REGENERATION OF WASTE LUBRICANT USING ACTIVATED CARBON FROM ENUGU COAL

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Abstract
In this work, coal based activated carbon was used to produce high quality lubricating oil from the waste. The raw coal was subjected to a modified form of chemical activation with KOH as the activating agent. The waste oil was pretreated by filtration, dehydration, centrifugation to eliminate impurities. Then, the oil subjected to acid treatment by combination with acetic acid.The bleaching was conducted by mixing the acidic oil with a coal-based activated carbon at temperature of 110^0C *at a specific time interval. Later, the bleached oil was neutralized using hydrated lime. The regenerated oil was characterized. The results showed that all the assessed properties of the regenerated lubricant such as viscosity, flash point, pour point, water content, density etc improved tremendously from the waste one. Further analysis of these essential characteristics of the refined oil revealed that each of them met the minimum specification of the standard lubricating oil.*

Keywords: Lubricant, waste oil, activation, regeneration, viscosity

INTRODUCTION
Lubricant is viscous liquid used to protect rubbing surfaces and promotes easier motion of connected parts. The principal functions are to minimize friction and reduce wears and tears, inhibit corrosion, serve as suspending agent, provide medium for heat transfer and temperature control (Echegi, 2024).

During usage, lubricants undergo changes such as degradation and contamination. The high temperature inside the machine triggers off isomerization, cracking and polymerization reaction [Mustapha et al, 2012]. Degradation causes the formation of low molecular weight compounds such as polycyclic aromatic hydrocarbon and oxidation products such as polymerized and condensed molecules called gums and sludge. As a result, the lubricating oil may gather some chips, combination of particles, water and dirts. Other contaminants are heavy metals – Fe, Cr, N, Cu, Zn, etc which result from wear and tear processes of the engine’s metal components [Ratiu et al, 2022].

With increased time of usage, the lubricant loses its functional properties due to build-up of the contaminants. These products of these degradation processes render the lubricating oil unfit for further usage and therefore have to be withdrawn from the machine and replaced with the fresh one. The fresh one can be obtained from either the virgin or regenerated oil. Due to various contending variables such as economy and environmental pollution, regeneration of waste oil has proved to be the most viable alternative [Echegi, 2024 and Oladimeji et al, 2018].

There are many methods of refining of waste lubricants. Recent advances on coal activation reveal that special forms of coal-based activated Carbon (CAC) of unique adsorptive characteristics can be synthesized from bituminous coal through the combination of different methods of carbonization and activation processes [Oladimeji et al, 2018]. This form of CAC product possesses liquid-phase adsorptive potentials suitable for modification of the constituent of organic solvent composition.

The recovery of base oil from waste one involves mechanisms and processes of eliminating all the contaminants including water, oxidation products, solid particles, soluble compounds, degraded additives to allow for the re-establishment of the original characteristics of the pure base oils. The three mechanisms that occur in succession are physical adsorption, chemical adsorption and molecular sieving.Physical adsorption involves the removal of dirt, sand-metal particles and combustible substances in unit operations of centrifugation, filtration, distillations and sedimentation. In chemical adsorption, there is the interplay of electrochemical bonding of adsorbates which entraps the contaminants under pressure inside the pores of the adsorbent. Generally, in adsorption treatment of oil, the adsorbent selectively extract resinous and sulphur containing compounds, unsaturated and polycyclic materials and organic residues of sulphuric acid as well as solvent from the oil [Udome et al, 2016].

There are many factors that determine the efficiency of the adsorption process including the nature and characteristics of adsorbent, type of oil and process conditions of temperature, contact time, dosage among others. These factors are the overriding variables that are considered in this work with a view to obtaining high qualities of refined lubricating oil.

MATERIALS AND METHOD

2.1 Preparation of Coal Sample

The raw coal sourced from Enugu Coal Mine, Enugu Nigeria was subjected to preliminary treatment of cleaning, drying, size reduction and sieving. The coal sample was washed with clean water to remove dirt particles and contaminants for the surfaces and sun-dried for 3 days at the interval of 6 hours. The dried sample was crushed and sieved to a mesh size of 1 – 5mm.

2.2 CHEMICAL ACTIVATION

The activation process was carried out in two steps, namely activation followed by carbonization in accordance with the procedures described by Echegi and Eze, 2018 as detailed below:
A measured amount of 2.0g of pre-treated coal sample was put into a volumetric flask and mixed with 50% activating agent solution of KOH at ratio of 4:1. A condenser was mounted to the flask to prevent evaporation. The mixture was boiled at a temperature of 80^0C for 2 hours in an oil bath. At the end of the period, the mixture was cooled to an ambient temperature, filtered by vacuum and dried at 110^0C for 24 hours in an oven. After the activation process, the sample was subjected to carbonization by placing it in a programmable tube furnace. The tube was programmed in such a way that the heating rate of 5^0C per minute was maintained. During carbonization, nitrogen was introduced to the system at a flow rate of $1000cm^3$/min and the heating continued to a temperature of 80^0C. The heating was maintained constant at this temperature for 2 hours. Later, the furnace and its content were allowed to cool to room temperature.

In order to purge out excess KOH, the carbonized sample was added 0.5N HCl and heated to 85^0C for a period of 30 minutes with constant stirring. After filtration, the sample was rinsed with distilled water several times until the pH of the activated carbon-distilled water mixture has exceeded 6. Then, the sample of activated carbon obtained was dried at 100^0C for 24 hours in an oven. Finally, the characterization tests to obtain the adsorption properties of the AC were carried out.

2.3 PRE-TREATMENT OF WASTE OIL

5 litres of spent (waste) lubricating oil, which has been used for over 2 months period, was first subjected to pre-treatment processes in order to enhance the quality of regenerated oil. The waste oil was first decanted, filtered and dehydrated in order to eliminate impurities, water, gasoline, glycol solvents and light hydrocarbon. Later, 30ml of xylene was added into 3 litres of waste lubricant in order to aid the precipitation of suspended solid and elimination of metals. The oil was thereafter subjected to centrifugation and filtration. The clean waste oil was stored in container.

2.4 REGENERATION OF WASTE OIL

It consists of three stages: acid treatment, bleaching and neutralization/filtration.

ACID TREATMENT:200ml of spent oil was measured into 500ml beaker, and placed on a hot plate. It was heated to a temperature of 40^0C - 45^0C. At this temperature range, 20ml of acetic acid was added to the oil. The heating was conducted for 10 minutes with constant stirring. During the heating, the acidic oil was allowed to settle for 24 hours to form sediment at the bottom of the beaker. The sedimented oil was decanted into another 500ml beaker using piece of cloth while the residue (acidic sludge) at the bottom of the beaker was discarded.

BLEACHING: The acidic oil was subjected to bleaching to obtain the refined oil. The oil was measured out and placed on a regulator hot plate and heated to a temperature of 110^0C. 10 wt% of activated carbon, was put into the oil and the mixture was continuously stirred for 20 minutes. At the end of the bleaching processes, the oil was subjected to neutralization and filtration.

NEUTRALIZATION/FILTRATION: Neutralization was carried out to adjust the pH of the oil to neutrality. In this case, 4 wt% of the hydrated lime was measured into the bleached oil. The bleached oil was neutralized with continuous stirring for 10 minutes. Thereafter, the oil was allowed to sediment in a beaker for 24 hours and then decanted into another beaker, while the residue at the bottom of beaker was discarded. The sedimented oil was filtered using a filter paper and the filtrate was collected and the residue (filter cake) was discarded. The clean regenerated oil was characterized to evaluate the properties and ascertain the impact of the work carried out. In this regards, the following properties of base oil such as viscosity, flash point, cloud point, density, viscosity index, TAN, TBN, metallic contents of Fe, Cr, Cu, etc were determined using the American Society of Testing Materials ASTM D1500, D1298, D445, D2896, D941 – 955

RESULT AND DISCUSSION

3.1 Properties of Raw Coal and CAC

Property	Moisture content (%)	Ash content (%)	Bulky density (g/cm^3)	pH	Iodine value (mg/g)	Surface area (m^2/g)	Fixed carbon (%)	Volatile matter (%)	Pore volume (Cm^2/g)	porosity
Raw coal	19.82	15.61	0.798	6.8	138	106	35.86	28.71	0.111	0.341
CAC	4.95	14.58	0.549	6.7	450.6	501.8	59.53	20.94	0.305	0.588

3.2 Characteristics of Lubricating Oil

Property	Waste Oil	Refined Oil	Virgin Oil
Density at 25^{0}C (g/cm^3)	0.947	0.889	0.867
Viscosity at 40^{0}C (cst)	120.00	104.4	91.00
Viscosity at 100^{0}C (cst)	15.08	12.18	10.54
Flash point (^{0}C)	186	212	230
Pour point (^{0}C)	-21	- 34	- 39
Water content (% vol.)	5.26	1.07	0.00
TAN (mg KOH/g)	4.6	2.1	0.00
TBN (mg KOH/g)	1.1	1.8	3.2
Sulphur (ppm)	6.3	2.4	–
Fe (ppm)	60.64	–	–
Cr (ppm)	4.0	–	–
Pb (ppm)	149.25	1.84	–
Cu (ppm)	20.83	2.56	–

Coal-based Activated Carbon (CAC)

The result of activation of Coal shows that there was tremendous improvement of the adsorptive property of the derived AC from its precursor. The adsorptive potentials of surface area, porosity, iodine volume, pore volume etc exhibited a remarkable performance from the activation process. The analysis shows that the least percentage increase of 69% was obtained from iodine value while the pore volume recorded the highest increment of 264%. This trend of result shows a little deviation from the work of Echegi and Eze (2018) in the evaluation of quality of activated carbon produced from coal. The effect of the oxidizing agent leads to discretive removal of successive layers of atoms from the carbon matrix. The oxidation selectively erodes the surfaces and creates the spaces between the elementary crystallites. The less organized, loosely bound carbonaceous materials are oxidized and cleared with the creation of channels, together with fissures within and parallel to graphitic planes, constituting the porous structure with large internal surface area and porosity [Echegi et al, 2019].

Flash Point: The flash point of lubricating oil is the lowest temperature to which the oil must be heated under specified conditions to give off sufficient vapour to form a mixture with air that can be ignited spontaneously by flame. A substantial low flash point is an indication that the oil has become contaminated with volatile substances such as gasoline, water and oxidation products. From Table 3.2, the value of treated oil was obtained as 212^{0}C while the waste one recorded 186^{0}C. The analysis shows that the refining process exhibited a favourable result when compared to the virgin one with value of 230^{0}C.

Density: The density or specific gravity of the regenerated oil could be lower or higher than that of the virgin oil depending on the type of contamination. If the oil is contaminated with higher carbon atoms the value of density will be higher than the virgin oil while the reverse is the case for the dilution or contamination with light oil or volatile component. The value obtained for the regenerated oil is very close to the virgin oil. A density of 0.889 was recorded for the regenerated oil while those of the waste and virgin oils were 0.947 and 0.867 respectively.

Viscosity: One of the important properties of lubricant is viscosity. Viscosity is the state of function of temperature, pressure and density and it varies inversely with temperature. Viscosity is affected by the nature of contaminant in the oil. The oxidized and polymerized products dissolved and suspended in the oil may cause increase in oil viscosity whereas the decrease may be as a result of fuel contamination or dilution. Oxidation of oil during use in automobile produces corrosive oxidized products, deposits, and varnishes which lead to an increase in the viscosity [Abu-Elella et al, Echegi et al, 2016].

As a function, the viscosity is evaluated at two temperatures of 40^0C and 100^0C. At 40^0C, the result for regenerated oil is 104 cst. The value for waste and virgin ones are 120 cst and 91 cstrespectively. The analysis shows that there was a remarkable improvement of this property by the regeneration process and an indication that CAC is suitable for the refining of waste oil. At 100^0C, there was substantial reduction in values of virgin, refined and waste. The values recorded are 15.08, 12.18 and 10.54 cst for waste, refined and virgin oils respectively.

The results produced the same trend of analysis and thus confirming the importance of regeneration process as one of the best methods of restoring the quality of waste oil. This can be attributed to the conversion of contaminants by the acidification and removal by filtration from the oil. This observation was corroborated by Echegi and Co-workers 2016) in the results obtained from the comparative analysis of regenerated lubricant with various activating agents.

Pour Point: Pour point measures the temperature of oil flow which is property of cold weather utilization of lubricant. The results show that regeneration process has the potentials to turn around the waste oil to wealth if properly executed. In this case, the value of waste oil of $–21^0$C was moderated to $–34^0$C by the refining processes. Even though, the exact value of the virgin oil could not be reached in this experiment, the analysis of result shows that the value obtained for refined oil fall within the specification of standard oil of –25 to $–46^0$C.

Total Base Number (TBN): Total base number (TBN) is a measure of reserved alkaline put into the lubricating oil to neutralize acids, retard oxidation and corrosion, enhance lubricity, improve viscosity characteristics and reduce the tendency of sludge build-up [Udonne et al, 2016]. It is a test to measure the ability to neutralize corrosive acids that may be formed during normal operation. The result of the analysis of TBN shows that both the waste and refined oils produced values lower than that of the virgin oil from this experiment. This is because some amount of the base has been used up to neutralize the acid formed during usage of the oil. After usage, the TBN for the waste oil decreased to 1.1 from 3.2mg KOH/g, and after treatment it appreciated to 1.8 from 1.1mg KOH/g.

Internal combustion engine, oils are designed for high alkaline base additives package to neutralize the acids products composition. TBN depletes in service and serves as one of the indicators for the measure of degree of oil deterioration and replacement. The depletion and deterioration of additive package are due to the combined effects of high temperatures, acidic effect of water and oxidant product contamination.

Total Acid Number (TAN): Acid Number (AN) and Base Number (BN) represent two of the most fundamental parameters used to characterize the quality of lubricants. Basically, AN represents acidic constituent in an oil while BN measures basic constituents usually added to neutralize acids accumulating in an oil. These two factors serve as complementary functions to each other and are commonly used in formulation of oxidative status or reserve alkalinity of lubricants.

From the result of TAN, it was observed that there is substantial increase from the virgin oil to that of the waste oil. This is due to the presence of organic, inorganic, heavy metal salts, ammonia derivatives, resin, water and corrosive materials which result from the oxidation process that occurred at elevated temperature in the engine. However, the value was regulated toward the required standard by the regeneration process to produce 2.1mg KOH/g. This is indeed, a recommendable achievement since the additives to be added at the formulation stage will neutralize the medium to the required standard specification of oil.

Sulphur Content: The result shows that sulphur content of the waste oil is much higher when compared to the virgin oil and standard specifications. This occurrence might be due to oxidation-reduction reaction taking place at the prevailing temperatures. Sulphur presence to any amount is never desirable because it reacts with the metal to form acids and compounds of low melting point that are readily sheared to induce unprecedented consequences. As corroborated by Udonne et al, (2016), corrosion in engines is caused by mineral acids formed by the oxidation of sulphur compounds in fuel of internal combustion engines.

Metal Content: The combustion chamber which consists of metal component such as Pb, Fe, Cu and Cr etc is subjected to wears and tears during usage. This effect leads to part per million of these metals liberated into the used/waste oil. The wears and tears of these metals is due corrosion caused by the presence of water and aided by fuel dilution during the piston and ring movement. The analysis of these metal contents in waste and regenerated oils reveals a high efficiency of removal of these contaminants during the experiment. Although, the total removal of some of these contaminants could not be achieved but a reasonable measure of success has been recorded which repositioned the refined oil to the standard limit of desired specification.

CONCLUSION

This study showed that high standard quality of lubricating oil can be produced from waste oil through refining process using activated carbon from coal. However, the activation of coal should be conducted in such manner so as to produce activated carbon of high adsorptive potentials.

In all the quality of oil assessed such as flash point, density, water content, sulphur content, pour point etc, the regenerated oil compared favourable with the virgin one. However, the viscosity value obtained, which is at the threshold of the minimum requirement can be improved upon by the formulated additive packages.

ACKNOWLEDGMENT
This research is sponsored by the Nigeria Tertiary Education Trust Fund (TETFUND). The authors hereby express their gratitude to this organization for providing all the assistance needed in research and development to scholars in tertiary institutions in Nigeria.

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