ADDIS ABABA UNIVERSITY
ADDIS ABABA INSTITUTE OF TECHNOLOGY (AAiT)
SCHOOL OF CHEMICAL AND BIO-ENGINEERING
(MSc. Program in Environmental Engineering)

Recycling of Used Lubricating Oil Using Acid-Clay Treatment Process

By

Hayalu Andargachew Mekonnen

Adviser: Dr.-Ing. Abubeker Yimam

OCTOBER 2014

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A Thesis Submitted in Partial Fulfilment of the Requirements for the Award of a Master's Degree in Chemical Engineering under Environmental Engineering

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Hayalu Andargachew

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ABSTRACT

Numerous industries are emerging in Ethiopia and urban developments are accelerated giving rise to multiple waste generations. As used lubrication oil is one of the hazardous wastes generated at different development sectors, it should not be utilized and/or disposed in ways which are unsafe to the environment hence calling for its proper management. This study primarily focuses on the recycling of used oil by applying acid-clay treatment process. Used engine oil properties gave expected undesired characteristics caused by oil deterioration. The characterization was indicative to the sources of contaminations from conditions during the oils application period. For instance, the lower flash point (132°C) indicated light fuel contamination effect; increased density (0.93 g/ml) and viscosity (kinematic Viscosity @ 40 °C was 126.41 cSt) showed possible oxidation and polymerization products dissolved and suspended in the used oil; and ash content (2.3%) indicated contamination from incombustible solid particles of dirt, dust, grit and metallic fragments. Similarly, deviations of other parameters also referred different contamination sources. Recycling experiments utilized 15, 20 and 25% acid and adsorbent (Bentonite clay) ratios with different combinations. Nine combinations with their respective triplicates were conducted. The experiments showed that the acid-clay treatment process was effective in recovering valuable oil from used oil samples with comparable qualities. From the twenty seven runs performed, yields within the range of 55% to 74.7 % was obtained. The run with acid percentage of 20% and adsorbent percentage of 15% was chosen as the optimum combination using statistical analysis that considered selected quality parameters of recovered oil i.e. density, kinematic viscosity @ 40 °C and ash content. The optimum combination gave a 69% yield; density of 0.886 g/ml; kinematic viscosity @ 40 °C of 94 cSt; and 0.34% ash content. Eight to ten percent of valuable light fuel was also recuperated from the vacuum distillation step of the process. The preliminary cost analysis showed, an estimated sum amount of 22.86 birr is expected to recover a liter of usable oil which is 61.64 birr less, relative to the amount required to import the original fresh oil that costs 84.5 birr/liter.

1. BACKGROUND

The demand for lubricants is continuously increasing with the increase in the establishment of factories and the tremendous increase in the number of vehicles and other means of transportation. Lubricant oils have been used primarily for reducing friction between moving parts of various machineries or equipment, minimizing material wear, and improving the efficiency of equipment /machineries which have consecutive significance in fuel and energy savings. Access to lubricants is essential to any modern society and not only does lubrication reduce friction and wear between moving surfaces, it also removes heat, keeps equipment clean, and prevents corrosion. But, the oil spent can be a great source of contamination if it is thrown as a waste or can be considered as a new resource if properly used, and all depend on the methods of how oil can be reused (Awaja & Pavel, 2006).

Used lubrication oil is a high pollutant material that requires responsible management. Used engine oil may cause damage to the environment when dumped into the ground or into water streams including sewers. This may result in groundwater and soil contamination. Recycling of such contaminated materials will have a significant positive impact on the environment and will be beneficial in reducing oil costs (Hamawand et al., 2013).

Used lubricating oil refers to the engine oil, transmission oil, hydraulic and cutting oils after certain period of application. It also refers to the degradation of the fresh lubricating components that become contaminated by metals, ash, carbon residue, water, varnish, gums, and other contaminating materials, in addition to asphaltic compounds which result from the bearing surface of the engines. These oils must be changed and removed from the automobiles, different machineries or utility equipment after certain period of application because they become inadequate from serious deterioration in service. These used lubrication oils have significant impact on both economic and environmental aspects. They cost millions of dollars to manufacture and represent a highly pollutant material when disposed of. If discharged on the land, water or even burnt as a low grade fuel, these may cause serious pollution problems since they release harmful metals and other pollutants into the environment (Hamawand et al., 2013).

1.1. Statement of the Problem

The hazard of environmental pollution through disposing used lubricating oils on the ground in many developing countries is of great concern to public health and ecology. Used lubricating oil contains a number of degraded additives, impurities, and residues resulting from the combustion process and frictions of mechanical parts. Some of these are poisonous or carcinogenic like PCB (poly-cyclic benzenes), PAH (poly-aromatic hydrocarbons) and heavy metals. It takes only one liter of oil to contaminate one million liters of water and the smallest single automotive oil change produces 4 to 5 liters of used oil. Similarly, one gallon of used oil is able to contaminate million gallons of drinking water and can form a thin layer of oil on the surface of the water which prevents oxygen from being dissolved in water. By this process, it hampers all kinds of aquatic life and the processes of photosynthesis. The carbohydrate content of plants grown in oil contaminated soils is significantly lower than that grown in plain soils (Nwachukwu et al., 2012).

In developing countries, used oils are utilized in road construction for dust control, for pest and weed control, wood preservation, as old engines emergency lubricants, for burners, boilers and furnaces which have multiple environmental effects on soil, land and air pollutions. Sometimes it is traditionally used for medication purposes on wound and cuts causing additional health effects (Nwachukwu et al., 2012).

Wise application and disposal of used lubricating oils will be of a great value from protecting the environment and utilizing resources in efficient and effective ways. Recycling makes more sense today than ever in this aspect. Recycling protects the environment by reducing waste generation and simultaneously saving expenses through increasing the reusable potential of once purchased resource several times.

Ethiopia is one of the developing nations in which numerous industries are emerging and urban development is increasing, giving rise to multiple waste generations. As used lubricating oil is one of the hazardous wastes generated at different development sectors, it should not be utilized and/or disposed in ways which are environmentally unsafe, therefore, requires proper management.

This research is based on addressing problems associated with improper application and/or disposal of used lubricating oils using a simple recycling technique which utilizes cheaper chemicals, utilities and equipment relative to other recycling or re-refining options for protecting our environment and conserving resources.

1.2. Objectives

1.2.1. General Objective

The general objective of the study will be to:

- Study the potential of recycling used lubricating oil through acid-clay treatment process

1.2.2. Specific Objective

The specific objectives of the study are the following:

1. To determine the contaminants that would characterize used generator engine oil.
2. Establishing the operating parameters of the acid-clay process experiment.
3. Assess the recovery capacity of the acid-clay process by characterizing the recovered oil and comparing it with the virgin oil.
4. Optimizing studied process parameters (acid ratio and adsorbent ratio) that would maximize the efficiency of the process.
5. Evaluating the preliminary cost analysis of the process from laboratory results.

1.3. Significance of the Study

The significance of this study will primarily circle around the protection of the environment through recycling resources and minimizing the amount of waste lubricating oil to be disposed which has a vital contribution in hazardous waste management in the country.

On the other hand, the fruitfulness of the study will demonstrate the basic hint of how different industries would benefit from reclaiming used oil for recurrent purposes and save expenses. Various factories could open separate processing plant that would assist the main process in this regard.

In addition to the environmental protection, the research will play a role in national research and development efforts to establish businesses henceforth creating job opportunities through small or large scale re-refining units for the future.

2. LITERATURE REVIEW

2.1. Lubricating Oil

Lubricating oil is the very stable, non-volatile and smallest fraction of crude petroleum. As petroleum products are essentially composed of hydrocarbons, lubricating oils have hydrocarbon structures, containing from 20 to 70 carbon atoms per molecule.

The lubricating oil molecules can be divided into three broad groupings i.e. paraffinic naphthenic and aromatic. Paraffinic molecules are predominantly straight chains, tend to be waxy, have a high pour point, good viscosity and better temperature stability. Naphthenic molecules are straight chains with a high proportion of five and to a lesser extent six membered ring structures. They tend to have a low pour point. For this reason they are used as refrigeration oils. They are highly carcinogenic and are little used in engine oil. Aromatics are straight chains with six membered ring benzene structures. In practice, no sharp distinction exists between these various groupings as many lubricating oil molecules are a combination, to varying degrees, of the different types of hydrocarbons (Yu-Lung Hsu & Chun-Chu Liu, 2010).

Lubricating oils are fluids such as engine oils, gear, hydraulic oils, turbine oils, etc., used to reduce friction between moving surfaces. They also serve to remove heat from working parts in machinery created by moving surfaces and provide a protective layer on the metal surfaces to avoid corrosion. They also act as a sealant to fill the microscopic ridges and valleys in any metal surfaces to increase the machinery efficiency. In addition, they serve as a cleaning agent to carry away dirt or other debris that may damage the bearings or other parts that are operated in tight tolerance. Debris is removed through the engine oil filter or the transmission filter.

Lubricating oils are usually blended with a number of chemical additives to provide products that last longer and allow the machinery to work better under severe operating conditions.

However, performance of the lubricants deteriorates over time as the additives are chemically changed and the oil becomes contaminated with various unwanted pollutants as a result of many physical and chemical interactions (Dennis W.Brinkman, 2010).

2.2. Used Lubricating Oil

During the usage of lubricating oil, it will age, deteriorate, and lose efficiency due to the mixture with foreign matters that contain metal powder, filings, and other oils as well as additives. If the lubricating oil is oxidized, its colour will become darker, and the acid value increases to generate precipitate, oil sludge, varnish, and hard varnish. If these materials deposit on the surface and in the flow passage and cleaner, it is likely to cause malfunctions of the machine and reduce the overall productive efficiency. At this point, the lubricating oil needs to be changed, so as to increase the work efficiency, and the replaced oil will be waste.

Generally lubricating oil becomes unfit for further use for two main reasons: accumulation of contaminants in the oil and chemical changes in the oil. These effects interfere with the basic properties of lubricating oil which are peculiar for their effective performance during application (Awaja & Pavel, 2006).

2.2.1. Lubricating oil Properties

In simple terms, the function of lubricating oil is to control friction and wear in a given system. The basic requirements therefore relate to the performance of the lubricant, i.e. its influence upon friction and wear characteristics of a system. Another important aspect is the oil quality which reflects its resistance to degradation in service. Most of the present day lubricant research is dedicated to the study, prevention and monitoring of oil degradation since the life-time of oil is as important as its initial level of performance. Apart from suffering degradation in service, which may cause damage to the operating machinery, oil may cause corrosion of contacting surfaces.

The fundamental physical properties such as viscosity, viscosity temperature dependence, viscosity index, pour point, flash point, volatility, oxidation stability, thermal stability, and etc., are the factors which determine the level of performance and quality of lubricating oil. During the oil application period, these properties may be lost or degraded (Chia-Yu, 2008).

2.2.1.1. Oil Viscosity

The parameter which plays a fundamental role in lubrication is oil viscosity. Different oils exhibit different viscosities. In addition, oil viscosity changes with temperature, shear rate and pressure and the thickness of the generated oil film is usually proportional to it. For engineering applications the oil viscosity is usually chosen to give optimum performance at the required temperature.

The viscosity of lubricating oils is extremely sensitive to the operating temperature. With increasing temperature the viscosity of oils fall quite rapidly. In some cases the viscosity of oil can fall by about 80% with a temperature increase of 25°C.

From the engineering viewpoint there was a need for a parameter which would accurately describe the viscosity-temperature characteristics of the oils. The viscosity index is an entirely empirical parameter which compares the kinematic viscosity of the oil of interest to the viscosities of two reference oils which have a considerable difference in sensitivity of viscosity to temperature.

Lubricant viscosity is also affected by pressure and increases with pressure. For most lubricants this effect is considerably larger than the effect of temperature or shear when the pressure is significantly above atmospheric.

There are several widely used oil viscosity classifications. The most commonly used are SAE (Society of Automotive Engineers), ISO (International Organization for Standardization) and military specifications (Chia-Yu, 2008).

2.2.1.2. Lubricant Density and Specific Gravity

Lubricant density is important in engineering calculations and sometimes offers a simple way of identifying lubricants. Density or specific gravity is often used to characterize crude oils. It gives a rough idea of the amount of gasoline and kerosene present in the oil. The oil density, however, is often confused with specific gravity.

Specific gravity is defined as the ratio of the mass of a given volume of oil at temperature '**t1**' to the mass of an equal volume of pure water at temperature '**t2**'. Density, on the other hand, is the mass of a given volume of oil [kg/m^3].

The density of a typical mineral oil is about 850 [kg/m^3] and, since the density of water is about 1000 [kg/m^3], the specific gravity of mineral oils is typically 0.85 (Chia-Yu, 2008).

2.2.1.3. Temperature Related Characteristics of Lubricating Oil

The temperature characteristics are important in the selection of lubricating oil for a specific application. In addition the temperature range over which the lubricating oil can be used is of extreme importance. At high temperatures, oils decompose or degrade, while at low temperatures oils may become near solid or even freeze. Oils can be degraded by thermal decomposition and oxidation. During service, oils may release deposits and lacquers on contacting surfaces, form emulsions with water, or produce foam when vigorously churned. These effects are undesirable and have been the subject of intensive research. The degradation of oil does not just affect the oil, but more importantly leads to damage of the lubricated equipment. It may also cause detrimental secondary effects to the operating machinery. A prime example of secondary damage is corrosion caused by the acidity of oxidized oils. The most important properties of lubricating oils and other lubricants, which are related to operating conditions, are its pour point, flash point, volatility, oxidation and thermal stability, neutralization number and carbon residue (Chia-Yu, 2008).

i. Pour Point and Cloud Point

Pour point is the lowest temperature at which the oil will just flow when it is cooled. This oil property is important in the lubrication of any system exposed to low temperature, such as automotive engines, construction machines, military and space applications.

Cloud Point is the temperature at which paraffin wax and other materials begin to precipitate. The onset of wax precipitation causes a distinct cloudiness or haze visible in the bottom of a jar. This occurrence has some practical applications in capillary or wick fed systems in which the forming wax may obstruct the oil flow. It is limited only to the transparent fluids since measurement is based purely on observation.

ii. Flash Point and Fire Point

Flash point is the temperature of oil at which its vapour will ignite. The fire point of oil is the temperature at which enough vapour is produced to sustain burning after ignition. Flash and fire points are very important from the safety view point since they constitute the only factors which define the fire hazard of a lubricant. In general, the flash point and fire point of oils increase with increasing molecular weight. For typical lubricating oil, the flash point is about 210°C whereas the fire point is about 230°C.

iii. Volatility and Evaporation

In many applications the loss of lubricating oil due to evaporation can be significant. The temperature has a controlling influence. At elevated temperatures in particular, oils may become more viscous and eventually dry out because of evaporation. Volatile components of the lubricant may be lost through evaporation resulting in a significant increase in viscosity and a further temperature rise due to higher friction which causes further oil losses due to evaporation. Volatility of lubricating oil is expressed as a direct measure of evaporation losses.

iv. Oxidation Stability

Oxidation stability is the resistance of lubricating oil to molecular breakdown or rearrangement at elevated temperatures in the ordinary air environment. Lubricating oils can oxidize when exposed to air, particularly at elevated temperatures, and this has a very strong influence on the life of the oil. The rate of oxidation depends on the degree of oil refinement, temperature, presence of metal catalysts and operating conditions. It increases with temperature. One way of improving oxidation stability is to remove the hydrocarbon type aromatics and molecules containing sulphur, oxygen, nitrogen, etc. This is achieved through refining. More refined oil has better oxidation stability. The products of oxidation usually consist of acidic compounds, sludge and lacquers. All of these compounds cause oil to become more corrosive, more viscous and also cause the deposition of insoluble products on working surfaces, restricting the flow of oil in operating units. This interferes with the performance of the unit. Oxidation stability is very important oil characteristic, especially where extended life is required; e.g. turbines, transformers, hydraulic and heat transfer units, etc. A lubricant with limited oxidation stability requires more frequent maintenance or replacement, resulting in higher operating costs. Under more severe conditions the required oil changes may become more frequent; hence the operating costs will even be higher.

v. Thermal Stability

When heated above a certain temperature oils will start to decompose, even if no oxygen is present. Thermal stability is the resistance of the lubricant to molecular breakdown or molecular rearrangement at elevated temperatures in the absence of oxygen. When heated to higher temperatures, mineral oils break down to methane, ethane and ethylene. Thermal stability can be improved by the refining process, but not by additives. Mineral oils with a substantial percentage of C-C single bonds have a thermal stability limit of about 350°C. Lubricating oils with aromatic linkages or with aromatic linkages and methyl groups as side chains exhibit a thermal stability limit of about 460°C. The additives used for lubrication improvement usually have a thermal stability below that of base oils. In general, thermal degradation of the oil takes place at much higher temperatures than oxidation. Thus the maximum temperature at which oil can be used is determined by its oxidation stability.

vi. Neutralization Number

The neutralization number refers to the acidity or alkalinity of lubricating oil. The results are reported as a Total Acid Number (TAN) for acidic oils and as a Total Base Number (TBN) for alkaline oils. TAN is a measure of acidic matter remaining in the oil and the TBN is the measure of alkaline matter remaining in the oil. In general, TBN applies only to the oil supplied with alkaline additives to suppress sulphur based acid formation in the presence of low grade fuels such as diesel engine lubricants. Thus TBN is a negative measure of oil acidity and a minimum value should be maintained. On the other hand the TAN number applies to most oils since they are normally weakly acidic.

vii. Carbon Residue

At temperatures of 300°C or more in the absence of air, oils may decompose to produce low molecular weight fragments from the large molecular weight species typically found in mineral oils. The fragmented or ‘cracked’ hydrocarbon molecules either recombine to form tarry deposits (asphaltenes) or are released to the atmosphere as volatile components. The deposits are undesirable in almost all cases and most lubricating oils are tested for deposit forming tendencies. The carbon residue is determined by weighing the residue after the oil has been heated to a high temperature in the absence of air. The carbon residue parameter is of little importance in the case of synthetic oils because of their good thermal stability. It is also infrequently used in characterizing well refined lubricants.

2.2.2. Degradation of Lubricating oil

Oils have a finite lifetime. As it is stated earlier, they will eventually degrade and/or become contaminated and will need to be changed. Lubricants consist of a base stock that can either be mineral or synthetic. In the case of synthetic base stocks, these are a family of compounds that are manufactured in a laboratory to have precisely the properties that the chemists and engineers want. Mineral base stocks are derived from crude oil that comes out of the ground and is refined to produce a base stock that can do the desired job. Synthetic bases are superior to mineral ones but are much more expensive.

The other component of a lubricant is the additive package. This is a range of twenty or more chemicals that the refinery blends with the base stock so that it can do its job. The additives are used to enhance the natural properties of the lubricating oil and to prevent some undesirable properties. The main additives for lubricating oil are oxidation inhibitor, detergent & dispersants, viscosity index improvers, pour point depressants, anti-foam agents, rust inhibitors, corrosion inhibitors and anti-wear additives.

Most additives are sacrificial in nature and this means that they get used up during the lifetime of the oil. As the oil is used to lubricate a piece of machinery, the additives become depleted and deactivated and eventually the oil will wear out and will need to be replaced.

Why oils degrade has been covered in numerous technical bulletins but this issue deals with how lubricants degrade, in other words, what are the mechanisms for additive depletion and degradation. The important mechanisms include oxidation, thermal degradation, neutralisation, shearing, hydrolysis, water washing, particle scrubbing, surface adsorption, rubbing contact, condensation settling, filtration, aggregate adsorption, evaporation, centrifugation and contamination.

Degradation of oil is also a complex web with many competing processes taking place at the same time. Even the best oil, in the best equipment, operating in an ideal environment with perfect maintenance practices will eventually degrade, wear out and need to be changed.

The next sub-sections will address the specifics of exactly what happens to motor oil during use in an internal combustion engine and what properties are violated.

2.2.2.1. Oxidation

Oxidation is the most important form of chemical breakdown of motor oil and its additives. The chemicals in motor oil are continuously reacting with oxygen inside an engine. The effects of oxidation due to this reaction as well as the by-products of combustion produce very acidic compounds inside an engine. These acidic compounds cause corrosion of internal engine components, deposits, varnish, sludge and other insoluble oxidation products that can cause a performance and durability degradation of an engine over a period of time. The products of oxidation are less stable than the original base hydrocarbon molecular structure and as they continue to be attacked by these acidic compounds can produce varnish and sludge.

Oxidation can cause changes in almost all properties of lubricating oils, especially on viscosity, pour point, flash point, volatility, and neutralization number.

2.2.2.2. Thermal Degradation

When motor oil is heated beyond a certain temperature it will start to degrade, even if there is no oxygen present. This is called thermal degradation and causes the oil to change viscosity. The thermal stability of motor oil cannot be improved by use of additives but it can be improved by refining out the same compounds that decrease the oxidation resistance. As temperatures increase, thermal degradation increases. In order for an oil to provide proper service and protection at high operating temperatures highly refined oils with plenty of anti-oxidants should be used. For average service less highly refined oils can be used.

In addition to changes on viscosity and oxidation stability, thermal degradation can significantly affect volatility and evaporation rate of lubricating oil and also increase carbon residue.

2.2.2.3. Corrosion

Petroleum oil that is new or kept clean by proper filtration is generally non-corrosive and will provide good protection against corrosion caused by the atmosphere. However, inside an engine oil oxidation by-products will attack internal engine steel and bearing materials that are typically manufactured with aluminium, copper, lead and tin.

Water present due to condensation caused by temperature and humidity changes or short ‘stop and go’ driving where the engine never reaches the proper operating temperature, although still hotter than the ambient temperature, can also cause corrosion. The hotter the oil is when water is present the more severe the chemical reaction is and corrosion related damage could definitely occur. In addition, water present in oil for an extended period of time can emulsify the oil and form a mixture which is much more corrosive than the two components alone and can then form sludge which may block oil filters or small passages.

Corrosion can accelerate oxidation & thermal instability, and further infringe all lubricating oil properties.

2.2.2.4. Contamination

Motor oil contamination also causes deterioration of the oil. Some of the more common contaminant sources include dirt, sand and dust from the air, soot, unburned fuel in the oil, water from condensation of the combustion process, wear metal particulates that the oil filter cannot trap and hold, corrosion by-products and additive elements that have degraded. In addition dirt, sand and dust can continue to enter the engine and, in addition to creating more wear debris, combine with other contaminants and cause more damage than they would separately.

One of the many by-products of combustion is soot. Soot can be highly abrasive as well as cause filters to become filled and/or plugged in extreme cases. Another contaminant is acidic by-products of combustion, which can produce a highly corrosive mixture and cause corrosion and pitting of internal engine components and additional generation of wear debris. These same acidic solutions can also mix with water inside the engine and form an emulsion that can cause problems with oil filters and passageways (Layzell, 2010).

Yet another source of contamination is fuel. A charge of fuel is rarely 100% burned during the combustion process. This unburned fuel can mix with the oil present in the cylinders. Fuel contamination can also be caused by worn sealing components such as excessive piston ring to cylinder clearances allowing unburned fuel to blow-by the rings.

When motor oil is diluted with fuel the viscosity is lowered. If this reaches extremes of contamination excessive wear and engine damage can take place and may lead to significant deterioration of the different properties of the oil (Chia-Yu, 2008).

2.2.3. Contaminants in Used Lubricating Oil

The main constituents of waste lubricating oils are the base oil, degraded additives, metallic debris, oxidation products and carbon soot. A large number of additives are used to impart performance characteristics to the lubricants. The main additives are antioxidants, detergents, anti-wear elements, metal deactivators, corrosion inhibitors, rust inhibitors, friction modifiers, extreme pressure withstanding elements, antifoaming agents, viscosity index improvers, demulsifying or emulsifying agents and stickiness improver.

During their use, these additives lose their characteristics rendering the lube oil non usable for lubricating purpose. In addition, during their use, the lubricating oils and the metal processing oils pick up fractions of various metals as a result of wearing out of components. The concentration of these impurities depends purely on the application to which the particular oil is put to (J. Diphare et al., 2013).

Generally, lubricating oil loses its effectiveness during operation due to the presence of certain types of contaminants. These contaminants can be divided into extraneous contaminants and products of oil deterioration.

Table 2-1: Typical contaminants found in used oils

Metals	Chlorinated hydrocarbons	Other organic compounds
Cadmium	*Dichlorodifluoromethane*	*Benzene*
Chromium	*Trichlorotrifluoroethane*	*Toluene*
Arsenic	*Tetrachloroethylene*	*Xylene*
Barium	*1,1,1- Trichloroethane*	*Benzo(a)anthracene*
Zinc	*Trichloroethene*	*Benzo(a)pyrene*
Lead	*Total Chlorine*	*Naphthalene*
		PCB's

2.2.3.1. Extraneous Contaminants

Extraneous contaminants are introduced from the surrounding air and from the engine during combustion. Contaminants from the air are dust, dirt, and moisture. These contaminants pass into the engine through the air-cleaner and may be composed of small particles of silicates. Air itself may be considered as a contaminant since it might cause foaming of the oil. The contaminants from the engine are:

(1) Metallic particles resulting from wear of the engine: Iron, copper and aluminium are released due to normal engine wear.

(2) Carbonaceous particles: soot and carbon originate due to incomplete fuel combustion especially during warm-up with a rich mixture.

(3) Metallic oxides present as corrosion products of metals,

(4) Water from leakage of the cooling system,

(5) Water as a product of fuel combustion: Fuel burns to CO_2 and H_2O. For every liter of fuel burnt, a liter of water is created. This normally passes out through the exhaust when the engine is hot, but when cold it can run down and collect in the oil.

(6) Fuel or fuel additives or their by-products, which might enter the crankcase of engines. Unburnt gasoline or diesel can pass into the lubricant, especially during start-up. Tetraethyl lead, which is used as an anti-knock agent in petrol, passes into the oil. Typical used engine oil may have contained up to 2% lead, but today any lead comes from bearing wear and is likely to be in the 2 - 12 ppm range.

2.2.3.2. Products of Oil Deterioration

Many products are formed during oil deterioration. Some of these important products are:

(1) Sludge: a mixture of oil, water, dust, dirt, and carbon particles that results from the incomplete combustion of the fuels and as result of oxidation. Sludge may deposit on various parts of the engine or remain in colloidal dispersion in the oil.

(2) Lacquer: a hard or gummy substance that deposits on engine parts as a result of subjecting sludge in the oil to high temperature operation.

(3) Oil-soluble products: result of oil oxidation products that remain in the oil and cannot be filtered out and deposit on the engine parts. The quantity and distribution of engine deposits vary widely depending on the conditions at which the engine is operated. At low crankcase temperatures, carbonaceous deposits originate mainly from incomplete combustion products of the fuel and not from the lubricating oil. While, at high temperature, increased lacquer and

sludge deposits may be caused by the lubricating oil. Some oil molecules, at elevated temperatures, will oxidize to complex and corrosive organic acids. (Awaja & Pavel, 2006).

2.2.3.3. Effects of Oil Contaminants

The lubricating oil properties are affected by any contaminants that may occur during motor operation. The effects of the contaminants are as follows:

(1) Water: Even in small amounts, water causes rusting of iron or steel. The water also results in forming water sludge (emulsions), which may clog oil passages, pump, valves and other oil handling equipment. Water also contributes to foaming problems.
(2) Solid particles of dirt, dust, grit and metallic fragments, which were circulated by the lubricant: these contaminants cause excessive wear, scoring of bearing surface, and possible failure due to seizing of metal fatigue. Soot and carbon make the oil go black.
(3) Sludge and lacquers: sludge deposits clog small oil passages and clearances. Lacquers or varnishes can cause sticking of valves, and resist against the continuous operation of oil pump.
(4) *Liquid contaminants:* such as unburned fuel from engines dilute lubricating oil and possibly reduce their viscosity beyond a safe load. Contaminants of the lubricant with heavier oil increase viscosity and interfere with the oil circulation. This affects the lubricating value and heat transfer capacity (Awaja & Pavel, 2006).

2.2.4. Physical and Chemical Tests of Used Lubricating Oil

Standard chemical and physical tests are used to evaluate the properties of the oil and the extent of the contaminants in the used automotive oils. These tests involve the following measurements:

(1) Viscosity: viscosity testing can indicate the presence of contamination in used lubricating oil. The oxidation and polymerization products that were dissolved and suspended in the oil cause the increase of oil viscosity. While a decrease in the viscosity of lubricating oil indicates the fuel contamination.
(2) Pour point: pour point is the lowest temperature at which the oil will flow. Low pour point indicates good lubricating oil.
(3) Flash point: flash point is the lowest temperature at which the vapours in air will burn momentarily if ignited by flame or spark. A decrease in flash point indicates contamination by

dilution of lubricating oils with unburned fuel. Increasing of flash point indicates evaporation of the light components from the lubricating oil.

(4) Acidity or neutralization number: this is a measure of the amount of alkali required to neutralize one gram of the oil. An increase in acid number indicates the extent in oxidation of lubricating oil.

(5) Ash content: the remaining solid ash, when the oil is completely burned, is a measure of oil purity and indicates contamination with metals.

(6) Carbon or coking test: this evaluates the solid residue obtained when the oil is heated to complete vaporization and it refers to the amount of deposit formed.

(7) Water content: this test is done by distillation and indicates the amount of water emulsified in the oil.

(8) Fuel contaminants: this test indicates the amount of fuel diluting in the lubricating oil during operation (Awaja & Pavel, 2006).

Refractive index, oil colour, sulphur content, chlorine content and metal contents of lubricating oils are tested through different techniques to characterize oil properties.

Table 2-2: Comparison of fresh base engine oil and used oil

Samples	**Base engine oil (Ravenol, VSi SAE 5W-40)**	**Used engine oil (being in use for 2000–3000 km)**
Flash point °C	232	158
Pour point °C	−13	−5
Kinematic viscosity@ (40 °C)	195.62	136.6
Kinematic viscosity@ (100 °C)	18	13.5
Viscosity index	100.27	89.11
Refractive index	1.4886	1.4763
Specific gravity	0.8818	0.9261
Water and Sediment (mL)	-	0.9
Carbon residue (wt %)	0.55	1.82
(TAN) mg KOH/ g(sample)	-	4.5
(TBN) mg KOH/ g(sample)	3.55	-
Metal Contents (ppm)		
• Cu	0	4.6
• Mg	72	81
• Cr	0	1.5
• Sn	0	1.6
• Pb	0	14.6
• Fe	0	72
• Zn	1200	1280

2.2.5. Impacts of Used Lubricating Oil

The contaminants in used oil have adverse environmental and health impacts. The presence of degraded additives, contaminants, and by-products of degradation render waste oils more toxic and harmful to health and environment than virgin base oils. If put into storm water drains or sewers, they can affect waterways and coastal waters. When dumped in soil or sent to landfill, they can migrate into ground and surface waters though numerous land treatment processes. In addition, uncontrolled used oils are a threat to plant and animal life, which can further result in economic losses, i.e. recreation and fishing industries. For example, used oil from internal combustion engines generally accumulates a variety of contaminants which increase the oil's toxicity (J. Diphare et al., 2013).

Improper application of used oil for multiple customary purposes also leads to various environmental degradations and health effects. Some local uses of changed oil and its direct and indirect adverse effects are shown in Table 2-3 (Nwachukwu et al., 2012).

According to EPA, just one quart of used oil is able to make one million gallons of water undrinkable. When used oil enters surface water, oil films will block sunlight, impair photosynthesis, and prevent the replenishment of dissolved oxygen, which lead to the death of aquatic plants and animals. When used oil is dumped down the drain and enters a sewage treatment plant, very small concentrations of oil in the wastewater (50 to 100 ppm) can foul

Table 2-3: Environmental impact assessment of local uses of changed engine oil

Local uses of used oil	*Application*	*Environmental effect*
Road construction	*On the ground*	*Soil pollution*
Rust prevention	*On a metal device*	*Stains on contact*
Old engines emergency lubricant	*Automobiles, generators*	*Air pollution, waste*
Wood preservation	*Timber; roofing, fencing*	*Land pollution*
Mixed with grease for gear oil	*Gear box lubricant*	*Spills; Soil pollution*
Production of grease	*Automobile lubricant*	*Stain on contact*
Burning, Boilers, furnaces	*Burners, bakery, incinerators*	*Off-gas, air pollution*
For pest, weed, and dust control	*Garden, workshops*	*Soil pollution*
Hydraulic oil	*Props, Lifts, Jacks*	*Spills*
Ball joint oil and nuts loosing oil	*Ball and socket joints, nuts*	*Stains on contact*
Block and Balustrade mold lubricant	*Block, bricks, balustrade molds*	*Spills*
Medication	*Wound and cuts*	*Additional Health effect*
Dust and tick control	*Land, floor*	*Land pollution, Stains*
Road construction	*On the ground*	*Soil pollution*

sewage treatment processes. Used oil drainage has been reported to account for more than 40% of the total oil pollution (the largest single source) to American waterways. Used oil filters are not even regulated as hazardous waste for most states and are allowed to be disposed in municipal landfills. Serious problems for the groundwater supplies surrounding the landfills are caused by residual oils from the filters that leach into the ground. Hence, practicing a good used oil recycling management is an important step for municipal solid waste reduction (Yang, 2008).

Used oil that is dumped onto soil can be washed into surface water by rain or snow, or it can seep through the soil into groundwater to contaminate our water sources. Used oil in the soil can also evaporate into the air. The contaminants in used oil that enter the air through evaporation or improper burning can then settle, or be washed by rain or melting snow, into surface water or onto soil. The only way to make sure that used oil will not contaminate either water, soil, or air is to make sure that it is not released into the environment at all.

Since used oil is generated in such large quantities, for example more than 1.5 billion gallons per year estimated in the U.S., the associated impact to the environment is tremendously serious when there is uncontrolled dumping and landfilling of used oil in the environment. EPA data show that more than 33% of used oils generated each year in the U.S. are illegally dumped. The most uncontrollable used oil source is those do-it-yourself oil changers (DIYers). According to EPA, only 5 percent of used oil generated by DIYers is recycled, and the rest is either burned onsite (4 percent), disposed of in trash (30 percent) or illegally dumped (61 percent). Lack of public education and awareness and shortage of convenient recycling centres are main reasons why many DIYers do not participate in the used oil collection program (F.Dalla et al., 2012). As shown in Table 2-4, there are many harmful constituents in used oil that may cause cancer or other health problems if they are inhaled or ingested. For example, it was reported that burning used oil tagged as the top source of airborne lead emissions, especially in those states where used oil is not listed as hazardous waste and lead concentration in used oil is not regulated. Used oil, therefore, is not prohibited for open burning even if lead is present at high concentrations. Typical levels of contaminants found in used oils are also summarized in Table 2-4.

Table 2-4: Typical levels of contaminants in used oils (Yang, 2008)

Category	Compounds	Automotive Used Oil Concentrations [ppm]	Industrial Used Oil Concentrations [ppm]
Metals			
	Cadmium	5 – 25	NG
	Chromium	50 – 500	NG
	Arsenic	2	NG
	Barium	3 – 30	NG
	Zinc	100 – 1200	NG
	Lead	100 - 1200	NG
Chlorinated hydrocarbons			
	Dichlorodifluoromethane	1000 – 4000	NG
	Trichlorotrifluoroethane		NG
	Tetrachloroethylene		1000 – 6000
	1,1,1- Trichloroethane		
	Trichloroethene		
	Total Chlorine	1000 – 4000	1000 – 6000
Other organic compounds			
	Benzene	100 – 300	100 – 300
	Toluene	500 – 5000	500 – 5000
	Xylene	500 – 5000	500 – 5000
	Benzo(a)anthracene	10 – 50	NG
	Benzo(a)pyrene	5 – 20	NG
	Naphthalene	100 – 1400	NG
	PCB's	NG – 20	100 – 1000

These contaminants not only cause problems when they are released into the environment through improper management, but sometimes also interfere with the recycling operations of used oils. At other times, they are found to be concentrated in the waste streams of the reprocessing or re-refining plants and can cause further disposal problems (Yang, 2008).

2.3. Used Oil Recycling and Reuse

A large range of used oils can be recycled and recovered in a variety of ways, either directly or after some form of separation and refinement. As per the waste management hierarchy, the first option is to conserve the original properties of the oil allowing for direct reuse. Other options could include recovering its heating value and/or using in other lower level applications. Certain types of waste oils, lubricants in particular, can be reprocessed allowing for their direct reuse. The use of used oils, after treatment, can be either as a lube base stock comparable to refined virgin base oil or as clean burning fuel.

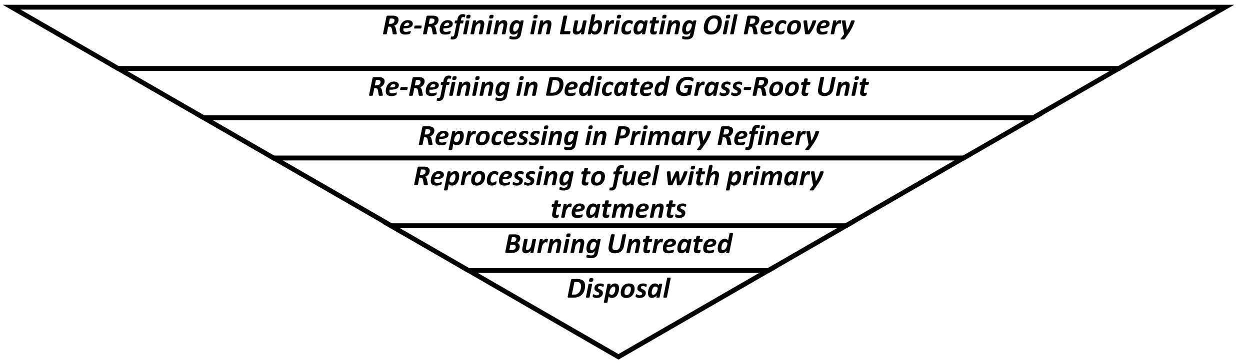

Figure 2-1: Waste oil treatment hierarchy

Used oils have been recycled for the past four decade. The idea of recycling used lubricating oil was presented in the year of 1930. Initially used lubricating oils were burnt to produce energy, and later these oils were re-blended to engine oils after treatment. Due to the increasing necessity for environmental protection and more stringent environmental legislation, the disposal and recycling of waste oils has become very important. The reuse of used lubricating oils can be accomplished through three basic methods, which are incineration, reprocessing, and re-refining.

Used oil can be thermally destroyed by incineration or combusted for energy utilization. Due to the economic benefit of recycling used oil, only a very small quantity of used oil is currently incinerated. Used oil that is incinerated generally has high concentrations of toxic contaminants that make recycling impractical or unsafe (J. Diphare et al., 2013).

Reprocessing technology provides a means where the waste oil is processed and burned for energy recovery. It involves removal of water and particulates so that used oil can be burned as fuel to generate heat or to power industrial operations. This form of recycling is not as preferable as methods that reuse the material because it only enables the oil to be reused once. Nonetheless, it is one of the economically attractive ways of managing used oil providing valuable energy i.e. about the same as provided by normal heating oil (Chia-Yu, 2008). A litre of used oil re-processed as fuel contains about 8,000 Kcal of energy, which is enough energy to light a 100 W bulb for one day or to operate a 1000W electric heater for 2 hrs. (Nwachukwu et al., 2012). Compared to direct burning, the major advantage from reprocessing used oil is that it improves the burning quality of used oil by removing/reducing some contaminants (Isah, 2013).

Used oil can also be re-refined back into base lube oil. Lube oil is a premium substance that can be re-refined and reused again and again. In general, water and dissolved low boiling point organic are removed by atmospheric or moderate vacuum distillation. Lube oil is then recovered using different treatments and/ or unit operations. Light end by-products are commonly used for plant combustion fuels. Diesel fraction and gas oil fractions can be recovered as high quality by-products after further advanced treatment. Residual streams from distillation can be used by asphalt industry as an asphalt flux to produce roofing asphalt, paving asphalt, insulating materials, and other asphalt based products. Re- refining involves treating used oil to remove impurities so that it can be used as a base stock for new lubricating oil. Re-refining prolongs the life of the oil resource indefinitely. This form of recycling is the preferred option because it closes the recycling loop by reusing the oil to make the same product that it was when it started out, and therefore uses less energy and less virgin oil (J. Diphare et al., 2013).

Table 2-5: Comparison of environmental aspect of treatment technologies (Yu & Chun, 2010)

	Recycling Technologies		
	Re-Refining	**Reprocessing**	**Incineration**
Acidic sludge	High	Low	-
Residual Sludge	High	Low	-
Harmful chemicals	Sulphuric acid	-	-
Pollution	Low	Low	high
Ash	-	-	High

Table 2-6: Comparison of economic aspect of treatment technologies (Yu & Chun, 2010)

	Recycling Technologies		
	Re-Refining	**Reprocessing**	**Incineration**
Technology Maturity	Plant Scale	Plant scale	-
Energy Demand	High	Low	-
Recovery rate	> 63%	> 74 %	-
Quality of reclaimed oil	Good	Fair	-
Equipment Demand	High	Low	Low
Operating Cost	High	Low	-

Table 2-7: Advantages and disadvantages of used oil recycling and reusing methods

Methods	Advantages	Disadvantages
Incineration	• Economically feasible at lower processing volumes • Cement factories are willing to procure waste oil • Less capital intensive than the other options • Concentrates waste oil disposal to limited sites that can be more easily regulated and controlled	• Air pollutant emissions, although minimal, still need to be addressed. • Opposition by regulatory and government institutions
Reprocessing	• Good substitute for second grade fuels • Limits the negative effects of the practice of uncontrolled burning of waste • The quality control of the re-processed fuel oil is monitored by the purchaser	• Requires a well-developed collection system • Requires extensive capital investment • Proper disposal of end waste residues are costly
Re-Refining	• Environmentally sound long term solution • Creates jobs • Reduces the amount of imported lubricant oil • Stripped light fuels and diesel give total self-sufficiency in fuel for the recycling plant	• Requires a well-developed collection system • Re-refined lube oil requires well developed market • Requires extensive capital investment • The re-refining option requires a reputable recycling company to ensure the marketability of the product • Proper disposal of end waste residues are costly

Ref: (J. Diphare et al., 2013)

2.3.1. Importance of Used Oil Recycling and Reuse

Used oil is definitely a vital source of energy. Oil doesn’t wear out; it just gets dirty after use. Used oil can be re-refined into base lube oil, reprocessed as fuel oil, or used as feedstock to produce petroleum-based products or other commercially valuable products via different methods. There are some facts about conserving resources by proper handling of used oil. Re-refining used oil takes about one-third of the energy needed to refine crude oil to lubricant quality; and one gallon of used lube oil that is re-refined produces the same 2.5 quarts of lubricating oil as 42 gallons of crude oil does. Collecting and recycling used oil, therefore, not only protects our environment from used oil contamination, but also conserves a valuable non-renewable resource.

From the standpoint of energy conservation, recycling used oil efficiently saves a precious, non-renewable resource. Only one out of 70 barrels of crude oil is processed into virgin lube stock. Many oil companies spend billions of dollars on exploring, recovering, and refining crude oil into quality lube oil. If the used oil generated by consumers can be recycled back to useful products such as pure lube oil again and again, tremendous time and money can be saved. More importantly, our natural resources will be conserved.

Therefore the management of used oil is particularly important because of the large quantities generated globally, the potential for direct re-use, reprocessing, regeneration and detrimental effects on the environment if not properly handled, treated or disposed of. Recycling of waste lubricants could result in both environmental and economic benefits (Yang, 2008).

2.3.2. General Regeneration Scheme

From the different used oil recycling treatment technologies, re-refining of waste oil to manufacture base oil conserves more resource than reprocessing the waste oil for use as a fuel. The energy required to manufacture re-refined oil from used oil is only one-third of the energy required to refine crude oil to produce virgin base oil. Therefore, re-refining is considered by many as a preferred option in terms of conserving resources, as well as minimizing waste and reducing damage to the environment.

At present, there are many waste oil re-refining technologies which include acid-clay treatment, solvent extraction, vacuum distillation with clay and hydrogenation finishing. But all technologies serve the mere purpose of generating lubricating oil for reuse. This is done in a four step process, in which water, solids, lighter oils, dissolved metals, degraded additives etc. are removed and finally the base stock is recovered (Udonne J. D., 2010).

The operational emphases of all technologies contain the following four points:

i. Dewater/defuel

In the use of lubricating oil, foreign matters are mixed into it under different circumstances; moisture is permeated into the lubricating oil in a long-term service. According to the definition, the fundamental components of light fuel are fuel and naphtha, which are mainly from the leakage of fuel for motor vehicle engine to the lubricating oil and the deterioration of components of lubricating oil. These foreign matters should be removed according to the difference between their physical properties and the lubricating oil (boiling point, specific gravity, being soluble in water or not).

ii. Deasphalting (Desludging)

As mentioned above, the lubricating oil would be mixed with different foreign matters during operation because of the environment. Beside liquid foreign matters such as moisture and light fuel, there are solid foreign matters such as metal powder derived from mechanical wear and additive added in the lubricating oil to generate deterioration products during operation leading to the formation of oxidative products such as organic acids, unsaturates, condensed aromatics and mercaptans, asphaltenes and petroleum resins. The removal of these compounds is known as deasphalting or desludging (Princewill & Sunday, 2010).

When dealing with this type of foreign matter, we can consider the different physical properties (different solubility and different boiling points) or use chemical method (add in chemical agent for reaction) to achieve deasphalting.

Early deasphalting was carried out mainly by adding in sulphuric acid or solvent treatment method; now, people adopt film separation or heat treatment.

Some processes carry out deasphalting through the fractionation step where the foreign matters remain as a residue during the distillation process.

iii. Fractionation

The fractionation classifies different materials based on different boiling points of different materials. Usually, a petroleum product is the mixture of diversified organic compounds (including lubricating oil), so to choose or remove a specific sort of material from the mixture, the materials can be obtained or removed by using fractionation.

iv. Finishing

After the aforesaid procedures, the final treatment is performed to remove some foreign matters, like chlorine, nitrogen, oxygen, and sulphur, which cannot be removed through the above method from the lubricating oil. Clay or hydro treatments are often used for the finishing procedure (Chia-Yu, 2008).

2.3.3. Acid-Clay Process

Acid-clay process is one of the popular treatment methods for re-refining used oil. In this process, the waste oil is treated with sulfuric acid. Sulphuric acid is a poly functional mineral acid which can act both as a sulphonating and an oxidizing agent. It can also act as a catalyst for some polymerization reaction of unsaturated hydrocarbons hence treatment of the used oil with sulphuric acid results sulphonation and oxidation of the degraded products (Princewill & Sunday, 2010).This acid reacts conversely with oxygen compounds and some sulfur- and nitrogen-based compounds to form sludge. Further refining is done in order to remove unsaturated hydrocarbons. Even after refining, there would be still some color and odor present in the oil which is later removed by treatment with activated clay. The problem with this method is that it produces a large volume of acid-sludge that is contaminated with petroleum. Due to these disadvantages, acid-clay process is now considered uneconomic since managing the residues incurs a huge cost (Udonne J. D., 2010). Nevertheless, Falah and Hussein (2011) demonstrated how this method could be used under different conditions and variables without bordering on the said disadvantages.

In the conventional acid clay process the used lubricating oil is settled or filtered after collection (J. Diphare et al., 2013). Then, the next step of re-refining involved removal of water from the used oil by atmospheric distillation. Thus, the used oil was distilled up to 200^{0}C and furthered fractionated under vacuum (5mmHg) to eliminate the light hydrocarbons. The residual fraction over 350^{0}C was obtained. The dehydrated oil (feed oil) was collected and sent to the next steps for further treatment. In the acid treatment, feed oil is treated with 98% concentrated sulphuric acid with a ratio 4:1, respectively. The mixture is then stirred for one hour at 50°C. The mixture was then allowed to cool and kept undisturbed for 24 hours for deasphalting and settling of acid sludge from acid treated oil. The next step of acid treatment was the clay percolation; an adsorption process would take place. Percolation technique is carried out via a continuous process. The treated oil by acid passed through adsorbent of activated clay in a double jacket long glass column. For each process, re-refined base-oil will be collected and analysed. ASTM standards will be used to determine various properties of the base-oil (Emam & Shoaib, 2012).

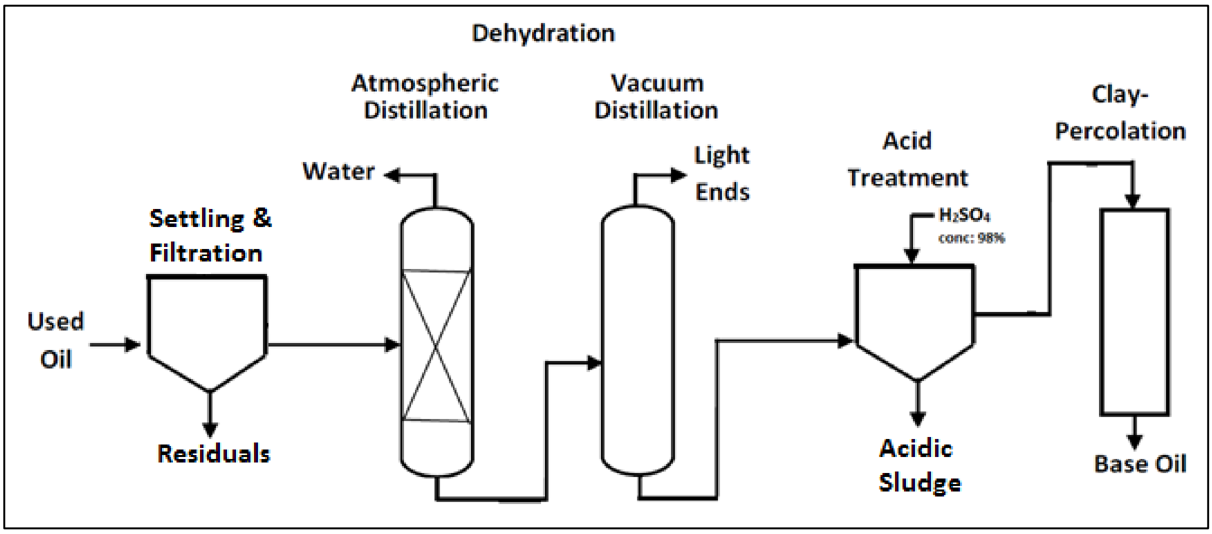

Figure 2-2: Typical acid-clay treatment process flow diagram

2.3.3.1. Basic Features of Acid-Clay Treatment

Acid-Clay Process for used oil recycling/reprocessing is the first used oil re-refining practice. It is the oldest and popular technology proven to have worked for many years worldwide. Regardless of some controversies, it has several features that distinguish it from other technologies.

Some of its features include:

- It can easily be set-up for very small capacity (F.Dalla et al., 2012). A practical example of small scale acid-clay process can be visited in Cairo. Installed equipment allows refining 3,000 litres of used oil in one batch (Nwachukwu et al., 2012).
- It requires low capital investment which makes it most cost effective for small and tiny scale plants (Mytol Petrotech , 2013). In Nigeria, a small-scale used engine oil recycling business in a mechanic village detailed to re-refining to lubricating oil is making annual turnover in excess of $2,234,375.00 at minimum cost. Besides, the environmental benefits of this recycling largely justify the efforts and the investments (Nwachukwu et al., 2012).
- The overall process is non-sophisticated and very simple process.

- It is simple to operate.
- It requires no advanced instruments which adds up for the reduction in initial investment costs
- It also requires no skilled operators (Mytol Petrotech , 2013).
- Its operating cost is lower. A mechanic village in Nigeria, operating a small scale re-refining unit, applies low treatment cost and energy use i.e. an average 105 kcal/ton of base oil distillation heat, and power consumption of 15 kWh/ton of base oil (Nwachukwu et al., 2012).

This process produces sludge in the following steps: dehydration, acid treatment and clay treatment steps. If disposed to the environment, separated sludge can cause severe pollution as they are concentrated forms of contaminants (which is also true for other technologies). However, pre-treatment steps and optimization of deasphalting and adsorption ratios has a significant result in acid contamination level and amount of acidic sludge disposed (Princewill & Sunday, 2010).

Once created, if carefully and wisely handled, this sludge can be used as a modifier for bituminous materials. It can also be used for the preparation of carbon rods as they are rich in carbon content (J. Diphare et al., 2013).

Moreover, the sludge is completely combustible with net heating values amounting up to 4,000 kcal/kg (Rahman et al., 2008). If burned, use of appropriate burners (e.g. cement kilns) and methods for pollution abatement is necessary.

Furthermore, it was concluded that treatment of acid sludge with different salt formulations provides a potentially lowest cost source of gilsonite varnish for news ink and also helps in reducing the environmental problem (Emam & Shoaib, 2012).

It is also criticized for its lower yield. But, although high yield means more available material to sell and it increases the motivation for production but it offset the quality as high yield mostly contributes to low quality. The lower yield with acid/clay percolation process is in fact referring to removal of a high amount of contaminants, sludge, and metals (Rahman et al., 2008). Judging from the results obtained in other studies (Udonne & Bakare , 2013); Sulphuric acid yields 90% while Nitric acid yields 70% to 80%. It is also recommended that nitric acid can be used in place of sulphuric acid and has proved to yield about 75% since it would cost less to obtain used oil. This may reduce the degree and nature of contamination, environmental/health risks associated with disposal.

2.3.3.2. Parameters Influencing Acid-Clay Treatment

There are several operating parameters which have significant effects on the final recycled product quality and sludge produced. Some of these major parameters are briefly discussed in this sub-section.

i. Distillation Temperature

There are two different distillation units in this acid-clay treatment process where water and light hydrocarbon fractions are separated from the used lubricating oil. These processes are evaporation and fractionation operations.

The atmospheric distillation (evaporation) removes free and emulsified water from the used oil. Temperature of this unit should be sufficient enough to completely vaporize water molecules. Since water boiling point is 100°C at STP, temperatures above this point are usually practical. To eliminate vapour shading effects of the oil and reduce evaporation time, temperatures up to 200°C are seldom applied. At higher temperatures, light hydrocarbon fractions are lost and the water is contaminated requiring thorough treatment. Lower temperatures increase the moisture content of recovered light ends affecting the energy value (Isah, 2013). In the research of regenerating base-oil from waste-oil under different conditions and variables, by Falah & Hussein (2011), the oil was heated to 140°C and under atmospheric pressure for a period of 1 h to eliminate the free water and emulsified water. The common process uses a temperature of 200°C to ensure dehydration of the used oil before fractionation of light ends, as mentioned earlier.

Hydrocarbons should not be heated to too high temperature due to cracking reactions that take place above about 400 °C. Coke deposits on piping and equipment increase maintenance costs and reduce process unit run-time. Therefore distillation is further processed in a vacuum system to recover light and heavy vacuum gasoil in lube-oil processing (neles, 2011).

Vacuum distillation temperature is usually maintained at below 340°C, to avoid vaporization of the lube oil base stock and ensure complete extraction of light hydrocarbons i.e. gasoline, kerosene, diesel etc. Oil which will normally boil at 500°C will boil at 300°C under the very high vacuum used. Under vacuum, boiling ranges are as follows (Layzell, 2010):

Gasoline	40 - 190 °C
Kerosene	190 - 260 °C
Diesel	260 - 330 °C
Lube oil	330 - 400 °C

While selecting vacuum distillation temperatures, oil degradation temperatures should also be taken into consideration. In obtaining final dehydration temperature, the optimum temperature depends on the amount of water and gasoline fractions in used oil as predetermined amount of oil sample is constantly heated at uniform rate (neles, 2011).

For 1.5 L of used oil and fixed heating rate of 600W, an optimum temperature of 215°C was obtained at 12 mBar. The used oil sample had 0.3 and 2 % w/w of fuel and water contaminants, respectively, before treatment (Awaja & Pavel, 2006).

ii. Vacuum Pressure

As mentioned earlier in the vacuum distillation, vacuum pressures also have similar effects on the distillation process. This is due to the fact that when vacuum pressure is increased, the boiling temperature of the crude oil component is increased which may lead to unexpected loss of the lube base stock. Thermal cracking and coking can be caused at extreme cases. So, vacuum distillation is usually carried out with absolute pressures of 10 to 40 mmHg at controlled temperature conditions in oil refineries (Wikipedia, 2014).

In the study made on used oil dehydration, three different vacuum pressures were tested (4, 8 and 12 mBar). The best dehydration results are obtained at the lower vacuum pressure, even though there is a wide range in boiling points between water, gasoline and the base oil cut. Also lower vacuum pressure is preferred to ensure that the temperature will not rise above 250 ◦C, which is the oil degradation temperature (Awaja & Pavel, 2006).

iii. Distillation Time

Distillation is usually carried out until no further distillate was produced. The dehydrated used oil was collected and then used for the next step of acid treatment (Awaja & Pavel, 2006). But for data recording purposes atmospheric distillation was conducted up to one hour and vacuum distillation was carried out between one and three hours, depending on the temperatures and vacuum pressures applied (Rahman et al., 2008). But extreme cases may result similar failures as discussed in distillation temperature and vacuum pressure extremes may effect since they are all interconnected in theory.

iv. Acid Ratio

The acid treatment process is conducted under the atmospheric pressure and the aim is to make the oil free of oxidized polar compounds, acidic products, additives and suspended particles and others and also, to keep the hydrocarbon families in the oil unmodified (Falah & Hussien, 2011). The removal of these compounds is accomplished with sulphuric acid and its ratio depends on the amount of the mentioned impurities. Undesirable components to be removed are relatively present in small amounts but large excesses amount of acid for efficient removal may cause changes in the remainder of the hydrocarbon mixture (G.Speight, 2009). From most literatures reviewed, the acid treatment is conducted with oil-to-acid ratio of 4:1.

However, optimum desludging ratios are obtained through experiments and results showed effective impurity removals even on larger ratios. A recovery of 83.7% was obtained for a ratio of 3:1, 88.40% for a ratio of 5:1, 89.40% for a ratio of 10:1, 90.7% for a ratio of 15:1 and 90.9% for a ratio of 20:1. This showed that the higher the ratio, the higher the recovery. The observed increase in recovery would depend on the grade of the acid used as well as the original source of the used oil, the level of contamination, and pretreatment steps (Princewill & Sunday, 2010).

v. Desludging Temperature

Since this step was exothermic, the dehydrated oil temperature should be lowered to 30°C. Temperature beyond 50°C would consume some of the hydrocarbons by introduction of sulphonation reactions (Rahman et al., 2008) . Paraffin and Naphthene hydrocarbons in their pure forms are not attacked by concentrated sulphuric acid at lower temperatures (G.Speight, 2009). Therefore, desludging temperature is maintained between 30 - 50°C to avoid the adverse effect of sulfuric acid oxidation of the oil at higher temperatures. However, at such low temperature the desludging reaction is slow. Hence sufficient time and rigorous agitation was employed to enable the reaction reach completion (Princewill & Sunday, 2010).

vi. Adsorption Ratio

The final treatment of the used oil recycling process is the de-colorization and neutralization. The compounds removed at this step include products of the oxidative degradation of base oil, such as organic acids, esters and ketones. It is also performed to adsorb some foreign matters, like chlorine, nitrogen, oxygen, sulphur, and some trace metals, passing the acid treatment step (Yu & Chun, 2010). Thus the amount of adsorbent used affects the elimination rate of these contaminants and the recovery efficiency of the process. Uneconomical usages of adsorbent also have a downside in producing excess sludge (contaminated clay).

From studies of Princewill & Sunday (2010), at uniform desludging ratio of 20:1, the adsorption ratio was varied to obtain different recoveries. The results show that for adsorption ratio of 3:1, a recovery of 66.7% was obtained; for the ratio of 5:1 a recovery of 74.8% and for a ratio of 10:1 a recovery of 82.9%. This showed that the recovery increases with adsorption ratio.

It was also reported that, in another research, types and particle size of adsorbent, adsorption time and adsorption temperatures have significant effects on the final recovered oil quality. To enhance adsorption, fine particles (- 75 to +150) of the adsorbent were used coupled with vigorous stirring. This step can be performed at room temperature using activated clay at a temperature of 120°C. Sufficient time was used so as to allow the adsorption reach completion (equilibrium). The oil from the adsorption stage was clear enough (Khan, 2009).

3. MATERIALS AND METHODS

The methodology that is used to generate data for this research is mainly through laboratory experiment. The general experimental procedure will follow three basic phases which are: (1) characterization of used engine oil (2) treatment of the used oil using acid-clay process (3) collection and characterization of the treated (recycled) oil.

The essential materials which are the necessary equipment and chemicals that will be required are discussed in this chapter. Detailed descriptions of the overall method of the experiment including the experimental design procedure followed are also included.

3.1. Materials

The used oil sample, for the experimental analysis of this research, is collected from Day light applied technologies P.L.C which is a glass container and crown cork manufacturing plant. The sample is directly drained from one of the three generators engine in the factory. The fresh oil is known as Rubia Tir 7400 and it was utilized for two thousand hours in the engine before being replaced as per the maintenance manual of the generator.

Table 3-1 Typical characteristics of RUBIA TIR 7400 oil *(Caltex lubricants, 2013)*

SAE grade	15W-40
Density @ 15 °C, g/mL	0.89
Base No., mg KOH/g	10.2
Flash Point, °C	> 215
Pour Point, °C	< -24
Ash content, %	-
Viscosity @ 40 °C, cSt	105
Viscosity @ 100 °C, cSt	15.1
Viscosity Index	137

As the recycling technique, which is being studied in this research, is the Acid-Clay treatment, some of the required equipment and chemicals are purchased from the market and some are obtained from the AAiT chemical and physical laboratories.

The various equipment and chemicals that are required for the successful completion of the experimental exercise are listed in Table 3-2.

Table 3-2: List of major equipment and chemicals

Item	**Purpose**
• **Equipment for sample characterization and acid-clay treatment**	
Measuring scale	Hydrometer
Viscometer	Viscosity determination
Furnace	Ash content determination
Tubular furnace	Carbon or coking test
Electric heater	Distillation
Vacuum pump	Vacuum distillation
Condenser	Distillation
Shaker	Acid, adsorption and neutralization treatment
Oven	Kaolinite clay activation
Centrifuge	Oil separation from clay
Thermometer (360 °C	Monitoring operating temperatures
• **Chemicals for characterization and acid-clay treatment**	
Potassium hydroxide	Total acid number analysis (characterization)
Sulfuric Acid (H_2SO_4)	Deasphalting and settling of acid sludge from used treated oil
Ethyl alcohol (Absolute)	Acid neutralization
Lime	Acid neutralization
Activated bentonite clay	Odor & Color treatment
• **Other appliances**	
Glass beakers	Sample and Product collection
Graduated cylinder	Sample measurement
Crucibles	Ash content measurement
Tong	Handling hot beakers
Gloves	Safety
Masks	Safety
Safety cloth	Safety

3.2. Methods

3.2.1. Characterization of Used Generator Engine Oil

The used generator engine oil has been tested to characterize the physical and chemical properties it has attained due to the different operational conditions and pollutant contaminations during its service period. Density, viscosity, pour point, flash point, acidity or neutralization number, ash content, coking test, water content and metal content analysis will be performed for adequate characterization of the sample. Some of these tests also give clues of the different sources of contaminations; as decrease in flash point indicates contamination by dilution of lubricating oils with unburned fuel and high ash content shows high metal content. After the complete characterization of the used oil sample, it is compared with the fresh oil specification listed on Table 3-1.

i. Density

A random volume of used oil sample was put into graduated cylinder and a density measuring device (hydrometer) was simply inserted at the top. While the device is floating, the point where the meniscus of the oil coincides is read on the hydrometer as the density of the oil.

ii. Viscosity

Kinematic viscosities of the oil at 40°C and 100°C are usually used to characterize oil quality. Dynamic viscosity at 40°C was measured using digital viscosity measuring device at which the viscosity was directly read from the display of the apparatus. Since the maximum temperature used while applying the viscometer is 60°C, the falling ball method was used to determine the dynamic viscosity at 100°C. In this method, a sample was poured in to a graduated tube channel containing the ball. Time taken by the ball to fall the height through the medium was recorded. The relation in Eqn. 3-1 was used to calculate the viscosity using the time data.

Finally the kinematic viscosity was obtained by dividing the dynamic viscosity with the respective density of the oil.

$$\eta = K(\rho_b - \rho)t \qquad (3\text{-}1)$$

Where; μ=viscosity (cP);
ρ_b=density of ball (8.53 g⁄ml)
ρ=density of liquid
t=time of descent (sec)
K=viscometer constant (1.238)

iii. Viscosity Index (ASTM D-2270)

The viscosity index is used to determine how much particular oil’s viscosity changes with temperature. It is a method of applying a number to this rate of change based on a comparison with two arbitrary selected oils (published in tables by the ASTM at a given temperature typically 40 °C and 100°C; see Appendix A) that have significant variations in viscosity index.

The reference oils have been selected in such a way that one of them has the viscosity index which is equal to zero (VI=0) and the other has the viscosity index equal to one hundred (VI=100) at 37.8°C but they both have the same viscosity as the oil of interest at 98.89°C. Viscosity Index is calculated using the following formula:

$$VI = \frac{(L-U)}{(L-H)} \times 100 \qquad (3\text{-}2)$$

Firstly the kinematic viscosity of the oil of interest was measured at 40°C (U) and at 100°C. Then from table (see Appendix A), looking at the viscosity at 100°C of the oil of interest, the corresponding values of the reference oils, ‘L’ and ‘H’ were read. Substituting the obtained values of ‘U’, ‘L’ and ‘H’ into the above equation yielded the viscosity index.

iv. Flash Point

The ‘flash point’ of the lubricant is the temperature at which its vapour will ignite. In order to determine the flash point the oil was heated at a standard pressure to a temperature which was just high enough to produce sufficient vapour to form an ignitable mixture with air.

The test specimen was put in an open cup and its temperature was gradually increased and monitored using a thermometer. At specified intervals a test flame is passed across the cup until the vapour of the test specimen of the sample ignites. The temperature at which a spark of fire is observed was recorded as the flash point.

v. Neutralization Number

The Neutralization Number or Total Acid Number (TAN) of the used oil was conducted using ASTM D974. It is the quantity in milligrams of potassium hydroxide (KOH) per gram of oil necessary to neutralize acidity. Two grams of used oil sample was weighed and mixed with 100 mL of the titration solvent (toluene and isopropyl alcohol containing a small amount of water) and 0.5 mL of the indicator solution (*p*-naphtholbenzein) and swirled until the sample was entirely dissolved by the solvent. The mixture assumes a yellow-orange colour and titrated with 0.1 M KOH solution in increments and mixed vigorously near the end point i.e. green colour. To observe the end point of dark-colored oil, the flask is shaken vigorously to produce momentarily a slight foam and the colour change occurs under a white fluorescent. The neutralization number or Total Acid Number (TAN) is calculated as;

$$TAN\left(\frac{mg\ KOH}{g\ sample}\right) = \frac{[(A-B)\times M \times 56]}{W} \qquad (3\text{-}3)$$

Where; A = KOH solution required for titration of the sample, mL,
B = KOH solution required for titration of the blank, mL,
M = molarity of the KOH solution, and
W = sample used, g.

vi. Coking Test

During a coking test (ASTM D524), the carbon residue is determined by weighing the residue after the oil has been heated to a high temperature in the absence of air. Three grams of used oil is measured on a crucible and put into a tubular stainless steel apparatus which was inserted into a tubular furnace. The apparatus was then flashed with N_2 gas so as to make the environment inside inert. The test is conducted at 550°C for thirty minutes. Finally the remaining residue is measured to calculate its percentage out of the total sample.

$$\%\ Carbon\ Residue = \frac{m_{Carbon\ residue}}{m_{initial\ sample}} \times 100 \qquad (3\text{-}4)$$

vii. Ash Content

There is some quantity of incombustible material present in a lubricant which can be determined by measuring the amount of ash remaining after combustion of the oil in a furnace (ASTM D482). Measured amount of used oil is put in a crucible and kept for five hours in the furnace at 800°C. Mass of the remaining ash was measured and its percentage is calculated by dividing it with initial mass of the sample.

$$\%\ Ash = \frac{m_{ash}}{m_{initial\ sample}} \times 100 \qquad (3\text{-}5)$$

viii. Water Content

Water content is the amount of water present in the lubricant. It is estimated by putting a measured amount of sample in an oven at 120°C for an hour. The dehydrated sample is then weighed to calculate the loss.

$$\%\ Water = \frac{m_{initial\ sample} - m_{final}}{m_{initial\ sample}} \times 100 \qquad (3\text{-}6)$$

ix. Metal Content

The metallic content analysis was performed by atomic absorption spectrometry using a fast sequential atomic absorption spectrometer. Before the analysis the used engine oil sample was heated to 60 °C and stirred to ensure homogeneity of the sample, it was then mixed with ten volumes of kerosene. Sets of organometallic standards of metal (Cu, Fe, Pb) 4-cyclohexylbutyric acid salts were prepared and metal concentrations were determined by introducing the test solutions of engine oil samples into the flame of the atomic absorption spectrophotometer and recording the responses. Metal concentrations were determined from the calibration curve that is obtained from standard solutions. Standard solutions for all metals in engine oil samples were prepared according ASTM D 4628-2.

3.2.2. Treatment of the Used Oil Sample

After characterization of the used oil, the treatment process will proceed to reduce or completely eliminate the various contaminants that are responsible for the inefficiency of the oil performance. The process will be conducted to recover the oil from the impurities and recycle it for relevant lubricating purposes. As the acid-clay technique is selected for the treatment of used oil in this research, the experimental procedure is based on the principles of this method which are described in the previous chapter.

Few but major rearrangements are made on the experimental steps for the laboratory tests relative to the steps recommended in acid-clay treatment process from literature reviews. For instance, the acid treatment is conducted in two stages with their respective neutralization steps. The first one is performed at the beginning of the treatment to improve the disturbing odor emission faced during the distillation step (the prior treatment step in a typical acid-clay treatment process) as witnessed in the trial runs of the research lab experiments. The second acid treatment is carried out after the vacuum distillation to react and settle out oxidation products during the heat up and other unreacted remaining contaminants from the first acid treatment. The neutralization steps are made with ethyl alcohol and lime for the first and second acid treatments, respectively. The second neutralization step is performed using lime to eliminate further recovery of ethyl alcohol which means additional distillation step. Lime also helps the following clay adsorption step. The laboratory experiment steps of this research are clearly discussed as follows:

Step 1: Acid treatment

The first step involved the acid treatment where 500 ml of feed oil is treated with 98% concentrated sulfuric acid at different testing ratios i.e. sulfuric acid being 10 – 20 % of the used oil sample. The mixture was then agitated and allowed to cool. The shaker temperature is fixed at 40°C and the agitation intensity was 250 rpm. The treated sample is then kept undisturbed for 24 hours for deasphalting and settling of acid sludge.

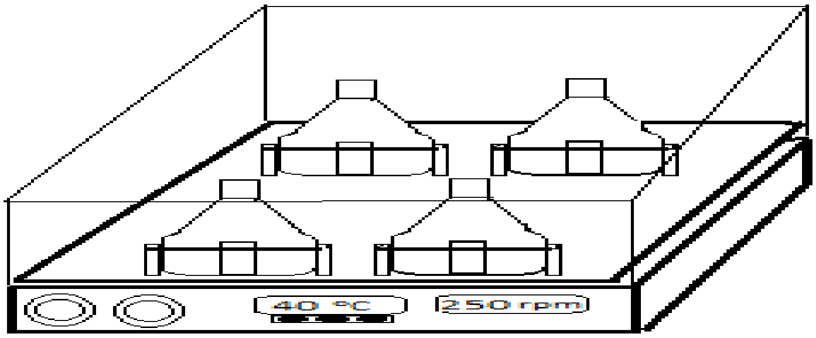

Figure 3-1: Acid treatment setup

The product from the acid treatment was separated from the sludge using a vacuum system. A hard rubber hose from the inlet of a vacuum pump was connected with a glass nozzle through which the supernatant is sucked out of a beaker where the settled sludge remains. A modified glass connector is applied to separate the product from the suction line.

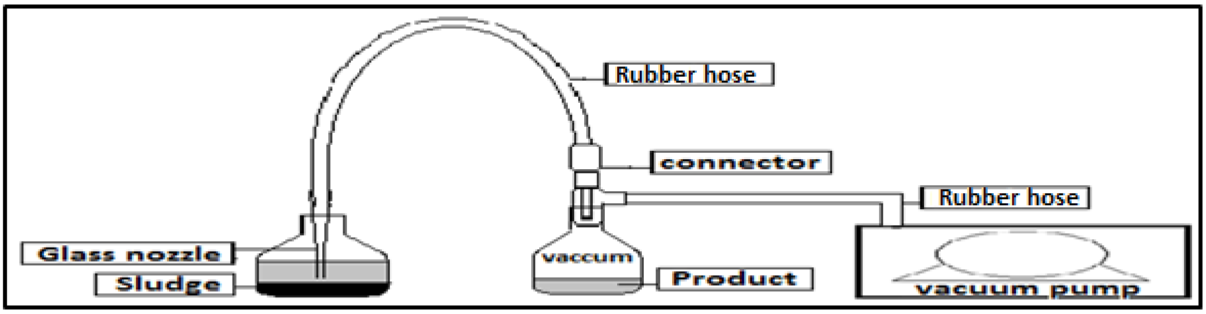

Figure 3-2: Product separation set-up

Step 2: Ethyl alcohol washing

After sludge removal, the treated oil was washed with ethyl alcohol absolute to react and eliminate the soluble acid still remained. Excess amount of ethyl alcohol is used for neutralization. Unreacted ethanol is recovered during the distillation step. Simple decantation was applied to separate the product from this step.

Step 3: Ethanol recovery & Water Removal

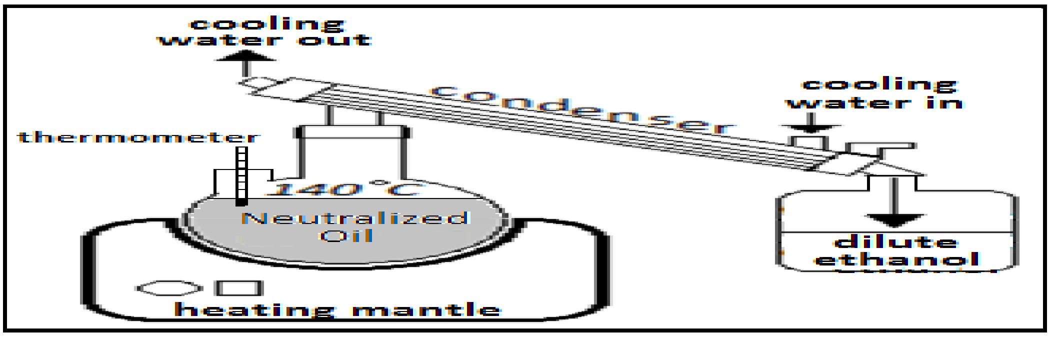

Figure 3-3: Atmospheric distillation experimental set-up

Ethanol recovery and complete removal of water is conducted using atmospheric distillation. Thus, the neutralized oil is heated with a heating mantle from 120°C to 140°C under atmospheric pressure, for an hour, to eliminate the mixture of ethanol and water. The ethanol is further concentrated by distilling it out using a water bath at 78°C.

Step 4: De-fuel

The dehydrated fraction is further treated under a vacuum of 0.5 bars to eliminate the light hydrocarbons at elevated temperatures of 330°C to 350 ^{0}C, until no observable condensate is left. This step is carried out with a distillation set-up comprising of a heating mantle, thermometer and a condenser with a nozzle in which vacuum pump line is installed. Then it is left to cool down to room temperature.

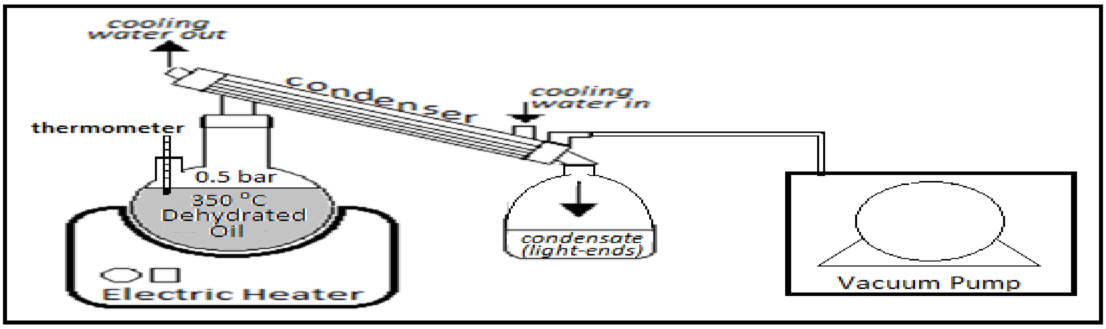

Figure 3-4: Vacuum distillation experimental set-up

Step 5: Secondary acid treatment

After removal of the light fractions, the remaining oil sample is treated with 5% concentrated sulfuric acid. Similar procedures are followed as the primary treatment step.

Step 6: Lime Neutralization

As in the ethyl alcohol washing, after sludge removal, the treated oil is mixed with excess amount of lime to neutralize any soluble acid still remained. The neutralization product (salts) and unreacted lime are left to settle down for 24 hrs.

Step 7: Clay Adsorption

Following secondary neutralization step, clay adsorption takes place. Acid activated bentonite clay was used at this adsorption step. The activated clay is used to improve color and oxidation stability of the acid treated oil. The oil is mixed with 15 - 25 % w/w of Bentonite clay. The mixture was performed at the room temperature on shaker with a constant stirring intensity of 300 rpm for an hour.

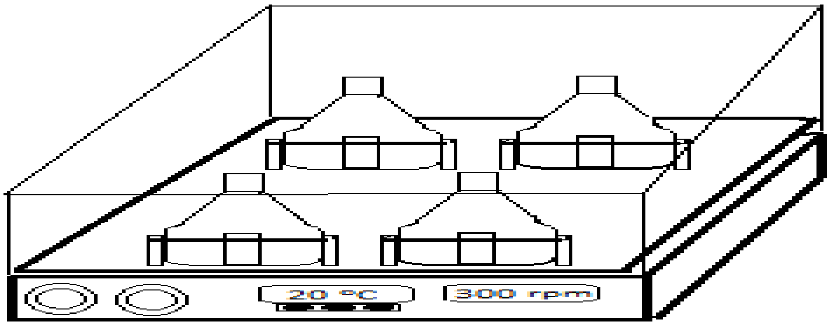

Figure 3-5: Clay adsorption set-up

Step 8: Centrifugation

The treated oil was separated by settling and centrifuging the supernatant oil to remove remaining suspended clay and other solids. This step is conducted at 5000 rpm for forty five minutes.

N.B. *As in the acid treatment step, similar separation technique was applied to separate products from the second neutralization and clay adsorption steps.*

3.2.3. Characterization of Treated Oil Sample

Recycled oil, collected at the last stage of the treatment process, is poured and collected in a clean beaker that will be ultimately analysed for final characterization. Some of the tests that were performed for the used oil characterization will be repeated to compare the results with the starting properties and observe similarities with the virgin oil standards. The major tests that will be conducted to characterize all processed samples include:

- Yield
- Density
- Kinematic Viscosity @ 40°C
- Ash content

Product sample which give relatively better results in the above four tests will be selected and further tests on flash point, kinematic viscosity @ 100°C, viscosity index, carbon or coking tests, neutralization numbert and metal content analysis will be made for full characterization of the recovered oil and comparison with the virgin oil.

3.3. Experimental Design

The laboratory experiment is based on a factorial design where the different treatment factors will be analysed for the different combinations of their test levels. The full factorial model is proposed to be used for the design of the experiment, analysis of response data and model fitting. The optimum combination of the operational factors will also be determined.

Randomization of experimental runs as well as appropriate analysis techniques are ensured through proper application of the software package – Design-Expert® Version 7.0.0.

3.3.1. Experimental Factors

The experimental factors which are investigated in this study are selected based on their influential rank in affecting used oil recovery ability of the acid-clay process and availability of required facility that allow monitoring and controlling. Hence, due to the high essentiality of their influences the effects of the following experimental factors were thus studied:

i. *Acid Ratio:* Sulphuric acid reacts with contaminants like alkenes, resinous, metals, nitrogen and partly sulphur compounds and etc. The extent of the treatment depends on the strength and quantity of the acid (G.Speight, 2009).
ii. *Adsorbent Ratio:* The compounds removed at this step include products of the oxidative degradation of base oil, such as organic acids, esters and ketones. It is also performed to adsorb some foreign matters, like chlorine, nitrogen, oxygen, sulphur, and some trace metals, passing the acid treatment step (Yu & Chun, 2010). Thus the amount of adsorbent used affects the elimination rate of these contaminants and the recovery

efficiency of the process. Uneconomical usages of adsorbent also have a downside in producing excess sludge (contaminated clay) (Princewill & Sunday, 2010).

Both acid and adsorbent ratios are varied in three levels. The experimental factors and their corresponding levels are listed in the table below.

Table 3-3: Experimental factors and corresponding levels

		Adsorbent Ratio (%)		
		15	20	25
Acid Ratio (%)	15	Run 1	Run 2	Run 3
	20	Run 4	Run 3	Run 6
	25	Run 7	Run 8	Run 9

As represented in the table above, nine runs are required to complete the overall factorial combination of both factors and their respective test levels. But triplicates of each run are performed to minimize experimental errors. The total experimental runs and randomization of the practical experiment can be referred in Table 4-2 of the results and discussion section.

Furthermore, there were other process conditions which had significant respective influences but not included in this study. Factors that were not studied and corresponding reasons for exclusion were:

1. *Distillation temperature*: Lack of temperature regulated heating mantle i.e. its temperature could not be set and monitored at fixed analysis point.
2. *Vacuum pressure*: Absence of adjustable vacuum pump with different setting capacities to be selected and fixed.
3. *Acid treatment temperature*: it was widely reported in literature reviews that desludging temperature is maintained between 30 - 50°C to avoid the adverse effect of sulfuric acid oxidation of the oil at higher temperatures and at lower temperature the desludging reaction is slow.
4. *Adsorbent particle size*: Absence of raw clay with different particle size which could be used in packed bed columns or batch mixing for adsorption.

3.3.2. Response Factors

Similarly, the response factors used for the study were selected primarily on basis of the objective set to identify the influence(s) of major process conditions on the final product after the acid-clay treatment process. Availability of required facilities, to easily conduct tests for all processed samples, was also taken into consideration. As stated in section 3.2.3 the response factors selected are discussed as follows:

i. *Yield:* Yield is a very important factor as it reflects the effectiveness of the process and has direct relation to the process cost as high yield means more available material to sell and it increases the motivation for production but it offset the quality as high yield mostly contributes to low quality (Emam & Shoaib, 2012).
ii. D*ensity:* Density of the oil is influenced by the chemical composition of the oil. Used engine oils density increases with the presence of increasing amounts of contaminants. One percent of weight of solids in the sample can raise the specific gravity by 0.007 g/ml (Hamawand et al., 2013).
iii. *Kinematic Viscosity:* Viscosity is the most important consideration of choosing lubricating oils. Viscosity testing can indicate the presence of contamination in used engine oil. The oxidized and polymerized products dissolved and suspended in the oil may cause an increase of the oil viscosity, while decreases in the viscosity of engine oils indicate fuel contamination (Emam & Shoaib, 2012).
iv. *Ash Content:* Ash content is a measure of oil purity and indicates contamination with metals and incombustible solid particles of dirt, dust, grit and metallic fragments. This test is vital in indicating metal residues whose experimenting facility is not easily accessible for all treated samples and analysis costs are higher (Awaja & Pavel, 2006).

All the other characterization tests are important in determining quality of all treated oil samples. But executing all tests would be costly since the budget allocated for the research was not sufficient enough for the purchase and installment of a number of equipment proposed to ensure comprehensiveness of the study's experiment. However, some tests were also relatively irrelevant with respect to the studied factors. For example, flash point would be a necessary factor if distillation parameters were included in the studied factors, since it is more related to the amount of fuel still remaining in the treated oil.

4. RESULTS AND DISCUSSIONS

4.1. Characterization of Used Lubricating Oil Sample

It is discussed in the previous chapters that the used oil is tested to determine its degradation and contamination level. Results from respective analysis that are used to characterize the experimental sample are given in Table 4-1 below.

Table 4-1: Used oil sample characterization results

Properties	Used engine oil sample (RUBIA TIR 7400)
Flash Point °C	132
Kinematic Viscosity@ 40 °C (cSt)	126.41
Kinematic Viscosity@ 100 °C (cSt)	16.9
Viscosity Index	127.9
Specific Gravity	0.93
Ash Content (%)	2.3
Water Content (%)	1.1
Carbon Residue (%)	4.68
(TAN) mg KOH/ g(sample)	5.62
(TBN) mg KOH/ g(sample)	-
Metal Contents (ppm)	
• Cu	6.2
• Pb	9.2
• Fe	54

From the above used oil analysis, it can be seen that there is a significant property alteration as compared to the fresh oil due to substantial deterioration during its application period. As mentioned in the literature review section, the lower flash point indicates light fuel contamination effect. Increased density and viscosity parameters show possible oxidation and polymerization products dissolved and suspended in the used oil. Similarly, the water content refers contamination from extraneous source; ash content indicates contamination from incombustible solid particles of dirt, dust, grit and metallic fragments; carbon residue indicates contamination with soot and carbon originating from incomplete fuel combustion and oil components breakdown; neutralization number indicates contamination from organic acids, soaps of heavy metals; and finally metal contents show contamination from engine parts wearing.

4.2. Experimental Results of Acid-Clay Treatment

The yield and results of selected quality evaluating properties of the recovered oil i.e. density, kinematic viscosity at 40 °C and ash contents obtained from each run are given in the following table.

Table 4-2: Experimental results of acid-clay treatment

Std.	Run	Acid Concentration (%)	Adsorbent Ratio (%)	Yield (%)	Density (g/ml)	Kinematic Viscosity @ 40°C (cSt)	Ash Content (%)
26	1	25%	25%	56.3	0.88	91.6	0.4
20	2	25%	15%	63.1	0.89	93.6	0.34
16	3	20%	25%	65.2	0.89	94.1	0.42
21	4	25%	15%	59.8	0.9	94.7	0.35
17	5	20%	25%	68.5	0.88	93.1	0.34
19	6	25%	15%	62.5	0.89	93	0.3
6	7	15%	20%	71.3	0.91	97.2	0.4
10	8	20%	15%	69.8	0.88	94.6	0.35
25	9	25%	25%	55	0.89	93	0.36
12	10	20%	15%	68	0.89	95	0.35
3	11	15%	15%	73.8	0.91	98.5	0.33
18	12	20%	25%	67.7	0.9	94.8	0.29
24	13	25%	20%	60.4	0.89	92.8	0.34
27	14	25%	25%	58.4	0.89	93.6	0.31
8	15	15%	25%	68	0.92	96.9	0.41
9	16	15%	25%	69.4	0.91	97	0.31
2	17	15%	15%	74.7	0.9	99.4	0.36
14	18	20%	20%	66.5	0.88	94.9	0.37
11	19	20%	15%	69.2	0.89	94.2	0.33
22	20	25%	20%	62.15	0.89	93.8	0.31
15	21	20%	20%	68.3	0.88	94.8	0.36
23	22	25%	20%	58.8	0.88	93.3	0.38
13	23	20%	20%	66.9	0.89	93.2	0.3
1	24	15%	15%	72.8	0.92	98.1	0.3
4	25	15%	20%	70	0.9	97.2	0.32
7	26	15%	25%	69.1	0.9	97.8	0.33
5	27	15%	20%	71.9	0.91	98.8	0.32

From the above results it can be observed that maximum yield is obtained (74.7 %) when used oil sample was treated with 15% acid and 15% adsorbent concentration. On the contrary minimum yield (55%) was obtained when both experimental factors were maximized to 25%.

Regarding the recovered oil properties, anonymous outcomes are realized which are discussed in subsequent sections.

4.3. Effects of Experimental Factors on Results

Amount of acid used and adsorbent ratio applied for different runs has shown significant effects on the yield of recovered oil as considered separately and interacting. Density, viscosity and ash contents are also influenced with different intensity as the concentration of the experimental factors are varied.

Effects on yield and quality of recovered oil distribution from variations in acid and adsorbent ratios are discussed under 4.3.1 and 4.3.2 below. Moreover, Figure 4-1 and 4-2 gives a set of graphs showing plots of obtained results.

4.3.1. Effects of Acid Quantity

From the experimental results analyzed for different acid percentages and constant adsorbent ratio, considerable variations are witnessed on recovery yields, densities and kinematic viscosities. Comparable ash contents were also observed with minimal distinctions.

Yield of the base-oil is found to be between 61.8 - 73.8 %, 60.5 - 71.1 %, 56.6 - 68.8 % for constant adsorbent ratios of 15%, 20% and 25%, respectively. As it can be referred from Table 4-3 and Figure 4-1, it increases as the quantity of acid used is decreased and vice-versa. For a constant 15% adsorbent ratio, the yields are 61.8%, 69.0% and 73.8% for acid percentages of 15%, 20% and 25%, respectively. Similarly, average yields of 60.5%, 67.2% and 71.1% for a constant adsorbent ratio of 20% and average yields of 56.6%, 67.1% and 68.8% for a constant adsorbent ratio of 25% are obtained with an increasing trend.

The density of the used oil sample is higher than the re-refined oils (Table 4-1 and Table 4-2) and the fresh base oil (0.89 g/ml). The average densities of recovered oils are between 0.88 – 0.91 g/ml. Relatively higher densities are observed with lower acid ratio (15%) i.e. 0.91 g/ml for all the different adsorbent percentages. As the acid ratio increased to 20%, densities of 0.89, 0.9 and 0.88 are obtained for adsorbent ratios of 15, 20% and 25%, respectively. Although minimal, a substantial decrease in density is seen towards the density of the virgin oil. Further increment on the acid concentration to 25%, gives similar results of 0.89, 0.9 and 0.89 g/ml. This clearly shows that an acid addition over 20% is insignificant.

Kinematic viscosity of the recovered oil is also influenced by the variation in acid ratio. As it can be observed from Table 4-1 and Table 4-2, the average kinematic viscosity at 40 °C is greatly reduced from the used oil (126.4 cSt) and also slightly decreased relative to the fresh oil (105 cSt). It is between 93.8 – 98.7 cSt, 92.7 – 97.7 cSt and 93.3 – 97.2 cSt for constant adsorbent ratios of 15, 20% and 25%, respectively. An increase in acid ratio gives a decreasing viscosity trend as it can be understood from Table 4-3 and Figure 4-1. This effect can be explained by improved removal of the oxidative products, unsaturated, condensed aromatics and mercaptans, asphaltenes and petroleum resins as the acid quantity is increased (Emam & Shoaib, 2012). The viscosity will later be improved towards the fresh oil by addition of viscosity index improvers.

Ash content is observed to seem constant for all acid concentration but has been considerably decreased as compared to the used oil sample (2.3%). It generally ranged between 0.33 to 0.36 % for all acid-to-adsorbent ratio combinations. Since there is no significant difference on ash content results at the various levels of acid ratio, further addition of acid, from the minimum quantity (15%) is not relevant.

As discussed previously, effects of acid concentration on yield and quality of recovered oil are summarized in Table 4-3 and Figure 4-1 below.

Table 4-3: Experimental results at different acid ratios

Acid Ratio *(%)*	**Adsorbent Ratio** *(%)*	**Average Yield** *(%)*	**Average Density (g/ml)**	**Average Kinematic Viscosity @ 40 °C (cSt)**	**Average Ash Content (%)**
15	15	73.8	0.91	98.7	0.33
20	15	69.0	0.89	94.6	0.34
25	15	61.8	0.89	93.8	0.33
15	20	71.1	0.91	97.7	0.35
20	20	67.2	0.88	94.3	0.34
25	20	60.5	0.89	93.3	0.34
15	25	68.8	0.91	97.2	0.35
20	25	67.1	0.89	94.0	0.35
25	25	56.6	0.89	92.7	0.36

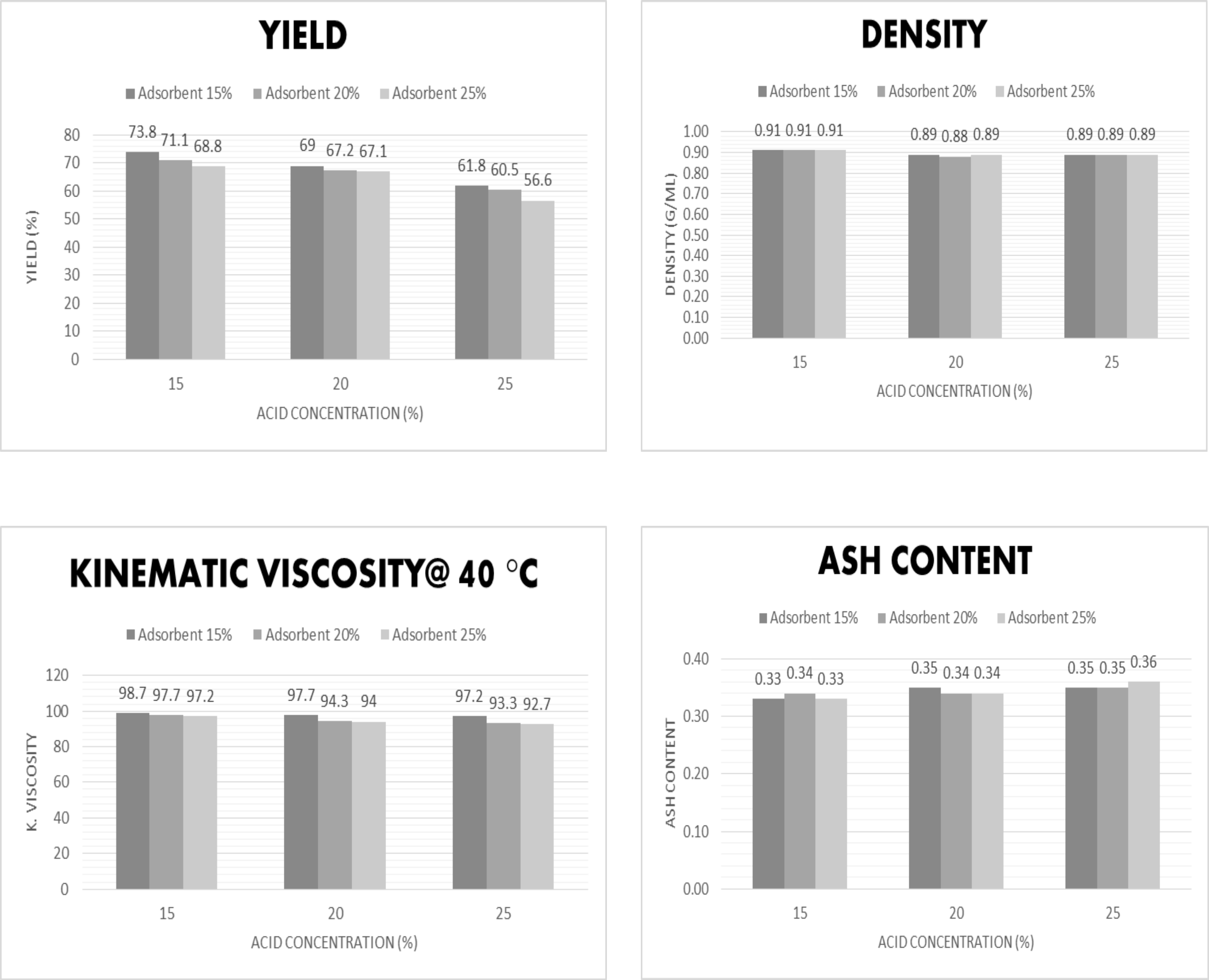

Figure 4-1: Effects of acid concentration

4.3.2. Effects of Adsorbent Ratio

It is clearly observed that as the amount of adsorbent used increased with constant acid concentration, the amount of recovered oil has considerably decreased. But it does not have significant effects on the selected quality parameters especially on density and ash contents.

Yield of the base-oil is found to be between 68.8 - 73.8 %, 67.1 - 69 %, 56.6 - 61.8 % for constant acid ratios of 15%, 20% and 25%, respectively. As it can be referred from Table 4-4 and Figure 4-2, it increases as the quantity of adsorbent used is decreased and vice-versa. For a constant 15% acid ratio, the yields are 73.8%, 71.1% and 68.8% for adsorbent percentages of 15%, 20% and 25%, respectively. The decreasing yield trend is observed to continue at all constant acid concentrations of 20% and 25%.

Density of recovered oil samples are not influenced for all adsorbent ratios at constant acid concentrations of 15%, 20% and 25%. This implies addition of adsorbent quantity, from the minimum ratio (15%) has no relevant effect on the density of the product.

Kinematic viscosity of the recovered oil has certainly improved as the amount of adsorbent is increased. At constant acid concentrations of 15%, 20% and 25%, average kinematic viscosities at 40 °C are found to be 97.2, 97.7 and 98.7; 94, 94.3 and 94.6; and 92.7, 93.3 and 93.8 cSt for adsorbent ratios of 15%, 20% and 25%, respectively. The slight increment in viscosity shows that remaining products of the oxidative degradation of base oil, such as organic acids, esters and ketones are removed to enhance the quality of the recovered oil (Yu & Chun, 2010).

Ash content exhibit unexpected outcomes giving higher results as adsorbent ratio is increased. Although the difference between ash contents is minimum, it shows an inclining trend. This can be explained by the inadequacy of the solid particles separation which may cause the increased adsorbent to add up on the ash content. Using accurate filtering and medium pressure, the filtration of ash content in the product could be substantially reduced.

Effects of adsorbent ratio on yield and quality of recovered oil are summarized in Table 4-4 and Figure 4-2 below.

Table 4-4: Experimental results at different adsorbent ratios

Adsorbent Ratio (%)	***Acid Concentration (%)***	***Average Yield*** (%)	***Average Density (g/ml)***	***Average Kinematic Viscosity @ 40 °C*** (cSt)	***Average Ash Content*** (%)
15	15	73.8	0.91	98.7	0.33
20	15	71.1	0.91	97.7	0.35
25	15	68.8	0.91	97.2	0.35
15	20	69.0	0.89	94.6	0.34
20	20	67.2	0.88	94.3	0.34
25	20	67.1	0.89	94.0	0.35
15	25	61.8	0.89	93.8	0.33
20	25	60.5	0.89	93.3	0.34
25	25	56.6	0.89	92.7	0.36

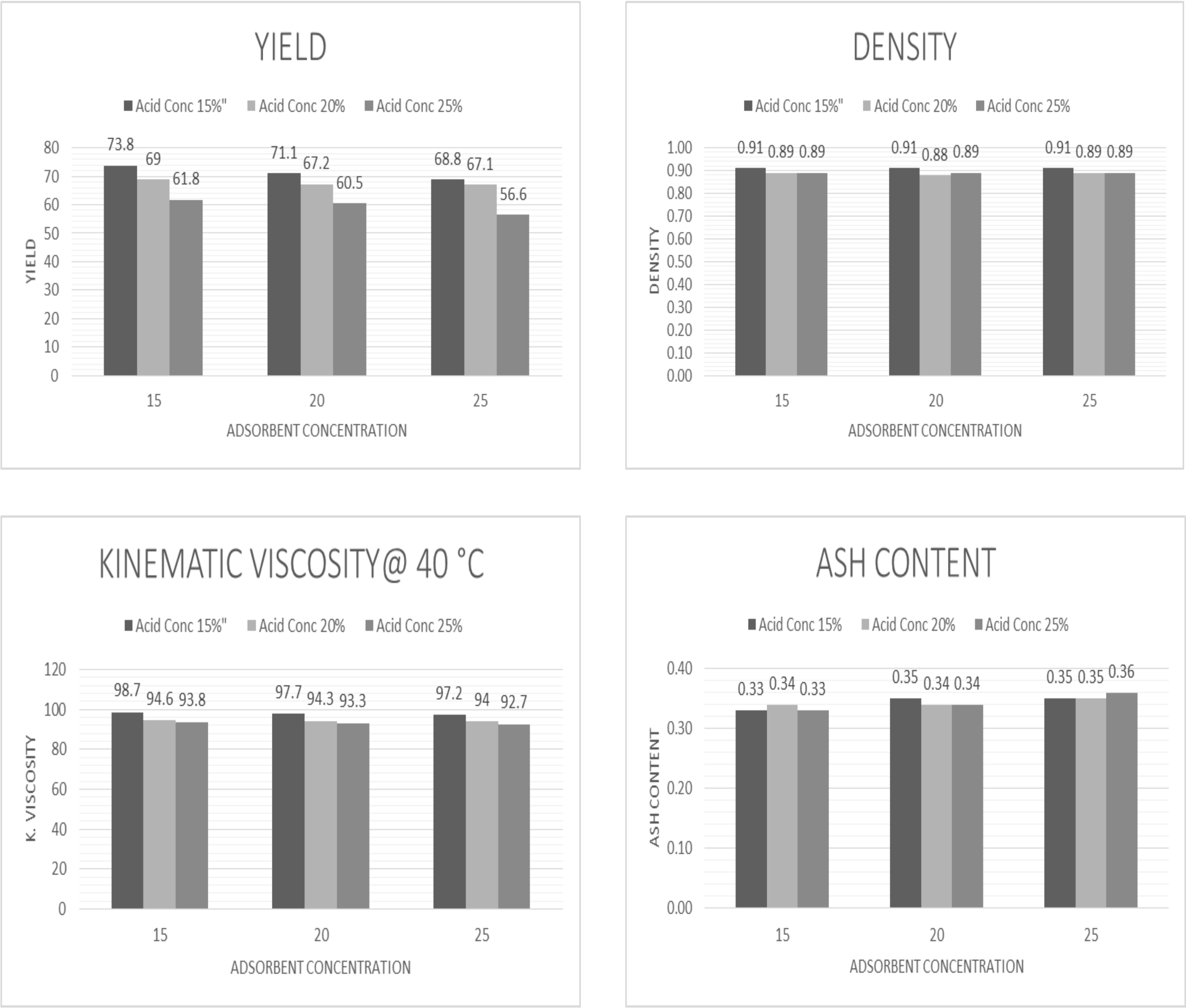

Figure 4-2: Effects of adsorbent ratio

4.3.3. Statistical Analysis

ANOVA and model fitting results of experimental data showed that amount of acid had the strongest effect on the yield (p-value < 0.0001) , density (p-value < 0.0001) and kinematic viscosity (p-value < 0.0001) of recovered oil but no significant influence on ash content (p-value= 0.9852). Adsorbent ratio also had significant effect on yield (p-value < 0.0001) and kinematic viscosity (p-value < 0.038) of recovered oil but not on density and ash contents. For model terms (experimental factors) to be influentially significant each of the terms need to have a p-value less than 0.05 or at least less than 0.10. It can be concluded that both acid and adsorbent ratios have no effect on ash content (response factor) since the model is analysed to be insignificant from ANOVA and model fitting results (see Table 4-5).

Table 4-5: Analysis of variance results summary

ANOVA for General factorial model					
Response 1: Yield					
Source	***Sum of Squares***	***df***	***Mean Square***	***F- value***	***P- value (Prob > F)***
Model	728.63	8	91.08	51.46	< 0.0001 - ***Significant!***
A-Acid Ratio	*641.11*	*2*	*320.55*	*181.13*	*< 0.0001*
B-Adsorbent Ratio	*72.43*	*2*	*36.21*	*20.46*	*< 0.0001*
AB- interaction	*15.09*	*4*	*3.77*	*2.13*	*0.1187*
Pure Error	31.85	18	1.77		
Cor Total	760.48	26			
Response 2: Density					
Source	***Sum of Squares***	***df***	***Mean Square***	***F- value***	***P- value (Prob > F)***
Model	2.874E-003	8	3.593E-004	6.47	0.0005 – ***Significant!***
A-Acid Ratio	2.696E-003	2	1.348E-003	24.27	< 0.0001
B-Adsorbent Ratio	9.630E-005	2	4.815E-005	0.87	0.4372
AB- interaction	8.148E-005	4	2.037E-005	0.37	0.8292
Pure Error	1.000E-003	18	5.556E-005		
Cor Total	3.874E-003	26			
Response 3: ***Kinematic Viscosity @ 40 °C***					
Source	***Sum of Squares***	***df***	***Mean Square***	***F- value***	***P- value (Prob > F)***
Model	110.71	8	13.84	23.12	< 0.0001 – ***Significant!***
A-Acid Ratio	105.39	2	52.70	88.04	< 0.0001
B-Adsorbent Ratio	4.72	2	2.36	3.94	0.0380
AB- interaction	0.60	4	0.15	0.25	0.9051
Pure Error	10.77	18	0.60		
Cor Total	121.49	26			
Response 3: ***Ash Content***					
Source	***Sum of Squares***	***df***	***Mean Square***	***F- value***	***P- value (Prob > F)***
Model	1.896E-003	8	2.370E-004	0.14	0.9964 - **Insignificant!**
A-Acid Ratio	5.185E-005	2	2.593E-005	0.015	0.9852
B-Adsorbent Ratio	1.430E-003	2	7.148E-004	0.41	0.6693
AB- interaction	4.148E-004	4	1.037E-004	0.060	0.9928
Pure Error	0.031	18	1.741E-003		
Cor Total	0.033	26			

After complete analysis of variance, from results of Run 8, 10 and 19 which were carried out for acid ratio of 20% and adsorbent ratio of 15%, the combination is selected as an optimum operating condition for the used oil recovery process. As presented in table, the combination has acquired the maximum desirability value of 0.637 than the rest of the combinations as per the optimization goal. The response factors i.e. yield, density, kinematic Viscosity @ 40 °C and ash content have given average results of 69%, 0.886 g/ml, 94.6 cSt and 0.34%, respectively.

Table 4-6: Optimization solution summary

Constraints:

Name	Goal	Lower Limit	Upper Limit	Importance
Acid Ratio	in range	15%	25%	3
Adsorbent Ratio	in range	15%	25%	3
Yield	maximize	55	74.7	5
Density	minimize	0.88	0.92	5
K.Viscosity @ 40°C	minimize	91.6	99.4	5
Ash Content (%)	minimize	0.29	0.42	5

Recommended Solutions:

No	Acid Ratio	Adsorbent Ratio	Yield (%)	Density (g/ml)	K.Viscosity @ 40 °C (cSt)	Ash Content	Desirability
1	20%	15%	69	0.886667	94.6	0.343333	0.637 – **Selected!**
2	20%	20%	67.233	0.883333	94.3	0.343333	0.621
3	20%	25%	67.133	0.89	94	0.35	0.612
4	25%	15%	61.8	0.893333	93.7667	0.33	0.557
5	25%	20%	60.45	0.886667	93.3	0.343333	0.503
6	15%	25%	68.833	0.91	97.2333	0.35	0.472
7	15%	20%	71.066	0.906667	97.7333	0.346667	0.462
8	15%	15%	73.766	0.91	98.6667	0.33	0.396
9	25%	25%	56.566	0.886667	92.7333	0.356667	0.321

4.4. Properties of Regenerated Base Oil

Using the optimization result summary, the base oil obtained from the selected experimental run is further analysed to fully describe its properties. Flash point, kinematic viscosity@ 100 °C, viscosity index (VI), total acid number (TAN), carbon residue, refractive index and metal contents (Cu, Pb, Fe) are the additional characteristics tested. This characterization helps to explain the quality improvement of the recovered base oil as compared to the properties of the used oil sample and fresh oil (see Table 4-7 below).

The flash points of the recovered oil is 209°C which is far better than the used oil (132°C) and slightly lower than the fresh oil (218°C). As stated in previous sections, the decrease in value of flash point for the used oil could be as result of the presence of light ends of oils. In essence, after undergoing combustion and oxidation at high temperature of the combustion engine, the oil breaks down into component parts, which include some light ends. The decrease in flash point for the used oil, may also be as a result of fuel dilution; that is, for an engine with bad piston rings. The flash point has greatly improved but not as good as the fresh oil which might be due to inadequate distillation process leaving trace amount of light ends in the oil. Nevertheless, the flash point is within acceptable range according to the ASTM D 4304 reference standard i.e.it should be greater than 180°C.

Table 4-7: Comparative properties of used oil, recovered oil and fresh oil

Properties	Used engine oil	Recovered oil	Fresh Oil
Flash Point °C	132	209	> 215
K. Viscosity @ 40°C (cSt)	126.41	94.6	105
K. Viscosity @100°C (cSt)	16.9	13.8	15.1
Viscosity Index	127.9	130.54	137
Density (g/ml)	0.93	0.886	0.89
Ash Content (%)	2.3	0.343	-
Carbon Residue (%)	4.68	0.84	1.12
(TAN) mg KOH/ g(sample)	5.62	1.1	-
(TBN) mg KOH/ g(sample)	-	-	10.2
Metal Contents (ppm)			
• Cu	6.2	0.4	-
• Pb	9.2	0.82	-
• Fe	54	0.71	-

The kinematic viscosities of the recovered oil, at 40°C and 100°C, are lower than the used and fresh oil. From the experimental observations, it can be understood that the used oil lost most of its viscosity due to contamination. Hence the treatment has remarkably reduced the viscosities indicating the removal of contaminants in the used oil. This effect can be justified by considering the viscosity index which upgraded relative to the used oil. Viscosity index is higher due to the presence of viscosity improvers in the fresh oil. Similarly addition of viscosity improvers may give better qualities to the recovered oil.

The density of the used oil is higher than fresh oil and the refined one. The results for the fresh and used lubricating oils are 0.89 and 0.93 respectively, while the re-refined oil has 0.886 g/ml. The treatment has effectively restored the oils density to that of the fresh oil.

Ash-content of the product oil has significantly reduced to realize the recovering capability of the acid-clay treatment process. Ash content of the re-refined base-oil was lowered to 0.343% from that of the used oil which was tested to be 2.3 %, at the beginning. As presumed earlier, the ash content might have been lowered using effective filtrations mechanism are applied. Since the metal content of the recovered oil is negligible, the rise in ash content, relative to the fresh oil, is due to clay particles which infiltrated through the final separation step.

The carbon residue in base oil produced is considerably lowered to 0.84 % lower than that of both the used oil (4.68 %) and fresh oil (1.12 %). The lower carbon residue can be explained by for example, an ash-forming detergent additive can increase the carbon residue value and yet removed during acid treatment (Hamawand et al., 2013).

As shown in Table 4-7, the TAN of the recovered oil is found to be 1.1 mg KOH/g. It can be concluded that the treatment has contributed in minimizing the TAN of used oil which was previously measured to be 5.62 mg KOH/g due to the possible presence of organic, inorganic, heavy metal salts, resin, water and corrosive materials which result from the oxidation process that occurred at elevated temperatures in the engine (Hamawand et al., 2013). The addition of sulphuric acid and incomplete neutralization of the process might also have contributed to increased TAN in the recovered oil. Internal combustion engine oils are formulated with a highly alkaline base additives package to neutralize the acidic products composition. As TBN is a measure of this package, its value is higher in the fresh oil and got depleted with time in service, in the used oil.

The recovery method also proved better metal content results when compared with the used oil showing low levels of contamination with iron, copper and lead.

4.5. Light Fuel Characterization

The vacuum distillation process has given a by-product of light fuel as expected, with a yield ranging between 8 -10 % in each experimental run. The product is tested for its ignitability by simply burning it in a laboratory. Other tests were also performed for the determination of its density, flash point, kinematic viscosity and calorific value to characterize the product in a more presentable way. The results gave 0.79 g/ml, 75 °C, 5.5 cSt, and 45MJ/kg for density at 20°C, flash point, kinematic viscosity at 40°C and calorific value, respectively.

4.6. Cost Analysis Consideration

The preliminary cost analysis is performed to estimate and compare costs incurred by the recycling process of used oil and the price of imported generator engine oil. This estimation of costs is necessary in giving information regarding the economic feasibility of the research.

Costs associated with the recycling process in the research include chemical costs, electrical power costs and labor costs where most of them are operating costs. Costs of different equipment which will be required for the construction and erection of the recycling plant can also be considered for a complete plant design, which is not the scope of this research.

It is to be noted that 69% recycling capacity is achieved from the selected optimum operational parameters i.e. 20% acid and 15% adsorbent. Using this yield as a basis for material balance evaluation (*see* Appendix C), the preliminary cost estimation of the process shows that a maximum sum amount of 22.86 birr is expected to recover a liter of usable oil from 1.33 liter of waste oil as summarized in Table 4-8. A barrel of engine oil is imported for 16,898 birr, which is 84.5 birr per liter.

Table 4-8: Chemical and energy costs estimation for recycling one liter of usable oil

	Amount required (from material balance)	Unit	Unit Cost (birr)	Total cost (birr)
Chemicals				
• Used oil	1.33	liter	3	3.99
• Sulfuric acid	0.266	liter	22.5	5.98
• Ethyl alcohol	0.0665	liter	60	4.38
• Lime	0.0196	kilogram	4	0.086
• Bentonite clay	0.133	kilogram	20	2.9
• Additives (5-8 %)*	0.08	liter	21	1.68
Energy required	0.04	Kwh	0.85	0.034
			Total	19.05
	Contingency	% total	0.20	3.81
			Grand Total	**22.86**

*Ref: (Caltex lubricants, 2013)

Eight percent light fuel is collected from the vacuum distillation. It can be used as an additional income source or save fuel energy requirements in the process compensating costs of the recycling. Using gasoil price (20 birr/liter), the recycling cost can be recalculated and reduced to give 21.26 birr.

5. CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

The study proved that the acid-clay treatment is a process that can effectively remove contaminants from used lubricating oil. The recovered oil has a comparable quality with the fresh oil indicating the possibility of reusing it.

Used engine oil properties were determined with standard chemical and physical tests. The characterization implied that the oil was contaminated with light fuel from extraneous and/or products of oil degradation; oxidation and polymerization products; water from extraneous source; soot and carbon originating from incomplete fuel combustion and oil components breakdown; organic acids and soaps of heavy metals; and metals from engine parts wearing.

Operational parameters were established in reference with the common acid-clay process and its modification. Acid and clay percentages of 15%, 20% and 25% were randomly selected to test the effects of these variable factors i.e. above and below the ratios in the common process (20%). Certain procedural rearrangements were made to overcome some difficulties faced during the experiment trial as mentioned in Section 3.2.2. The acid treatment was performed twice in the experiment. The first one was performed at the beginning of the treatment to improve the disturbing odor emission faced during the distillation step. The second acid treatment was carried out after the vacuum distillation to react and settle out degraded products formed during the heat up. The acid treatments were conducted for an hour on a shaker at 40°C (recommended) and 250 rpm. Two neutralization steps, with ethyl alcohol and lime, were conducted for the two acid treatment steps, respectively. Vacuum distillation was carried out at 0.5 bar for at 330-350°C for extended seven hours. The time delay was needed since the vacuum created was not low enough and the condenser setup was inadequate due to unavailability of required equipment. Bentonite clay, activated at 120 °C, was used at room temperature and agitation intensity of 300 rpm for three hours to facilitate the adsorption rate.

Effects of acid and adsorbent ratios were studied on the recovery of usable lubricating oil from spent engine oil. The results showed that the efficiency of the recycling operation depends on these reagent ratios. It was noted that the recovery yield increases with decreased percentage in these ratios. A maximum recovery of 74.7% was obtained when both acid and clay to oil proportion was minimum i.e. 15% and vice-versa. Some of the oil properties were also consistently influenced by acid and adsorbent variations. Maximum average density (0.91 g/ml) was observed when 15% acid and 15% adsorbent is used. The other combinations gave relatively lower values especially when the acid percentage was above 15%. Samples were not influenced by adsorbent ratio variation implying it had no significant effect on the density of the product. Kinematic viscosity of the recovered oil was improved as the percentage of acid and adsorbent increased. Lower kinematic viscosity of 92.7 cSt and higher viscosity of 98.6 cSt was obtained for equal acid and adsorbent ratio of 25% and 15%, respectively. The decreasing viscosity trend could be explained by improved removal of contaminants that gave rise to the increased viscosity of the used oil. It was also concluded that viscosity would later be improved towards the virgin oil value by addition of viscosity improvers. Ash content was significantly reduced from 2.3% in used oil but the variation in acid and adsorbent ratio did not considerably influence the results. Ash contents were between 0.33- 0.356% for all combination of the experimental factors.

Optimization of the experimental results was conducted using design expert software through complete analysis of variance. The combination which applied acid ratio of 20% and adsorbent ratio of 15%, was selected as an optimum operating condition for the used oil recovery process. The combination gave the maximum desirability value of 0.637 than the rest of the combinations as per the optimization goal. The response factors i.e. yield, density, kinematic Viscosity @ 40 °C and ash content gave average results of 69%, 0.886 g/ml, 94.6 cSt and 0.34%, respectively.

Characterization of the product from the optimum experimental run presented relatively better results as compared to the fresh oil. This proved the effectiveness of the acid-clay treatment process to recover usable oil from spent engine oil.

Valuable light fuel oil was also recuperated from the vacuum distillation step. This product had similar characteristics that was comparable with gas oil. It could be used to supply the energy requirement in the larger scale recycling plant.

Regarding cost effectiveness of the process, the difference in the imported oil price and the cost incurred for reclaiming used oil increased the appeal of the recycling process to be implemented and gave an insight of its potential and opportunities for scale up.

5.2. Recommendations

Further research is required in order to take this process to the commercial stage. However, while few variables have been studied in this research, there are many others that need thorough investigation such as temperature, pressure, settling time, mixing, centrifugation speed & time and type & size of adsorbent which will have significant effects on the yield and recycled oil qualities. In addition, the following aspects are important concerning the general characteristics of the treatment and recycling of used oils sector:

- Detailed statistical analysis on waste oil generation, from the different development sectors in Ethiopia, will be essential in giving a better insight for the significance of oil recycling and provide concrete justification of its implementation in this country.
- A study on different recycling techniques is necessary to practically evaluate and compare efficiencies to recommend the best method for implementation.
- Sludge analysis should be performed to propose efficient disposal or application area.
- A study on the different additives and their formulation is required to give the recycled oil identical properties as that of the fresh oil or deliver a desired product of interest.
- Exclusive investigation on used oil will help to identify components that are responsible for bad odour emission during distillation step and gives an indication to come up with effective solutions.
- The experiment in this study should be re-demonstrated with an appropriate distillation setup having a vacuum pump of desired capacity, temperature regulated heater and efficient condenser to observe results of final temperature and time taken. It may also have considerable effect on proceeding steps and final product quality.
- Proper scale up of the recycling process can be proposed from which required equipment, machineries and utilities will be clearly identified.
- Detailed cost benefit analysis evaluation can be made that compares the potential benefits of used oil recycling with the anticipated costs of construction and erection of the scaled up plant.
- Further character testing may also be executed to evaluate oxidation stability, thermal stability and foaming character of the recycled oil. If possible practical application of the recovered oil in a real engine system should be experimented.

- Different response factors can be analysed which may be significantly influenced by the variation in experimental factors. Results may be used to compare results with this study and come up with another optimum operating conditions. Similarly, different experimental factors can be variably examined.
- During experiment, proper safety equipment should be strictly applied to avoid possible irritations on eyes, skin and breathing system.

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APPENDIX A: Viscosity Index Evaluation Data

v_{100}	L	H	v_{100}	L	H	v_{100}	L	H	v_{100}	L	H	v_{100}	L	H
2.00	7.994	6.394	8.3	106.9	63.05	14.6	283.0	143.9	21.8	575.6	261.50	41.0	1810	676.6
2.10	8.640	6.894	8.4	109.2	64.18	14.7	286.4	145.3	22.0	585.2	264.90	41.5	1851	689.1
2.20	9.309	7.410	8.5	111.5	65.32	14.8	289.7	146.8	22.2	595.0	268.60	42.0	1892	701.9
2.30	10.00	7.944	8.6	113.9	66.48	14.9	293.0	148.2	22.4	604.3	272.30	42.5	1935	714.9
2.40	10.71	8.496	8.7	116.2	67.64	15.0	296.5	149.7	22.6	614.2	275.80	43.0	1978	728.2
2.50	11.45	9.063	8.8	118.5	68.79	15.1	300.0	151.2	22.8	624.1	279.60	43.5	2021	741.3
2.60	12.21	9.647	8.9	120.9	69.94	15.2	303.4	152.6	23.0	633.6	283.30	44.0	2064	754.4
2.70	13.00	10.25	9.0	123.3	71.10	15.3	306.9	154.1	23.2	643.4	286.80	44.5	2108	767.6
2.80	13.80	10.87	9.1	125.7	72.27	15.4	310.3	155.6	23.4	653.8	290.50	45.0	2152	780.9
2.90	14.63	11.50	9.2	128.0	73.42	15.5	313.9	157.0	23.6	663.3	294.40	45.5	2197	794.5
3.00	15.49	12.15	9.3	130.4	74.57	15.6	317.5	158.6	23.8	673.7	297.90	46.0	2243	808.2
3.10	16.36	12.82	9.4	132.8	75.73	15.7	321.1	160.1	24.0	683.9	301.80	46.5	2288	821.9
3.20	17.26	13.51	9.5	135.3	76.91	15.8	324.6	161.6	24.2	694.5	305.60	47.0	2333	835.5
3.30	18.18	14.21	9.6	137.7	78.08	15.9	328.3	163.1	24.4	704.2	309.40	47.5	2380	849.2
3.40	19.12	14.93	9.7	140.1	79.27	16.0	331.9	164.6	24.6	714.9	313.00	48.0	2426	863.0
3.50	20.09	15.66	9.8	142.7	80.46	16.1	335.5	166.1	24.8	725.7	317.00	48.5	2473	876.9
3.60	21.08	16.42	9.9	145.2	81.67	16.2	339.2	167.7	25.0	736.5	320.90	49.0	2521	890.9
3.70	22.09	17.19	10.0	147.7	82.87	16.3	342.9	169.2	25.2	747.2	324.90	49.5	2570	905.3
3.80	23.13	17.97	10.1	150.3	84.08	16.4	346.6	170.7	25.4	758.2	328.80	50.0	2618	919.6
3.90	24.19	18.77	10.2	152.9	85.30	16.5	350.3	172.3	25.6	769.3	332.70	50.5	2667	933.6
4.00	25.32	19.56	10.3	155.4	86.51	16.6	354.1	173.8	25.8	779.7	336.70	51.0	2717	948.2
4.10	26.50	20.37	10.4	158.0	87.72	16.7	358.0	175.4	26.0	790.4	340.50	51.5	2767	962.9
4.20	27.75	21.21	10.5	160.6	88.95	16.8	361.7	177.0	26.2	801.6	344.40	52.0	2817	977.5
4.30	29.07	22.05	10.6	163.2	90.19	16.9	365.6	178.6	26.4	812.8	348.40	52.5	2867	992.1
4.40	30.48	22.92	10.7	165.8	91.40	17.0	369.4	180.2	26.6	824.1	352.30	53.0	2918	1007
4.50	31.96	23.81	10.8	168.5	92.65	17.1	373.3	181.7	26.8	835.5	356.40	53.5	2969	1021
4.60	33.52	24.71	10.9	171.2	93.92	17.2	377.1	183.3	27.0	847.0	360.50	54.0	3020	1036
4.70	35.13	25.63	11.0	173.9	95.19	17.3	381.0	184.9	27.2	857.5	364.60	54.5	3073	1051
4.80	36.79	26.57	11.1	176.6	96.45	17.4	384.9	186.5	27.4	869.0	368.30	55.0	3126	1066
4.90	38.50	27.53	11.2	179.4	97.71	17.5	388.9	188.1	27.6	880.6	372.30	55.5	3180	1082
5.00	40.23	28.49	11.3	182.1	98.97	17.6	392.7	189.7	27.8	892.3	376.40	56.0	3233	1097
5.10	41.99	29.46	11.4	184.9	100.2	17.7	396.7	191.3	28.0	904.1	380.60	56.5	3286	1112
5.20	43.76	30.43	11.5	187.6	101.5	17.8	400.7	192.9	28.2	915.8	384.60	57.0	3340	1127
5.30	45.53	31.40	11.6	190.4	102.8	17.9	404.6	194.6	28.4	927.6	388.80	57.5	3396	1143
5.40	47.31	32.37	11.7	193.3	104.1	18.0	408.6	196.2	28.6	938.6	393.00	58.0	3452	1159
5.50	49.09	33.34	11.8	196.2	105.4	18.1	412.6	197.8	28.8	951.2	396.60	58.5	3507	1175
5.60	50.87	34.32	11.9	199.0	106.7	18.2	416.7	199.4	23.0	963.4	401.10	59.0	3563	1190
5.70	52.64	35.29	12.0	201.9	108.0	18.3	420.7	201.0	29.2	975.4	405.30	59.5	3619	1206
5.80	54.42	36.26	12.1	204.8	109.4	18.4	424.9	202.6	29.4	987.1	409.50	60.0	3676	1222
5.90	56.20	37.23	12.2	207.8	110.7	18.5	429.0	204.3	29.6	998.9	413.50	60.5	3734	1238
6.00	57.97	38.19	12.3	210.7	112.0	18.6	433.2	205.9	29.8	1011	417.60	61.0	3792	1254
6.10	59.74	39.17	12.4	213.6	113.3	18.7	437.3	207.6	30.0	1023	421.70	61.5	3850	1270
6.20	61.52	40.15	12.5	216.6	114.7	18.8	441.5	209.3	30.5	1055	432.40	62.0	3908	1286
6.30	63.32	41.13	12.6	219.6	116.0	18.9	445.7	211.0	31.0	1086	443.20	62.5	3966	1303
6.40	65.18	42.14	12.7	222.6	117.4	19.0	449.9	212.7	31.5	1119	454.00	63.0	4026	1319
6.50	67.12	43.18	12.8	225.7	118.7	19.1	454.2	214.4	32.0	1151	464.90	63.5	4087	1336
6.60	69.16	44.24	12.9	228.8	120.1	19.2	458.4	216.1	32.5	1184	475.90	64.0	4147	1352
6.70	71.29	45.33	13.0	231.9	121.5	19.3	462.7	217.7	33.0	1217	487.00	64.5	4207	1369
6.80	73.48	46.44	13.1	235.0	122.9	19.4	467.0	219.4	33.5	1251	498.10	65.0	4268	1386
6.90	75.72	47.51	13.2	238.1	124.2	19.5	471.3	221.1	34.0	1286	509.60	65.5	4329	1402
7.00	78.00	48.57	13.3	241.2	125.6	19.6	475.7	222.8	34.5	1321	521.10	66.0	4392	1419
7.10	80.25	49.61	13.4	244.3	127.0	19.7	479.7	224.5	35.0	1356	532.50	66.5	4455	1436
7.20	82.39	50.69	13.5	247.4	128.4	19.8	483.9	226.2	35.5	1391	544.00	67.0	4517	1454
7.30	84.53	51.78	13.6	250.6	129.8	19.9	488.6	227.7	36.0	1427	555.60	67.5	4580	1471
7.40	86.66	52.88	13.7	253.8	131.2	20.0	493.2	229.5	36.5	1464	567.10	68.0	4645	1488
7.50	88.85	53.98	13.8	257.0	132.6	20.2	501.5	233.0	37.0	1501	579.30	68.5	4709	1506
7.60	91.04	55.09	13.9	260.1	134.0	20.4	510.8	236.4	37.5	1538	591.30	69.0	4773	1523
7.70	93.20	56.20	14.0	263.3	135.4	20.6	519.9	240.1	38.0	1575	603.10	69.5	4839	1541
7.80	95.43	57.31	14.1	266.6	136.8	20.8	528.8	243.5	38.5	1613	615.00	70.0	4905	1558
7.90	97.72	58.45	14.2	269.8	138.2	21.0	538.4	247.1	39.0	1651	627.10			
8.00	100.00	59.60	14.3	273.0	139.6	21.2	547.5	250.7	39.5	1691	639.20			
8.10	102.30	60.74	14.4	276.3	141.0	21.4	556.7	254.2	40.0	1730	651.80			
8.20	104.60	61.89	14.5	279.6	142.4	21.6	566.4	257.8	40.5	1770	664.20			

APPENDIX B: Experimental Design and Analysis Data

B.1. ANOVA Table

Response 1 Yield

ANOVA for selected factorial model

Analysis of variance table [Classical sum of squares - Type II]

Source	***Sum of Squares***	***df***	***Mean Square***	***F- value***	***P- value (Prob > F)***
Model	728.63	8	91.08	51.46	< 0.0001 - ***Significant***
A-Acid Ratio	*641.11*	*2*	*320.55*	*181.13*	*< 0.0001*
B-Adsorbent Ratio	*72.43*	*2*	*36.21*	*20.46*	*< 0.0001*
AB- interaction	*15.09*	*4*	*3.77*	*2.13*	*0.1187*
Pure Error	31.85	18	1.77		
Cor Total	760.48	26			

The Model F-value of 51.46 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

Std. Dev.	1.33	R-Squared	0.9581
Mean	66.21	Adj R-Squared	0.9395
C.V. %	2.01	Pred R-Squared	0.9058
PRESS	71.67	Adeq Precision	22.394

The "Pred R-Squared" of 0.9058 is in reasonable agreement with the "Adj R-Squared" of 0.9395. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 22.394 indicates an adequate signal. This model can be used to navigate the design space.

Term	**Coefficient Estimate**	**df**	**Standard Error**	**95% CI Low**	**95% CI High**
ntercept	66.21	1	0.26	65.67	66.74
A[1]	-5.81	1	0.31	-6.47	-5.15
A[2]	-0.79	1	0.18	-1.17	-0.41
B[1]	-2.01	1	0.31	-2.66	-1.35
B[2]	-0.022	1	0.18	-0.40	0.36
A[1]B[1]	-0.075	1	0.38	-0.88	0.73
A[2]B[1]	-0.54	1	0.22	-1.00	-0.070
A[1]B[2]	-0.25	1	0.22	-0.72	0.22
A[2]B[2]	-0.15	1	0.13	-0.42	0.12

Final Equation in Terms of Coded Factors:

Yield =+66.21-5.81* A[1]-0.79 * A[2]-2.01 * B[1]-0.022 * B[2]-0.075 * A[1]B[1]-0.54 *A[2]B[1]-0.25 * A[1]B[2]- 0.15* A[2]B[2]

Response 2 Density

ANOVA for selected factorial model

Analysis of variance table [Classical sum of squares - Type II]

Source	*Sum of Squares*	*df*	*Mean Square*	*F- value*	*P- value (Prob > F)*
Model	2.874E-003	8	3.593E-004	6.47	0.0005 – ***Significant!***
A-Acid Ratio	2.696E-003	2	1.348E-003	24.27	< 0.0001
B-Adsorbent Ratio	9.630E-005	2	4.815E-005	0.87	0.4372
AB- interaction	8.148E-005	4	2.037E-005	0.37	0.8292
Pure Error	1.000E-003	18	5.556E-005		
Cor Total	3.874E-003	26			

The Model F-value of 6.47 implies the model is significant. There is only a 0.05% chance that a "Model F-Value" this large could occur due to noise.
Values of "Prob > F" less than 0.0500 indicate model terms are significant.
In this case A are significant model terms.
Values greater than 0.1000 indicate the model terms are not significant.
If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

Std. Dev.	7.454E-003	R-Squared	0.7419
Mean	0.89	Adj R-Squared	0.6272
C.V. %	0 .83	Pred R-Squared	0.4192
PRESS	2.250E-003	Adeq Precision	6.197

The "Pred R-Squared" of 0.4192 is not as close to the "Adj R-Squared" of 0.6272 as one might normally expect. This may indicate a large block effect or a possible problem with your model and/or data. Things to consider are model reduction, response tranformation, outliers, etc.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 6.197 indicates an adequate signal. This model can be used to navigate the design space.

Term	**Coefficient Estimate**	**df**	**Standard Error**	**95% CI Low**	**95% CI High**
Intercept	0.89	1	1.434E-003	0.89	0.90
A[1]	-0.010	1	1.757E-003	-0.014	-6.309E-003
A[2]	4.074E-003	1	1.014E-003	1.943E-003	6.205E-003
B[1]	-5.556E-004	1	1.757E-003	-4.246E-003	3.135E-003
B[2]	1.296E-003	1	1.014E-003	-8.347E-004	3.427E-003
A[1]B[1]	-1.667E-003	1	2.152E-003	-6.187E-003	2.854E-003
A[2]B[1]	-1.111E-003	1	1.242E-003	-3.721E-003	1.499E-003
A[1]B[2]	0.000	1	1.242E-003	-2.610E-003	2.610E-003
A[2]B[2]	-1.852E-004	1	7.172E-004	-1.692E-003	1.322E-003

Final Equation in Terms of Coded Factors:

Density = +0.89 -0.010 * A[1]+4.074E-003* A[2]-5.556E-004* B[1]+1.296E-003*B[2]-1.667E-003* A[1]B[1]-1.111E-003 * A[2]B[1] +0.000 * A[1]B[2]-1.852E-004* A[2]B[2]

Response 3 Viscosity @ 40 degree C

ANOVA for selected factorial model

Analysis of variance table [Classical sum of squares - Type II]

Source	*Sum of Squares*	*df*	*Mean Square*	*F- value*	*P- value (Prob > F)*
Model	110.71	8	13.84	23.12	< 0.0001 – *Significant!*
A-Acid Ratio	105.39	2	52.70	88.04	< 0.0001
B-Adsorbent Ratio	4.72	2	2.36	3.94	0.0380
AB- interaction	0.60	4	0.15	0.25	0.9051
Pure Error	10.77	18	0.60		
Cor Total	121.49	26			

The Model F-value of 23.12 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant.
In this case A, B are significant model terms.
Values greater than 0.1000 indicate the model terms are not significant.
If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

Std. Dev.	0.77	R-Squared	0.9113
Mean	95.15	Adj R-Squared	0.8719
C.V. %	0.81	Pred R-Squared	0.8005
PRESS	24.24	Adeq Precision	13.284

The "Pred R-Squared" of 0.8005 is in reasonable agreement with the "Adj R-Squared" of 0.8719.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 13.284 indicates an adequate signal. This model can be used to navigate the design space.

Coefficient Term	**Estimate**	**df**	**Standard Error**	**95% CI Low**	**95% CI High**
Intercept	95.15	1	0.15	94.84	95.46
A[1]	-2.31	1	0.18	-2.69	-1.92
A[2]	0.42	1	0.11	0.20	0.65
B[1]	-0.51	1	0.18	-0.89	-0.13
B[2]	0.019	1	0.11	-0.20	0.24
A[1]B[1]	0.100	1	0.22	-0.37	0.57
A[2]B[1]	-0.11	1	0.13	-0.38	0.17
A[1]B[2]	-0.044	1	0.13	-0.32	0.23
A[2]B[2]	9.259E-003	1	0.074	-0.15	0.17

Final Equation in Terms of Coded Factors:

Viscosity @ 40 degree C =+95.15-2.31 * A[1]+0.42 * A[2]-0.51 * B[1]+0.019 * B[2]+0.100 * A[1]B[1]-0.11 * A[2]B[1]-0.044 * A[1]B[2]+9.259E-003 * A[2]B[2]

Response 4 Ash Content

ANOVA for selected factorial model

Analysis of variance table [Classical sum of squares - Type II]

Source	*Sum of Squares*	*df*	*Mean Square*	*F- value*	*P- value (Prob > F)*
Model	1.896E-003	8	2.370E-004	0.14	0.9964 - **Insignificant!**
A-Acid Ratio	5.185E-005	2	2.593E-005	0.015	0.9852
B-Adsorbent Ratio	1.430E-003	2	7.148E-004	0.41	0.6693
AB- interaction	4.148E-004	4	1.037E-004	0.060	0.9928
Pure Error	0.031	18	1.741E-003		
Cor Total	0.033	26			

The "Model F-value" of 0.14 implies the model is not significant relative to the noise. There is a 99.64 % chance that a "Model F-value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant.
In this case there are no significant model terms.
Values greater than 0.1000 indicate the model terms are not significant.
If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

Std. Dev.	0.042	R-Squared	0.0571
Mean	0.34	Adj R-Squared	-0.3620
C.V. %	12.14	Pred R-Squared	-1.1216
PRESS	0.071	Adeq Precision	1.107

A negative "Pred R-Squared" implies that the overall mean is a better predictor of your response than the current model.

"Adeq Precision" measures the signal to noise ratio. A ratio of 1.11 indicates an inadequate signal and we should not use this model to navigate the design space.

Term	**Coefficient Estimate**	**df**	**Standard Error**	**95% CI Low**	**95% CI High**
Intercept	0.34	1	8.029E-003	0.33	0.36
A[1]	5.556E-004	1	9.834E-003	-0.020	0.021
A[2]	-9.259E-004	1	5.678E-003	-0.013	0.011
B[1]	8.889E-003	1	9.834E-003	-0.012	0.030
B[2]	-3.704E-004	1	5.678E-003	-0.012	0.012
A[1]B[1]	1.667E-003	1	0.012	-0.024	0.027
A[2]B[1]	2.778E-003	1	6.954E-003	-0.012	0.017
A[1]B[2]	1.111E-003	1	6.954E-003	-0.013	0.016
A[2]B[2]	-7.407E-004	1	4.015E-003	-9.175E-003	7.694E-003

Final Equation in Terms of Coded Factors:

Ash Content = +0.34 +5.556E-004*A[1]-9.259E-004*A[2]+8.889E-003*B[1]-3.704E-004*B[2]
+1.667E-003*A[1]B[1]+2.778E-003* A[2]B[1]+1.111E-003 * A[1]B[2]-7.407E-004*A[2]B[2]

B.2. Diagnostic Plots

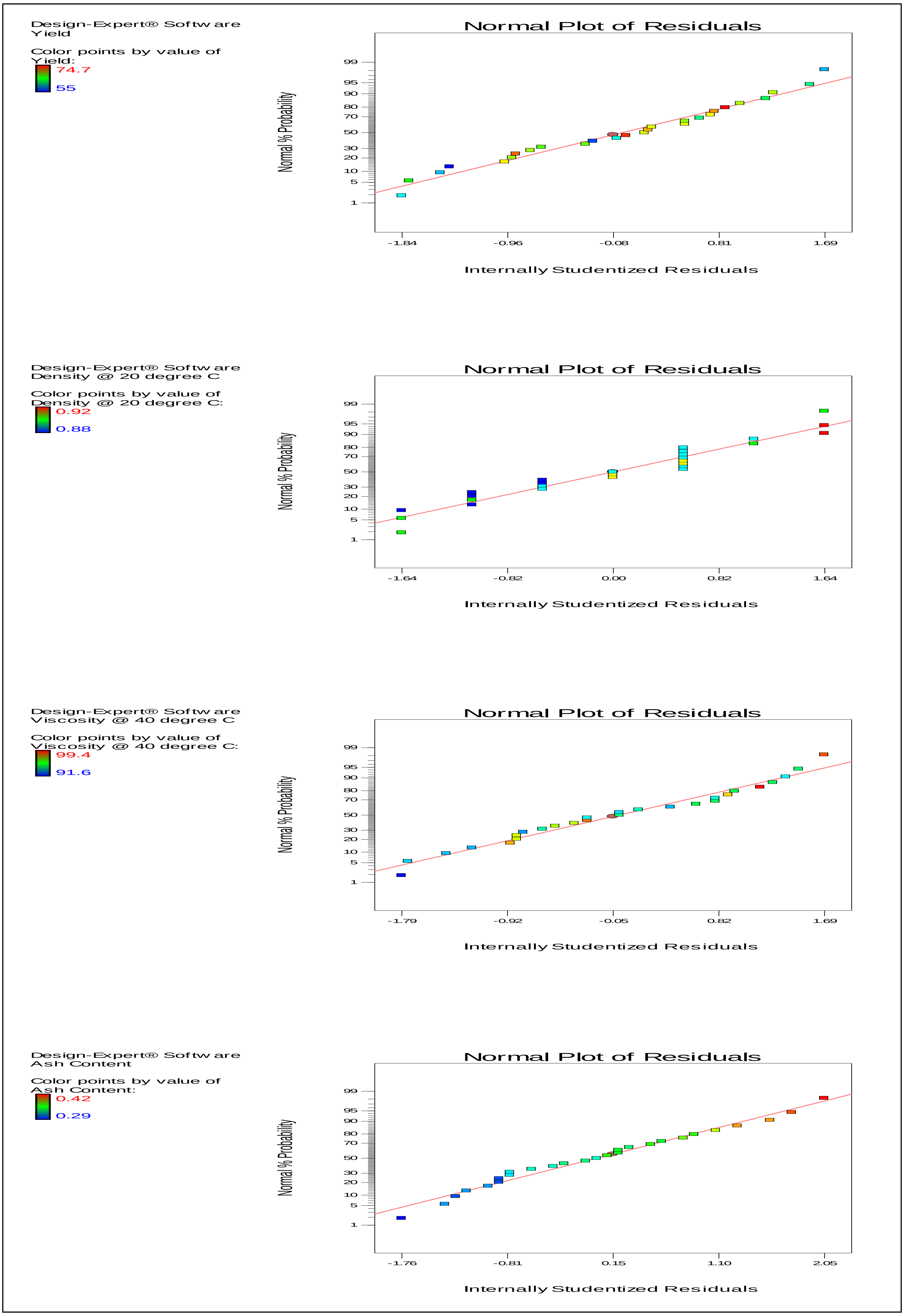

Figure B-1: Normal plot of residuals

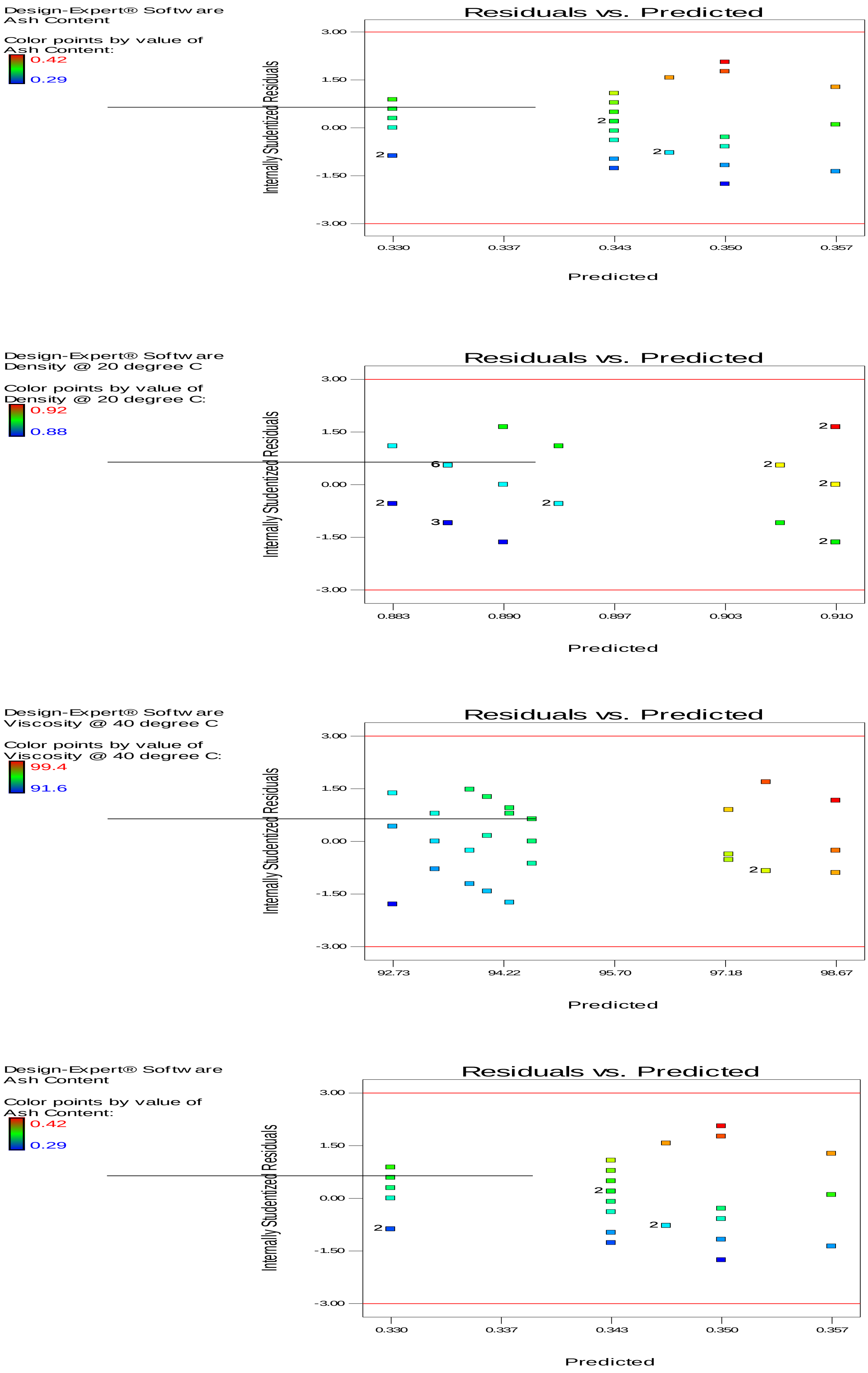

Figure B-2: Plot of residuals vs. predicted values

APPENDIX C: Material Balance & Energy requirement

C.1. Material Balance

The material balance of the process is considered based on the selected optimum operational conditions of the variable factors. These are:

- Acid percentage =20 %
- Adsorbent (clay) percentage = 15 %

Other operational parameters discussed in section 3.2.2 are kept constant for all runs.

Table C-1: Material balance results of the selected optimum experimental run

Major Process Steps	Input	Output	Oil recovered (%)
Primary acid treatment	• Used oil = 500 ml • Sulphuric acid= 75 ml	• Oil = 446 ml • Sludge = 92 ml	89.2
Ethyl Alcohol Neutralization	• Recovered oil = 446 ml • Ethanol = 22 ml	• Oil + ethanol = 455 ml • Sludge= 14 ml	91
Atmospheric Distillation	• Oil + ethanol = 455 ml	• Oil = 443 ml • Diluted ethanol = 12 ml	88.6
Vacuum Distillation	• Oil = 443 ml	• Oil = 394 ml • Light fuel= 40 ml	78.8
Secondary Acid Treatment	• Oil = 394 ml • Sulphuric acid= 25 ml	• Oil = 375 ml • Sludge = 32 ml	75
Lime Neutralization	• Oil = 375 ml • Lime = 9.1 g	• Neutralized oil = 360 ml • Sludge =21 g	72
Adsorption	• Neutralized oil = 360 ml • Bentonite Clay = 48.6 g	• Recovered oil = 345 ml • Sludge = 63 g	69

Using a basis of one liter of product yield:

Used oil required for the process can be calculated as;

- $\mathrm{U} = \frac{1-\mathrm{X}}{0.69} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots .. (1)$

Where: U = used oil requirement

X = additive requirement (8 % (Caltex lubricants, 2013))

- $\mathrm{U} = 1.33 \text{ liters}$

Sulphuric acid requirement;

- $\mathrm{S.A.} = \mathrm{U} \times \mathrm{a.r} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots .. (2)$

Where; U = used oil requirement

a.r = acid ratio; 20 % (from optimum condition)

- $\mathrm{S.A.} = 267 \text{ ml}$

Ethyl Alcohol requirement;

For the first acid treatment (step-1), three-fourth of the total acid is used. Therefore 200 ml of sulphuric acid is consumed. By assuming one-fourth of the acid may not react, equivalent amount of ethanol is applied for neutralization. From the chemical equation, the amount of ethanol is calculated.

$$\underset{(98g)}{H_2SO_4} + \underset{(46g)}{C_2H_5OH} \rightarrow\rightarrow C_2H_5-O-SO_3H + H_2O \quad \ldots\ldots.\ldots(3)$$

Using the above stoichiometry, for ethanol concentration of 95% and acid concentration of 98.5%, the total requirement will be calculated as;

- $E = \frac{(0.985)200}{(0.95)4} \times \frac{46g}{\rho_E} \times \frac{\rho_a}{98g} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.\ldots\ldots..\ldots(4)$

Where; $\rho_a = \text{density of sulfuric acid, } 1.84\ g/ml$

$\rho_E = \text{density of ethanol, } 0.789\ g/ml$

- $E = 57ml$

Lime requirement;

Similarly, in the secondary acid treatment (step-5), one-fourth of the total acid is used. Therefore 67 ml of sulphuric acid is added to the product of vacuum distillation. By assuming one-third of the acid may not react (since more acid is used) equivalent amount of lime is applied for neutralization. From the chemical equation, the amount of ethanol is calculated.

$$\underset{(98g)}{H_2SO_4} + \underset{(56g)}{CaO} \rightarrow\rightarrow CaSO_4 + H_2O \quad \ldots\ldots\ldots\ldots..\ldots\ldots\ldots\ldots..\ldots(5)$$

From the above stoichiometry, for Lime purity of 95% and acid concentration of 98.5%, the total lime requirement will be calculated as;

- $L = \frac{67\times0.985\times\rho_a}{(0.95)3} \times \frac{56\ g}{98\ g} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.\ldots\ldots\ldots...\ldots(6)$

Where; $\rho_a = \text{density of sulfuric acid, } 1.84\ g/ml$

- $L = 24.4\ g$

Adsorbent requirement;

After the lime neutralization, 360 ml of oil is recovered which is 72 % from the total amount of used oil applied at the beginning of the experiment. From the selected optimum operational condition, the quantity of clay needed for the adsorption process is 15%. Using this data, the adsorbent clay requirement is calculated as;

- $\mathrm{C.R} = 1.33 \times (\frac{1000\ \mathrm{ml}}{\mathrm{L}}) \times 0.72 \times 0.15 \times \rho_{\mathrm{oil}} \ldots\ldots\ldots (7)$

Where; $\rho_{\mathrm{oil}} = 0.9\ \mathrm{g/ml}$ [assumed between 0.886 (recovered oil) and 0.93 (used oil)]

- $\mathrm{C.R} = 129.3\ \mathrm{g}$

The vacuum distillation step approximately gave 40 ml of light fuel which is 8 % of the total used oil which is initially applied for the experiment. For the material balance based on one liter product yield, the amount of light fuel expected can be calculated as;

- $\mathrm{L.F} = 1.33 \times \left(\frac{1000\ \mathrm{ml}}{\mathrm{L}}\right) \times 0.08 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$
- $\mathrm{L.F} = 106.4\ \mathrm{ml}$

The amount of additives required for blending with the recovered oil is assumed to be 8 %, based on the fresh oil composition.

Table C-2: Material balance based on one liter product yield

Material required	Unit	Amount required
Used oil	Liter	1.33
Sulphuric Acid	Liter	0.267
Ethyl Alcohol	Liter	0.057
Lime	gram	24.4
Bentonite clay	gram	129.3
Additives (8 %)	Liter	0.08

C.2. Energy Requirement

The major energy requirement for the recycling process is electrical power that is used for distillation step. This energy can be approximated using quick estimates of wattage requirements from the following equation (Watlow , 2014);

- $\mathrm{Power\ (kW)} = \frac{\mathrm{Liters} \times \mathrm{Temperature\ rise\ (°C)}}{1680 \times \mathrm{heat\ up\ time\ (hrs)}} \ldots\ldots\ldots\ldots (9)$

The distillation steps totally took seven hours and a maximum temperature of 350 °C was attained. The amount of oil fed to the distillation system is 91% as referred in Table B-2. Therefore;

- $\mathrm{input\ oil} = 1.33 \times 0.91$
- $\mathrm{input\ oil} = 1.21\ \mathrm{liters}$

The power required will be;

- $\mathrm{P} = \frac{1.21(\mathrm{ltr}) \times (350 - 15)°\mathrm{C}}{1680 \times 7(\mathrm{hrs})}$
- $\mathrm{P} = 0.04\ \mathrm{KW}$