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An Alternate Acid Cleaning Process (Glacial Acetic Acid) for the Regeneration of Waste Engine Oil and A Proposed Procedure for the Safe Disposal of Produced Sludge

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Abstract

Generally, in undeveloped countries used motor oil cleaning operations are carried out in batch containers. Pollutants such as oxidized metallic carbon compounds and moisture is removed by simple heating and then sulphuric acid is gradually added at room temperature. This nonstandard processing approach also harms the environment as per environmental regulations. The aim of our study is to suggest a biodegradable acid (which does not affect the environment) for the regeneration of used engine oil. Briefly, the water was first removed from the used oil by simple heating until the knocking noise stopped. The dehydrated oil was then treated with glacial acetic acid (instead of sulphuric acid) for an hour at room temperature. Reddish brownish (top) and black (bottom) layers were developed following a 24 hour settling period. After collecting the top layer, fuller earth (Multani metti) was gradually added while being constantly stirred. The engine oil was finally filtered at room temperature to remove existing particles. About 53% v/v of the engine oil was recovered with the proposed cleaning methodology. The residual sludge is a mixture of biodegradable species that contains mainly acetic acid. Furthermore, the cement can be blended with the sludge to make concrete blocks for its proper safe disposal.

Keywords: Used motor oil, Sulphuric acid, Acetic acid.

1. Introduction:

Lubricating oils are one of the widely used fraction of the petroleum refinery products [1]. Each year tons of lubricating oil is needed for the vehicles, process industry, and different machines [2]. Essentially, these viscous oil forms a very thin layer between the sliding metal faces which are in direct contact with each other [3]. The very thin oil film takes away the frictional heat and keeps the contact surfaces well intact. These oils are usually blended with many other chemical additives in order to improve the operational life and its performance under rough operating conditions [4].

The boiling point of lube oils is usually between 300 C to 565 C [5]. In any case, with the passage of time the oil losses the lubrication ability because of physical and chemical deteriorations [5, 6]. The presence of metal particles, ash, carbon residue, varnishes, water, gums, and asphaltic sediments are detrimental to the contact surfaces of the engine parts or any machinery [7]. Thus, these lube oil are replaced with the fresh oil after a certain time of continuous operations [8]. The oil taken out

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from the machinery or engine is termed as used/waste/spent engine oil [9].

It is crucial to ensure that the used lubricant is properly disposed because improper handling can seriously harm the environment [10, 11]. For example, a discharge of a small amount of oil into the soil or water can lead to severe toxification for many living species [12, 13]. On the other hand, they are high value compounds and, ideally, most should be recovered or recycled [14]. Based on a rough estimate in Pakistan, 80,000 tons of used engine oil are processed each year for many applications [15]. In general, the transport industry is a major center of our growing economy and therefore the amount of used motor oil is constantly increasing [16].

The presence of lubrication oil in the combustion engine is essential for the proper operation of the vehicle [17, 18]. Engine oil keeps metallic contact surfaces in a state where erosion and friction heat generation are minimized [19]. Additionally, a high quality lubricant can help increase fuel economy by reducing friction between moving components of the shaft that steers the piston inside the combustion chamber [20]. In the open market, a number of motor oil brands are available with slightly different formulations [21]. As a rule, engine oil is used to reduce friction, wear, and overheating of engine parts. A good grade oil also avoids the corrosion, cools the engine, cleans certain engine components, do not let the clogs, and provide sealing to minute clearances near the combustion cylinders [22].

Lubricating oil is a mixture of n-paraffin, iso-paraffin, naphthenes, and aromatics [23]. The fraction of each group affects the ultimate physico-chemical properties of lubrication [24]. Inside the engine, undesirable species such as dust, fuel, ash, coolant, humidity and acids may mix with lubricating oil during normal operation [25]. In addition, under certain extreme conditions, soot particles, exhaust gases and metallic particles may also become a homogeneous part of the lubricating oil [26]. These undesirable alteration is a reason for replacing a contaminated oil with the fresh quality oil [27]. In brief, the lubricating oil loses its effectiveness when the concentration of impurities is raised from a certain value. Not only does it lose its ability to maintain the engine at maximum performance, but it is also lethal to the sliding surfaces [28]. The taken out engine oil contains polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), heavy metals like lead, arsenic, cadmium, soot, and acid contaminants. Thus, a proper processing is essential to limit the chances of the dirty oil spillage into the environment.

In any case, the decision of the extent of oil cleaning is taken on the basis of market requirement [28, 29]. For example, the waste lubricating oil can be burnt (heat production), regenerated, recycled, mildly treated, or severely treated to reproduce fine hydrocarbons [30]. The regeneration is a term used when the process treatment yields the lubricating oil of almost the same properties as it was new. Ideally, the regeneration is the ultimate goal however the amount of contaminants in the collected waste oil decides whether the process is economical viable [14]. The acid and clay treatment process is the oldest and the simplest method for the reclamation of the waste oil [31]. Briefly, a sulphuric acid is added to a contaminated oil and after proper mixing the sludge settles in the container. The disposal of the sludge is of great concern because it contains the spent mineral acid with many impurities [32]. In this work we cleaned the waste lubricating oil with glacial acetic acid. The glacial acetic is biodegradable and thus comparatively considered as less harmful to the environment. Furthermore, safely disposing of the harmful sludge is one of our key goals. To ensure that the toxins will not spill into the environment or for safe disposal, this sludge can be transformed into concrete blocks by simply combining it with cement.

2. Methodology:

One liter samples of used engine oil were collected from three different petrol stations situated close to the Peshawar University Forest Bazaar. Thus a total of three-liter sample was homogeneously mixed in one main container. A volume of 100 ml was then taken out in five different beakers. Each beaker was heated to a temperature of 150 °C for one hour. As indicated in Figure 1, the water and the other volatile components evaporated and roughly after an hour the knocking sound disappeared. The reason for this knocking sound is that oil has a higher boiling point than the water. At 150 °C, the oil swiftly transforms the water into steam, resulting in the knocking sound. This is an indication that the oil is now separated from the water and other volatile components. These beakers were then cooled to a room temperature which was 16 °C.

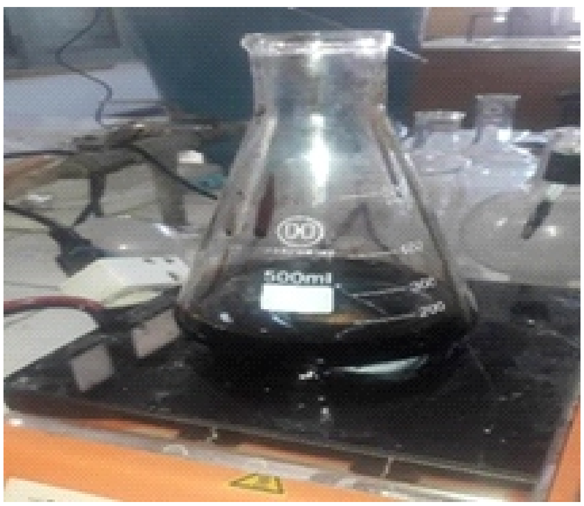


Figure 1: *Moisture and volatile components removal from the waste lubricating oil*

After that the dehydrated oil was mixed with different volumes of the glacial acetic acid that is 20 ml, 25 ml, 30 ml, 35 ml and 40 ml in the first, second, third, fourth, and fifth beaker, respectively and stirred at 150 rpm. The temperature of the stirring was 25 °C as shown in Figure 2. The mixtures were left for 24 hours at room conditions. The top layer was separated from that of the bottom sludge. The bottom sludge was collected and measured.

Figure 2: Treatment of the glacial acid with the dried lubricating oil

Moreover, the top layer oil was collected in a separate container and was further cleaned from the viscous components with the help of a centrifuge machine. These labeled containers were placed in fixed holders of the centrifuge equipment model number RC-50 as shown in Figure 3. The revolving speed of a 300 rpm was fixed for an hour. Again two layers of different densities were formed. The relatively clean oil was separated from the remaining settled viscous oil.

Figure 3: Centrifuge machine for the separation of oil mixer

Lastly, the top layer oil was mixed with activated fuller earth (local name Multani meti) in a ratio of 1gm per 2.5 ml separated oil with continuous stirring. The temperature of the mixer was heated to 250 °C for one hour as shown in Figure 4. The fuller treated oil was again centrifuged to collect a top regenerated oil which was then further filtered to obtain clean engine oil.

Figure 4: Treatment of the lubricating oil with fuller earth at a temperature of 250 °C.

By heating the sludge mixer to a temperature of 120 °C, a fraction of acetic acid was extracted from the produced sludge. The condensed acetic acid was recovered in a round bottom flask. Figure 5 depicts the setup used to recover the heating and condensed acetic acid. The heating sludge took 30 minutes total at a temperature of 100 °C. The acetic acid extraction was approximately completed in less than 10 minutes.

Figure 5: Acetic acid recovery from the produced sludge.

The flash point was determined using an instrument model number 123, a test method known as closed cup tester, which is a small container with a lid that is heated at a controlled rate until the liquid gives off enough vapour to form an ignitable mixture with air. At this temperature, the flash point was noted for all the tested samples. Similarly, pour point testing was performed by slowly cooling the oil and measuring the temperature at which the oil became too thick to flow. These tests were typically carried out in accordance with ASTM D97. The Redwood viscometer, also known as the Redwood viscosity apparatus, was used to determine a fluid's kinematic viscosity. The time it takes for a specific volume of fluid to flow through a calibrated orifice at a constant temperature was measured. Finally, the density in a graduated cylinder was determined by measuring volume and mass.

To solidify the produced sludge, the residual viscous sludge was mixed with sand and cement. For each bonding process, an equal ratio of cement and sand (1: 1) were homogeneously mixed with the sludge and then dried in the sun for 10 days. For example, three compositions were created: 20 g sludge and 10 g cement and sand, followed by 20 g sludge and 15 g cement and sand, and lastly 20 g sludge and 20 g cement and sand. Finally, the solid block impact was tested by dropping them from a height of 6 feet.

3. Results and Discussions:

Five waste oil samples of 100 ml were taken in five different beakers. 20 ml of glacial acetic acid was added in the first beaker, 25 ml was added in the second, 30 ml was added in the third, 35 ml was added in the fourth and 40 ml was added in the fifth. Total volume of the oil sample added with glacial acetic acid was 120 ml, 125 ml, 130 ml, 135ml and 140 ml in the five beakers respectively. The oil separated (clean oil) was 90 ml and the settled oil (sludge) was 30 ml with fraction of the top layer 0.75 percent in the 120 ml beaker. 92 ml separated oil and 33 ml settled oil with 0.73 percent top layer fraction was found in the 125 ml beaker. There was 88 ml separated oil and 42 ml settled oil with 0.67 percent top layer fraction in the 130 ml beaker. 91 ml separated oil and 44 ml settled oil with 0.67 percent top layer fraction in the 135 ml beaker and 94 ml separated oil and 46 ml settled oil with 0.67 percent top layer fraction was found in the 140 ml beaker. The analysis in the Table 1 showed that after a certain limit the separation of oil and sludge becomes constant as after the third beaker which contained 130 ml volume the top layer fraction was constant at 0.67 percent.

Table 1: Separation of top and viscous bottom layer hydrocarbons by using a glacial acetic acid treatment of the used motor oil.

S.No	Volume of the sample oil (ml)	Volume of the acetic acid (ml)	Total volume of sample plus acetic acid (ml)	Separated oil (ml)	Settled oil (ml)	Fraction of the top layer (Separated oil/total volume of sample and acetic acid
1.	100	20	120	90	30	0.75
2.	100	25	125	92	33	0.73
3.	100	30	130	88	42	0.67
4.	100	35	135	91	44	0.67
5.	100	40	140	94	46	0.67

Additionally, the relatively clean oil that was separated during the acid treatment procedure was added to five different beakers, each of which had 90, 92, 88, 91, and 94 ml of oil. These five beakers underwent centrifugation in order to be further separated. The denser phase, which contained all of the contaminants, was separated from the relatively clean oil using a centrifugal force. Data from Table 2 demonstrates that more sludge is formed during subsequent centrifugal separation when more acid was introduced. For instance, when 20 ml of acid is present (Table 1), 39 ml of total sludge is formed (Table 2), while adding 25 ml of acid (Table 1) results in 43.12 ml (Table 2) of total sludge and 40 ml of acid (Table 1) results in 61.98 ml (Table 2) of total sludge.

Table 2: Separation of clean and viscous oils using centrifugation of the comparatively clean engine oil.

S.No	Separated oil from the acid treatment process (ml)	Top layered (ml)	Settled sludge (ml)	Total sludge (ml)	Fractional recovery (Fraction of the top layer (top layer oil/total volume of sample and acetic acid.
1.	90	81	9	39	0.67
2.	92	81.88	10.12	43.12	0.65
3.	88	73.04	14.96	56.96	0.56
4.	91	73.71	17.29	61.29	0.67
5.	94	78.02	15.98	61.98	0.55

For the quantification of the separated acetic acid from the sludge, a sludge mass of the serial number 5 of the Table 2 was heated to a temperature of 120°C. The separation of the acetic acid in terms of grams was fast in first 10 minutes. After sometime the mass separated was approximately stagnant as shown in Figure 6.

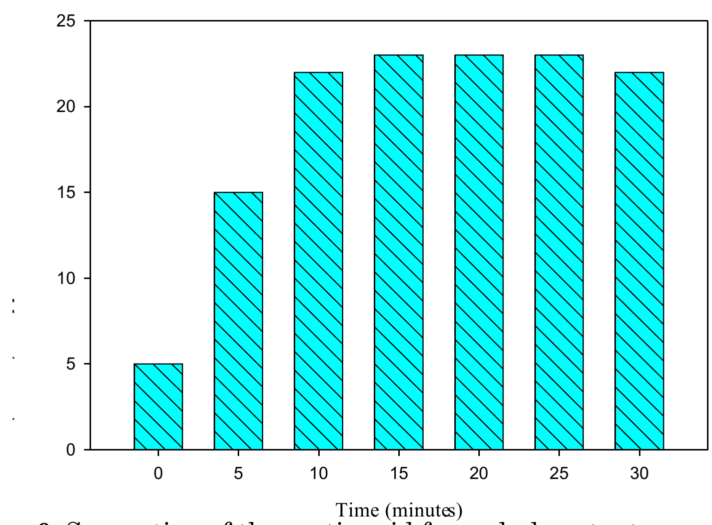


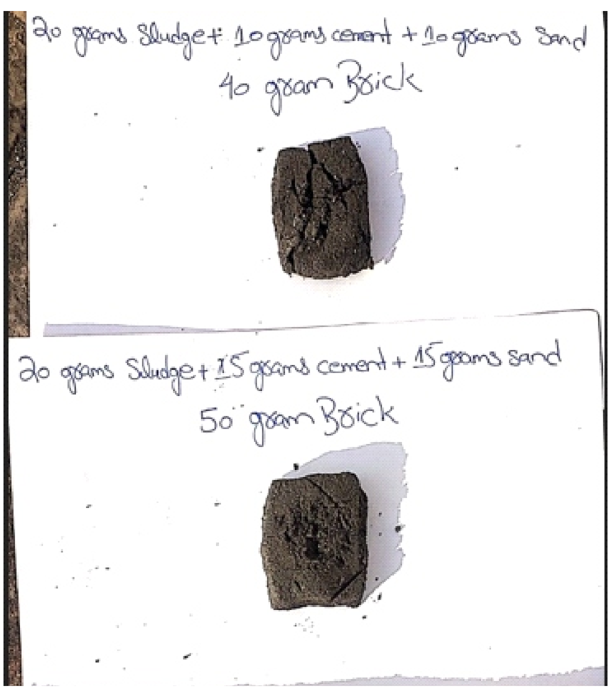
Figure 6: Separation of the acetic acid from sludge at a temperature of 120 °C,.

As shown in Table 3, fresh engine oil was compared to used engine oil, top layer separated oil after acid treatment, and top layer separated oil after centrifugation in terms of flash point, pour point, kinematic viscosity, and density. Fresh engine oil had a flash point of 209 °C, a pour point of - 12 °C, a kinematic viscosity of 87 cst, and a density of 826 kg/m^3. The flash point of used engine oil was 160 °C, the pour point was -45 °C, the kinematic viscosity was 24 cst, and the density was 788 kg/m^3. The flash point of the top layer separated oil after acid treatment was 179 °C, the pour point was -28 °C, the kinematic viscosity was 44 cst, and the density was 800 kg/m^3. The separated oil had a flash point of 200 °C, a pour point of -15 °C, a kinematic viscosity of 72 cst, and a density of 815 kg/m^3. These analyses revealed that this treatment restored nearly all of the properties of the waste engine oil, as the fresh oil and treated oil values are very similar.

Table 3: Analysis of the physical properties of the lubricating engine oil.

No	Sample	Flash point ℃	Pour point ℃	Kinematic viscosity @ 40 ℃	Density (kg/m^3)
1	Fresh engine oil	209	-12	87	826
2	Used engine oil	160	-45	24	788
3	Top layer separated oil after acid treatment	179	-28	44	800
4	Top layered Separated oil after centrifugation	200	-15	72	815

Finally, sand and cement were used to solidify the contaminated sludge in order to dispose it properly. There were three sun-dried brick samples created. 20 g of sludge, 10 g of cement, and 10 g of sand made up the first brick. 20 g of sludge, 15 g of cement, and 15 g of sand made up the second brick. The third brick was made out of 20 g each of sludge, cement, and sand. For ten days, all of these bricks were allowed to dry. Their strength was put to the test by being thrown from a height of 6 feet after ten days. There were many cracks in the 40 g block. Few cracks could be seen in a 50 g block. The strength of the third brick (60 g) was demonstrated by the absence of cracks as shown in Figure 7.



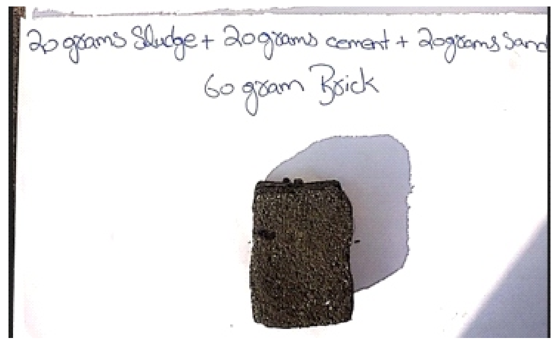


Figure 7: Structural strength of the produced brick from the sludge cement and sand.

4. Conclusions:

In several parts of Pakistan, the sulphuric acid processing method is frequently used to recycle used motor oil. Toxics are created during the cleaning procedure, which eventually harms the ecosystem. Huge capital investment is needed to implement the modern technologies, which is beyond the means of the majority of small business owners. Acetic acid can be used in the interim to extract usable hydrocarbons from used lubricating oil. To save the energy Atmospheric pressure and temperature are used during the treatment procedure. The simple processing consists of a mixture of acetic acid and old motor oil. This cleaning process recovers about 53% of the lubricating oil in terms of volume. The possibility of environmental deterioration can be decreased by turning the created sludge into solid blocks.

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