CONFERENCE PROCEEDINGS FOR THE 44TH ANNUAL CONFERENCE OF THE NIGERIAN SOCIETY OF CHEMICAL ENGINEERS HELD AT IMO CONCORDE HOTELS OWERRI FROM 20TH TO 22ND NOVEMBER 2014

APPLICATION OF ACID TREATED CLAY IN THE RECYLING OF USED ENGINE OIL

By
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Abstract:
This research investigates the effect of acid treatment on the physio-chemical properties of clay by applying the modified clay in treating waste lube oil. Clay sample was obtained, prepared and treated with sulphuric acid (H_2SO_4) at different concentrations, activation temperature and time. The modified clay samples obtained were used to treat waste engine oil. Thereafter, the properties of the treated oil samples analyzed and compared with the used engine oil in order to determine the adsorption capacity of the clay. The result of the analysis on the oil samples showed an improvement in the quality of the treated oil properties when compared with the untreated used oil and fresh oil. The increase in acid concentration, activation time and temperature is associated with an increase in flash point, cloud point and a decrease in metal content and viscosity. Therefore, activation time, temperature and acid concentration are proved to be good parameters that can be used to improve the adsorption capacity of clay.

Keywords: Activation, Clay, Used Oil,

1.0 Introduction

Governments, environmentalist and researchers all over the world are looking for ways to reduce or eliminate environmental pollution of which spent engine oil contributes a lot. This is due to the fact that only a very small percentage of the billions of gallon of waste lube oil are been discharged into the environment every year is been recycled (Bromilow; 1990). Most of the used oils discharged into the environment inappropriately are often leached into underground water and other fresh water bodies, thereby endangering the lives of aquatic animals and contaminating the water being consumed by humans (Cutler, 2009).

Water polluted with high chemical content poses great danger for plants. Another area of concern to governments and industrialists is how to conserve the ever depleting crude oil reserves as a result of continuous exploitation. This research therefore justifies the problems which have been highlighted above and is also capable of proffering lasting solutions to these problems. In addition, it impacts Nigeria’s economy through reduced importation of lubricating oil by regeneration of useful hydrocarbon resources that can be further processed into new lube oil product by addition of additives. The regeneration of oil also has the potential of creating jobs through the construction and operation of recycling plants which can reduce the high rate of unemployment in the country (Udonne; 2011).

Several methods of recycling waste lubricating oil have evolved over time and these include: acid method, distillation/clay method, acid/clay method, activated charcoal/clay method among others (Scapin et al; 2007, Rincon et al; 2005, Hamad et al; 2005). Since the inception of waste lube oil recycling, clay has been one of the most important and widely used adsorbent materials for the renewal of the oil.

Infact, clay/acid method was the earliest method employed in the recycling of used engine oil. This is attributed to its adsorption property, clay is able to remove most of the metal build up in the spent engine oil. Research in the world today is also focusing on how the absorption properties of clay can be improved, so as to enhance its application in the petrochemical industry (Cutler; 2009). To this end, acid modified clay has shown that it possess properties which have made it an important adsorbent material generating world-wide interest in the industry. Plasticity, fineness of grain, hardness, cohesion, de-coloration, capacity of surface, shrinkage under firing and air drying and impermeability are some of the many characteristics of clay which makes them suitable for their numerous applications (Varga; 2007, Mako et al; 2005, Harvath et al; 2003). The improved properties achieved through acid modification of clay is now generating a renewed interest by researchers in the recycling of waste engine oil because of the potential of producing a high quality base stock oil. Acid modified clay also hold a promising potential as an alternative to zeolite in its useful application as catalyst.

This research paper is aimed at investigating the absorption capacity of clay treated with sulphuric acid using chemical activation method. In addition, this work seek to study the effect of varied concentration of the acid, treatment time and temperature on the recycling of used engine oil using acid treated clay.

2.0 METHODOLOGY

2.1 Materials and Methods

The clay sample and the spent engine oil used in this work were sourced from Badaggi and Automobile workshop, Minna, Niger state respectively. The glasswares and some of the equipments were provided by the Chemical Engineering Department Laboratories of Federal University of Technology, Minna.

2.1 Clay Preparation

The untreated clay sample was ground and then mixed with distilled water to form a solution. Impurities such as sand, stone and other particles settled at the bottom of the cylinder and were separated by decanting off the clay particles. The slurry was then kept in an oven to dry up. The dried clay was thereafter sieved into very fine particle size using 75 µm mesh size sieve.

2.2 Clay Treatment and Activation

100g of the untreated clay sample was weighed using a digital weighing balance, and poured into a double neck round bottom flask with 250 ml of 0.5 mol/dm^3 H_2SO_4 acid solution added. A reflux condenser was connected to the flask at one neck, while a thermometer set at room temperature was inserted at the side neck of the flask. The setup was placed in a water-bath on a magnetic stirrer. The bottom opening of the condenser was connected to a source of running cold water and the top opening connected to a sink. The setup was clamped firmly to the magnetic stirrer set at 800 rpm and was run for 30 minutes.

The same procedure was repeated at varying acid concentration, treatment time, and temperatures. The varied concentration were 0.5 mol/dm^3 and 3.0 mol/dm^3, while the varied time and temperature were 30 minutes, 60 minutes, 180 minutes and 60 ^oC, 90 ^oC, 90 ^oC respectively. A total of 18 experimental runs of treated clay samples were obtained with each of the sample having one of the parameter constant and others varied as shown in Table 1.

At the end of each experimental run, the mixture of the clay and acid was washed thoroughly with distilled water until the pH of the washing water was found neutral. The washed clay samples were then dried in an oven at a temperature of 110 ^oC for about 1 hour and the dried clay samples ground and sieved into fine particles.

Table 1: Experimental Controlled Variables

Sample No	Concentration (mol/dm^3)	Time (min)	Temperature (^oC)
C	0.0	0.0	0.0
1	0.5	30	30
2	0.5	30	60
3	0.5	30	90
4	0.5	60	30
5	0.5	60	60
6	0.5	60	90
7	0.5	180	30
8	0.5	180	60
9	0.5	180	90
10	3.0	30	30
11	3.0	30	60
12	3.0	30	90
13	3.0	60	30
14	3.0	60	60
15	3.0	60	90
16	3.0	180	30
17	3.0	180	60
18	3.0	180	90

Note: Sample C represents the unmodified clay (raw)

2.3 Characterization of Clay and Oil samples

The analyses of clay and oil samples were carried out according to the standard procedures stated in Awaja and Pawal (2006) and Coyler (2000). Generally, lubricants are characterized by certain properties that make them suitable for their lubricating functions in the internal combustion engine of various machines. Some of these properties include; viscosity index, flash point, cloud point, pour point, water content, specific gravity, total acid number (TAN), total base number (TBN), ash content and so on. (Udonne, 2012).

2.4 Purification Process of the Spent Engine Oil

The percolation method of treatment as described by Grim, (1962) was employed in the purification of the oil. The spent oil was preheated for about 7 minutes in order to reduce its viscosity and increase its penetration power. 30 g of each of the treated clay samples were packed in a plug flow funnel (funnel inserted with a filter paper). 80 ml of the preheated spent oil was measured and poured over the clay bed in the funnel and allowed to filter through the bed into a conical flash. The clay bed was then disposed off after the filtration and the treat oil samples were labelled accordingly. The untreated clay sample was also used to treat the spent engine oil at a particle size of < 75um. In all, 18 treated oil samples were generated by varying 2 parameters and keeping one constant during clay activation. Sample A and B were the fresh lubricating oil and the spent untreated oil respectively. Sample C was generated by treating the waste oil with the raw clay.

3.0 Results and Discussion

The analysis of the chemical elements as shown in Table 2 revealed that the clay used for the adsorption process has considerable high amount of iron, magnesium, aluminium and silica ions. However, the clay contains low quantity of sodium and potassium ions. These are the elements that can possibly leach when the activated clay is treated with oil.

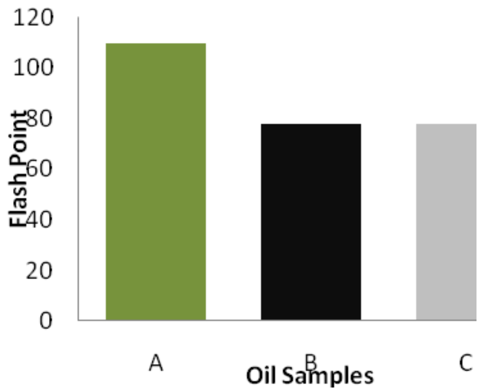
Table 2: Identified elements and amounts present in untreated clay sample

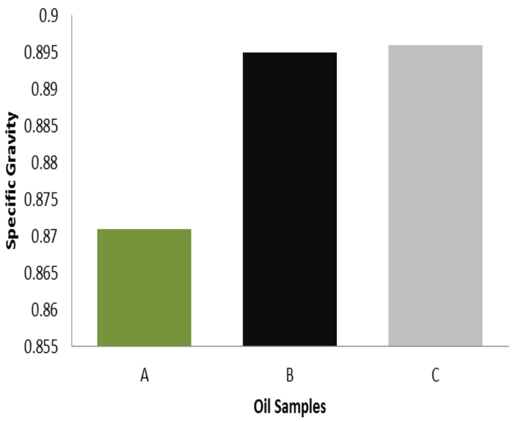
Element	Metal Oxide	Amount (Wt %)
Sodium(Na)	Na_2O	0.391
Potassium(K)	K_2O	0.194
Calcium(Ca)	CaO	1.420
Magnesium(Mg)	MgO	9.545
Iron(Fe)	Fe_2O_3	70.379
Silicon(Si)	SiO_2	11.401
Aluminium(Al)	Al_2O_3	6.670

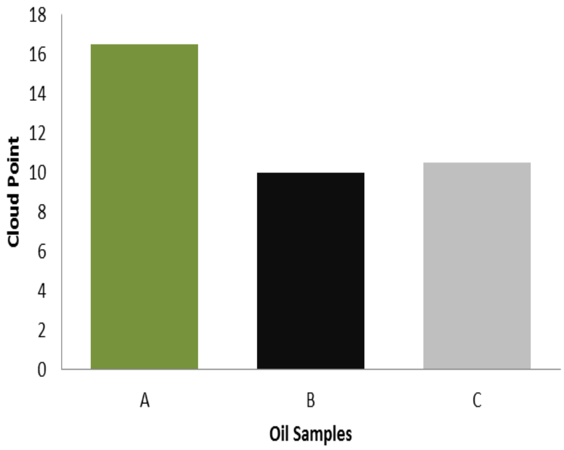
Figures 1(a – e) give the comparison between the properties of fresh oil, used oil and used but treated oil with raw clay. As shown in Figure 1(a), the flash points of the fresh and used lube oil were 110 ^oC and 78 ^oC, respectively. The decrease is attributed to the presence of light fuels in the used oil (Rincon et al; 2005) produced by the combination of combustion and oxidation processes that occurred in the internal combustion chamber of the engine.

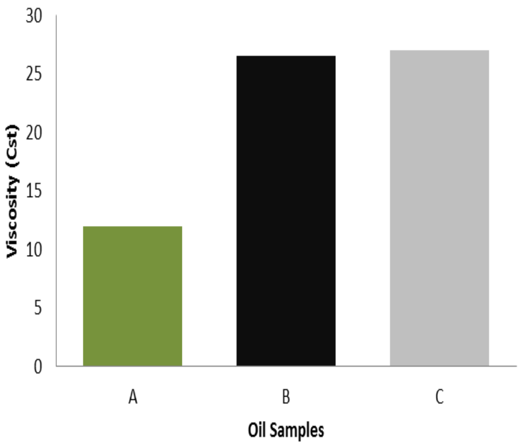
During these processes, the oil is broken down into smaller parts which give rise to the presence of light fuels. In addition, the flash point of the used oil when treated with raw clay remained at 78 ^oC. This is an indication that the raw clay has no effect on the flash point of the used oil. Figure 1(b) showed that the raw clay possessed a low adsorption capacity because it slightly affects the specific gravity of the treated oil. The increase in viscosity from 12 cst to 26.5cst for fresh oil and used untreated oil respectively as shown in Figure 1(c) is attributed to oxidation or contamination of oil that resulted in the formation of light fuel (Scapin et al; 2007).

The increase in cloud point as shown in Figure 1(d) is as a result of the presence of suspended contaminants that acts as pour point depressants. The cloud point of the treated refined oil sample with raw clay was observed to be the same with that of the untreated used oil, and this confirmed that the raw clay has a low adsorption capacity. Figure 1(e) shows that the iron content of the fresh oil was 0.0 ppm and that of the used oil was 27.0 ppm, while the treated oil with raw clay was 21.1 ppm. This is because of the accumulation of metals particles such as iron, lead and aluminium in the engine oil as a result of corrosion in the internal combustion chamber of the engine. The slight reduction in the iron content of the treated oil on comparison with used oil confirmed the low adsorption capacity of the raw clay


120
100
80
60
40
20
0
Flash Point
A
B
C
Oil Samples


0.9
0.895
0.89
0.885
0.88
0.875
0.87
0.865
0.86
0.855
Specific Gravity
A
B
C
Oil Samples


18
16
14
12
10
8
6
4
2
0
Cloud Point
A
B
C
Oil Samples


30
25
20
15
10
5
0
Viscosity (Cst)
A
B
C
Oil Samples

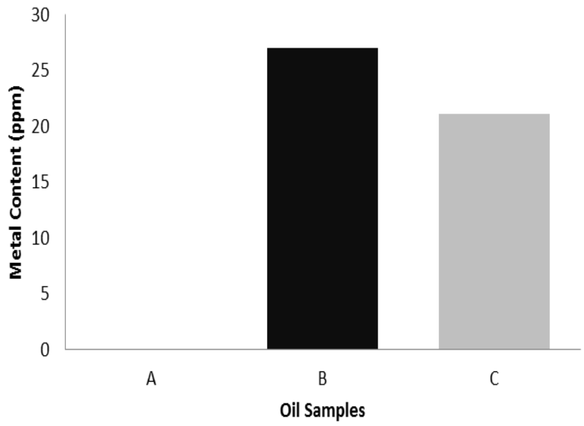


Figure 1: Comparism of the properties of fresh oil; used oil and used but treated with raw clay.
A: Fresh oil; **B**: Used oil; **C**: Used but treated with raw clay.

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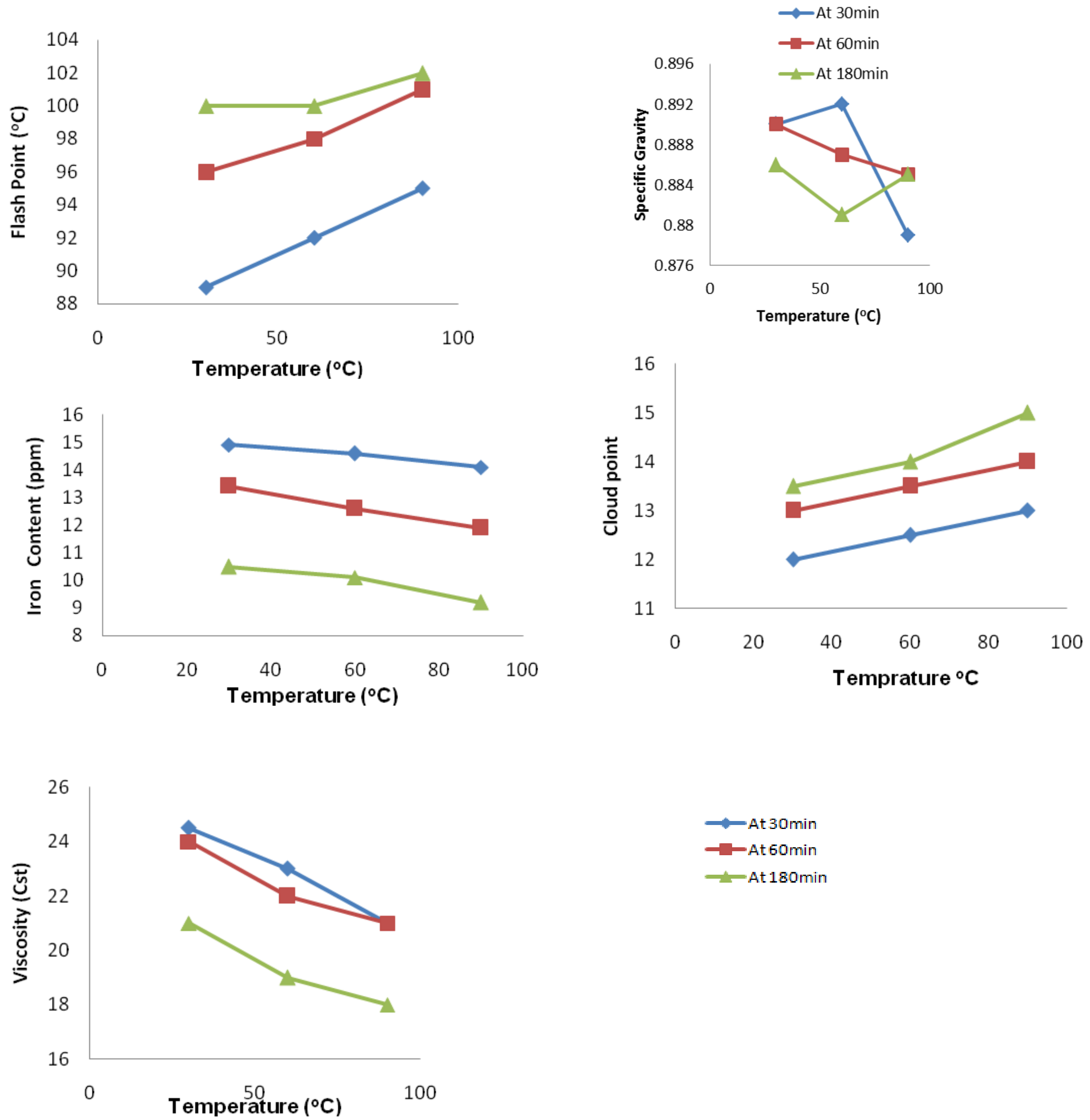


Figure 2: Effect of activation temperature on the properties of the treated oil at a constant concentration of 3.0 mol/dm^3 of H_2SO_4

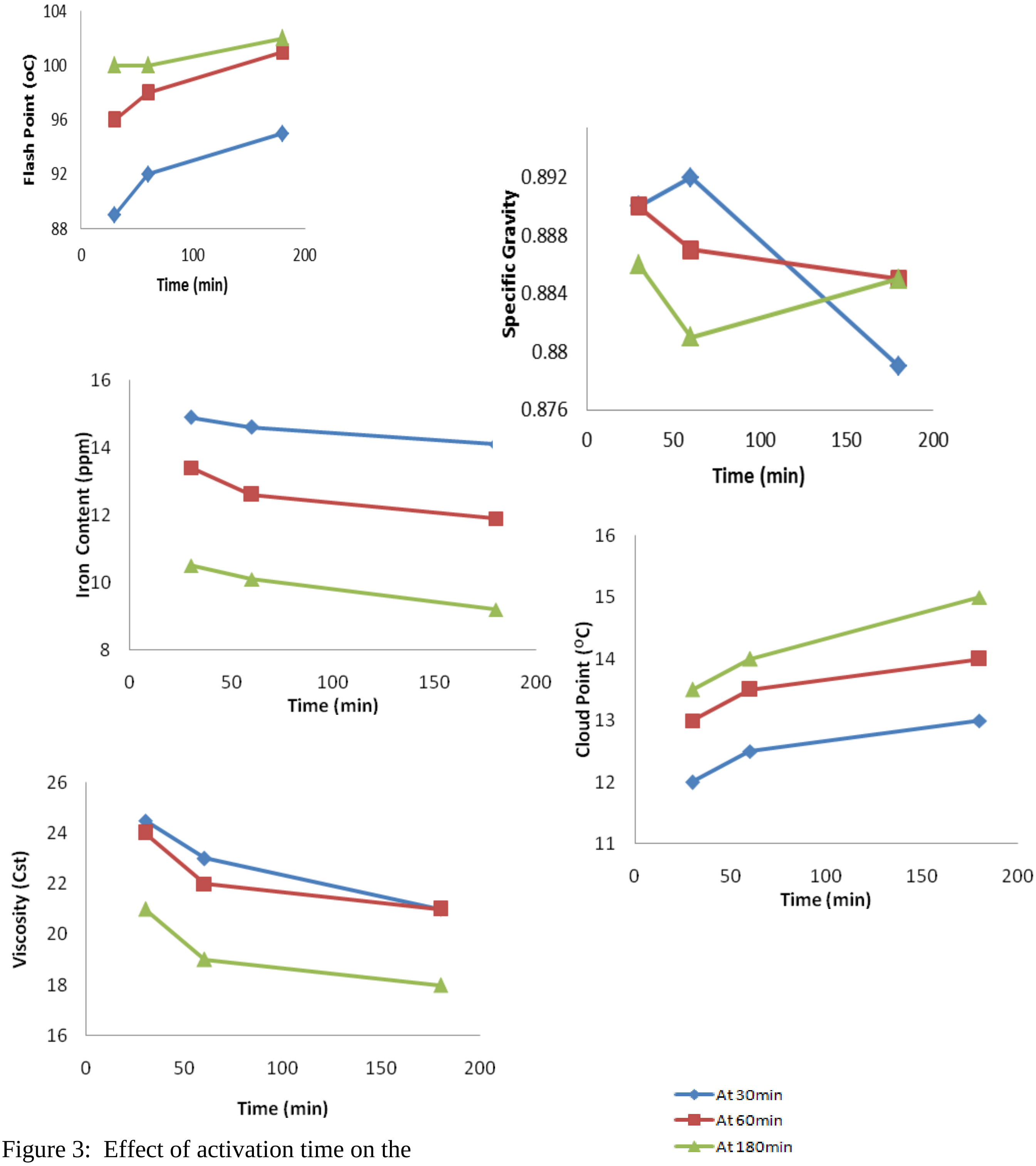
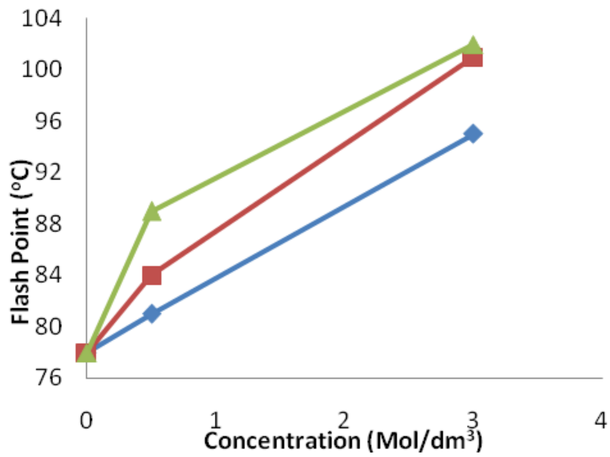
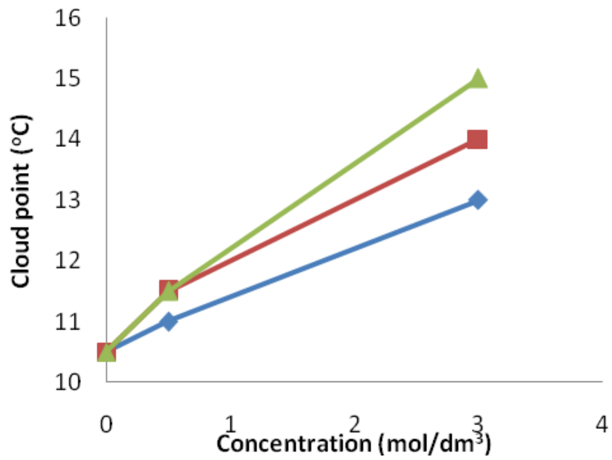
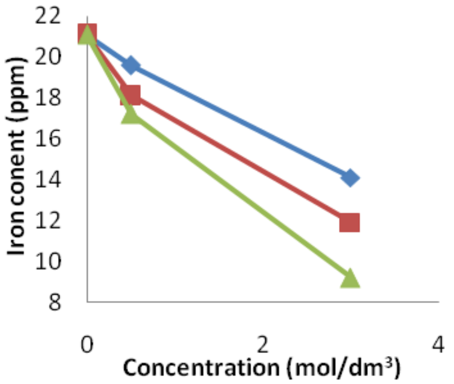
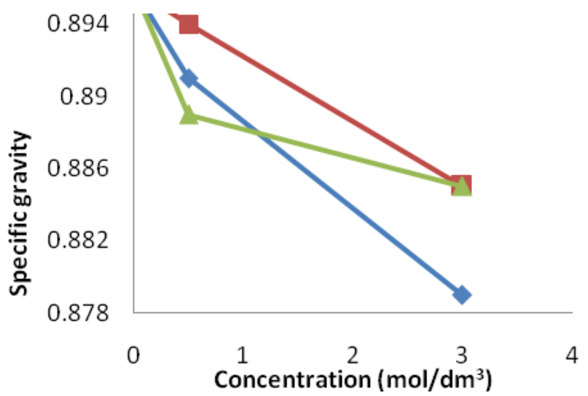


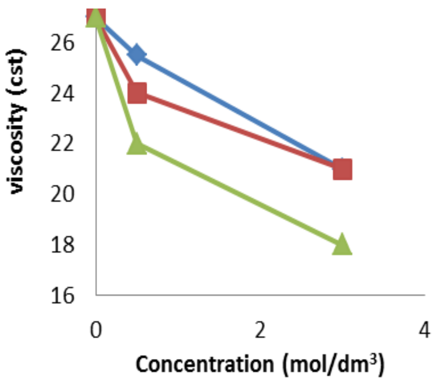
Figure 3: Effect of activation time on the properties of treated oil at 3.0 mol/dm^3 of H_2SO_4


Flash Point (°C)
104
100
96
92
88
84
80
76
0
1
2
3
4
Concentration (Mol/dm3)


Cloud point (°C)
16
15
14
13
12
11
10
0
1
2
3
4
Concentration (mol/dm3)


Iron conent (ppm)
22
20
18
16
14
12
10
8
0
2
4
Concentration (mol/dm3)


Specific gravity
0.894
0.89
0.886
0.882
0.878
0
1
2
3
4
Concentration (mol/dm3)


viscosity (cst)
26
24
22
20
18
16
0
2
4
Concentration (mol/dm3)

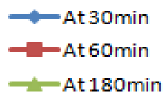

At 30min
At 60min
At 180min

Figure 4: Effect of concentration on the properties of the treated oil at constant temperature of 90 ^{o}C

Figures 2 to 4 give the graphical representations of the effects of activation temperature, time and concentration on the physio-chemical properties of the treated oil respectively. As shown in Figure 2, properties such as flash point and cloud point showed an upward trend as temperature increased at a constant concentration of 3.0 mol/dm^3 of H_2SO_4. However, the value of viscosity and iron content of the treated oil decrease with an increase in the temperature. There is a combination of both upward and downward trend in the plot of specific gravity aganist temperature.

Figure 3 is a plot that showed the effect of activation time between 30, 60 and 180 min at 3.0 mol/dm^3 of H_2SO_4 on the properties of treated oil. As activation time increase, there is an increase in flash point and cloud point of the treated oil. However, there is a decrease in the metal content and viscosity of the treated oil as activation time increases. There is a combination of both upward and downward trend in the plot of specific gravity aganist activation time.

Figure 4 showed how the adsorption capacity of the clay was improved as the acid concentration was increased from 0.5 mol/dm^3 to 3.0 mol/dm^3. There is an upward trend in the flash point and cloud point as concentration of the acid increases. However, a downward trend was observed in metal content, specific gravity and viscosity of the treated oil as concentration of the activating acid increases.

Conclusions

In general, all the graphs showed that acid treatment of clay improves the adsorption capacity of the treated clay. By using activated clay to treat used oil, the effect of activation temperature, time and concentration of the acid on the properties of treated lube oil were investigated. The results are summarized as follows; Acid concentration, activation time and temperature proved to be good parameters that can be used improve the adsorption capacity of clay in the treatment of used oil. At activation temperature of 90 ^{0}C, time of 180 minutes and acid concentration of 3.0 mol/dm^3, the adsorption capacity of the clay was observed to be highest as reflected in the properties of the treated used engine oil. Acid activated clay proved to be a good adsorbent that can be used to recycle used engine oil.

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