic sludge) at the bottom of the beakers were carefully discarded (*2*).

2.2.7 Acidified Clay Treatment Procedure

The process involves packing the acidified clay (30g) after grinding it to a particle size of 74µm into a buckner funnel, with a filter paper inserted in it. Then the funnel was connected to a vacuum pump which allowed the sulphuric acid treated oil to pass through the clay bed. This procedure was repeated for all the acids (*12*).

2.2.8 Neutralization Procedure

To neutralize the acid in the three oil samples, 100cm3 of 10% NaoH was added. After which the oil was left to settle for 24 hours and then decanted into a beaker while the residue at the bottom was discarded. Also, the pH of the decanted oil was recorded and noted to check if neutralization was completed (*2*). Finally, the resulting purified lubricating oil was obtained and ready for analysis as reported by (*9*).

3.0 RESULTS AND DISCUSSION

The clay mineral was characterized using BET analysis to determine the change in the surface area, pore volume and pore diameter between the untreated clay and treated clay mineral similarly the used and purified engine oil samples were characterized to determine the changes in their physiochemical properties when compared to the corresponding fresh oil. The result obtained is discussed below: -

3.1 Characterization Of Clay Sample Using Brunauer-Emmett-Teller (BET)

The Brunauer-Emmett-Teller theory (BET) is commonly used to estimate specific surface area (SSA) of solid materials, extending the Langmuir monolayer adsorption model to multilayer adsorption. SSA is a crucial morphological characteristic in applications involving porous structures, like industrial adsorbents, catalysts, and polymers. Pores are classified based on their size: micropores (dpore < 2 nm), mesopores (2 to 50 nm), and macropores (>50 nm), with further divisions into ultra-micropores, medium-sized micropores, and super-micropores (*13*).

The results in Table 1 shows a significant increase in the surface area of clay after acidification, increasing from 53.308 m²/g for untreated clay to 89.513 m²/g for acidified clay. This increase in porosity is attributed to the acidification process at high temperatures, which partially dissolves exchangeable cations, creating more surface area for adsorption (*14*). This aligns with previous research, which noted that the adsorptive capacity of an adsorbent is directly linked to its surface area. The pore volume also increases, from 0.025 cm³/g for untreated clay to 0.211 cm³/g for acidified clay, in line with similar studies (*14*). Additionally, the pore diameter decreases from 160.253 nm for untreated clay to 153.720 nm for acidified clay, as the activation process involves breaking up agglomerates, allowing plate separation (*14*). These findings are consistent with previous research (*14, 15*), albeit partially agreeing with others (*4, 16*) that reported a significant increase in surface area of activated clay.

Table 1: Result of the Characterization of Clay Mineral

	SURFACE AREA((m2g-1)	PORE VOLUME((cm3g-1)	PORE DIAMETER((nm))
UNTREATED CLAY	53.308	0.025	160.253
ACIDIFIED CLAY	89.513	0.211	153.720

3.2 Characterization of Fresh, Used and Purified Engine oils using Quality test procedures

3.2.1 Kinematic viscosity:

Viscosity, the measure of a fluid's resistance to flow, serves as a crucial indicator of spent engine oil quality, allowing the detection of contaminants and oxidation products. Contaminants like soot, dirt, glycol, and water, as well as fuel dilution and shearing of viscosity index improvers, can influence viscosity. A higher viscosity reflects a stronger oil film, which is essential for effective lubrication (*2*). The study tested the kinematic viscosities of spent, purified, and fresh oil samples at 40°C and 100°C and found that the type of acid and clay used in the treatment of used engine oil significantly impacts viscosity. Spent oil had kinematic viscosities of 118.9 cSt and 13.9 cSt, in agreement with previous findings (*17*), while the purified oil samples showed higher viscosities than spent oil and were closer to fresh oil as shown in Figure 1. This increase in viscosity in purified oil is attributed to the conversion and removal of impurities by acids and filtration. Notably, the results suggest that the purification of spent engine oil using organic acetic acid and mineral sulfuric acid with acidified clay is effective in removing contaminants, with sulfuric acid showing advantages over other methods (*2*).

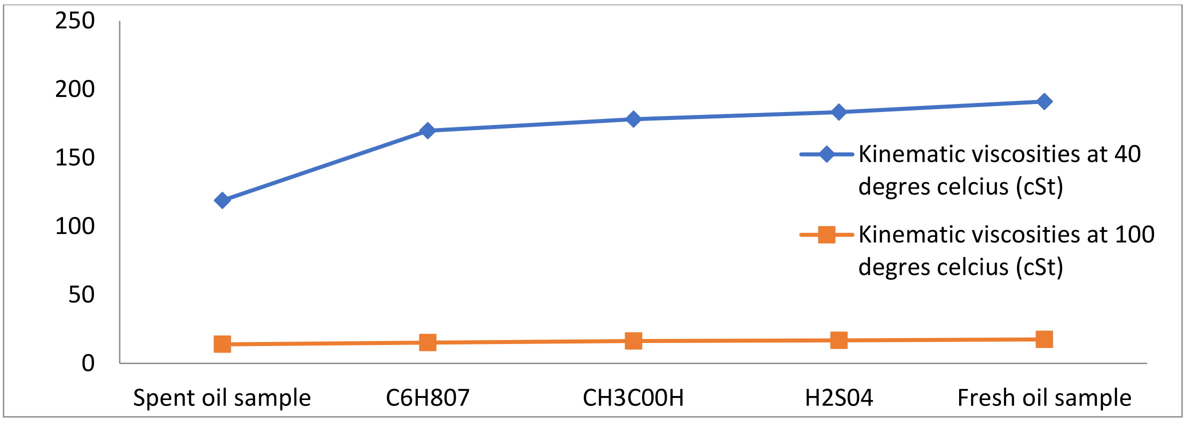

Figure 1: Kinematic Viscosities of Spent, Purified and Fresh Engine oil samples at 40 ^{O}C and 100 ^{O}C

3.2.2 Flash point:

The flash point, indicating the lowest temperature at which air vapors from a substance will briefly ignite upon exposure to flame or spark, serves as a significant marker of a lubricating oil's quality. A lower flash point often signals contamination with volatile substances like gasoline, making it a reliable indicator of oil condition (*18*). Figure 2 illustrates the flash point results for spent engine oil, purified oil samples, and fresh engine oil. The flash point of spent engine oil is 106°C, while purified oil samples exhibit values within the range of 133°C to 189°C. This increase in flash point is attributed to the reduction of contaminants through the purification process, in line with prior research (*4*). Fresh engine oil, with a flash point of 201°C, surpasses that of spent oil, a decrease in flash point attributed to dilution by unburned fuel during engine operation (*3*). The flash points of the purified engine oil and fresh engine oil samples consistently exceed that of spent engine oil, aligning with earlier studies (*3, 11, 17*). Furthermore, the flash points achieved through purification with organic acetic acid and mineral sulfuric acid closely resemble those of fresh engine oil, highlighting their effectiveness in purifying contaminated engine oil.

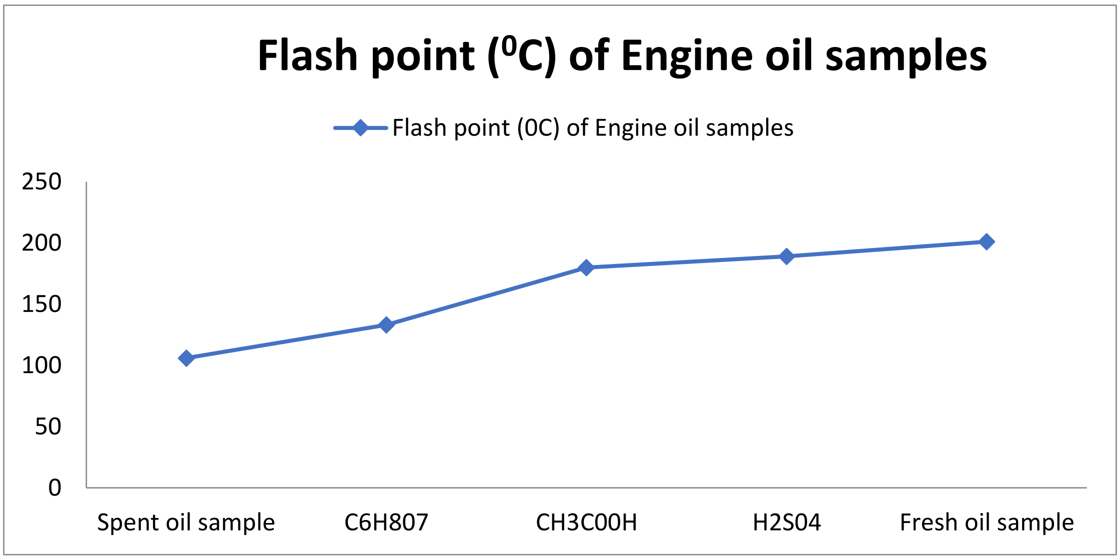

Figure 2: Flash Point (^{O}C) of Spent, Purified and Fresh Engine oil Samples

3.2.3 Pour point

The pour point, a critical parameter, signifies the lowest temperature at which lubricating oils remain functional for specific applications, with significant implications for their flow characteristics, especially in cold conditions. Engine base oils often contain waxes and paraffins that solidify at low temperatures, leading to higher pour points, particularly in oils with high wax and paraffin content. The study's results, as depicted in Figure 3, reveal that purified oil samples exhibit pour point values ranging from -11°C to -9°C, surpassing the -15°C pour point of spent engine oil, aligning with previous research (*12, 19*). Notably, when the acidified clay treatment employs organic acetic acid and mineral sulfuric acid as washing agents, the resulting pour point values closely match those of fresh engine oil, highlighting the efficacy of these agents in purifying spent or contaminated engine oil.

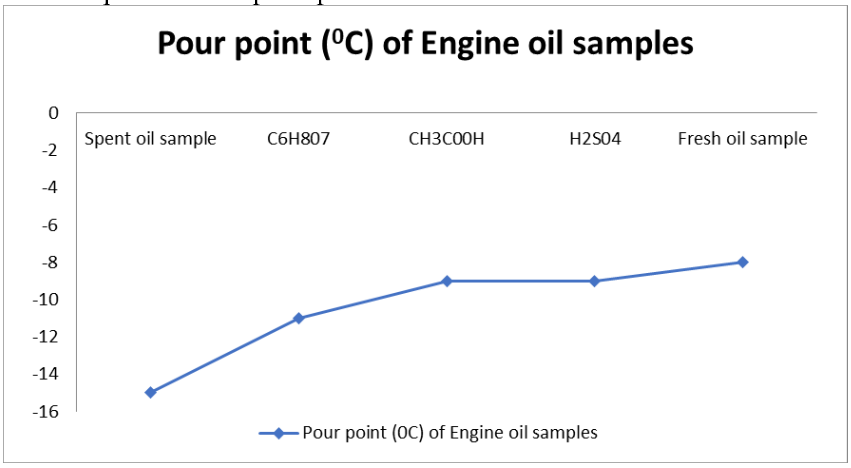

Figure 3: Pour point (^{O}C) of Spent, Purified and Fresh Engine oil Samples

3.3 Metal Content Determination Using Atomic Absorption Spectrometry (AAS)

3.3.1 Determination of Iron (Fe):

The most common wear metal in a car's engine that is introduced into the engine oil after a period of use is iron. Iron comes from many various places in the engine such as liners, camshafts and crank shaft, pistons, gears, rings, and oil pump (*3*). Figure 3 shows that the Iron concentration for the spent engine oil is high while that of the purified engine oil samples have lower iron concentrations. The purified oil sample using acidified clay with organic acetic acid gives the lowest iron concentration of 0.851ppm which can be compared to the iron concentration of the fresh engine oil sample. Fe concentration in used oil sample should fall within 100-200ppm range reported by (*9*), very high iron amounts indicate excessive wear of engine parts. The result obtained is in agreement with the result of (*3, 11, 20*)

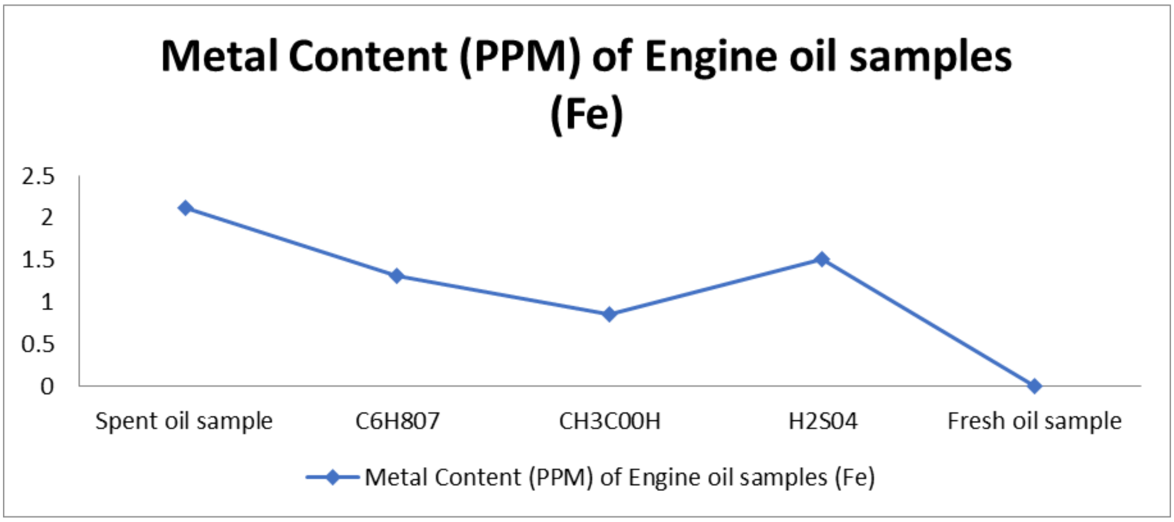

Figure 3:Iron (Fe) Content (PPM) of Spent, Purified and Fresh Engine oil Samples

3.3.2 Determination of Manganese (Mn):

Manganese is a rear metal that is usually introduced into the spent engine oil in small amounts. Manganese (Mn) is introduced from wear of cylinder liners, valves, and shafts (*3*). Figure 4 shows that the purification process was able to reduce the manganese concentration of spent engine oil however the purified engine oil using acidified clay with organic citric acid and acetic acid gives a manganese concentration of 1.764ppm and 1.941ppm respectively. Which are lower than the values obtained for Mineral sulphuric acid acidified clay treatment. Therefore, purification with organic citric and acetic acid proves to be more effective for the removal of manganese in spent engine oil. The result obtained is in agreement with the result reported by (*3*).

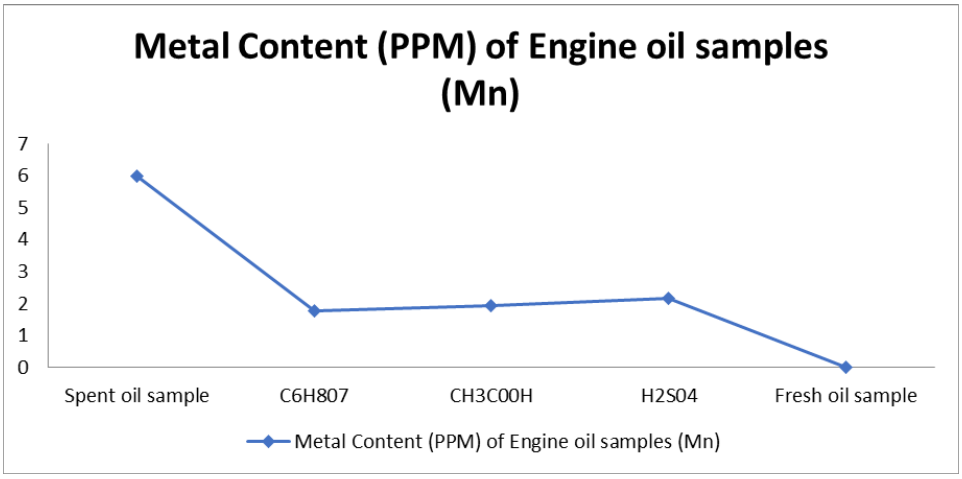

Figure 4:- Manganese (Mn) Content (PPM) of Spent, Purified and Fresh Engine oil Samples

4.0 CONCLUSIONS AND RECOMMENDATION

The study explored the efficacy of 1M acidified clay, using mineral sulfuric acid, organic acetic acid, and organic citric acid as a novel washing agent, for the purification of spent Shell Helix(20W-50) engine oil. A comprehensive characterization, encompassing kinematic viscosities at 40°C and 100°C, pour point, flash point, and metal content analysis via AAS, was conducted to assess the effectiveness of these acids in the purification process. Additionally, the porosity of the acidified bentonite clay used in the process was characterized using BET analysis, revealing its high porosity, falling within the macropores category with a diameter exceeding 50 nm.

The findings indicate that acidified clay treatment with mineral sulfuric and organic acetic acids yielded results comparable to fresh engine oil in the purification process, significantly enhancing the quality of the spent engine oil. However, the use of acidified clay with organic citric acid showed less effectiveness in the quality improvement of the purified oil. The AAS analysis demonstrated a measurable reduction in metal content after purification, with acetic acid being particularly effective in decreasing iron (Fe) concentration, and organic citric acid proving the most efficient in reducing manganese (Mn) content.

This study therefore recommends the use of mineral sulphuric acid and organic acetic acid in the purification of spent engine oil using acidified clay treatment technique.

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