Application of response surface methodology in optimizing the process conditions for the regeneration of used mobil oil using different kinds of acids

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ARTICLE INFO

Keywords:
Chemical engineering
Petroleum engineering
Environmental science
Mobil oil
Acid/clay method
Process conditions
Optimization
Regeneration

ABSTRACT

Optimization of process parameters for the regeneration of used mobil oil by acid/clay method using sulphuric acid as washing agent was successfully carried out. Used mobil oil was characterized before and after regeneration to determine the changes in the physicochemical properties of the oils. The viscosity, flash point and fire point of the oil increased after regeneration while the specific gravity and sulphur content decreased. The Atomic Absorption Spectrometry (AAS) carried out revealed the presence of eight different metals in the fresh mobil whose concentration increased during use but reduced after regeneration. The FTIR instrumentation analysis revealed that the used mobil oil has high concentration of some ester groups, aromatic materials, glycol and sulphur oxidation products while the proportion of these materials plunged significantly after treatment. Changes in the process conditions like acid concentration, settling time and bleaching temperature affected the effectiveness of the regeneration process by affecting the desired changes in the physicochemical properties. The process parameters were optimized using Central Composite Rotatable Design (CCRD) of Response Surface Methodology (RSM), with the aid of design expert. The design, which use purity as the response of the experiment, considered three independent factors of acid concentration, settling time and bleaching temperature; and the effects of these factors on the response are significant since their P-values are less than 0.05. An optimum theoretical purity of 0.86 was obtained at 6.5mol/lit acid concentration, 5.5hours settling time and 95.5°C bleaching temperature, which agreed excellently with 0.85 actual purity obtained at the same conditions. Therefore, the regenerated mobil oil at these optimal conditions is capable of meeting commercial expectations.

1. Introduction

Mobil oil, one of the best products of Exxon Mobil, is an excellent lubricant for most automobiles and internal combustion engines. Lubricating oils are predominantly complex mixtures of hydrocarbons with more than 20 carbon atoms per molecule. Generally, the hydrocarbon molecules range from low viscosity oils with 250g as molecular weight to highly viscous lubricants whose molecular weights reached 1000g. Lubricating oils are heavy oils obtained from crude oil over the temperature range of 350–500°C (Ababio, 2001). Doaa et al. (2017) have opined that lubricating or motor oil is the most important fraction of petroleum because it is extensively used in all automobile, machines and internal combustion engines. Its function includes reducing friction, carrying away heat, protecting against rust, wear and removing contaminants from the engine. The oil is used to ensure the smooth performance and prolong the good condition of the vehicles and machines (Udonne, 2011; Ogbeide, 2011). It is estimated that about 1.7–3.5 million tons of engine oils are collected annually across United States of America and Europe, which is quite sizeable (Hamawand et al., 2013). Nigeria alone generates and sells more than 300 million litres of motor oil every year out of which about half of the total amount of motor oil sold is being generated annually (Opeyemi, 2004). Though this estimate cannot say to be 100% accurate, because Nigerians have widespread habit of re-using already used oil in other automobiles and machines and even blend it with new motor oils, instead of trying to regenerate it first. However, this quantitative measure is still significant for estimating roughly. Furthermore, Boughton and Horvath (2004) opined that less than 45% of spent engine oil is collected globally for regeneration annually while the end users throw the remaining 55% into the immediate environment, which is a serious environmental threat. Engine oil in

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https://doi.org/10.1016/j.heliyon.2020.e05062
Received 27 April 2020; Received in revised form 30 May 2020; Accepted 22 September 2020
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cn-nd/4.0/).
its purest form, is a valuable resource to the engine. Generally, engine oil is slippery and gets dirty with time as it is being used. This implies that the lubricating property of the oil diminishes as it is being used; and at the same time, its tendency to act as a potential pollutant increases since it gets more contaminated with dust particles, combustion and oxidation products as well as worn out metal parts. Therefore, used engine oil could be considered as a high pollutant that needs urgent and adequate attention because it can contaminate the environment and water bodies when carelessly disposed (Eldeen et al., 2017). The chemical elucidation done using FTIR revealed that the level of unsaturation in the used Mobil oil is high because of the carbonyl groups deposited during use by chemical oxidation processes (Kadam and Zingde, 1985; Vazquez-Duhalt and Greppin, 1989) while the AAS revealed the metal constituents in the oil and how they increase during use as well how regeneration process causes them to plummet.

Research has shown that used engine oils can be effectively regenerated for further use since oil does not wear out. This means that the chemical composition of lubricating oils is always preserved for a long time due to high thermal stability of the heavy compounds contained in the oil (Hussein et al., 2014). regeneration of used engine oil could be seen as the process of using sulphonating agents, such as sulphuric acid, oleum or sulphuric trioxide to remove impurities from the oil (Isah et al., 2013). This process guards our environment from the toxic effects of releasing this spent lubricant into it (Adeyinju et al., 2016). The regeneration of the used engine oil is important for two main reasons: It ensures a cleaner way of maintaining a safe working and pollution free environment by avoiding unwarranted disposal of used oil contaminants into the environment stream and other water bodies. It also provides an affordable and a sustainable approach to the conservation of this natural resource (fresh motor oil) since it is a finite and non-renewable resource. This is achieved through viable recycling of used motor oils using adequate techniques. Hamawand et al. (2013) had earlier reported that the use of acid-clay method in recycling used lubricant has lasted for many years. The regeneration of used Mobil oil using acid-clay mixture operates by the principle of adsorption, in which the acid acts as an adsorbent; adsorbing impurities from the oil. This method is cheaper compared to other methods though it has some limitations.

The regeneration of used engine oil is subject to certain reaction conditions that must be carefully met to give the desired product. These reaction conditions may also depend on the type of regeneration process been employed. Based on literatures, some of the dominating factors include solvent ratio, acid concentration, bleaching temperature and reaction time. This research considered bleaching temperature, settling time and acid concentration as the factors affecting the regeneration process because the first two are often the likely ones being studied in every regeneration process while acid concentration was also since acid was used as the washing agent. In addition, they are the main factors affecting the regeneration of used mobil oil. These three independent variables must be optimized in order to establish the most acceptable conditions for the process. According to Datta (2011), optimization is a unique decision-making technique, which focuses on establishing the best results under a set of conditions. Every optimization problem consists of the objective function, which is a term that describes the main problem to be optimized. The other important components are the constraints and the variables. Also, we know that problems involving optimization could be linear, non-linear, geometric or quadratic (Asadu et al., 2019). In this study, these process conditions were optimized using central composite design (CCD) of response surface methodology (RSM). RSM is defined as the collection of basic and mathematical techniques, which is used to build, ameliorate and optimize a given process (Montgomery, 2004; Myers and Montgomery, 2002). RSM, as a tool, is used to establish the relationship between the independent variables (process conditions) and the dependent variable(s) (response(s)). It is primarily aimed at creating an empirical model for a given system or process, based on the experimental outcomes. The preference of RSM for this optimization study is because RSM makes it easier to determine how the independent variables interact both with each other and the response, and RSM is economical both in terms of reduction of time and the number of experimental runs needed to analyze all the factors (Boyaci, 2005). Thus, RSM suits the studying of the effects of many input variables and their interactive effects on one or more output variable(s). Furthermore, RSM is very suitable for development of a fitting mathematical model for the system and estimates error using the method of least squares. Adeyanju et al. (2016) had opined that RSM connects items properties by using regression analytical equations, which shows the relationship between information factors and item properties. In other words, this work is not only focused on the processes of regenerating used Mobil oil by acid-clay method, but also the use of CCD of RSM in studying the effects of these reaction conditions on the process response (purification) as well as establishing the optimal values at which the best purified Mobil oil is obtained.

2. Materials and methods

2.1. Materials

Used Mobil oil was collected from mechanic workshop in Nsukka industrial site. Other materials used included; cotton wool, sulphuric acid, hydrochloric acid, acetic acid, sodium hydroxide (all manufactured by BDH Chemicals Ltd Poole, England), activated clay, activated charcoal and distilled water. The equipment includes: magnetic stirrer, weighing balance, conical flask, viscometer, test cup, Pensky martin flash point apparatus (PM-93), test tubes, beaker, Bunsen burner, tripod Stand, stop watch, hot plate, crucible, thermometer, syringe, electric oven, thermometer, Atomic Absorption Spectrophotometer (Model 230ATS), Fourier Transform Infrared Spectroscopy (Model: M30).

2.2. Methods

2.2.1. Purification procedure

Acid/clay method using sulphuric acid as washing agent was used in purifying used mobil oil. Normal procedure for the purification of used mobil oil was followed. Here, 300 ml of used was measured into a 500 ml beaker using a measuring cylinder. Thereafter, 30 ml of sulphuric acid was measured separately into a 50 ml beaker. The regulator hot plate was switched on and the 300 ml of used mobil oil in the beaker was placed on top. The used engine oil was heated for about 5 min until temperature of 45–50 °C was attained; after which each acid was gently poured and the whole mixture continuously stirred for 10 min. It was then allowed to settle for 24 h to form two layers: upper and lower sediments. The acidic-oil mixture was properly decanted into another 500 ml beaker using a piece of cloth while the residue (acidic sludge) at the bottom of the beaker was discarded. The decanted oil layer was maintained in an electric oven at a temperature at 100 °C and then bleached by adding 20 g of activated clay. The resulting mixture was continuously stirred for at least 10 min after which it was neutralized by adding 100 ml of the solution of 15 % Caustic soda (NaOH). The mixture obtained was constantly stirred again for 10 min and allowed to settle for 24 h in a beaker without agitation after which it was decanted into another beaker. It was finally filtered using a filter cloth and the filtrate was collected in a filtration flash while the residue was discarded. The same procedure was repeated using the other acids respectively as washing agents. The filtered residues and acidic sludge can be buried underground in a sanitary landfill where is thought to be adequate and necessary.

2.2.2. Characterisation of used and regenerated mobil oil

Physicochemical properties such as specific gravity, viscosity, flash point, fire point of the fresh, used and regenerated mobil oils were determined using standard ASTM D2974-07 (ASTM, 2007). The metal contents of the different samples of mobil oil were analysed using Atomic absorption spectrophotometer.
2.2.3. Preparation of samples for FTIR spectroscopic analysis

The Fourier Transform Infrared Spectroscopy is a good analytical tool used to analyze a sample to discover the functional group present in the sample. The FTIR spectra of fresh, used, and regenerated mobil oil samples were recorded with Buck Scientific Infra-red Spectrophotometer (Model: M530) over a wavelength range 4000–500cm⁻¹. 1g of each sample was mixed with 0.5g of Potassium Bromide (KBr); after which 1ml of Naplo (a solvent for preparation of sample by Buck 530 IR – Spectrophotometer) was pipetted into the sample mixture with the aid of a syringe to form a paste before introducing into the instrument sample mould and allowed to scan at a wavelength of 600–4000nM to obtain its spectra wavelength.

2.2.4. Design of experiment

Central Composite Design (CCD) of the Response Surface Methodology (RSM) was used in optimizing the reaction conditions for the regeneration of used Mobil oil using acid/clay method. These reaction conditions are bleaching temperature, acid concentration and settling time. The experimental design done with the aid of design expert version 11, considered three independent factors of bleaching temperature, acid concentration and settling time as shown in Table 1.

The response of the experiment is the purity which is given on a scale of zero to one (0–1); with lower values indicating high impurity while the higher values (values close to 1) indicate high purity. The purity was based on the difference between unity and impurity removal (1 - impurity removal). Having chosen 1 as the reference, then it means at any point, the sum of impurity and purity is 1. Therefore, when the purity is high the impurity is low and vice versa.

The impurity removal was calculated using Eq. (1):

\[ \text{Impurity removal} = \frac{S_{go} - S_{gt}}{S_{go}} \]

(1)

Where \( S_{go} \) = Specific gravity of used mobil oil.

\( S_{gt} \) = Specific gravity of mobil oil regenerated at any time t.

The specific gravity was used to develop this model equation because the difference between the specific gravities of used and regenerated oils is mainly attributed to the removal of most of impurities during the regeneration processes. The specific gravity can be used as a useful parameter for purity if we remember that impurity generally increases the physical properties, such as density and boiling point of most substances. Practically, the specific gravity of a pure substance rises when the substance is contaminated because the presence of impurities increases the overall the mass of the substance. Therefore, high specific gravity is one of the major indications that the oil is contaminated (Udonne, 2011). Thus, as the oil is being regenerated, its specific gravity decreases because of the removal of the impurities. Hence, validating the use of specific gravity as a measure of the purity of the oil during regeneration.

3. Results and discussions

3.1. Characterization of fresh, used and regenerated mobil oils

A dimensionless ratio of the density of a certain substance to that of water is known as specific gravity or relative density. Density of a substance depends on a number of factors such as changes in temperature, presence of impurities mainly aromatic compounds, etc. Temperature and density are inversely related. An impure material tends to have higher density than that of the same pure material. For the engine oil, an increase in the number of aromatic compounds in the oil would lead to an increase in its density and hence specific gravity. According to Udonne (2011), used engine oils have higher specific gravities because of the deposition of impurities such as metals and degraded products during usage. The specific gravities of the regenerated oils are lower than those of the used oils because of the removal of most of the contaminants in the oils during the regeneration process. According to Abro et al. (2013), based on the nature and kind of impurity in the used engine oil, the specific gravity of the regenerated used engine oil could be lower or higher than fresh engine oil. Generally, used lubricants contaminated with heavy metals, aromatic compounds and other highly unsaturated compounds tend to have lower specific gravity than fresh lubricants after regeneration. These explains why regenerated mobil oils in Table 2 have lower specific gravities than fresh engine oils.

It is already a known fact that viscosity is a measure of opposition to flow in fluid system. The higher the viscosity, the higher is its resistance to flow. Emman and Abeer (2012) noted that viscosity is proportional to the strength of the oil film. Furthermore, Abu-Elella et al. (2015) had opined that viscosity is a state function of density, temperature and pressure. Thus, viscosity varies inversely as the temperature of the engine oil. Udonne and Bakera (2013) inferred that the oxidation or contamination of the fresh motor oil with insoluble matter could result in increase in its viscosity while dilution of the oil with light fuel could bring down its viscosity. Table 2 also unveiled that the viscosity of used engine oils is far lower than that of their corresponding fresh oils. This could be due dilution with light fuel from thermal decomposition of hydrocarbons (Ajemba, 2012). In addition, Isah et al. (2013) also suggested that apart from the effect of dilution with light fuel, the decrease in viscosity of the used oils may also be attributed to the degradation or thermal cracking of the fresh oils during application. The Table vividly revealed that the viscosity of the regenerated Mobil oil is higher than that of their used oil counterparts but lower than the fresh oil. The higher viscosity in regenerated oils is also an indication that the regeneration processes were able to restore the properties of the oils. Thus, the regenerated oils have higher viscosities than the used oil due to the fact that the arrangement of molecules is unperturbed by the chemical treatment and filtration (Isah et al., 2013).

The flash points and the fire points of the used oils are generally lower than those of their corresponding fresh oils. According to Abu-Elella et al. (2015), a very low flash point of engine oils indicates that they have been contaminated with volatile materials like gasoline. The flash point and fire point of the regenerated oils are higher than that of their used oil counterparts because the regeneration processes succeeded in reducing the number of contaminants. Thus, the regeneration of the used oils tends to take their flash point and fire point closer to those of their fresh oil counterparts.

Furthermore, Table 2 showed that sulphur content is highest in the used oil. The high sulphur content in used oils could be attributed to the wear caused between the moving parts of the engine or machine during application. Low melting point sulphur compounds are formed when sulphur reacts with most metals. These sulphur compounds are the major cause of corrosion in automobiles' engines because they are unstable and easily oxidized in the internal combustion engines during use (Rincon et al., 2005). On treatment, the sulphur content of the used oil reduces due to the reduction of the wear and also because of the removal of these oxidized sulphur compounds by washing agents.

| Table 1. Design of experiment. |
|-----------------------------|---|---|---|
| Factors               | Symbols | Unit | -1 | 0 | 1 |
| Bleaching temp         | A     | °C  | 70 | 90 | 110 |
| Acid conc              | B     | mol/lit | 3 | 5 | 7 |
| Time                  | C     | Hrs | 2 | 4 | 6 |
Another vital information demonstrated by Table 2 is that regenerated oil using sulfuric (H2SO4) acid has relatively the best physico-chemical properties which are closer to those of the fresh oil. This is a suggestion that sulfuric acid is better than the other acids used as washing agents. This high efficacy of sulfuric acid as a washing agent than other acids used in this research could be attributed to the strength of the acids. Sulfuric acid is the strongest acid among the three acids used and therefore gave the best regenerated used Mobil oil. The fact that the performance of sulfuric acid as a washing agent is closely followed by hydrochloric acid performance also supported the earlier notion that the acid strength played a role in their efficacy. Furthermore, it is also known that stronger acids are more reactive in chemical reactions than weaker acids.

3.2. AAS characterization results

The Atomic Absorption Spectrometry (AAS) analysis was carried out to identify and determine the number of chemical elements present in fresh, used and purified mobil oils. According to Table 3, AAS revealed the presence of about eight different metals in the different samples of mobil oil. The AAS indicates that the concentration of metal is higher in the used oil than in the fresh oil. This is so because during the use of the engine oil as a lubricant for engines or other machines, worn out metal pieces and other impurities were deposited (Hamad et al., 2005; Jha, 2005; Abro et al., 2013; Isah et al., 2013). Zinc has the highest proportion in most fresh motor oil because it is part of additives added to ameliorate the oil performance (Hamawand et al., 2013). The rise in the concentration of Zinc in spent oil could be attributed to the galvanized pipe wearing and decomposition of anti-wear additives, whose main element is Zinc (Dabai and Bello, 2019). Manganese normally results from the wearing of cylinder liners valves and shafts (Łukasiewicz and Buell, 1977). The presence of Iron in engine oil is dependent on the conditions of the bearings inside the engine (Bartels and Kiss, 1970), however, in used oil, the rise in Iron content comes from various parts of the engine such as camshafts, liners, gears, pistons, rings and crank shaft (Dabai and Bello, 2019). The range of Iron content in used mobil oil is in close concord with the earlier report by Friday et al. (2008). According to the discoveries made by Bertrand et al. (1980), Lead in engine oil is connected with source of fuel (leaded gasoline), bearing wear and impurities resulting from the use of galvanized containers. Copper is also present in the motor oil after used from bearings and valve guides (Dabai and Bello, 2019). Cassap (2008) also noted the possibility of copper content increasing from engine oil coolers. The copper in the different oil samples is very small compared to Zinc, Iron and Lead contents, which could mean that it may have been introduced by the decomposition of additives added in minute quantities or piton and valve guides wearing (Dabai and Bello, 2019). The analysis done also demonstrated that there is a reduction in metal traces after regeneration. Thus, Table 3 revealed clearly that the regeneration of the used oil by acid/clay method is a success and that engine oil treated with sulfuric acid/clay had the least metal impurities or contaminants, especially because precipitates are formed when sulphuric acid reacts with Zinc and copper respectively (Dabai and Bello, 2019).

3.3. FTIR analysis of the different samples of mobil oil

Van de Voort and Sedman (2006) opined that Fourier Transform Infrared Spectroscopy is a useful tool for determining the qualitative and quantitative features of IR-active molecules in organic and inorganic materials irrespective of their state. Analyzing the oil lubricants using FTIR provides a means to track many features, which indicates the state or level of oil contamination, starting from soot to nitration (Van de Voort and Sedman, 2006). The spectra of fresh, used and regenerated mobil oil samples are shown in Figures 1a, b and c.

Figure 1a shows FTIR spectrum of fresh mobil oil. Peak 771.3081cm-1 shows the presence of halo compound (Chloro compound) in the oil while 867.0094cm-1, 1271.145cm-1 and 1866.837cm-1 reveal that there is an ester in the oil. The bands of 1431.615cm-1, 2698.142cm-1 and 2997.08cm-1 indicated the presence of saturated alkanes in the oil. This makes the oil flow at a definite condition. The bands of 1614.672cm-1, 1957.168cm-1, 3081.791cm-1 and 2179.048cm-1 indicate the presence of alkene and alkyne compounds but no presence of carbonyl compounds. The peak at 3251.4cm-1 to 3790.729cm-1 shows the presence of nitrogen compounds in the oil.

FTIR spectrum of used mobil oil is shown in Figure 1b. Peak 698.5016cm-1 shows that there is halo group (Bromo compound) in the used oil, while peaks at 855.4864cm-1, 1059.41cm-1 and 1397.833cm-1 reveal the presence of sulphur oxidation products. Sulfate material is as a result of sulphur in the base oil and additives. The bands at 1145.381cm-1 and 2677.425cm-1 show the presence of phosphate compound. The phosphate compound is as a result of anti-wear agents in the oil additives. At peaks of 1304.958cm-1, 1610.495cm-1, 2454.07cm-1 and 2833.35cm-1, there is presence of carbonyl containing degradation products in the oil from esters, aldehydes or acids (Kadam and Zingde, 1985), which are commonly by oxidation processes in engine oils (Vazquez-Duhalt and Greppin, 1989). The bands of 1975.185cm-1, 2182.834cm-1, 3010.207cm-1 and 3173.84cm-1 reveal the presence of products of soot. This is due to incomplete combustion of fuel. The peaks

| Properties       | Fresh Mobil oil | Used Mobil oil | Regenerated oil by acid/clay method |
|------------------|-----------------|----------------|-------------------------------------|
|                  |                 |                | H2SO4     | HCl       | Acetic acid |
| Specific gravity | 0.89            | 0.93           | 0.78      | 0.73      | 0.71        |
| Viscosity (Ns/cm²) at 40 °C | 82.6          | 37.8           | 73.36     | 70.10     | 65.8        |
| Flash point (°C) | 189             | 146            | 176       | 173       | 169         |
| Fire point (°C)  | 191             | 158            | 180       | 176       | 174         |
| Sulphur Content (%) | -              | 0.78           | 0.521     | 0.572     | 0.621       |

Table 2. Results on characterization of fresh, used and regenerated Mobil oil samples purified by acid/clay methods.

Table 3. AAS characterization results of different samples of mobil oil.

| Samples               | Cu(ppm) | Cr(ppm) | Fe(ppm) | Mg(ppm) | Mn(ppm) | Pb(ppm) | Sn(ppm) | Zn(ppm) |
|-----------------------|---------|---------|---------|---------|---------|---------|---------|---------|
| Fresh oil             | 0.0647  | 0.0583  | 0.6114  | 0.5281  | 0.4326  | 0.0000  | 0.0524  | 1.9009  |
| Used oil              | 0.0970  | 0.1167  | 1.9563  | 0.7586  | 0.8635  | 0.0064  | 0.0819  | 3.1082  |
| Purified with H2SO4 + clay | 0.0716  | 0.0841  | 0.9814  | 0.3108  | 0.5847  | 0.0000  | 0.0608  | 1.6015  |
| Purified with HCl + clay | 0.0788  | 0.0961  | 1.2638  | 0.3826  | 0.6413  | 0.0038  | 0.06914 | 1.9864  |
| Purified with Acetic acid + clay | 0.0874  | 0.1010  | 1.4028  | 0.4215  | 0.7082  | 0.0052  | 0.07318 | 2.2607  |
Figure 1. a) FTIR spectrum of fresh mobil oil, b) FTIR spectrum of used mobil oil, c) FTIR spectrum of used mobil oil regenerated with H₂SO₄.
at 2058.84 cm⁻¹ and 3419.058 cm⁻¹ are the results of nitrogen oxide fixation into the oil. The peak at 1856.448 cm⁻¹ indicates the presence of aromatic material in the oil. Each of the peak values at 3290.979 cm⁻¹, 3532.59 cm⁻¹ and 3739.649 cm⁻¹ reveals the presence of water and glycol contamination in the oil.

As indicated in Figure 1c, the spectrum of used mobil oil regenerated by acid/clay method using H₂SO₄ revealed the absence of some compounds found in used mobil oils. Example of those compounds include Phosphonic acid (POH), esters (S-OR) and allene (C=CH=CH₂) and carbonyl compounds. The IR spectra revealed the presence of thiols (S-H) at a peak value of 2593.8020 cm⁻¹. The peak value of 1065.7080 cm⁻¹ indicates the presence of primary hydroxyl group, while the peak values 3700.2430 cm⁻¹ and 3819.6850 cm⁻¹ reveal the presence of other alkanol group. The absence of carbonyl group, ester group and some of the Sulphur oxidation compounds found in used Mobil oil indicated the effectiveness of the acid in regenerating the used mobil oil. Therefore, the regenerated oil has peaks closer to the fresh oil. Hamawand et al. (2013) obtained similar result of absence of carbonyls for used motor oil at 2359.56 cm⁻¹, treated with sulphuric acid.

Table 4 revealed the different compounds in the based lubricant as well as the additives used in packaging the fresh Mobil oil. Comparing the compounds and functional groups present in the fresh, used and purified mobil oil samples, it can easily be seen that carbonyl group is present only in used Mobil oil. According to Vazquez-Duhalt and Greppin (1989), carbonyl compounds are often present in used engine oil because they are formed by processes involving chemical oxidation. Used Mobil oil has more peaks than purified Mobil oil because of other products, which are oxidized at high temperatures (Dabai and Bello, 2019).

### 3.4. Effects of variation of process conditions

The effects of variation of bleaching temperature, acid concentration and settling time on the purification of used mobil oil were studied, by determining how they affect the physicochemical properties of the oil. This section presents the results of the laboratory experiments carried out at some of the selected design points, generated by the design expert. The essence is to determine the correlation between the actual purity and the predicted purity at the different points, with a view to finding the range at which the optimal reactions conditions are obtainable. Another crucial point which this analysis indicated is how the process conditions interacted with each other and with the response (purity). This was achieved by maintaining any two parameters (say acid concentration and settling time) constant while varying the third parameter (for example bleaching temperature). It is also pertinent to note that only sulfuric acid was used in studying the effects of process conditions and the optimization because it has already been established that sulfuric acid is the best acid among three acids used in this experiment, for the regeneration of used engine oil.

#### 3.4.1. Effect of variation of concentration of the acid at constant bleaching temperature (90 °C) and settling time (4hrs)

Table 5 shows that varying the concentration of the acid affected the regeneration of the used mobil oil, as shown by changes in the properties of the oil at different acid concentrations. The flash point, fire point, viscosity and pH increase while the specific gravity and sulphur content of the oil plummet as the concentration of the acid increases during regeneration. It could also be seen that between 5-6 concentrations of acid, there is no considerable changes in each of the physicochemical properties. This could mean that the optimum acid concentration occurred within the range. The results obtained are used to plot Figures 2, 3, 4.

Figure 2 easily revealed that the flash point and fire point of the purified mobil oil increase with increase in the concentration of the sulfuric acid. Rincon et al. (2005) have already opined that used motor oils have lower low flash points due to the contamination by light fuels. In other words, the concentrated sulphuric acid, which was added as the washing agent, washes away most of the light fuels and other oxidation products thereby increasing the flash points of the purified oils. The figure also revealed that at any given acid concentration, the fire points are higher. This could be attributed to the fact that the fire point of the fresh and used mobil oils was even higher than the flash point at the beginning.

The graph reveals that there is an inverse relationship between the acid concentration and specific gravity or sulphur content. Thus, as the

| S/N | Compounds of fresh Mobil oil/Peaks or Wavelengths (cm⁻¹) | Compounds of used Mobil oil/Peaks or Wavelengths (cm⁻¹) | Compounds of used Mobil oil purified with H₂SO₄/Peaks or Wavelengths (cm⁻¹) |
|-----|--------------------------------------------------------|-------------------------------------------------------|--------------------------------------------------------------------------------|
| 1   | Cloro compound C-Cl stretch/771.3081                   | Bromo compound C-Br stretch/698.5016                  | Bromo compound C-Br stretch/693.5941                                          |
| 2   | Esters/867.094                                        | Ester/855.4846                                        | Alkane/882.8400                                                                |
| 3   | R₂ alcohol OH stretch/1159.1670                       | Sulphate/1059.4110                                    | Primary alcohol compound/1065.7080                                            |
| 4   | Aromatic/1274.1450                                    | Phosphate/1145.5810                                   | Sulphate/1402.6850                                                             |
| 5   | Methyl C-H asymmetrical/symmetrical bend/1431.6150   | Carboxyl compound/1304.9580                          | Alkene C-CH stretch/1628.5770                                                  |
| 6   | Alkene/1614.6720                                      | Sulphate/1397.8830                                    | Aromatic compound C-CH stretch/1885.1700                                       |
| 7   | Cyclic ester CO stretch/1866.8370                     | Ketone/1610.4950                                      | Isothiocyanate/2049.6430                                                       |
| 8   | Allene/1957.1680                                      | Aromatic/1856.4480                                    | Carboxylic acid/2443.7540                                                      |
| 9   | Isothiocyanate/2058.1600                               | Allene/1975.1850                                      | Thiols/2593.8020                                                               |
| 10  | Alkyn/2179.0480                                       | Isothiocyanate/2058.8480                              | Aldehyde C-H stretch/2270.4780                                                 |
| 11  | Nitrile CN stretch/2499.9320                          | Alkyn/2182.8340                                       | Methyne C-H stretch/2904.1960                                                  |
| 12  | Carboxylic acid/2613.7980                             | Carboxylic acid/2454.0710                             | Alkene C-H stretch/3014.5830                                                   |
| 13  | Aldehyde/2698.4120                                     | Phosphonic acid/2677.4250                             | Alkene C-H stretch/3120.2330                                                   |
| 14  | 1° Methyne CH stretch/2881.9130                       | Aldehyde CH stretch/2833.3510                         | Carboxylic acid OH stretch/3256.6990                                           |
| 15  | 2° Methyne CH stretch/2997.0800                       | Alkene – CH stretch/3010.2070                         | Amine/3480.1720                                                               |
| 16  | Alkene CH stretch/3081.7910                           | Alkene C-H stretch/3173.8410                          | 3° Alcohol/3700.2430                                                          |
| 17  | Alcohol OH stretch/3251.4600                          | Alcohol OH stretch/3290.9790                          | 3° Tertiary Alcohol/3819.6850                                                  |
| 18  | Alcohol OH stretch/3512.446                           | Amine/3419.0580                                       |                                                                                  |
| 19  | 1° Alcohol OH stretch/3690.9430                       | 2° Alcohol OH stretch/3532.5900                       |                                                                                  |
| 20  | 2° Alcohol OH stretch/3790.7290                       | 3° Alcohol OH stretch/3739.6490                       |                                                                                  |
concentration of the acid increases, the specific gravity as well as the sulphur content decline. As already noted, used mobil oils have higher density and sulphur fresh oil due to the presence of impurities and wears respectively. However, as the concentration of the acid is being increased during the regeneration of the oil, the tendency for removal of more of the impurities would be high. There was a steeper decrease in sulphur content between 3-5 acid concentrations after which the rate of decrease started slowing down, showing that the reaction has reached optimum. The specific gravity continued to decrease sharply from 3-6 acid concentration but showed lower changes after that because the process is attaining its completion.

Figure 4 shows that an increase in concentration of the sulphuric acid will lead to a rise in the viscosity as well as the pH of the mobil oil. As more of the acid penetrates the used mobil oil during the treatment phase, viscosity and pH of the oil rise because the more the acid the more the removal of the light fuel components, which is responsible for low viscosity in used engine oil (Ajemba, 2012).

### Table 5. Varying acid concentration at constant temperature and time.

| Conc. of Acid (M) | Flash Point (°C) | Fire Point (°C) | Viscosity (Ns/cm²) | Specific gravity | Sulphur content (%) | pH*10⁻¹ |
|------------------|-----------------|-----------------|-------------------|------------------|---------------------|---------|
| 3                | 154             | 171             | 56.8              | 0.91             | 0.76                | 77      |
| 4                | 162             | 186             | 63.4              | 0.86             | 0.62                | 84      |
| 5                | 176             | 194             | 68.7              | 0.71             | 0.53                | 85      |
| 6                | 180             | 202             | 72.2              | 0.60             | 0.51                | 87      |
| 7                | 186             | 213             | 79.3              | 0.52             | 0.50                | 91      |

3.4.2. Effect of variation of settling time at constant bleaching temperature (90°C) and acid concentration (5mol/lit)

Table 6 revealed how the changes in the settling time during purification affected the properties of the oil. These changes in properties at different settling times are represented in Figures 5 and 6 (see Figures 7 and 8; Table 7).

During purification, the flash point and fire point of the oil increase as the time of settling of the bleached oil increases. This is because as the purified oil is allowed to stand for few hours, the impurities settle at the bottom of the container and can easily be filtered off. The figure also
revealed that the fastest increase in flash point occurred at settling time in the range of 3–5 h. The figure also showed that the fire point increased at equal amount for a settling time of 2–4 h, with the fastest increase occurring between 5-6 h settling time.

Here, the specific gravity, sulphur content and viscosity are plotted respectively against the settling time at constant temperature and acid concentration. There is a decrease in both the specific gravity and sulphur content as settling time increases. However, the viscosity increases with settling time. The fall in specific gravity and sulphur content as well as the increase in viscosity at higher settling time could be because at high settling time, the acid, which acts as a washing agent penetrates more of the internal structure of the used Mobil oil and is able to remove most of the impurities. The fastest increase in viscosity of the oil was observed as the settling time rises from 3-5 h. The rate at which viscosity increases reduced after this time. This could be because the reaction is almost at the point of completion.

3.4.3. Effect of variation of bleaching temperature at constant acid concentration (5 mol/lit) and settling time (4 h)

The flash point and the fire point are plotted against the bleaching temperature. The high flash point and fire point at high bleaching temperature depicts that the used Mobil oil has been purified. At high temperature, some if not all the volatile components of the used motor oil will probably gain enough kinetic energies to easily escape from the oil. This would in turn ameliorate the flash and fire points respectively. There was a steady rise in both flash point and fire point as the temperature kept rising from 70-110 °C, although the increase in flash and fire points with temperature was more pronounced between 90-110 °C because the oil molecules must have gained enough energies to become freer, which would lead to swift vaporization of the more volatile components.

The bleaching temperature has an inverse relationship with the specific gravity and the Sulphur content respectively. High bleaching temperature causes the bulk mass of the motor oil to melt and possibly leads to evaporation of some molecules because the binding forces on the molecules of the oils will reduce. Therefore, it is right to say that as the bleaching temperature soars during the purification, the specific gravity and the Sulphur content would become lower.

Figure 9 shows the effect of bleaching temperature on viscosity and pH of the oil. From the plot, it could easily be seen that there is a slight increase in the pH of the oil as the temperature rises from 70-110 °C. On the order hand, the viscosity of the oil falls as the bleaching temperature increases. The fall in viscosity is highest between 90-100 °C but reduces after this temperature. Actually, this decrease in viscosity is not desirable but its effect is being reduced by other process conditions. Therefore, there is a general rise in viscosity of the oil after regeneration.

3.5. Optimization

The response of the experimental design conducted based on the design matrix of the CCRD is shown in Table 8. The response, which is the purity, calculated according to Eq. (1) above, was keyed into the Design Expert and the analysis was done (see Table 9).

Table 8 shows that the values of some factors are not round numbers. This was generated by the design expert and it could be attributed to the alpha value for three factors, which is 1.682. Hence, the three decimal places in some values are due to the three decimal places in the alpha value.

3.5.1. The response model and analysis of variance (ANOVA)

According to the design expert software, the model selected based on the fitness of the experimental data is quadratic. The ANOVA is essential for understanding the P-value, F-value and Lack of fit. The statistical relationship between the independent process variables and the response (purity) is explained by a second order polynomial expression as follows:

Table 6. Varying settling time at constant temperature and acid concentration.

| Time (hr) | Flash Point (°C) | Fire Point (°C) | Viscosity (Ns/cm²) | Specific gravity x10² | Sulphur content x 10⁻² |
|-----------|------------------|-----------------|--------------------|----------------------|-----------------------|
| 2         | 156              | 178             | 53.6               | 84                   | 71                    |
| 3         | 167              | 184             | 58.2               | 81                   | 66                    |
| 4         | 173              | 186             | 71.5               | 76                   | 56                    |
| 5         | 182              | 191             | 75.0               | 64                   | 52                    |
| 6         | 187              | 203             | 79.0               | 60                   | 47                    |
\[
Purity = 83.98 + 6.66A + 5.93B - 2.25AB - 1.25AC - 1.50BC - 6.23A^2 - 6.59B^2 - 6.41C^2
\]  
(2)

Normally, a significant level of 95% is wholly accepted; therefore, any term is considered significant if its P-value is less than 0.05 significant level (Onukwuli and Obodo, 2015). F-values were also used in predicting the significance of a parameter while the lack of fit-test is necessary in evaluating the adequacy of the models. Thus the significance of a term could be accurately described by its P-value of F-value; and according to Shrivastsvs et al. (2008), the lower the P-value (higher F-value) of a model, the better the significance of the effect of the input variable(s) on the response(s). The model with F-value of 229.59 and P-value less than 0.0001 indicated high accuracy of the model, high relevance in the prediction of the response by the independent input variables and as the correctness of the model equation in predicting the response (purity) by

Figure 5. Effect of variation of settling time on flash point and fire point at constant temperature and acid concentration.

Figure 6. Effect of variation of settling time on the specific gravity, sulphur content and viscosity at constant temperature and acid concentration.

Figure 7. Effect of variation of bleaching temperature on flash point and fire point at constant acid concentration and settling time.

Figure 8. Effect of variation of bleaching temperature on specific gravity and Sulphur content at constant acid concentration and settling time.
99.99% accuracy. The linear independent term of temperature (A), concentration (B) and time (C) as well as the interactive term of temperature and concentration (AB), temperature and time (AC) and concentration and time (BC) have high significance level of more than 95% as their P-values are less than 0.05. Moreover, the P-values of the quadratic parameters in terms of temperature (A²), concentration (B²) and time (C²) are all less than 0.05 (P-value < 0.05); implying that they have significant effects on the response (purity).

The coefficient of determination value (R²) reveals the fitness of the model to the experimental data. R² value is very good since its value is very close to unity. Moreover, the predicted and the adjusted R² values have excellent agreement with each other and they are close to unity (Bas and Boyaci, 2007). They therefore indicate that the model is good and valid for predicting the response. The signal to noise ratio is measured by the adequate precision. Taran and Aghaie (2015) stated that adequate precision ratio above 4 is desirable because it shows the required model efficacy. In addition, the adequate precision is very useful in comparing the range of the predicted values at the design points to the mean prediction error. Another important parameter contained in Table 10 is the coefficient of variation, abbreviated as C.V. Chen et al., (2011) defined it as a measure of the repeatability and reproducibility of the models. It could also be described as the ratio of the standard deviation of the estimate to the mean value of the observed response (Asadu et al., 2019).

According to Chen et al. (2011), any CV value less than 10% is reproducible. Therefore, this model is reproducible since its CV is 1.76. The plot reveals that the data points are well distributed; which suggested an excellent correlation between the experiment and predicted values. Also, this confirmed that the selected quadratic model was adequate in predicting the response of the experimental data.

### Table 7. Varying bleaching temperature at constant time and acid concentration.

| Temperature (°C) | Flash Point (°C) | Fire Point (°C) | Viscosity (Ns/cm²) | Specific gravity | Sulphur content | pH x 10⁻¹ |
|------------------|-----------------|-----------------|--------------------|-----------------|-----------------|----------|
| 70               | 149             | 167             | 78.4               | 0.76            | 0.75            | 63       |
| 80               | 156             | 179             | 72.6               | 0.70            | 0.73            | 64       |
| 90               | 167             | 184             | 68.2               | 0.62            | 0.66            | 66       |
| 100              | 175             | 196             | 57.8               | 0.56            | 0.61            | 69       |
| 110              | 184             | 212             | 54.5               | 0.48            | 0.54            | 71       |

### Table 8. The Response of the CCRD for optimization experiment.

| Std | Run | Factor 1   | Factor 2   | Factor 3 | Factor 4 |
|-----|-----|------------|------------|----------|----------|
|     |     | A:Temp degree | B:Conc mol/l | C:Time hrs | Purity   |
| 1   | 20  | 70         | 3          | 2        | 0.40     |
| 2   | 12  | 110        | 3          | 2        | 0.62     |
| 3   | 5   | 70         | 7          | 2        | 0.60     |
| 4   | 3   | 110        | 7          | 2        | 0.70     |
| 5   | 4   | 70         | 3          | 6        | 0.61     |
| 6   | 9   | 110        | 3          | 6        | 0.75     |
| 7   | 10  | 70         | 7          | 6        | 0.72     |
| 8   | 8   | 110        | 7          | 6        | 0.80     |
| 9   | 16  | 56.364     | 5          | 4        | 0.55     |
| 10  | 15  | 123.636    | 5          | 4        | 0.77     |
| 11  | 18  | 90         | 1.636      | 4        | 0.54     |
| 12  | 19  | 90         | 8.363      | 4        | 0.76     |
| 13  | 6   | 90         | 5          | 0.636    | 0.56     |
| 14  | 2   | 90         | 5          | 7.364    | 0.75     |
| 15  | 7   | 90         | 5          | 4        | 0.84     |
| 16  | 11  | 90         | 5          | 4        | 0.84     |
| 17  | 17  | 90         | 5          | 4        | 0.84     |
| 18  | 13  | 90         | 5          | 4        | 0.84     |
| 19  | 1   | 90         | 5          | 4        | 0.84     |
| 20  | 14  | 90         | 5          | 4        | 0.84     |
Table 9. The Analysis of Variance (ANOVA) for the Quadratic model.

| Source       | Sum of Squares | Df | Mean Square | F-value | P-value | Remark   |
|--------------|----------------|----|-------------|---------|---------|----------|
| Model        | 3207.03        | 9  | 356.34      | 229.59  | <0.0001 | Significant |
| A-Temp       | 606.35         | 1  | 606.35      | 390.67  | <0.0001 |           |
| B-Conc       | 480.41         | 1  | 480.41      | 309.53  | <0.0001 |           |
| C-Time       | 566.45         | 1  | 566.45      | 364.96  | <0.0001 |           |
| AB           | 40.50          | 1  | 40.50       | 26.09   | 0.0005  |           |
| AC           | 12.50          | 1  | 12.50       | 8.05    | 0.0176  |           |
| BC           | 18.00          | 1  | 18.00       | 11.60   | 0.0067  |           |
| A²           | 559.82         | 1  | 559.82      | 360.69  | <0.0001 |           |
| B²           | 625.14         | 1  | 625.14      | 402.77  | <0.0001 |           |
| C²           | 592.03         | 1  | 592.03      | 381.44  | <0.0001 |           |
| Residual     | 15.52          | 10 | 1.55        |         |         |           |
| Lack of Fit  | 15.52          | 5  | 3.10        |         |         |           |
| Pure Error   | 0.0000         | 5  | 0.0000      |         |         |           |
| Cor Total    | 3222.55        | 19 |             |         |         |           |

3.5.2. The independent factors effects on the purification of used mobil oil

The significance of the parameters can be evaluated by F-values or the
p-values. A parameter is significant if the F-value is higher than the F-
critical or if the p-value is less than the significance level of 0.05. In other
words, the p-value is the probability of the F-critical being greater than
the F-values of the parameters. If the probability is more than the signi-
cance level, it means the parameter is not significant else the parameter
is significant. They are all significant since their p-values are less than 0.05. In other words, they significantly and positively affect the
purification of Mobil oil.

3.5.3. The interactive effects on the purification of used mobil oil

Figures 10a to c are the response surface diagrams, which are also
known as three dimensional (3-D) diagrams. The purity, which is the
response, is expressed in percentage. They show how the independent
and dependent variables interact with each other. These can be plotted
by keeping one variable at its null point, while carefully varying the other
two variables within experimental range (Asadu et al., 2019).

Figure 10(a, b and c) depict how temperature and acid concentration
(AB), temperature and time (AC) and acid concentration and time (BC)
affects the purity of the oil respectively. From the Figures, there is high
levels of interactions between temperature and concentration, tempera-
ture and time and concentration and time as their contour lines are
somewhat curved. Moreover, the 3D plots are all domes and concave
inwards showing high interactions and none is flat. The ANOVA table
revealed that all these interactive factors on the response are signifi-
cant, as their P-values are less than 5%. For example, Figure 10a shows that the
purity of the Mobil oil at a certain period of time depends on the tem-
perature and the acid concentration. In other words, as the bleaching
temperature is being increased, the degree of purity of the motor oil
undergoing regeneration also increased with increasing concentration of
the acid. The increase in percentage purity with both variable continued
until a certain optimum was reached after which further increase resulted
in decrease in percentage purity. This happened at acid concentration of
6.5mol/lit and temperature of above 103 °C. The same increase in per-
centage purity of the motor oil, followed by a slight decrease after
reaching a certain point, was observed for other interactive factors. The
fact that the contour lines are not parallel but curved in most cases meant
that there is high interaction between the factors and they have the
desired influence on the used mobil regeneration (Asadu et al., 2019).

3.5.4. The optimum values and validation

According to Agu et al. (2015), optimization is interactive and tries to
negotiate the statistical agreement between the basic variables and the
response(s). This means that in this experiment, RSM was used to model
the relationship between the process conditions (acid concentration, settling time and bleaching temperature) and the response (purity). The
design expert analysis generated about 100 optimum solutions from
which one was selected and presented in Table 11. The purification was
carried out at the optimum conditions to verify the selected solution by
determining actual purification. The actual purity obtained is 0.85, and
this agreed excellently with the theoretical percentage purity. This was
equally confirmed by the alignment of the data points of the predicted and
actual values (Figure 11).

4. Conclusions

It can be deduced from this experimental study that the quality of
used mobil oil can be improved by the mineral acids used in this research
tough sulphuric gave the best regenerated Mobil oil as a washing agent.
Changes in the properties of the oil are an indication of the effectiveness
of the purification method in purifying the used oil. Generally, during the
purification of the used Mobil oil, its specific gravity and sulphur content
decrease while its viscosity, flash point and fire point increase. The fact
that the physicochemical properties of the oil vary when the process
conditions like acid concentration, bleaching temperature and settling
time vary meant that they affect the purification of the oil. Optimization
studies carried out on the process conditions using central composite
design of response surface methodology revealed that the optimal con-
ditions for the purification of used Mobil oil, based on the factors studied
are 95.5  °C, 6.5M H₂SO₄ and 5.5hours, which gave almost the same
theoretical and experimental value as the response (purity), depicting the
congeniality of the empirical model with the experimental data. Thus,
analysis of the physicochemical properties of the purified Mobil oil at
these optimal conditions demonstrated that the oil has desirable prop-
erties for industrial use.

Table 10. The quadratic model parameters.

| Std. Dev. | 1.25 | R² | 0.9952 |
| Mean     | 70.85 | Adjusted R² | 0.9908 |
| C.V. %   | 1.76 | Predicted R² | 0.9612 |
| Press    | 57   | Adeq Precision | 49.1105 |
Figure 10. a) 3D plot of temperature and concentration interaction against purity in percentage, b) 3D plot of temperature and time interaction against purity in percentage, c) 3D plot of time and concentration interaction against purity in percentage.

Table 11. The optimum solution.

| Bleaching temperature (°C) | Acid concentration (mol/lit) | Time (hrs) | Theoretical purity | Actual purity (%) | (%) Deviation |
|---------------------------|-----------------------------|------------|--------------------|-------------------|--------------|
| 95.5                      | 6.5                         | 5.5        | 0.86               | 0.85              | 1.1          |
Declarations

Author contribution statement

UGWELE, F. O. & CHIME, T. O: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data.
ANINWEDE, C. S: Performed the experiments; Contributed reagents, materials, analysis tools or data.
CHRISTIAN O. ASADU: Performed the experiments; Wrote the paper.
INNOCENT S, IKE: Analyzed and interpreted the data; Wrote the paper.

Funding statement

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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