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# USED AUTOMOTIVE LUBRICANT TREATMENT USING ACID-CLAY METHOD

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

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# Acronyms

Cst- centi stoke

TBN-Total Base Number

SDG- sustainable development goals

S- Spark

C- Compression

API-  American Petroleum Institute

ASTM- American Society of Testing and Materials

SAE- Society of Automotive Engineers

VI- viscosity Index

TAN- Total Acid Number

PAH- Polycyclic aromatic hydrocarbon

PCB- Polychlorinated biphenyl

BTEX- Benzene, Toleune, Ethylbenzen and Xylene

# ABSTRACT

Used lubricating oil has been the subject of much debate over recent years in Ethiopia. The amount of lubricating oils disposed annually in the country is considerably large. This amount of waste lubricating oil has a significant impact on both economic and environmental aspects. In this research Acid-clay technology has been tested for re-refining used lubricating oils, usually Total Rubia Tir 7400 15W-40 and Total Quartz 5000 20W-50 by varying acid ratio between 10-20% and adsorbent ratio between 15-25%. The result showed that the efficiency of the recycling operation depends on these two reagent ratios. Increasing the acid concentration showed a significant difference over the yield, kinematic viscosity and other physicochemical properties, however increasing the amount of acid over the optimum point made no significant change. Better bleaching and yield and other physicochemical properties were achieved with increasing adsorbent ratio. A maximum yield of 71.45% was obtained for Rubia Tir 7400 15W-40 at acid ratio of 15% and 25% adsorbent. Whereas a minimum yield is obtained 42.6% at acid ratio of 10% and 15% adsorbent ratio. For Quartz 5000-20W-50 a maximum and minimum yield, and other physicochemical properties were obtained at 15:25 and 10:15 acid adsorbent ratio respectively with72.5% and 49% yield. All metal contaminants are substantially removed; total base number is enhanced while carbon residue is significantly reduced for both lubricants suggesting the method works effectively regardless of the lubricant type.

# 1. Background

As the second largest population and the tenth largest land territory occupation in Africa; Ethiopia, being one of the fastest growing economies in the world, has witnessed a rapid growth in the industrialsector which can be seen by the different establishments of industrial cities, factories to meet ends of the country's demands. The country's development driven economy has benefited as well affected the country in a paradoxical way. This economic growth has also resulted in an increase in population, urbanization especially in the capital which lead to rapid increase in automobile transportation.

Road transportation service accounts for handling 95% of the mobility in the country. The capital, Addis Ababa hold 54% of the total fleet transportation. Transport authority of the country estimates that the total number of vehicles in the country as of July 07 2015 is 587,454 where most of these automobiles are older than 15 years of production date. These cars are responsible for using 37,000 ton oil per year; the volume of lube oil that is sold in the country is around 3milion litres per year alone by Total Ethiopia.[1]

Used oils are consumed as either a source of energy for furnaces creating smoke and soot and other toxic metals or to be put up in as a waste on the ground or water bodies thus leading to environmental Pollution. One gallon of oil is able to contaminate million gallons of drinking water and can form a thin layer of oil on the surface of water which prevent oxygen from being dissolved in water, which then retards all kind of aquatic life and the process of photosynthesis.[1]

Ethiopia, aiming to become a middle income country in 2025 and developing a green economy meeting the SDG, is facing challenges on its environment from the transportation sector; this trivial but yet important matter has to be mitigated by using different environmentally friendly methods. This research tries to meet amends that are the result of 'lubricant' related problems.

The management of waste oils is particularly important because of the large quantities generated nationally through transport and Industrial activities. These waste oils may have detrimental effect on the environment if not properly handled, treated or disposed. In recent decades a number of treatment technologies have been developed that promise to solve technical, economic and environmental problems associated with used oil management. This research investigates one of the different technologies namely acid clay. This method is an old and popular one, a proven technology that had been worked for many years worldwide. This technology is set up for very small capacity, low capitalinvestment cost making it most cost effective for small plants, non-sophisticated, very simple process to operate, no advance technology and skilled operators are required.

## 1.1- Statement of the problem

Ethiopia and particularly in Addis; the city's booming sectors for industrial, transportation and building sectors are responsible for potential sources of rising greenhouse gas emissions coupled with the increasing activity in key social and economic sectors. Vehicular emission is becoming number one cause for pollution in Ethiopia and contributing significantly to health hazards which has gradually grown into major environmental concern for policy makers and environmental experts.

The disposal of the used oil for engines have great effect over the environment, some will be disposed into the aquatic bodies some will be released directly to the atmosphere and some will just enter the soil and generally disrupt the natural cycle of these systems.Owning this fact different process had been implemented through time to overcome such a problem that is to re-refine oil for the clean-up of the environment before disposal and as well for utilized use of treated oil as good as virgin oil. This thesis will focus on the acid clay treatment/Acid clay re-refining of lubricant/.

Acid clay technology is chosen because of its very simple and low operating and equipment cost. Compared to other methods it has a low energy demand, good recovery rate and quality of reclaimed oil. Major drawback of this process is its high sludge formation which with further study could be easily managed and this by-product can be turned into utilizable product.

## 1.2 Significance of the study

Completion of this research will play an important role by providing a study report on acid clay treatment and how this process can achieve best operating condition while reducing the need for extraction of crude oil extraction which is associated with environmental impacts of the activity, protecting the environment from toxic and hazardous chemicals. Acid-clay process is easily manipulated process which will help to enhance development especially in our country in a cheap way.

## 1.3 Objectives

### 1.3.1- General objective

The general objective of this research is to re-refine used automobile engine oil by using Acid Clay treatment technology.

### 1.3.2- Specific Objective

This research paper will focus on the following specific points

- Characterization of used automobile lubricants
- Laboratory setup of acid clay treatment technology
- Treatment of used lubricant ( Diesel and Gasoline engine lubricants)
- Optimization of the process parameters that affect used oil treatment
- Evaluation of physicochemicalproperties (Flash Point, TBN, Viscosity, Metal content) of the filtered lube oil.
- Comparison of the treated oil with that of the virgin oil

## 1.4Scope of the study

The research emphasise on treatment of used automotive motor oil through recycling by cheap adsorbent and acid that is abundantly found in the country. Through this research it is expected to minimize the amount of waste automotive lubricating oil generated in the country and as well reduce the amount of foreign currency spent by the country in order to buy a new lubricant. The scope of this study is limited to picking the best operating condition, treatment of the used oil to be used again and removal of all contaminant metals and enhancing some of the fundamental physicochemical properties that describe lubricants.

# 2. LITREATURE REVIEW

A lubricant (engine oil) can be defined as an oil products that separates the metal parts of an engine, reduce friction and keep it clean. Lubricant deals with the application of lubricating oil to machine. [2]. Lubricants were at one time exclusively animal or vegetable oils of fats, but modern requirement in both nature and volume have petroleum as the main source of supply, lubricating oil can be produced by modern method of refining from most crude and they range from thin easily flowing spindle oils to tank cylinder oils.[3].

The lubrication system of engine is intended to avoid the increase of wear, overheating and seizure of rubbing surfaces to reduce the expenditure of indicated power on overcoming mechanical losses in the engine and also to remove wear products of a machine [4].

Lubricant oil is used in automobile engines to lubricate moving parts of engine, reducing friction, protect, against wear, and removing contaminants from the engine, act as a cleaning agent, and act as an anticorrosive and cooling agent. It picks up a number of impurities and additional components from engine wear. These components include metal particles (iron, steel, copper, lead, zinc, etc.) and other compounds of barium, sulphur, water, dirt, burnt carbon, and ash, most of them are highly toxic in nature; therefore these contaminants must be separated in order to reuse the engine oil.[5]There are four major types of lubricant, namely – liquid, solid, and gaseous and plastics Lubricant, example of lubricants include oil, grease, air and graphite. Liquid and plastics lubricant are the most commonly used lubricant in industries because they are inexpensive, easily applied and good coolants while Gaseous and Solid lubricant are recommended only in some special application.[6]In view of the problem encountered, lubricating oil is designed to impact various properties and to protect engine in so many ways. Lubricating oil is highly specialized product carefully developed to perform many essential functions among which are the following.

- Permit easy starting of engine,
- Reduced friction,
- Protecting machine against rust and corrosion,
- Lubricating of engine parts etc [7]

## 2.1 History of Lubricant

The use of animal fats, vegetable and olive oils as lubricants in the rolling wheels of carts was developed in the Middle East. This has since advance from the use of animal fat, vegetable and olive oils to refined mineral oil free from unstable compounds which have negative effect on the service life of the bearings. However, in 1947 the inter-industry needs for the system which would include other factors for improved engine oil performance other than viscosity was adopted by the American Petroleum Institute (API), hence the introduction of API classification systems which established three types of crank engine oils as Regular containing no additive, Premium containing oxidation inhibitors and Heavy duty type containing oxidation inhibitors and detergents/dispersant additives.

Consequently, in 1969, the tripartite of the American Petroleum Institute (API), American Society for Testing and Materials (ASTM), and the Society for Automotive Engineers (SAE) cooperated in establishing an entirely new classification system. The new classification system was based on engine design and construction, fuel type, operating conditions and the base oil stock. Base oil stock selected became important because the characteristics and performance of the finished oil depends on the crude oil source, the refining method used and the additive incorporated. This new classification enables engine oils to be more precisely defined and selected according to their performance characteristics and easily related to the type of service for which each is intended. The system uses letter designations for each category to enable automobile engines manufacturers use the letter to indicate the class or classes of engine oil suitable for the engine. As of today, there are fifteen classes of API engine service classification systems, eight of which are spark ignition (petrol or gasoline) engines while seven other classes are the compression ignition (Diesel) engines. They are normally identified with presiding letters “S” and “C” meaning spark and compression respectively. Unlike the 1885 ancestors, the challenges for the design of modern car engines were meeting the emission requirements, increased speeding, engine weight reduction, production cost reduction, operating cost and fuel economy, then oils are not oil, just as the modern automobiles have advanced from raw base oil to pre 1947 to those containing additives to help achieve the performance advantage required by the modern automobile.[8]

## 2.2 Mineral and synthetic Lubricant Base oils

Lubricant technology has evolved since the mid-1800s, when petroleum-based mineral oils (i.e., refined distillates of petroleum) first replaced animal fats, vegetable oils and marine oils as lubricants. Industrial development during the 19th century created an increased demand for lubricants, but the introduction of the gasoline-powered internal combustion engine is what caused the demand for lubricants to rapidly exceed the supply of natural oils. The refining of crude oil to produce gasoline as fuel for internal combustion engines also provided a source of mineral oil for lubrication purposes [9].

Automotive lubricant oils are typically 75 to 85 percent base stock (i.e., crude oil-derived product) combined with performance enhancing additives. The base stock may consist of a mineral oil, synthetic oil, or a blend of both. The additives may contain zinc, magnesium, molybdenum, phosphorus, and sulphur and bromine compounds. The base oil, in combination with the additives, determines the flow characteristics of the finished lubricant, its volatility and its oxidation stability (sludge and deposit-forming tendency) [10].

Mineral base oils are manufactured by the distillation of crude oils, followed by further refining of the distillates via separation or other conversion processes (e.g., hydrocracking, hydrogen reforming, and wax isomerization). These oils are mixtures of paraffin's (straight-or branched-chain hydrocarbons), naphthenic (ring forms of paraffin's) and aromatics (alkyl benzenes and multi-ring aromatics). Mineral base oils break down in extreme heat and congeal in extreme cold. In addition, mineral oil base stocks contain undesirable impurities such as sulphur, trace metals and carbon residues which can limit the performance capabilities and useful service life of the resulting blended lubricant oils [11]. Synthetic base oils can be substituted for conventional mineral base oils. Most synthetic lubricants are fabricated by polymerizing short chain hydrocarbon molecules called alpha-olefins into longer chain hydrocarbon polymers called poly-alpha-olefins (PAOs). The degree of variation in molecular size, chain length and branching in synthetically produced fluids is much less than occurs in base stocks extracted from crude oil[12]. While they appear chemically similar to mineral oils refined from crude oil, PAOs do not contain the impurities or waxes inherent in conventional mineral oils. PAOs constitute the most widely used synthetic lubricants in the U.S. and Europe.

Synthetic lubricant technology allows the products to be designed for particular lubrication applications and, in combination with additives, provides targeted performance. Synthetic lubricants are frequently blended with mineral oil in order to provide desired combinations of properties[9]. Among the advantages for synthetic lubricants over mineral base oils are: low temperature fluidity and thus better cold weather performance; low volatility (i.e., low tendency to evaporate); high-temperature thermal stability (high "viscosity index"); oxidation resistance (of the oil itself); and high natural detergent characteristics (resulting in a cleaner engine with less additive content[10]. The "green" advantages that accompany the use of synthetic oils include improved fuel economy, decreased oil consumption and extended oil change intervals.[13]

## 2.3 Principle of Manufacturing of Base oil

The base oil used for the production of engine oils are obtained as distillate from the vacuum distillation. The raw material for this vacuum distillation is the atmospheric residue obtained at temperatures above 380°C. The products of vacuum distillation include the diesel fuel, the distillate of base oil, asphalt and bitumen. The distillates of the base oil are further treated in the three stages below:

a) **De-asphalting:** This is the process of treating the vacuum residue to eliminate resins and asphaltic substances. These asphaltic substances are extracted from the vacuum residue by treating with propane. The removal of sulphur and oxygen containing compounds improves the colour and quality of the base oil. The extracted asphalt is used in manufacturing bitumen.

b) **Furfural treatment:** The objective of this treatment is to do away with the aromatic substances whose viscosity indexes are low. Furfural is a hydro cyclic aldehyde, which is a bi-product of processing cereal wastes in paper-pulp production. Furfural preferentially dissolves hydrocarbons not needed. The base oil obtained has a high viscosity index but this index is also dependent on the type of crude oil processed.

c) **De-waxing:** The objective of de-waxing is to eliminate the long straight chain paraffinic hydrocarbons called petroleum waxes; these waxes are responsible for the high pour-point when present. The principle of de-waxing is simple; the raffinate is cooled so that the wax in the form of crystal crystallizes which is separated by filtration. However, doing this is difficult because wax and raffinate form a spongy mass that is hard to filter. Solvent de-waxing is preferred since it can de-wax stocks from light distillate to heavy residues. The solvent used is a blend of methyl-ethyl ketone and toluene.

d) **Hydro-finishing:** The final treatment is hydro finishing. It means getting rid of the least impurities not yet eliminated in the form of volatile products. These impurities include sulphur, nitrogen and oxygen products. The oil is hydrogenated in the presence of a catalyst at a temperature of 25°C and a pressure of 40 bars after which a good quality mineral base oil is obtained. The grade of the base oil obtained include 85, 100, 150, 330, 600NS (neutral solvent) and BSS (bright stock solvent). The NS 85 is of a lower viscosity while BSS is the most viscous of the base stocks. However, 500 NS is base oil blended of NS 330 and NS 600. This is because this blend is important due to its range of viscosity which its use is important more than the 300 and 600 Neutral Solvents.

### 2.4 Additives

Additive are materials which are not normally present in oil and which when added in it, improves its physical and chemical properties. They are used to obtain results not attainable by refining methods alone or to partially replace refining methods; the use of additives gives a desired result in a cheaper and economical way. The primary objectives of additives in the base oil are:

a) To prevent undesirable changes taking place during services.

b) To improve the original properties of the product.

**Types of Additives.**

**a) Anti-oxidants:** It would be highly desirable if the engine oil could maintain its original physical properties without a change for an infinite period of time. However, the hydrocarbon nature of petroleum oil makes it readily susceptible to oxidation, particularly when subjected to high temperature in the presence of certain oxidation catalysts which are usually associated with its use. Oxidation of petroleum oil results in marked changes taking place in both its physical and chemical properties. The oil becomes more viscous in nature; it develops corrosive acid and deposit insoluble sludge and lacquer-like material. Anti-oxidants are meant to inhibit the deterioration of oils by oxidation during service. Some anti-oxidants are meant to stabilize the oil under relatively mild conditions while some are meant to stabilize the oil that will encounter high temperature and severe conditions. This work is based on the later since the lubricants used in the internal combustion engines encounter temperatures of the order of 150 – 250°C in the piston zone and much higher than this in the combustion chamber itself. Examples of this anti-oxidants are dithiophosphate, 2, 3- tert-butyl para cresol etc.

**b) Detergents:** The rapid development of the small high-speed diesel engine during the past decade has been accompanied by the evolution of the so called “detergent” or “heavy duty” type lubricating oil designed to prevent excessive piston and ring zone deposits which were found to be prevalent in this type of engine. Materials of this type are generally molecules having a large hydrocarbon tail and a polar head group. The tail section, an olephilic group serves as a stabilizer in the base fluid, while the polar group is attracted to contaminants in the lubricant. Although these compounds are commonly called detergents, their functions appear to be dispersing of the particulate matter rather than cleaning up existing dirt and debris. Therefore, it is more appropriate to classify them as dispersants. Examples are sulphates, salicylates, phenates and phenol sulphide salts.

**c) Dispersants.** A major development in the additive filed was the discovering and the use of ash-less dispersants. These materials may be categorized into two broad types; high molecular weight polymeric dispersants used to formulate multi grade engine oils and lower molecular weight additives for use where viscosity modification is not necessary. Examples of these dispersants are high molecular weight esters, high molecular weight alkylated phenols, polymetric dispersants etc.

**d) Anti-wear additives**. Wear is the loss of metals with subsequent change in clearance between surfaces moving relative to each other. If continued, it will result in equipment malfunction. Among the principal factors causing wears are metal to metal contact, presence of abrasive particulate matters, and attack of corrosive acids. Example of material used here to prevent wear is di-thio-phosphates.

e) **Viscosity modifiers.** Viscosity modifiers or viscosity index improvers as they were formally known, comprises a class of materials that improves the viscosity/temperature characteristics of the lubricant. This modification of rheological properties result in increased viscosity index of the engine oil. Viscosity modifiers are generally oil soluble organic polymers with molecular weight ranging from about 10,000 to 1 million.

f) **Antifoam agents.** Oil foaming was not formally considered a problem, but with the use certain additives which seems to stabilize form, and with changes in engine design it has become serious in recent years. Excessive foaming of engine oil may cause failure of feeding mixtures of oil and air to the pressure pumps, or by displacement and loss of oil from the lubricating system, or by giving erroneous reading of oil level in the oil and air pressure pumps, or by giving erroneous reading to the oil level in the supply system. Anti-foam agents prevent foaming by destroying bubbles when they reach a free surface almost as rapidly as they are formed. Many materials have some anti-foaming ability, the most effective product so far found are the silicon polymers (polymethylsiloxanes) and these have found extensive use in engine oils.[8]

## 2.5 Composition of Engine oil

The most important consideration in engine oil is the reduction of friction and control of wears [14]where viscosity is the primary factor performance which was obtained by blending base stock or base oil with various compositions of various additives. So achieving the right viscosity relies on selecting the right base stocks and blending item with performance additives to enhance functional performance with the advancement in refinery technologies specifically in lube processing, a sophisticated refining technique e.g. Hydro treating/hydro cracking have been introduced to convert the undesirable components of the base stocks. United State Environmental Protection Agency reported that, the base stocks used in the formulation of this engine oil are either of mineral (petroleum) or synthetic origin. Table 2.1 below shows the physical composition of mineral based oil.[6].

Table 2.1 Physical Composition of Mineral Based oil[6]

| **Characteristics** | **100N** | **150N** | **250N** | **500N** | **BS** |
|---|---|---|---|---|---|
| Kinetic viscosity (cst) | 3.9-4.3 | 4.9-5.5 | 6.9-7.7 | 108-120 | 305-325 |
| Viscosity Index | 95 | 95 | 95 | 95 | 95 |
| Flash Point(°C) | 193 | 204 | 210 | 221 | 226 |
| Fire point(°C) | 198 | 210 | 217 | 236 | 234 |
| Pour point(°C) | -9 | -9 | -9 | -9 | -9 |
| Appearance | Clear and bright | Clear and bright | Clear and bright | Clear and bright | Clear and bright |
| Water content | None | None | None | None | None |

- N-Neutral Solvent
- BS- Bright Stock Solvent

### 2.5.1 Classification of Engine oil

Engine oil is normally specified in terms of their performance and viscosity grade [15]Table 2.2 shows the engine oil viscosity classifications, three types of automotive lubricants have been defined and classified by the Society of Automotive Engineers (SAE):

I- Crankcase oil
II- Transmission and axle lubricant
III- Fluids for hydraulic torque converters and fluid coupling

### Table 2.2- Engine Oil Viscosity Classification[15]

| **SAE Viscosity Grade** | **Viscosity @temperature** | **BorderlinePumping Temperature** | **Viscosity (ASTM d-45cSt)** | |
|---|---|---|---|---|
| | Cp@°C Max. | °C Max. | Max | Min |
| 0w | 3500@-30 | -35 | 3.8 | <3.3 |
| 5w | 3500@-25 | -30 | 3.8 | <2.5 |
| 10w | 3500@-20 | -25 | 4.1 | <3.5 |
| 15w | 3500@-15 | -20 | 5.6 | <4.9 |
| 20w | 4500@-10 | -15 | 5.6 | <4.6 |
| 25w | 6000@-5 | -10 | 9.3 | <8.5 |

## 2.6 Lubricating oil properties

**Density and specific gravity:** Density is the ratio of mass of a substance to the volume of the substance. Specific gravity is the ratio of density of substance to the density of water determined at the same temperature. The level of impurities in the used oil is indicated by the density and specific gravity. The specific gravity increases with the increase of aromatic content in the oil. Used engine oil has higher density and specific gravity due to the presence of contaminants in it.

**Viscosity:** Viscosity is the resistance offered to the flow of fluid. Viscosity testing of oil indicates the presence of contaminants in it. The viscosity of the lubricating oil decreases due to the addition of fuel, water and other contaminants added to it during its time inside the engine. Viscosity of the oil plays a cardinal role in reducing friction and it should be high. [16]

**Viscosity index:** Viscosity index is a number that indicates the change in viscosity at different temperatures. If the viscosity index is high, the viscosity change with the temperature is less. This means that the oil has higher thermal stability and provides good engine protection.

**Flash point:** Flash point is the minimum temperature at which the vapour produced by heating the oil produces a momentary flame when introduced to an ignition source. A low value of flash point indicates the addition of volatile products to the lubricating oil and the presence of contaminants.

**Total acid/base number:** The Total Acid Number (TAN) indicates the amount of acid content present in the oil. The TAN is the amount of potassium hydroxide required to neutralize the acid present in one gram of the oil. The engine oil undergoes oxidation at elevated temperatures producing carbonyl products and carboxylic acid. Higher TAN indicates the higher acid content and the oil needs replacement.[16]

## 2.7 Used Lubricant

With increasing new industries, increase in number of vehicles and mechanization of agriculture, and the volume of used lubricating oil produced each year is also increasing. Generated used oil can be considered as a source or as a source of pollution. The used oil contains water; salt, broken down additive components, varnish, gum and other materials. Also, due to oxidation or thermal degradation, a lot of impurities are generated in lubricating oil, during its application in internal combustion engines.

Used oil is a valuable resource and a vital source of energy; it still has lubricating value and heat value. Following the proper treatment to remove contaminants, 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 processes. The high contamination levels in some used oils, however, increase the difficulties in the operations and generate hazardous by-products as secondary pollutants. A large portion of the recycled used oil is combusted for energy utilization (often creates air pollution problems) or thermally destroyed by incineration (only when the oil has a high concentration of toxic contaminants that makes recycling impractical or unsafe). The contaminants in the used oil are toxic to the bacteria strains used in the biochemical process and lower product yields. Another concern is the potential bioaccumulation of these toxins in the bio products. A proper pre-treatment process is necessary to remove these toxins from the used oil stock to enhance the yield efficiency of the bioconversion process and improve the quality of the bio products. These impurities contain: unsaturates, aldehydes, phenolic compounds, alcohols, acidic compounds, non-stable products of hydrocarbons. In addition, used oil absorbs nitrogen oxides and the acidic fuel combustion exhaust gas.

These compounds besides dust, fuel, lubricating oil additives degradation products, and fuel additives regularly decrease the lubricating oil performance. Moreover, the viscosity increases by production of an asphalt-like sludge, which a metallic scrapings act as catalysts at the high operating temperature and oxygen vicinity. This used oil needs proper management to make it a valuable product by minimizing the quality of oil being improperly disposed of and reducing the waste oils environmental burden. Therefore, recycling of used oil justifies the interest in elimination of pollution. [17]

### 2.7.1 History of Recycling of Lubricant

The recycling of used oil has more than a four decade tradition. The idea of recycling of used oil was presented in the year of 1930. Initially the used oil was burned to produce energy, and later this oil was re-blended to engine oil after treatment. Recycle of used oil has been carried out by several methods. Recycling technology is the most important used oil re-refining. During re-refining the mechanical, physical and chemical contaminations are removed with the following processes: distillation, acidic refining, solvent refining, clay treatment, hydrogenation, or combinations of the formers. These processes have different yield and product properties, construction and operational cost. Target contaminants that need to remove from used oil include heavy metals, chlorinated hydrocarbons, BTEX compounds, PAHs, and PCBs.[17]

If used oil is mismanaged, the effects upon the environment will be detrimental. The reason behind this statement is that it contains metals, chlorinated hydrocarbons and other organic compounds including many that are listed in the US EPA. Spilled or dumped used oil on land can reduce soil productivity and seep into the groundwater to contaminate our water sources. According to EPA, just one quarter of used oil can make 1 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 sewage treatment processes.

Two major sources of used oil are automotive and industrial used oil. Automotive used oil tends to have a high concentration of potentially hazardous heavy metals, usually as the result of the engine or bearing wear, or the inclusion of these metals in oil additives. Industrial used oil tends to have a high level of chlorinated hydrocarbons and PCBs through careless management practices. The presence of other toxic organic compounds like benzene or naphthalene is usually associated with the oil formulation itself. [17]

Simply one gallon of waste oil can ruin the taste of a million gallons of drinking water. Films of oils on the surface of water prevent the replenishment of dissolved oxygen thereby hamper aquatic life, impair photosynthetic processes and block sunlight. Studies showed that, significant long-term effects have been observed in freshwater fishes with concentration of oil of 310 ppm and in marine life forms at concentration of oil of only 1 ppm.

Waste oil is also used as fuel for industrial furnaces. Combustion of waste oil destroys valuable resources and also represents a significant threat to the environment. All the toxic components present in the waste oil reach to the environment with the flue gas. In extreme cases, these contaminants damage the furnace, leading to increased environmental pollution. Emission of Zn can be as high as 600 times and Cu can be 2100 times if waste oil is burnt instead of re-refining.

Waste oil can be a very valuable resource, if managed properly. It has very refined fractions of petroleum and its recovery possibilities are extremely high. Average crude oils have 3-8% base-oil, whereas lube crudes typically have 12-16% base-oil. This compares with 65-75% recoverable base-oil content in used automotive oils, which if burnt or dumped would mean the loss of a valuable natural resource. Re-refining of waste oil is energy efficient; less energy (about one third) is used to produce a gallon of base stock from waste oil than to produce the same gallon from crude oil. It is also environment friendly. [18]

When used, blended lubricating oil goes through normal degradation and about 50% of it is consumed in the process. The rest of the oil picks up number of contaminants from the working environment, such as, residual components of engine fuels, solids from wear processes along with corrosion products and dirt, soot, combustion products etc. [18]

Currently, the recycling and reuse of used oil are limited to a few options. From the standpoint of energy conservation, recycling used oil efficiently saves a precious, non-renewable resource. The most encouraged option, even by governments, for reuse of the used oil generated by consumers, is to recycle it back to base lube oil. It does not only save a tremendous amount of time and money, but more importantly helps to conserve our natural resources. Used oil can be combusted for energy utilization or thermally destroyed by incineration. Due to the economic benefit of recycling used oil, only a very small quantity of used oil is currently incinerated. The oil that is incinerated generally has a high concentration of toxic contaminants that makes recycling impractical or unsafe. One of the most common applications for recycled oils is reprocessing them to be used as fuels. In some cases, however, the contamination levels in used oil are too high. As a result, it increases the difficulties in the reprocessing operations. Moreover, the hazardous by-products generated in the recycling processes become secondary pollutants that are even more difficult to handle. [17]

There are basically three options to deal with the regarding waste oil in the world:

a) Dumping the waste oil on land, garbage heap and sewerage system,

b) Regeneration of base-oil from waste oil and

c) Extracting of heat value of waste oil through combustion process.

### 2.7.2 Source and Collection of Spent Engine Oil

Used oils originate from diverse sources. These include petroleum refining operations (including sledges containing appreciable amounts of oil originating from the various parts of petroleum plants such as sumps, gravity separators, and the cleaning of storage tanks), the forming and machining of metals, small generators (do-it-yourself car and other equipment maintenance) and industrial sources, and the rural farming population. Collecting used oil from non-industrial sources and local/small generators is very difficult and requires a well-established and efficient infrastructure to accomplish the task. In this regard, it is important to develop adequate reuse or recycling options, to properly handle the collected volume of oil, to address the specific properties of the concerned waste and assess the degree to which used oils could be treated. A major source of oily wastes arising worldwide is the sludge recovered from tanks used for the storage of leaded petrol. These sludge which are normally produced by high pressure water jet cleaning of storage tanks consist of iron oxide corrosion product and sediments, onto which organic and inorganic lead compounds have been ab/adsorbed mixed with fuel. The free fuel is usually readily removed by gravity or mechanical separation and used as an energy source. The highly toxic organic lead compounds associated with the sludge have to be chemically or thermally oxidised (calcined) to inorganic lead compounds to facilitate its disposal.[19]. Essentially, the source of used oil varies with the point of use and the roles the virgin oil performs [20] Table 2.3 shows the classification of spent engine oil and their source.

**Table 2.3 Possible source of used lubricant**

| **lasses of waste** | **Characteristics** | **Probable source point** |
|---|---|---|
| Aqueous waste | Waste water containing oil and Morehighly contaminated waste | Refineries and petrochemical facilities, oil storage installation vehicles or car wash park |
| Spent motor oil | Contains contaminants which are volatile (waterand fuel)soluble (oil additives) and insoluble(carbon particles), metal oxides including lead oxide together with a large number of other trace metal and detergent | Garages, commercial transport , undertakings, service stations, industrial sites) |
| spent oil emulsion | Mainly water soluble cutting oil, wastes containing dispersed mineral oils in water, soap type emulsifiers, Lube oil additives and other contaminants like tramp oil. | Metal working industries machine shops, manufacturing industries, Engineering activities. |
| Non- emulsified oils mixtures | Mainly mineral oil waste containing 10%-90% oil, water, oxidized lubricant materials, sediment metal particles and tramp oils | Metal working industries, energy sectors, manufacturing industries. |

### 2.8 Characterization of waste lubrication 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. Some contaminants, such as chlorinated solvents, water, unburned fuel, carbon and dust are also picked up by the waste oil during use or during storage.

### A- Environmental pollution

The contaminants in waste 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, for example, recreation and fishing industries. For example, used oil from internal combustion engines generally accumulates a variety of contaminants, which increase the oil's toxicity.

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 2.4[21].

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 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.[22]

Table 2.4- Direct and indirect effects of Used Lubricant.

| 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 |

### B- Importance of used oil recycling

A large range of waste 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 waste oils, after treatment, can be either as a lube base stock comparable to refined virgin base oil or as clean burning fuel.

## 2.8.1 Treatment technologies

Used oils have been recycled for the past six decade. The idea of recycling used lubricating oil was presented in the year of 1930. Initially the 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 recycling of waste lubricating oils can be accomplished through three basic methods, which are reprocessing, re-refining and destruction.

### A- Reprocessing

The objective of re-processing is to produce a finished fuel oil that is low in basic sediment and water content, and that will not clog burners, foul boiler tubes, or cause sediment build-up in customer tanks. As such, the process requires filtration and removal of coarse solids that can pose environmental hazard or operational problems. Treatment options include mainly physical processes like settling, filtration, or a combination of these operations. Unfortunately, these processes alone are not sufficient to remove all chemical contaminants in the oil, and inclusion of further treatment processes such as clay contacting and distillation would reduce the competitive advantage of waste oil processors.

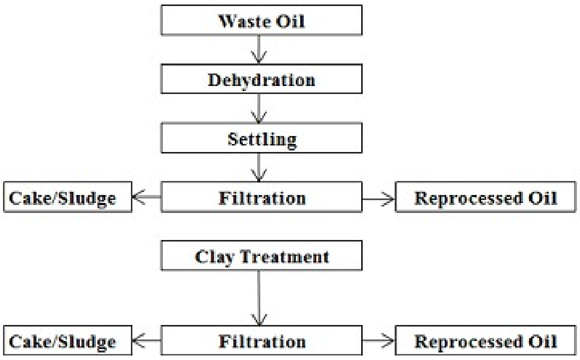

Figure 2.1 Block diagram of oil reprocessing of used lubricating oil

### B- Re-refining

Over the years several re-refining technologies have been proposed for waste oil recycling. Re-refining is the use of distilling or refining processes on used lubrication oil to produce high quality base stock for lubricants or other petroleum products. The use of this method has increased tremendously in developed countries, some countries reaching up to 50% of the country's need for lubricating oil. There are various methods developed by different western countries in the treating of used lubricating oil for reuse. It requires the conversion of waste oil to a product with similar characteristics to those of virgin oil. The process typically involves, but is not limited to, pre-treatment by heat or filtration, followed by either vacuum distillation with hydrogen finishing or clay, or solvent extraction with clay and chemical treatment with hydro-heating. Vacuum distillation followed by clay contacting offers a less polluting and more economical solution to the re-refining process, particularly for small-scale plants with a capacity range between 10000 and 30000 tons. The resulting residual by-product is well compacted and baled in thick plastic sheets prior to disposal in landfills.Participation of a reputable recycling company can play an important role in enhancing the trust factor.

### C. Incineration

This method is preferable when the waste oil is highly contaminated, particularly with polychlorinated by phenyls (PCB) and polychlorinated terphenyls (PCT). In the absence of hazardous waste incinerators, controlled high temperature incineration at cement factories is recommended.

Temperatures at the flame end of rotating cement kilns ranges between 2000 and 2400°C. This high temperature is adequate to destroy organics and neutralize acid compounds. The heavy metals content is reduced considerably as their concentrations remain very low compared to those found in the natural material used in the cement production process. Note, however, that continuous monitoring of gas emissions at the cement factories would be required to ensure compliance with air quality standards.

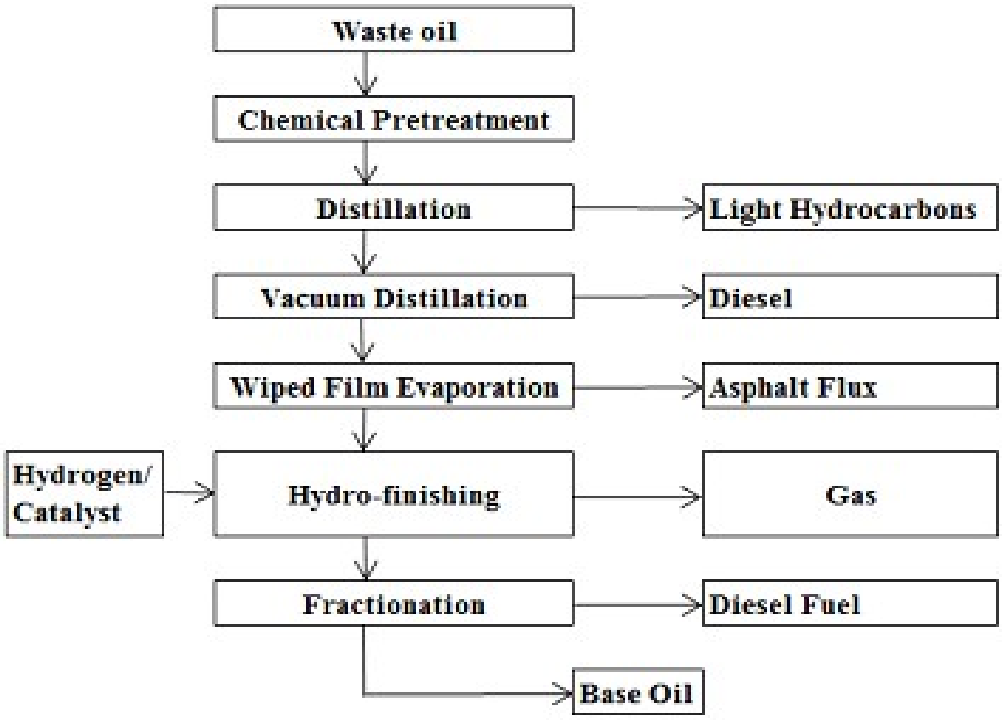

Figure 2.2- Block Diagram of used lubricating oil

## 2.9 Re-refining Technologies

With increasing prices of base raw material i.e. crude oil, recycling of waste oil has become an economically attractive proposition, in as much as it is a way of minimizing the environmental hazards and conservation of scarce non-renewable resource. The recycling of used lubricants has been practiced to various degrees since the 1930s and particularly during the Second World War when the scarcity of adequate supplies of crude oil encouraged the reuse of all types of materials including lubricants. In the earlier part of the 20th century, the lubricating oils contained few or no additives at all. Recycling these oils usually involved some basic and simple processes which were a combination of heating to remove volatile components; settling to separate water, dirt, and sludge; and centrifuging or filtering to remove most of the remaining insoluble contaminants. By this limited processing, recycled oils could not match the original oil quality. Technological improvements have now enabled the quality of recycled oil at par with virgin oils.

In recent years environmental considerations regarding the conservation of resources have further boosted interest in recycling. Recent developments, particularly, stress on waste recovery has led to further renewed interest in recycling the used oil. In some developed countries up to 50% of the countries' need for lubricating oil is met through recycled oils.

There are different methods used by different countries for recycling used oils. It has been established that almost 85 to 90% of the dehydrated Waste Oils can be converted in to useful products, be they the Base Oils for further processing in to lubricating oils or as fuel. [22]

### 2.9.1 The acid / clay re-refining method

The acid/clay process has a long operational history, it is not highly sophisticated and is appropriate to a wide range of circumstances and is thus readily operable in most countries.[19]In this process which has been widely used by re-refining facilities, used oil is initially subjected to filtration and dewatering mechanisms. Light products (Ethane, Methane etc.) are removed at the initial distillation step. It is then contacted with sulphuric acid which extracts oxygen compounds, asphalt, resin derivatives, other nitrogen and sulphur based compounds and metal contaminants from the oil. At the end of this process, desirable concentrations of paraffin and naphtalene molecules remain in the oil.

Vacuum distillation involves the distillation of oils under sub-atmospheric pressure which lowers the necessary operating temperature and reduces problems of thermal breakdown. The use of wiped film equipment which allows material with significant solid contents to be more readily processed with reduced thermal breakdown is increasing. Clays with high adsorptive capacity are used to remove impurities such as heavy metals and breakdown products arising in the use of oil. They are frequently used to give recovered oil a final polish.Next, the oil is mixed with active clay to remove the colour and odour. After the filtration step, the product has the necessary qualifications to produce base oil.

This invention relates to the production of acid-activated decolorizing clays and more particularly relates to a process for the acid activation of sub-bentonite type clays, It is well established that there are many naturally occurring clays and earths which possess potential utility as decolorizing agents or catalytic materials for a variety of purposes. These products have broad utility in a number of industries, one of particular importance being the re-refining of petroleum and other oil products.

Quite often these clays do not in their natural state possess the properties desired, at least not to the extent which would render their use practical or economical. Accordingly it has been necessary to treat clay materials by a variety of processes in order to bring out to the best advantage their potentials for the use intend.While the treatment varies according to the end use of the product, it is conventional to treat the clay by acid activation, heat, or both.[23].

Acid clay process for used recycling is an old and popular method, a proven technology that had been worked for many years worldwide. This technology can be set up for a very small capacity, low capital investment cost making it most cost effective for small scale plants, non-sophisticated, very simple process to operate, No advanced technology and skilled operators are required. The following flow diagram shows how the process works.

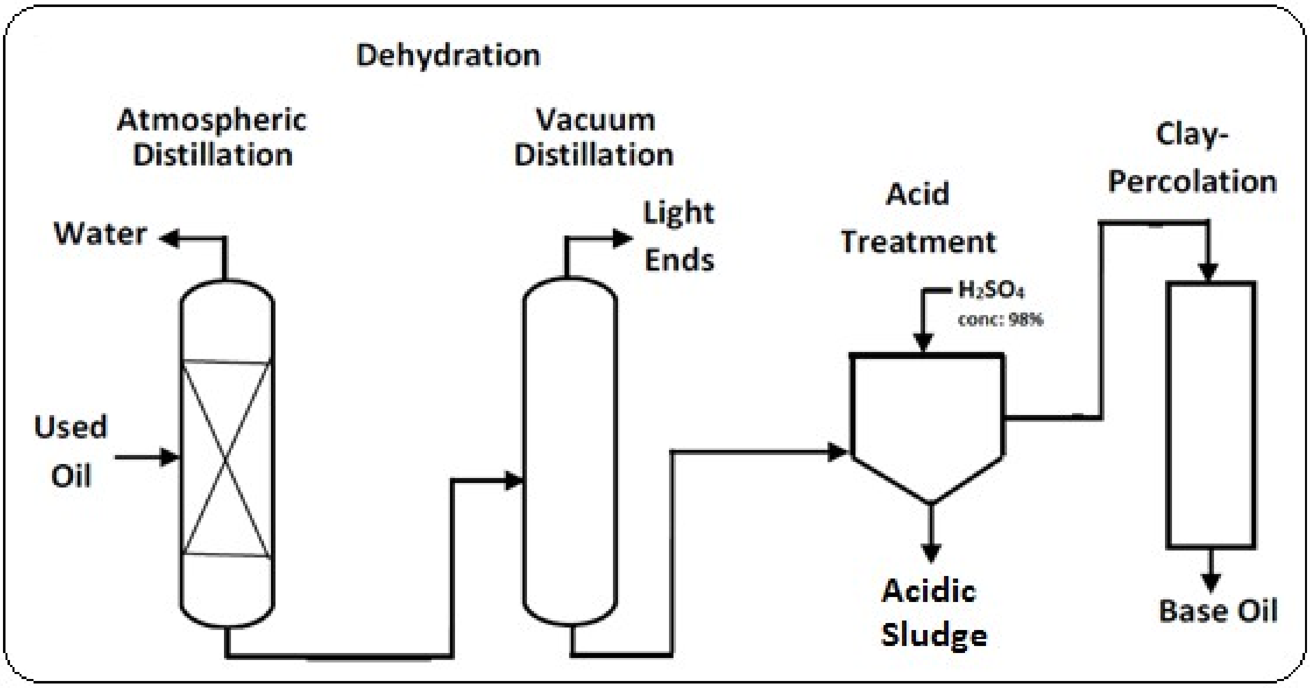

Figure 2.3 Flow chart of Acid/Clay Treatment process.

One of the main drawbacks of this process is that it causes environmental pollution due to generation of acid sludge and acid gas emission. Both residues are considered as hazardous waste as they contain toxic metals and sulphuric acid and disposal costs are high. Therefore, many countries have banned this process. However, it is still used in countries like Brazil, India and China to produce low quality market product. Spent clay is usually used in ceramic and cement industries. [24]

Different studies show that the acidic sludge, as a by-product (industrial waste), could be converted to the valuable products and raw materials of other processes, such as manufacturing processes, including organic fertilization, explosive materials, paint, ink, chemical fibre and industrial detergent. Processing of acidic sludge produces different commercial products such as surfactants, sulphuric acid, light hydrocarbons, coke, activated carbon, furnaces fuel and boilers, types of bitumen and asphalt and thermal insulation, etc. Also acidic sludge can be used as the amending of bitumen materials and preparation of carbon rods. Based on the studies of technical and economical view-point that have been conducted by the Iranian industries organization, the bitumen materials as a raw material or the additives for cycle of production are used in different industries such as wool fibers, booklet, laminated paper envelopes, asphalt heat insulation, plastic bags, automotive fan belt, PVC flooring, proof insulated pipe covers, blown bitumen, emulsion bitumen, polymer bitumen, complementary of bitumen refinery, motorcycle battery, paint, ink, printing ink and liquid bitumen, etc. [25]

## 2.10Parameters 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. [26]

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. [26]

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 [27]. 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[28].

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 follow[26]:

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

### II- Vacuum Pressure

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.[26]

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[29].

### 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[29]. Atmospheric distillation is normally conducted up to one hour and vacuum distillation was carried out between one and three hours, depending on the temperatures and vacuum pressures applied[30].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[31].The removal of these compounds is accomplished with sulphuric acid and its ratio depends on the amount of the mentioned impurities. The undesirable components to be removed are relatively present in small amounts but large excesses amount of acid for efficient removal which may cause marked changes in the remainder of the hydrocarbon mixture[32]. 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. [26]

### 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 [30] . Paraffin and Naphthene hydrocarbons in their pure forms are not attacked by concentrated sulphuric acid at lower temperatures[32].Therefore, desludging temperature should be maintained between 30 - 50°C to avoid the adverse effect of sulfuric acid oxidation of the oil at higher temperatures. [33].

### 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[34].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.

To enhance adsorption, fine particles (- 75 to +150) of the adsorbent used coupled with vigorous stirring. This step can be performed at room temperature using activated clay at a temperature of 120°C[26].

# 3. Materials and Methods

This research was carried out in the school of Chemical and Bio Engineering Laboratory, Addis Ababa Institute of Technology, Addis Ababa University and the following procedures had been followed:

- ✓ Characterization of the Used Lubricating oil
- ✓ Acid- clay treatment of the used oil
- ✓ Final characterization of the treated oil

The different equipment and the chemical that were used for the research is discussed thoroughly in the following section.

## 3.1 Materials

Two types of lubricants (Total Rubia Tir 7400 15 W- 40 and Total Quartz 5000-20W-50) were used in the Acid- Clay treatment. Virgin and used lubricants of these were obtained from Total Ethiopia's oil company. Characterizations of virgin and used Total Ethiopia's Rubia and Quartz were undertaken before the treatment was carried out. While the rest of the chemicals had been purchased from the market, Bentonite Clay (Bleaching Clay) was collected from Addis Mojo Edible Oil Company for the research.

### 3.1.1 Characteristics of the virgin Rubia Tir 7400 15W-40

Total Rubia Tir 7400 15w-40 is a mineral lubricant used in on-road diesel technology. It is recommended to euro 3, and previous engines of most European and American manufacturers. It is also adapted to euro 5 and previous engines of some manufacturers with appropriate oil drain intervals. Total Rubia Tir 7400 15w-40 enables coverage some fleet of mixed brands (American and European manufacturers) with a minimal number of products. [35]. Table 3.1 shows that characterisation of the virgin Rubia Tir 7400 15W-40.

**Table 3.1 characterisation of Virgin Rubia Tir 7400 15W-40**

| TOTAL RUBIA TIR 7400 15 W-40 | | Method | Value |
|---|---|---|---|
| Density at 15 C | $\frac{kg}{m^3}$ | ASTM D1298 | 888 |
| Kinematic viscosity at 40◦C | $\frac{mm^2}{s}$ | ASTM D445 | 98.7 |
| Kinematic viscosity at 100◦C | $\frac{mm^2}{s}$ | ASTM D445 | 13.4 |
| Viscosity index | - | ASTM D2270 | 136 |
| Flashpoint | ◦C | ASTM D92 | 236 |
| Pour point | ◦C | ASTM D97 | -30 |
| T.B.N | $\frac{mgKOH}{g}$ | ASTM D2896 | 11 |

### 3.1.2 Characterisation of Quartz 5000-20W-50

Total quartz 5000 20w-50 has been developed to cover the most stringent requirements of both gasoline and diesel engines (passenger cars and light industrial vehicles). Total quartz 5000 20w-50 is particularly suited to turbocharged engines. [35] Table 3.2 shows that characterisation of the virgin Quartz 5000-20W-50.

**Table 3.2 characterisation of Virgin Quartz 5000 20 W-50**

| **TOTAL QUARTZ 5000-20W-50** | | **Method** | **Value** |
|---|---|---|---|
| Density at 15 C | $\frac{kg}{m^3}$ | ASTM D1298 | 892.1 |
| Kinematic viscosity at 40◦C | $\frac{mm^2}{s}$ | ASTM D445 | 176.4 |
| Kinematic viscosity at 100◦C | $\frac{mm^2}{s}$ | ASTM D445 | 19.1 |
| Viscosity index | - | ASTM D2270 | 123 |
| Flashpoint | ◦C | ASTM D92 | 240 |
| Pour point | ◦C | ASTM D97 | -24 |
| Viscosity grade | - | SAE J300 | 20W-50 |

The equipment's and the chemicals that had been used for this research are the following.

## Table 3.3 Equipment's used for the laboratory

| Equipment | Measuring unit | Use |
|---|---|---|
| Weighing balance | gm | To weigh out samples |
| Filtering paper | | To filter out |
| Vacuum pump | 20mm Hg | For vacuum distillation |
| Beaker | 50ml- 2 L | Measuring samples |
| Measuring cylinder | 50ml | Measure out acid |
| Heating mantel | - | - |
| Distillation set up | - | Removal of light fuels |
| Centrifuge | 3600rpm | Forced Settling |
| Magnetic stirrer | - | Thoroughly mix acid with sample |
| Different flask | - | To store samples |
| Thermometer | °C | Measure temperature |
| Chemicals | | |
| Sulphuric acid | ml | Used to de-asphalting |
| Sodium hydroxide | gm | Neutralization |
| Activated bentonite clay | gm | For bleaching |
| Safety equipment's | | Safety equipment's are used to overcom working hazards. |
| Gloves | | |
| Safety clothes | | |
| Googels | | |
| Mouth mask | | |

## 3.2- Method

### 3.2.1- Methods used for characterization of used Lubricant

Used Lubricant has to be tested in order to analyse and characterise the physical and chemical properties that is found what has formed under the operational condition and service period of the lubricant. These conditions are stated in chapter two as Density, flash point, viscosity and neutralization number. These parameters are used in order to analyse the amount of contaminant that is found under the used lubricant. Finally these results are going to be used for comparison against the newly treated lubricant.

### i- Density

Density determination by pycnometer is a very precise method. It uses a working liquid with a well-known density, such as water. The pycnometer is a glass flask with a close fitting ground glass stopper with a capillary hole through it. This fine hole releases a spare liquid after closing a top-filled pycnometer and allows for obtaining a given volume of measured and/or working liquid with a high accuracy.

$$v=\frac{m_l}{p_l} \quad ........3.1$$

Density was measured by using Pycnometer (50ml), a very simple procedure in which the different weight of the different versions were measured and subtracted from the initial mass of the pycnometer then divided by the total volume of the pycnometer.

$$\rho=\frac{m_{v'}-m_{py}}{v_{py}} \quad .....3.2$$

Where

$m_{v'}=mass\ of\ diffrent\ version$

$m_{py}=initial\ mass\ of\ pycnometer$

$v_{py}=volume\ of\ pycnometer$

### ii- Viscosity

Kinematic viscosity is required at 40° and 100 ◦. Different researches suggest that these values are usually used in order to characterise oil quality. The Laboratory vibro visocometer is used to measure the dynamic viscosities. Therefore density will be used in order to convert this dynamic viscosity into Kinematic viscosity by using a simple equation.

$$v=\frac{\mu}{\rho} \quad .........3.3$$

Where $v = kinematic\ viscosity$

$\mu = dynamic\ viscosity$

$\rho = density$

### iii- Carbon Residue

The carbon residue value of the various petroleum materials serves as an approximation of the tendency of thematerial to form carbonaceous type deposits under degradation conditions and can be useful as a guide in manufacture of certain stocks.
Calculating the mass % carbon residue in the original samplecarbon residue as follows:

$$\% \text{ carbon residue} = \frac{(A*100)}{W} \quad \ldots\ldots\ldots\ldots 3.4$$

Where
$A$ = carbon residue, g, and
$W$ = sample used, g.

### IV- Viscosity index (VI)

It is the rate of change of viscosity between two temperatures. The lower the VI the more the drop in viscosity as the oil warms up. The higher the VI value, the less the drop in viscosity as the oil warms up.

As stated above, the oil’s viscosity will thin out rapidly at first when cold, the rate of thinning then slowing as the engine warms up and will stabilize as running temperature is reached. It is during the cold start where the concern is greatest owing to the heavy drag from the treacle like oil. It can take up to 90sec for the oil to properly circulate in an engine following a dry start from the cold.

The VI scale was set up by the SAE, the temperatures chosen arbitrary for reference are 100and 210 °F (38°C and 98 °C). The original scale only stretched between VI=0(lowest VI oil, naphthenic) and VI=100 (best oil, paraffinic) but since the conception of the scale better oils have also been produced, leading to VI’s greater than 100.

VI improving additives and higher quality base oils are widely used nowadays which increases the Vis attainable beyond the value of 100. The Viscosity index of synthetic oils range from 80 to over 400.

$$\text{VI} = 100\frac{(L-U)}{(L-H)} \quad \ldots\ldots\ 3.5$$

Where VI- viscosity index

$U = oil's\ kinematic\ viscosity\ at\ 40\,°c$

$L = oil's\ kinematic\ viscosity\ at\ 40\,°C\ for\ oils\ of\ VI = 0$

$H = oil's\ kinematic\ viscosity\ at\ 40\,°C\ for\ oils\ of\ VI = 100$

### V- Neutralization Number- TBN

The Neutralization Number (TBN) 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 MKOH 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 (TBN) or Total Acid Number (TAN) is calculated as;

$$\text{TBN}\ \left(\frac{mg\,KOH}{g\,sample}\right) = \frac{\left[\left(A - B\right) \times M \times 56\right]}{W} \quad \ldots\ldots\ldots\ldots\ldots 3.6$$

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- 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.

### VII- 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.

## 3.3 Acid-Clay Treatment of Used Lubricants

The whole process is stated in this section but the whole process is as follows:

**Step one: -Settling, Filtering and Dehydration**

The used motor lubricant that is freshly collected is let to settle for 24hrs before filtering it to remove impurities such as metal chips, sand, dust, micro impurities and solid particles that might be found along the used oil. After that, the used lubricant is taken at 2 litres per batch within an open beaker on a heating mantel for dehydration at 140°C for about 90 minutes.This process significantly reduces impurities in waste oil such as antifreeze, water and other solvents.

**Step two: - Distillation (Atmospheric and Vacuum)**

After the used lubricant is dehydrated the flask is closed by using cork and is further distilled at a temperature of 250°Cto remove the light fuel, Vacuum is used to elevate the temperature to remove the rest of the light fuels and the hydrocarbon that till there is nothing to recover after condensation.

Figure 3.1- Distillation setup

**Step three: - Acid Treatment**

Distilled oil is left to cool down and settle for at least 24 hours, then concentrated sulphuric acid (98%) in the ratio of 10-20 % is used to desphalte the burnt hydrocarbons inside the oil and this mixture is stirred thoroughly for at least an hour to ensure a complete homogeneous mixing.The compounds removed at this step are mainly products of the oxidative degradation of the base oil, such as organic acids, esters, ketones etc. It was then allowed for the mixture to settle for at least 72 hours for the acid to act upon the degraded oil in which the two layers were formed in which the sludge is removed from the bottom by decanting the top oil into a clean beaker for neutralization and removing the sludge.

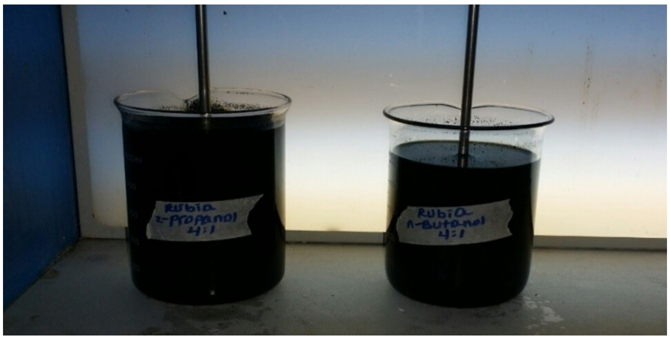

Figure 3.2- Stirring of Acid treated lubricant

**Step Four:-Neutralization**

Hereafter the settling of the degraded oil, the suspended oil is then decanted slowly into a clean beaker. This sample is neutralized by using sodium hydroxide pellets and this mixture is let down to settle for 24 hours.

**Step Five: - Adsorption**

The Neutralized oil is treated with Bentonite Clay 15- 25% of the treated lubricant with respective to the amount of acid used for treatment. The mixture is left for stirring for an hour for complete mixing then it is left for 3-7 days.

Figure 3.3 Adsorption of Clay treated lubricant

**Step Six:-Centrifuge**

The final treated oil is slowly decanted in a clean flask/Beaker and sent to centrifuge at 3600RPM for two hours.

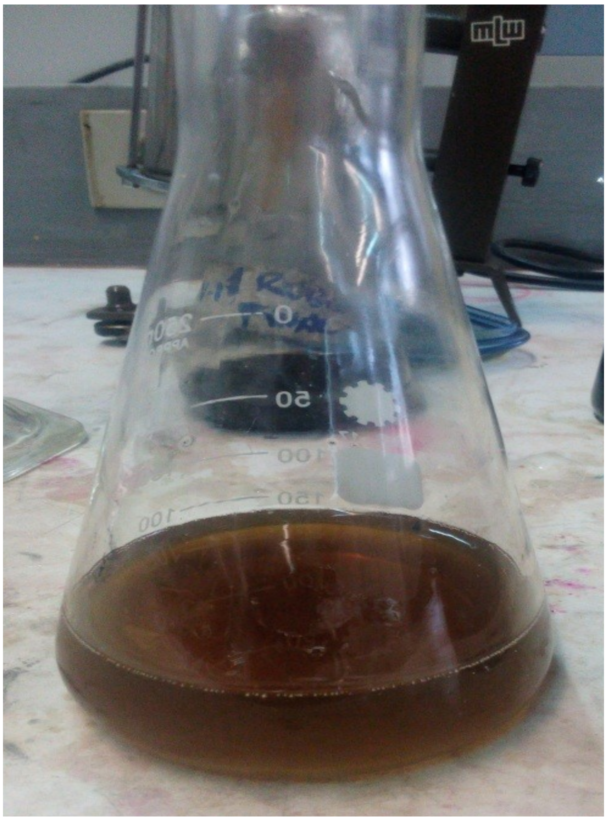

Figure 3.4 Final Treated lubricant

### 3.3.1- Treated automotivelubricant samples

The treated lubricant oil is collected by using clean beakers for it to be ready for characterisation and analysis. These experimental runs were all duplicated to ensure the consistency of the overall work. The Main tests that were gone through include the following

- ⇒ Kinematic viscosity @ 40 °C
- ⇒ Yield
- ⇒ Density

Run tests which showed better comparative results in the above main tests were selected for further treatment of Metal content, viscosity index, total acid and base number, ash content, flash point thus will be compared with the virgin and used lubricant.

### 3.4- Experimental design

Two factors were chosen for the experimental design in this study,acid and adsorbent to sample ratios which are considered to have a significant effect on the treatment as had been discussed in the previous chapters. The experimental factors and their corresponding levels are given in the table below for both Rubia Tir 7400 15W-40 and Quartz 5000-20W50 lubricants.

| **Acid Ratio** | **Adsorbent Ratio** | | |
|---|---|---|---|
| | 15% | 20% | 25% |
| **10%** | Version 1 | Version 4 | Version 7 |
| **15%** | Version 2 | Version 5 | Version 8 |
| **20%** | Version 3 | Version 6 | Version 9 |

**Table 3.5 Experimental Factors with levels.**

# 4 Result and Discussion

## 4.1 Characterization of used automotive lubricant

This chapter discusses on the outcomes of the laboratory analysis, characterisation of the used oil and finally comparing and contrasting these values and giving a detailed discussion over the results.

From the below tables the virgin oil, the used oil and treated oil analysis, it can be seen that there is a significant property alteration during application and treatment.

## 4.2 - Experimental result of treated Rubia Tir 7400 15W-40 lubricant

Some of the properties such as density (g/ml), kinematic viscosity@40 (Cst) and Yield % were evaluated for the different runs that were used in the experimental analysis.

From table 4.1 amount of Adsorbent and acid ratio's used in different runs have a significant effect on the yield, Density and kinematic viscosity. It can be deduced maximum yield, kinematic viscosity@40°c and optimum density for Rubia Tir7400 were obtained at 15% acid ratio and 25% Adsorbent ratio while minimum yield, kinematic viscosity @40°c and density were obtained at 10% Acid ratio and 15% Adsorbent ratio .

**Table 4.1- Experimental analysis result of Rubia Tir 7400**

| Std | Run | Block | Factor:Acid % | Factor:Adsorbent Ratio% | Response :Yield % | Response Density g/ml | Response 2 Kinematic Visocisty @40°C |
|---|---|---|---|---|---|---|---|
| 7 | 1 | Block 1 | 10% | 20% | 66 | 0.887594 | 60.22 |
| 14 | 2 | Block 1 | 10% | 25% | 62.4 | 0.873682 | 55.44 |
| 12 | 3 | Block 1 | 20% | 20% | 66 | 0.86972 | 53.22 |
| 18 | 4 | Block 1 | 20% | 25% | 44 | 0.883 | 60.249 |
| 9 | 5 | Block 1 | 15% | 20% | 70 | 0.873682 | 62.75 |
| 8 | 6 | Block 1 | 10% | 20% | 61 | 0.88421 | 59.714 |
| 10 | 7 | Block 1 | 15% | 20% | 69.8 | 0.8756 | 61.557 |
| 3 | 8 | Block 1 | 15% | 15% | 40 | 0.87602 | 52.96 |
| 17 | 9 | Block 1 | 20% | 25% | 44 | 0.8841 | 61.192 |
| 5 | 10 | Block 1 | 20% | 15% | 48 | 0.87878 | 59.22 |
| 16 | 11 | Block 1 | 15% | 25% | 70.1 | 0.8746 | 63.229 |
| 6 | 12 | Block 1 | 20% | 15% | 50.9 | 0.8871 | 58.602 |
| 13 | 13 | Block 1 | 10% | 25% | 55 | 0.8694 | 56.7 |
| 1 | 14 | Block 1 | 10% | 15% | 42 | 0.87478 | 58.16 |
| 2 | 15 | Block 1 | 10% | 15% | 43.2 | 0.87378 | 57.909 |
| 11 | 16 | Block 1 | 20% | 20% | 65.4 | 0.871 | 54.9 |
| 4 | 17 | Block 1 | 15% | 15% | 52.1 | 0.877 | 54.275 |
| 15 | 18 | Block 1 | 15% | 25% | 72.8 | 0.8771 | 65.23 |

### 4.2.1- Effects of Amount of Acid on Rubia Tir 7400

The experimental analysis indicated that acid percentages have a significant effect over Kinematic viscosity, density and yield while holding the adsorbent ratio constant.

From table 4.2 Yield is found to be between 42.6-49.45%, 63.5-69.9, and 44-71.45 % for constant adsorbent ratio of 15%, 20% and 25% respectively and acid ratio between 10-20%. For acid percentage of 10% 15% 20 % and a constant adsorbent of 15% ratio the yields are 42.6%, 46.05% and 49.45%. Likewise for constant adsorbent ratio of 20% and varying ratio of acid with 10%,15% and 20% the average yield was found to be 63.5%, 69.9% and 65.7% similarly for acid ratio of 10%, 15%, 20% and a constant adsorbent ratio of 25% the average yield is calculated to be 58.7%,71.45% and 44%.

The average density recovered are between 0.87-0.89 the acid ratio is comparatively lower when acid ratio is at 15% there is a comparative increment in average density while acid ratio was at 10% but then again there was no significant change in addition of acid to a higher ratio of 20% over the average densities.

Kinematic Viscosity of the treated Rubia Tir7400 is affected by the amount of acid used. For constant adsorbent ratio of 15, 20 and 25% while the acid ratio at 10% average kinematic viscosity @40° C, 58.0345 Cst, 59.967Cst and 56.05 Cst. At acid ratio of 15% average viscosity with constant adsorbent ratio of 15, 20, 25% it's observed the kinematic viscosity improved to 53.6175 Cst, 62.1535 Cst and 66.8345 Cst. Similarly at acid ratio of 20% and Adsorbent ratio of 10, 15 and 20% the following was observed 58.911 Cst, 53.71Cst and 60.7205 Cst indicating increment of acid ratio doesn't make a significant difference as it did for the other characteristic factors .

**Table 4.2- Average Experimental results of different amount of acid ratio for Rubia Tir7400**

| Acid Ratio % | Adsorbent Ratio % | Average Yield (%) | Average Density(g/ml) | Average Kinematic Viscosity @40°C(Cst) |
|---|---|---|---|---|
| 10 | 15 | 42.6 | 0.89 | 58.0345 |
| 15 | 15 | 46.05 | 0.87 | 53.6175 |
| 20 | 15 | 49.45 | 0.88 | 58.911 |
| 10 | 20 | 63.5 | 0.89 | 59.967 |
| 15 | 20 | 69.9 | 0.87 | 62.1535 |
| 20 | 20 | 65.7 | 0.88 | 53.71 |
| 10 | 25 | 58.7 | 0.89 | 56.05 |
| 15 | 25 | 71.45 | 0.87 | 66.8345 |
| 20 | 25 | 44 | 0.88 | 60.7205 |

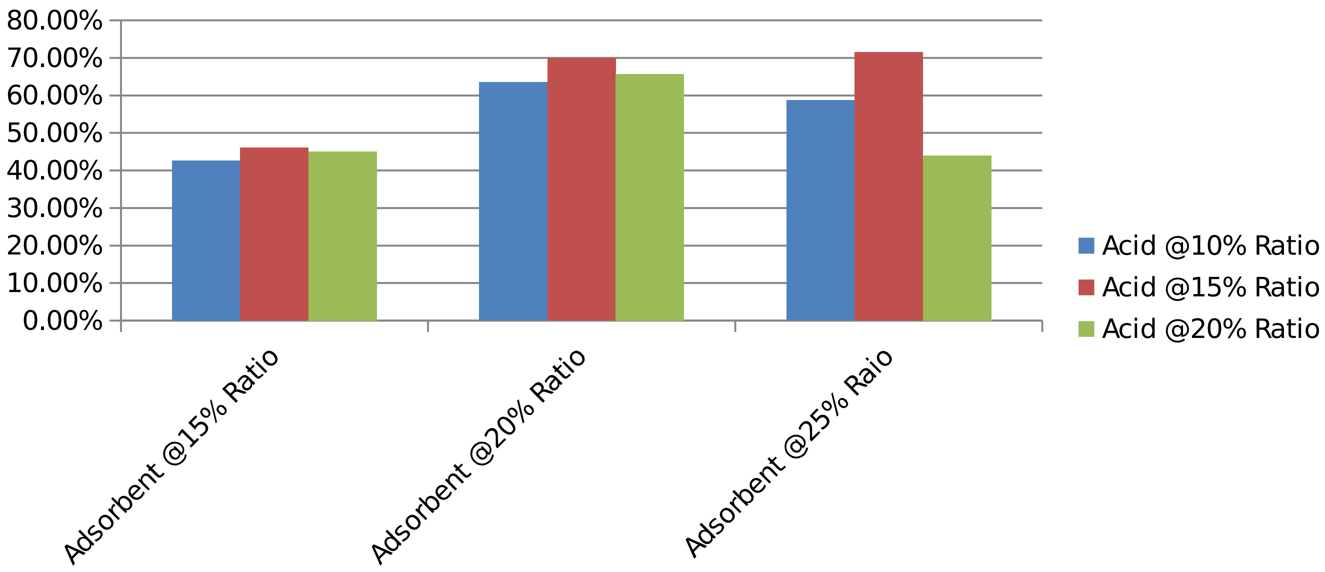

**Figure 4.1 Experimental Chart results of average Yield on different acid ratio and constant adsorbent ratio**

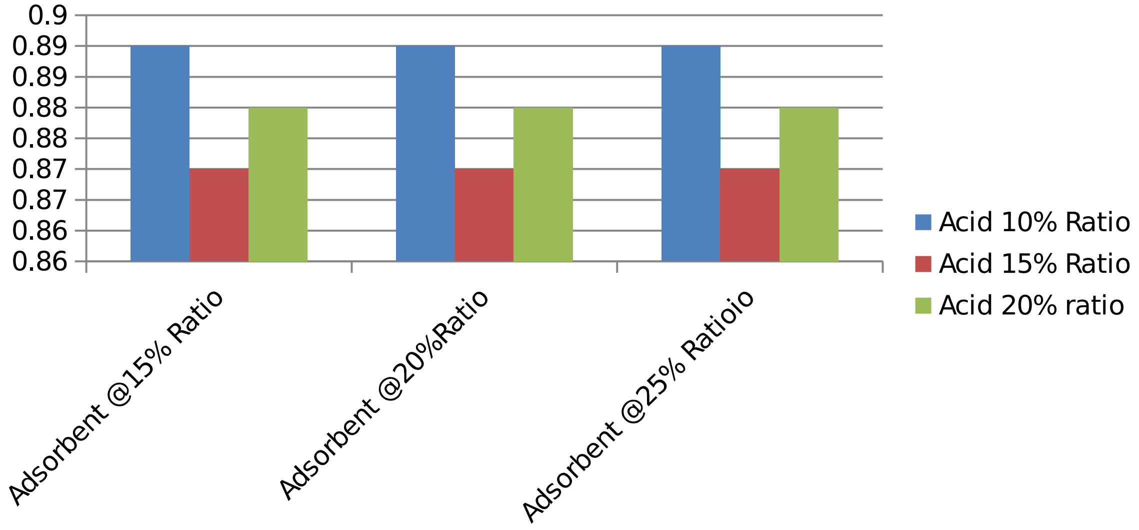

**Figure 4.2 Experimental Chart results of average density on different acid ratio and constant adsorbent ratio**

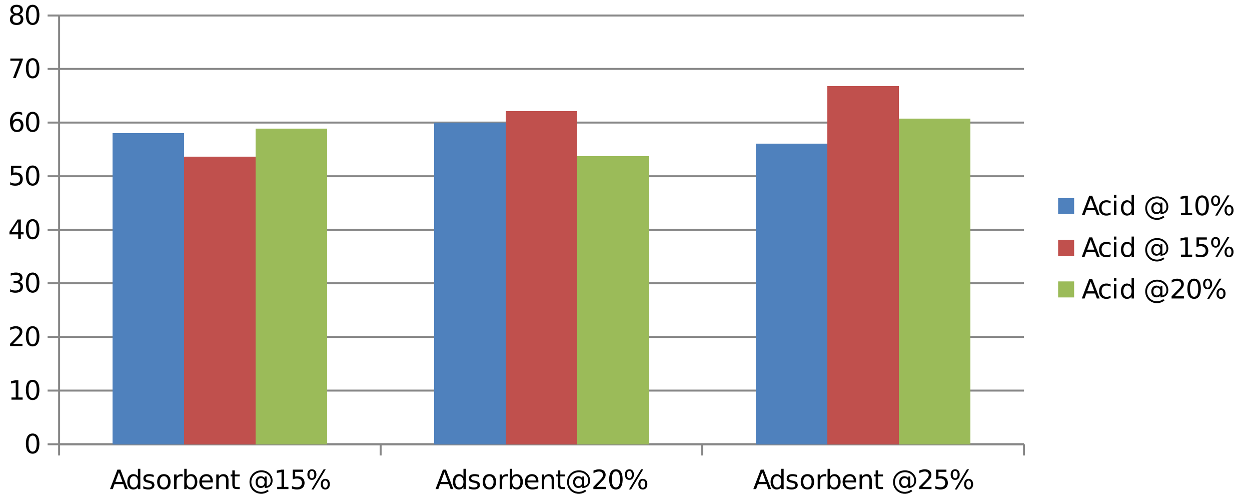

**Figure 4.3 Experimental Chart results of average kinematic viscosity@40°C on different acid ratio and constant adsorbent ratio**

### 4.2.2- Effects of Adsorbent Ratio on Rubia Tir 7400

It is noted that the effect of adsorbent ratio have much effect over the selected parameters of the oil with the amount of acid used however with the amount of acid ratio above 15% the amount of acid ratio used didn't have much effect over the treated oil.

Yield is found to be between 42.6-63.5%, 46.05-71.45, and 44-65.7% for constant acid ratio of 10%, 15% and 20% respectively and adsorbent ratio between 15-25%. From the table below for adsorbent ratio of 15% 20% 25 % and a constant adsorbent of 10% ratio the yields are 42.6%, 63.5% and 58.7%. Likewise for constant acid ratio of 15% and varying ratio of adsorbent with 15%20% and 25% the average yield was found to be 46.05%, 69.9% and 71.45% similarly for acid ratio of 20% and adsorbent ratio of 15 , 20, 25% the average yield is calculated to be 49.45%,65.7% and 44%.

The average density recovered is between 0.87-0.89, it shows that it is not that different from the analysis given for Effect of Acid ratio.Kinematic Viscosity of the treated Rubia Tir7400 is affected by the amount of adsorbent used. For constant acid ratio of 10, 15 and 20% while the adsorbent ratio at 15% average kinematic viscosity @40° C, 58.0345 Cst, 53.6175 Cst and 58.911Cst. At adsorbent ratio of 20% average viscosity with constant acid ratio of 10, 15, 20% it's observed the kinematic viscosity improved to 59.967 Cst, 62.535 Cst and 53.71 Cst. Similarly at adsorbent ratio of 25% and Acid ratio of 10, 15 and 20% the following was observed 56.05Cst, 66.8345Cst and 60.7205 Cst indicating increment of adsorbent ratio make a significant difference in obtaining a better quality treated oil which is observed visually.

**Table 4.3- Average Experimental results of different amount of adsorbent ratio for Rubia Tir7400**

| Adsorbent Ratio % | Acid Ratio % | Average Yield(%) | Average Density(g/ml) | Average Kinematic Viscosity @40°C(Cst) |
|---|---|---|---|---|
| 15 | 10 | 42.6 | 0.89 | 58.03 |
| 20 | 10 | 63.5 | 0.89 | 59.96 |
| 25 | 10 | 58.7 | 0.89 | 56.05 |
| 15 | 15 | 46.05 | 0.87 | 53.61 |
| 20 | 15 | 69.9 | 0.87 | 62.15 |
| 25 | 15 | 71.45 | 0.87 | 66.83 |
| 15 | 20 | 49.45 | 0.88 | 58.91 |
| 20 | 20 | 65.7 | 0.88 | 53.71 |
| 25 | 20 | 44 | 0.88 | 60.72 |

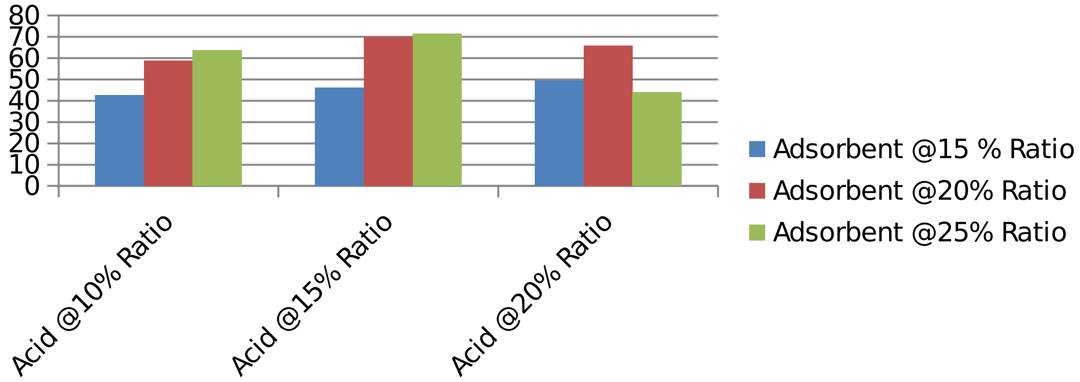

**Figure 4.4 Experimental Chart results of average yield on different adsorbent ratio and constant acid ratio**

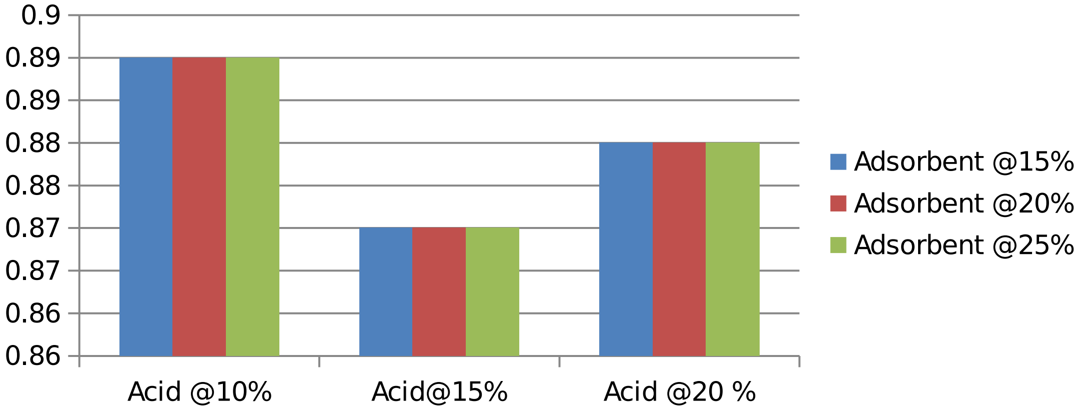

**Figure 4.5 Experimental Chart results of average density on different adsorbent ratio and constant acid ratio**

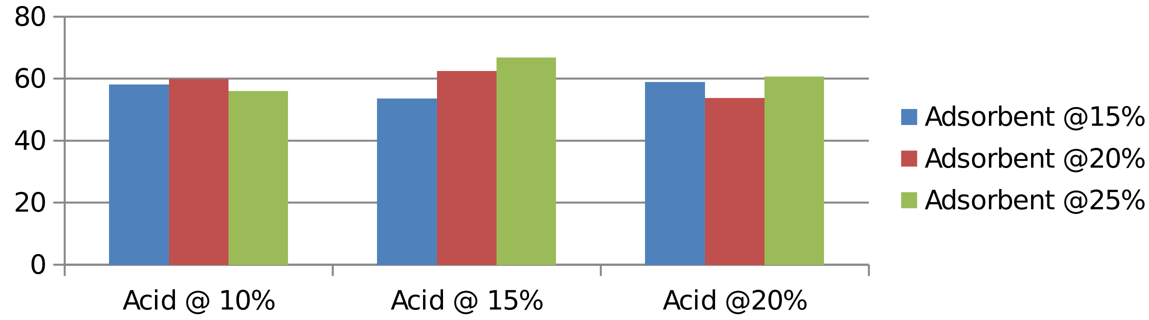

**Figure 4.6 Experimental Chart results of average kinematic viscosity @40°C on different adsorbent ratio and constant acid ratio**

## 4.3 - Experimental analysis result of Quartz 5000-20W-50 by using Acid Clay treatment

For the experimental analysis of the lubricant Quartz the same principle applies used for Rubia in the previous section. Again it can be deduced maximum yield, kinematic viscosity@40°Cis obtained at 15% acid ratio and 25% Adsorbent ratio while minimum yield, kinematic viscosity @40°Cand density were obtained at 10%Acid ratio and 15% Adsorbent ratio .

**Table 4.4- Experimental analysis result of Quartz 5000-20W-50**

| Std. | Run | Block | Factor1:Acid ratio% | Factor2: Adsorbent Ratio % | Response1 Yield% | Response 2 Density(g/ml) | Response3: Kinematic Viscosity @40° Cst |
|---|---|---|---|---|---|---|---|
| 6 | 1 | Block 1 | 20% | 15% | 62 | 0.893 | 108 |
| 8 | 2 | Block 1 | 10% | 20% | 59 | 0.891 | 99.1 |
| 10 | 3 | Block 1 | 15% | 20% | 64 | 0.894 | 105 |
| 9 | 4 | Block 1 | 15% | 20% | 66 | 0.889 | 107.9 |
| 1 | 5 | Block 1 | 10% | 15% | 48 | 0.8913 | 101.1 |
| 11 | 6 | Block 1 | 20% | 20% | 60 | 0.889 | 107.2 |
| 13 | 7 | Block 1 | 10% | 25% | 69 | 0.889 | 102.7 |
| 17 | 8 | Block 1 | 20% | 25% | 48 | 0.891 | 106.7 |
| 3 | 9 | Block 1 | 15% | 15% | 64 | 0.8936 | 107 |
| 12 | 10 | Block 1 | 20% | 20% | 54 | 0.891 | 106 |
| 4 | 11 | Block 1 | 15% | 15% | 53 | 0.892 | 102 |
| 2 | 12 | Block 1 | 10% | 15% | 50 | 0.8912 | 103 |
| 14 | 13 | Block 1 | 10% | 25% | 68 | 0.893 | 101.4 |
| 5 | 14 | Block 1 | 20% | 15% | 60 | 0.8907 | 106 |
| 18 | 15 | Block 1 | 20% | 25% | 49 | 0.893 | 106 |
| 16 | 16 | Block 1 | 15% | 25% | 73 | 0.8901 | 110 |
| 15 | 17 | Block 1 | 15% | 25% | 72 | 0.887 | 109.6 |
| 7 | 18 | Block 1 | 10% | 20% | 62 | 0.894 | 100.1 |

### 4.3.1- Effects of amount of acid and adsorbent on Quartz 5000-20w-50

The experimental analysis here as well indicated that acid percentages have a significant effect over Kinematic viscosity and yield while holding the adsorbent ratio constant.

From Table 4.5, yield is found to be between 49-61%, 57-65, and 48-72.5 % for constant adsorbent ratio of 15%, 20% and 25% respectively and acid ratio between 10-20%. Average kinematic viscosity is found to be 102.05-107 %, 99.61-106.59 %, 102.04-109.83 % for constant adsorbent ratio between 15-25% and acid ratio between 10-20% respectively.It is noted that the effect of adsorbent ratio have much effect over the selected parameters of the oil with the amount of acid used ; with the amount of acid ratio above 15% the amount of acid ratio used didn't have much effect over the treated oil as like Rubia Tir7400.

From Table 4.6 Yield is found to be between 49-68.5%, 58.5-72.45, and 48.5-61% for constant acid ratio of 10%, 15% and 20% respectively and adsorbent ratio between 15-25%. Kinematic Viscosity of the treated Quartz 5000-20W-50 is affected by the amount of adsorbent used. For constant acid ratio of 10, 15 and 20% while the adsorbent ratio at 15% average kinematic viscosity @40° C, 102.05 Cst, 104.5 Cst and 107Cst. At adsorbent ratio of 20% average viscosity with constant acid ratio of 10, 15, 20% it's observed the kinematic viscosity improved to 99.605 Cst, 106.45 Cst and 106.59 Cst. Similarly at adsorbent ratio of 25% and Acid ratio of 10, 15 and 20% the following was observed 102.04Cst, 109.825 Cst and 106.355 Cst. indicating increment of adsorbent ratio make a significant difference in obtaining a better quality treated oil.

Table 4.5- Average Experimental results of different amount of acid ratio for Quartz 5000-20W-50

| **Acid Ratio %** | **Adsorbent Ratio %** | **Average Yield (%)** | **Average Density(g/ml)** | **Average Kinematic Viscosity @40°C(Cst)** |
|---|---|---|---|---|
| 10 | 15 | 49 | 0.89125 | 102.05 |
| 15 | 15 | 58.5 | 0.8928 | 104.5 |
| 20 | 15 | 61 | 0.89185 | 107 |
| 10 | 20 | 60.5 | 0.8925 | 99.61 |
| 15 | 20 | 65 | 0.8915 | 106.45 |
| 20 | 20 | 57 | 0.89 | 106.59 |
| 10 | 25 | 68.5 | 0.891 | 102.04 |
| 15 | 25 | 72.5 | 0.88855 | 109.83 |
| 20 | 25 | 48.5 | 0.892 | 106.35 |

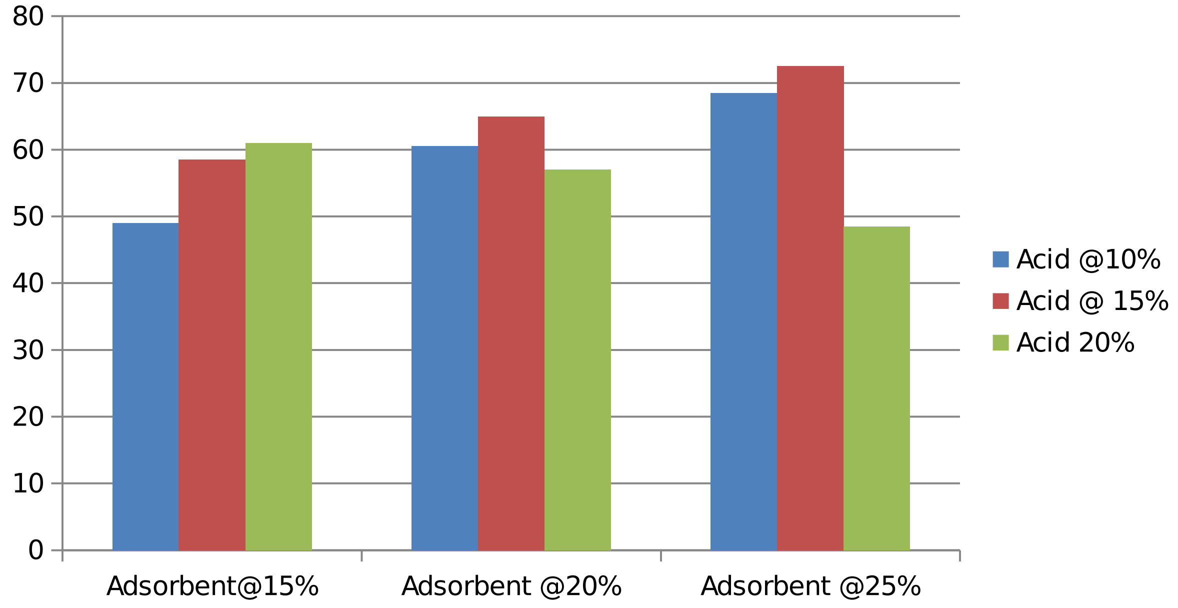

Figure 4.7 Experimental Chart results of average yield on different acid ratio and constant adsorbent ratio

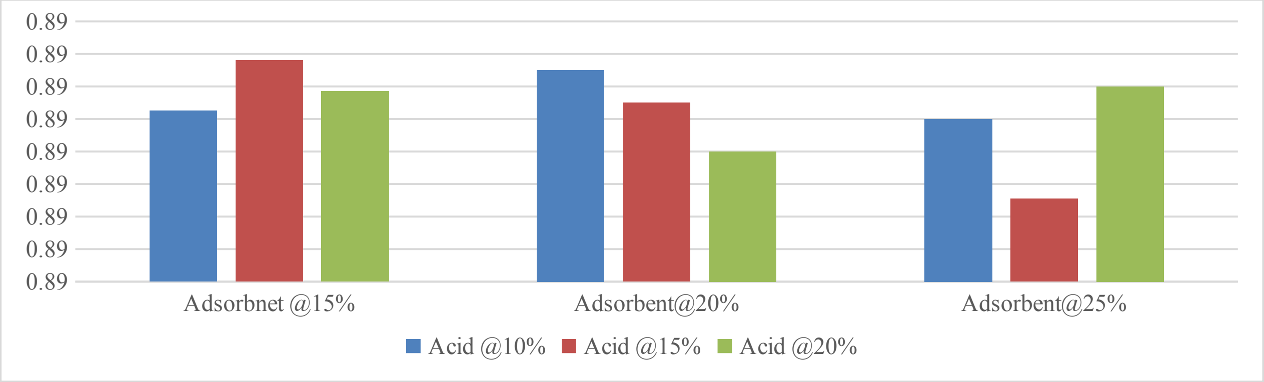

Figure 4.8 Experimental Chart results of average densities on different acid ratio and constant adsorbent ratio

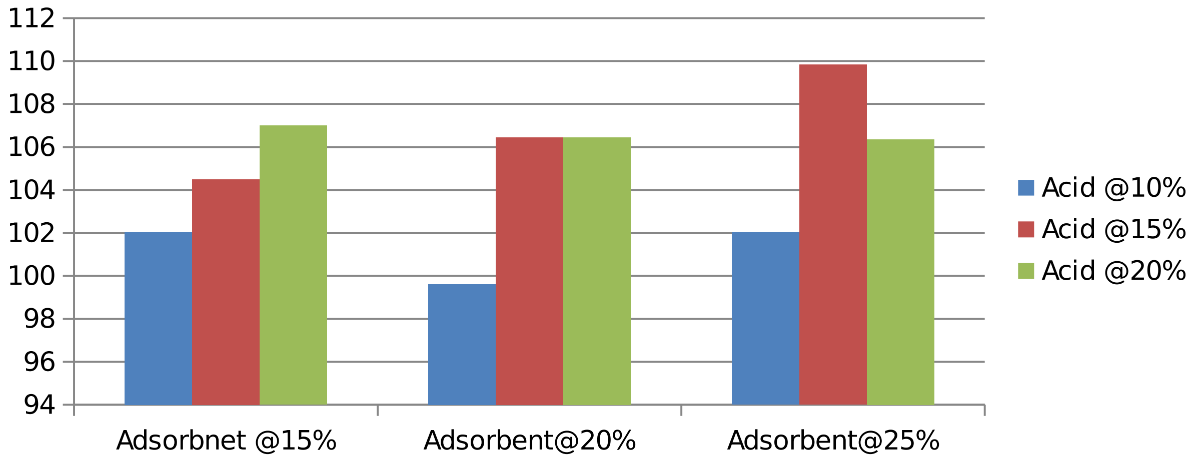

**Figure 4.9 Experimental Chart results of average kinematic viscosity @40 on different acid ratio and constant adsorbent ratio**

Table 4.6- Average Experimental results of different amount of adsorbent ratio for Quartz 50W-20

| Adsorbent Ratio % | Acid Ratio % | Average Yield (%) | Average Density(g/ml) | Average Kinematic Viscosity @40°C(Cst) |
|---|---|---|---|---|
| 15 | 10 | 49 | 0.89125 | 102.05 |
| 20 | 10 | 60.5 | 0.8925 | 99.605 |
| 25 | 10 | 68.5 | 0.891 | 102.04 |
| 15 | 15 | 58.5 | 0.8928 | 104.5 |
| 20 | 15 | 65 | 0.8915 | 106.45 |
| 25 | 15 | 72.5 | 0.88855 | 109.825 |
| 15 | 20 | 61 | 0.8915 | 107 |
| 20 | 20 | 57 | 0.89 | 106.59 |
| 25 | 20 | 48.5 | 0.892 | 106.355 |

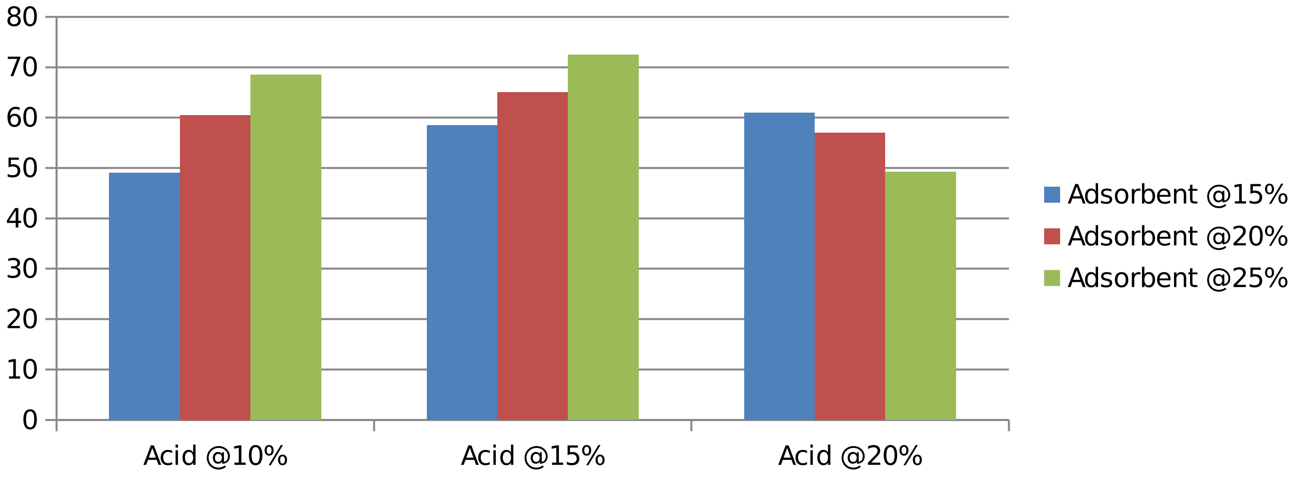

Figure 4.10 Experimental Chart results of average yield on different adsorbent ratio and constant acid ratio

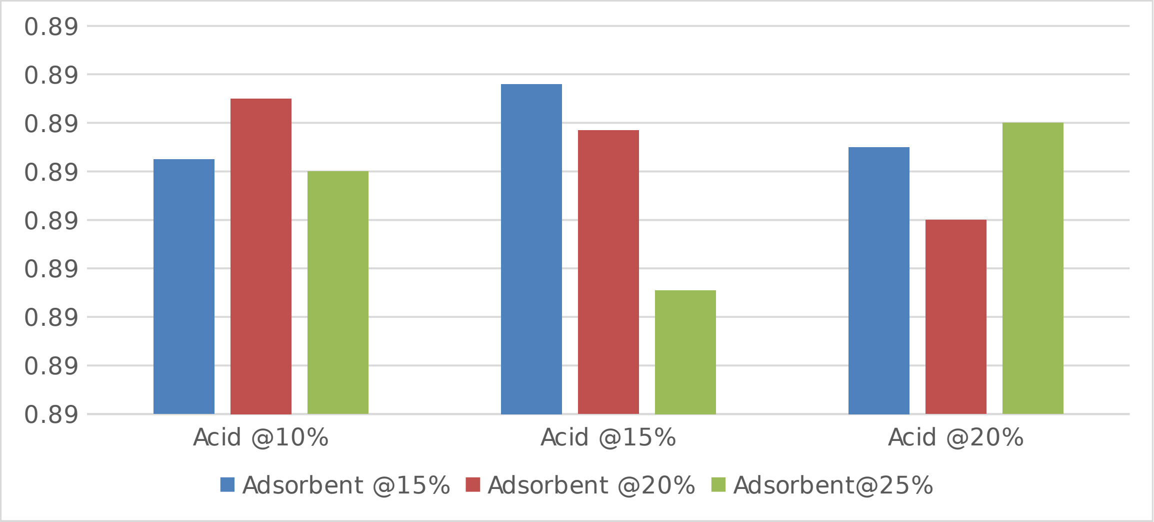

Figure 4.11 Experimental Chart results of average density on different adsorbent ratio and constant acid ratio

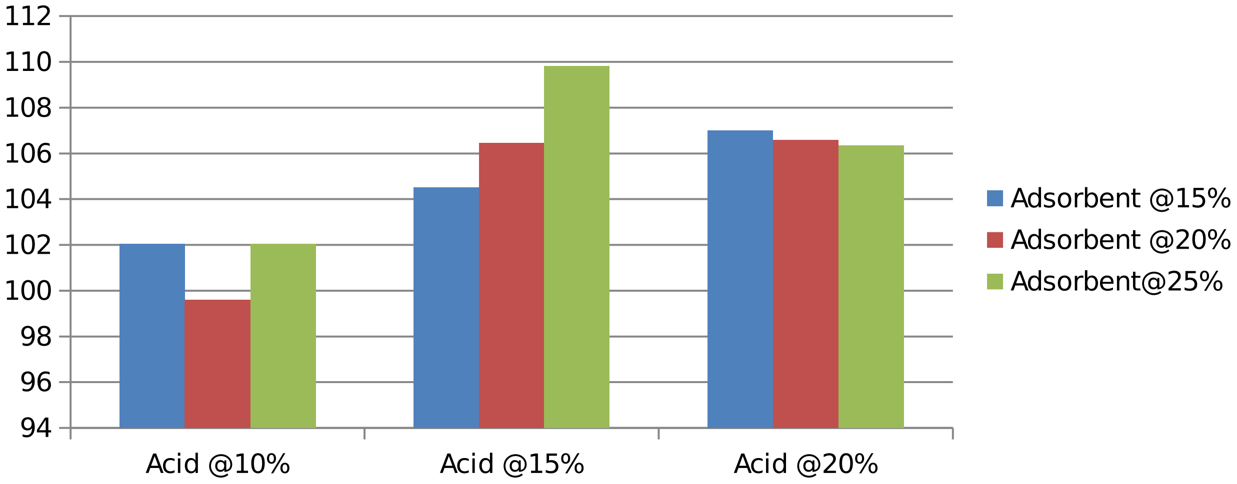

Figure 4.12 Experimental Chart results of average kinematic viscosity @ 40 °C on different adsorbent ratio and constant acid ratio

## 4.4Interpretation of the Results

Table 4.7 and 4.8 shows the comparative result that was gathered from the laboratory treatment, used oil characterization and Virgin oil guideline for both Rubia and Quartz.

From the above it can be seen that the viscosity testing results indicates the presence of contamination in used lubricant. The oxidized and polymerized products dissolved and suspended in the oil may cause and increase of the oil viscosity, while decrease in the viscosity of engine oils indicate fuel contamination.

Oxidation of base oils during use in an engine environment produces corrosive oxidized products, deposits and varnishes which led to an increase in the viscosity[36]. From table 4.1 Kinematic viscosity @ 40°C increment from initial virgin oil value of 98.7 Cst to 102 Cst is indicative of oxidation and suspension of polymerized products; treated oil resulted 65.23 Cst which is the result of the destructive nature of sulphuric acid removing the oxidized products, deposits and varnishes from the used oil the same principle applies when kinematic viscosity is @100°C reducing the contaminant from 13.4 Cst to 14.2 Cst. This may also mean removing the additives which have been added to enhance the viscosity.

With the same conceptual basis; Table 4.2 tells the kinematic viscosity @40°C increased from the initial 176.4Cst to 180.4Cst due to oxidation while after treatment it has decreased to 110.68 Cst at the same time the viscosity @100°C changed from 24Cst to 11.473Cst after treatment.

A substantially low flash point of engine oil is a reliable indicator that the oil has become contaminated with volatile products such as gasoline. Lowering the value of flash point of used engine oil is because of presence of light fuels. The flash point of fresh Rubia and Quartz oils are 236°C and 240°C respectively because they contain different additives which contribute to improving the flash point. Table 4.1 shows that the used oil's flash point had decreased to 170 °C but after treatment it has significantly increased to 220°C, while in table 4.2 flash point increased from 167.8 °C to 220°C.

TBN is a measure of alkaline base additives package to neutralize the acidic products composition and is used as an indication for the engine oil's replacement time. This is because TBN depletes with time in service; higher TBN values are more effective at neutralizing acids for a longer period of time. The rate of consumption of the additives is an indication of the projected service life of the oil[36]. From the table 4.1 the virgin and the treated oil both have higher values, this is due to the presence of a high alkaline additive package that was not depleted and has the ability to neutralize large quantity of acids, organic, inorganic bases including amino compounds and certain heavy metals, whilst used oils TBN is low due to the depletion of the additive package as a result of the high temperature and the acid effect of water and oxidant product contamination. The results increased from 5.3 to 9.3 for Rubia Tir 7400 and TBN for Quartz increased from 5.3 to 8.08 respectively.

Density is influenced by the chemical composition of the oil. An increase in the amount of aromatic compounds in the oil results in an increase in the density, while an increase in the saturated compounds results in a decrease in the density. Used oil density increases with the presence of increasing amounts of solids in the used engine oil.[37]. Table 4.1 showed used oil increase in density of 0.946268g/ml from 0.888g/ml virgin oil to 0.8746g/ml for treated oil. Table 4.2 showed used oil increment to 0.94834g/ml from 0.8921 g/ml Virgin oil to 0.889g/ml treated oil.

Metal contents had significantly reduced for both Quartz 50W and Rubia Tir 7400 and it's thoroughly discussed here.

Copper (Cu) is introduced to the engine oils after use from bearings and wearing's, engine oil coolers can also contribute to copper content along with some oil additives. The recycled refined oil has a copper concentration of 0.47ppm compared to 42.17ppm of used oil for table 4.1 whereas for table 4.2 Copper concentrations decreased from 12.84 ppm to 0.86ppm. Lead (Pb) is associated with bearing wear, fuel source and contamination due to the use of galvanized containers. [38]. Lead concentration decreased after treatment to less than 0.01 ppm from 0.03 ppm for both tables. Iron (Fe) concentration in engine oil depends on the bearing conditions inside the engine. If the bearings fail, iron concentrations in used engine oil increases. In the engine the wear rises at a faster rate during the starting of the engine.[39]. Table 4.1 shows the concentration of iron decreasing from 283.48ppm to 50.62ppm while table 4.2 shows decrease in concentration of iron from 583.39ppm to 62.63ppm. Cadmium is introduced in the engine oil as a contaminant during usage. Base oils are free from cadmium.[40]. In Table 4.1 Cadmium accounts less than 0.2 ppm in the treated oil while the used was found to be 0.46ppm, in Table 4.2 it accounts less than 0.2ppm in treated and 0.2 ppm in the used oil. Zinc (Zn) and Calcium (Ca) are introduced into the base oil as a form of additive package as anti-oxidant, corrosion inhibitor, anti-wear, detergent and extreme pressure tolerance [41]. From Table 4.1 zinc was reduced to 0.46ppm from 105.83 ppm while Ca was reduced to lesser than one ppm from 175.06ppm and for Table 4.2 Zinc was reduced from 105.83ppm to 4.33ppm while calcium was reduced from 201.6 to less than one. Nickel was reduced from 0.53ppm to 0.3ppm in Table 4.1 and from 0.48ppm to less than 0.5ppm in Table 4.2. Magnesium (Mg) and Molybdenum (Mo) was reduced from 9.35ppm to 7.64ppm and 52.56 ppm to 3.02ppm respectively in Table 4.1. Table 4.2 showed that Magnesium (Mg) and Molybdenum (Mo) were reduced from 8.36ppm to 6.6ppm and 74.76 ppm to 1.92ppm respectively.

Table 4.7 Results of Rubia Tir 7400 virgin oil, used oil and treated oil

| Property | Virgin oil | Used Oil | | Treated Oil |
|---|---|---|---|---|
| | | Test Method | Result | |
| **Flash Point** | 236 | ASTM (04.04)D92 | 170 | 220 |
| **Kinematic-viscosity @40° (Cst)** | 98.7 | D 445 | 102.21 | 65.23 |
| **Kinematic-viscosity @100°(Cst)** | 13.4 | D 445 | 14.2 | 8.21 |
| **Viscosity Index** | 136 | D 2270 | 141.86 | 92.472 |
| **Density (g/ml)** | 0.888 | D 4052 | 0.94 | 0.8771 |
| **TBN[mg KOH/g(sample)]** | 11 | ASTM D2896rev.11 | 5.3 | 9.85 |
| **ConradsonCarbon Residue (%)** | - | D189 | 1.83 | 0.48 |
| **Calcium (ca)** | - | ASTM(04.04)D92 | 175.06 | <1.00 |
| **Zinc (Zn)** | - | ASTM(04.04)D92 | 105.83 | 0.46 |
| **Arsenic (As)** | - | EPA(GFAAS) | <0.5 | <0.1 |
| **Cadmium(Cd)** | - | EPA(GFAAS) | 0.46 | <0.2 |
| **Chromium(Cr)** | - | ASTM(04.04)D92 | <1.00 | <0.5 |
| **Lead** | - | ASTM(04.04)D92 | 0.03 | <0.01 |
| **Copper** | - | ASTM(04.04)D92 | 42.17 | 0.47 |
| **Iron** | - | ASTM(04.04)D92 | 283.48 | 50.62 |
| **Nickel** | - | EPA (GFAAS) | 0.53 | 0.3 |
| **Magnesium** | - | ASTM(04.04)D92 | 9.35 | 7.64 |
| **Molybdenum** | - | EPA(GFAAS) | 52.56 | 3.02 |

Table 4.8 Results of Quartz 20-W50 virgin oil, used oil and treated oil

| Property | Virgin oil | Used Oil | | Treated Oil |
|---|---|---|---|---|
| | | Test Method | Result | |
| **Flash Point** | 240 | ASTM (04.04)D92 | 167.8 | 220 |
| **Kinematic viscosity @40** | 170.4 | D 445 | 180.4 | 110.68 |
| **Kinematic viscosity@100** | 19.1 | D 445 | 24 | 11.473 |
| **Viscosity Index** | 123 | D 2270 | 163.195 | 88.882 |
| **Density (g/ml)** | 0.8921 | D 4052 | 0.94 | 0.889 |
| **TBN[mg KOH/g(sample)]** | 12 | ASTM D2896rev.11 | 5.3 | 8.08 |
| **ConradsonCarbon Residue (%)** | - | D189 | 3.02 | 0.4 |
| **Calcium (ca)** | - | ASTM(04.04)D92 | 201.6 | <1.00 |

| | | | | |
|---|---|---|---|---|
| **Zinc (Zn)** | - | ASTM(04.04)D92 | 105.83 | 4.33 |
| **Arsenic (As)** | - | EPA(GFAAS) | <0.5 | <0.2 |
| **Cadmium(Cd)** | - | EPA(GFAAS) | <0.2 | <0.2 |
| **Chromium(Cr)** | - | ASTM(04.04)D92 | 0.01 | <0.01 |
| **Lead** | - | ASTM(04.04)D92 | 0.03 | <0.01 |
| **Copper** | - | ASTM(04.04)D92 | 12.84 | 0.86 |
| **Iron** | - | ASTM(04.04)D92 | 583.39 | 62.63 |
| **Nickel** | - | EPA (GFAAS) | 0.48 | <0.5 |
| **Magnesium** | - | ASTM(04.04)D92 | 8.36 | 6.6 |
| **Molybdenum** | - | EPA(GFAAS) | 74.76 | 1.92 |

# 5- Conclusion and Recommendation

## 5.1- Conclusion

This research has shown that used engine oil can be recycled by using acid clay treatment. The method produces base oil comparable to that produced using conventional methods. Optimum conditions for recycling used engine oil using this method are simple, it only requires settling of the used oil, dehydration, distillation (atmospheric and /vacuum), mixing with bentonite clay and finally centrifugation. The base oil produced by this method has a potential to be used in car engines after the proper additive addition.

The results have showed that during purification of fuel oil there is an improvement in viscosity @40°C, viscosity @ 100°C, density, flash point, carbon residue, TBN, and metal contents as a major impurity is significantly reduced.

The extent at which these impurities were removed depends on the amount of acid (in ratio) and the amount of adsorbent (in ratio) that was used.

The effect of acid and adsorbent ratio was studied on the recovery of base oil from the used oil. From the results gathered the efficiency depends on the adsorbent and acid ratios. It was observed the recovery generated increased with increasing acid concentration till the optimum acid concentration was achieved but using more acid beyond this optimum value was fruitless. Whereas yield recovered showed better bleaching and yield percentage with increasing adsorbent ratio.

Maximum average recovery for Rubia Tir 7400, of 71.45 % was obtained when acid ratio was at 15% while adsorbent ratio at 25%, whereas the minimum recovery yield of 40% of recovery at 10% acid and 15% adsorbent ratio. Maximum average Density was 0.87g/ml where 66.8345Cst was maximum kinematic viscosity. Minimum average density and Kinematic viscosity was recovered to be 0.89g/ml and 58.0345 Cst respectively at 10% Acid and 15% adsorbent ratio.

For Quartz 50W-20 Maximum average recovery yield, of 72.5 % was obtained when acid ratio was at 15% while adsorbent ratio at 25%, whereas the minimum recovery yield of 49% of recovery at 10% acid and 15% adsorbent ratio. Maximum average Density was 0.89g/ml where 109.83 Cst was maximum kinematic viscosity. Minimum average density and Kinematic viscosity was recovered to be 0.89g/ml and 102.05 Cst respectively at 10% Acid and 15% adsorbent ratio.

Optimization of the experimental results was conducted using Design Expert software through complete analysis of variance. 15% acid ratio and 25% adsorbent ratio combination was selected as an optimum operating condition for the used oil recovery process for both Rubia Tir 7400 and Quartz 50W-20. The combination gave maximum desirability of 0.941 and 0.924 for Rubia and Quartz respectively. The desirable yield, density and kinematic viscosity for Rubia Tir 7400 commergave71.45%,0.88g/ml,64.229 Cst respectively. Quartz 50W-20 le yield, density and kinematic viscosity 72.5%, 0.89 g/ml and 109.825Cst respectively.

## 5.2- recommendation.

From this thesis it is recommended to broaden the scope of study to enhance it to industrial scale. Parameters such as temperature, pressure, mixing temperature and time, desludging period, contact time of adsorbent, speed and time of centrifuge have to be thoroughly studied. Some of the things to be suggested other than the operating parameters are the operating condition.

⇒ The major drawback of this technology is the production of acidic sludge. As acid sludge composition is similar to bitumen, as it had been suggested in section 2.9.1 of this research, the hazardous by product can be transformed into different useful materials, however a research had to be done fully.

⇒ It is noticed during experiment that the volume and size of the beakers and flasks used showed a significant difference over the treatment procedure; therefore further study should be put into it.

⇒ The type/origin/ and particle size of the clay that will be used for percolation have to be thoroughly studied.

⇒ This study have to be done in a better quality laboratory setup with proper distillation and vacuum set up with digital temperature and pressure display.

⇒ Study has to compromise the addition of additives to enable comparison with the treated and virgin oil.

⇒ Investigation on the distilled light fuel for proper reuse.

⇒ Capital costs should be studied for erecting and running of the plant

⇒ The procedure had to be done in a hood to minimize contamination of the working environment including operating personnel health and safety; while distilling for removal of the light fuels awful and hazardous gases can emit thereby affecting the surrounding. Therefore it is highly recommended for proper safety equipment.

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# APPENDIX-A

## A1- Experimental Design and Analysis of Data for Rubia Tir 7400

ANOVA

**Response1 : Yield**

**ANOVA for Selected Factorial Model**

**Analysis of variance table [Partial sum of squares]**

| **Source** | **Sum of Squares** | **DF** | **Mean Square** | **F-Value** | **Prob > F** | |
|---|---|---|---|---|---|---|
| Model | 2098.01 | 8 | 262.25 | 19.37 | <0.0001 | - significant |
| *A* | *297.94* | *2* | *148.97* | *11.00* | *0.0038* | |
| *B* | *1254.02* | *2* | *627.01* | *46.31* | *< 0.0001* | |
| *AB* | *546.04* | *4* | *136.51* | *10.08* | *0.0022* | |
| Pure Error | 121.85 | 9 | 13.54 | | | |
| Cor Total | 2219.86 | 17 | | | | |

The Model F-value of 19.37 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, AB 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. | 3.68 | R-Squared | 0.9451 |
| Mean | 56.82 | Adj R-Squared | 0.8963 |
| C.V. | 6.48 | Pred R-Squared | 0.7804 |
| PRESS | 487.42 | Adeq Precision | 11.088 |

The "Pred R-Squared" of 0.7804 is in reasonable agreement with the "Adj R-Squared" of 0.8963.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 11.088 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 | 56.82 | 1 | 0.87 | 54.85 | 58.78 |
| A[1] | -1.88 | 1 | 1.23 | -4.66 | 0.89 |
| A[2] | 5.65 | 1 | 1.23 | 2.88 | 8.42 |
| B[1] | -10.78 | 1 | 1.23 | -13.56 | -8.01 |
| B[2] | 9.55 | 1 | 1.23 | 6.78 | 12.32 |
| A[1]B[1] | -1.55 | 1 | 1.73 | -5.47 | 2.37 |
| A[2]B[1] | -5.63 | 1 | 1.73 | -9.56 | -1.71 |
| A[1]B[2] | -0.98 | 1 | 1.73 | -4.91 | 2.94 |
| A[2]B[2] | -2.12 | 1 | 1.73 | -6.04 | 1.81 |

Final Equation in terms of coded Factors

Yield =+56.82-1.88* A[1]+5.65 * A[2]-10.78 * B[1]+9.55 * B[2]-1.55 *A[1]B[1]-5.63 *A[2]B[1]-0.98 * A[1]B[2]-2.12 * A[2]B[2]

**Response 2: Desnity**

**ANOVA for Selected Factorial Model**

**Analysis of variance table [Partial sum of squares]**

| **Source** | **Sum of Squares** | **DF** | **Mean Square** | **F Value** | **Prob > F** | |
|---|---|---|---|---|---|---|
| Model | 4.902E-004 | 8 | 6.128E-005 | 9.70 | 0.0013 | significant |
| *A* | *3.235E-005* | *2* | *1.618E-005* | *2.56* | *0. 1318* | *0.1318* |
| *B* | *3.505E-006* | *2* | *1.752E-006* | *0.28* | *0.764* | |
| *AB* | *4.544E-004* | *4* | *1.136E-004* | *17.98* | *0.0003* | *0.0003* |
| Pure Error | 5.687E-005 | 9 | 6.319E-006 | | | |
| Cor Total | 5.471E-004 | 17 | | | | |

The Model F-value of 9.70 implies the model is significant. There is only a 0.13% 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 AB 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. | 2.514E-003 | R-Squared | 0.8960 |
| Mean | 0.88 | Adj R-Squared | 0.8036 |
| C.V. | 0.29 | Pred R-Squared | 0.5842 |
| PRESS | 2.275E-004 | Adeq Precision | 8.744 |

The "Pred R-Squared" of 0.5842 is not as close to the "Adj R-Squared" of 0.8036 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 8.744 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 | 0.88 | 1 | 5.925E-004 | 0.88 | 0.88 |
| A[1] | -4.500E-005 | 1 | 8.379E-004 | -1.941E-003 | 1.851E-003 |
| A[2] | -1.619E-003 | 1 | 8.379E-004 | -3.515E-003 | 2.765E-004 |
| B[1] | 6.240E-004 | 1 | 8.379E-004 | -1.272E-003 | 2.520E-003 |
| B[2] | -3.183E-004 | 1 | 8.379E-004 | -2.214E-003 | 1.577E-003 |
| A[1]B[1] | -3.585E-003 | 1 | 1.185E-003 | -6.266E-003 | -9.043E-004 |
| A[2]B[1] | 2.190E-004 | 1 | 1.185E-003 | -2.462E-003 | 2.900E-003 |
| A[1]B[2] | 8.979E-003 | 1 | 1.185E-003 | 6.299E-003 | 0.012 |
| A[2]B[2] | -7.077E-004 | 1 | 1.185E-003 | -3.388E-003 | 1.973E-003 |

**Final Equation in Terms of Coded Factors:**

Desnity =+0.88-4.500E-005 * A[1]-1.619E-003 * A[2]+6.240E-004 * B[1]-3.183E-004 *B[2]-3.585E-003 * A[1]B[1]+2.190E-004 * A[2]B[1]+8.979E-003 * A[1]B[2]-7.077E-004 *A[2]B[2]

**Response 3: Kinematic Viscosity @40°C**

**ANOVA for Selected Factorial Model**

**Analysis of variance table [Partial sum of squares]**

| **Source** | **Sum of Squares** | **DF** | **Mean Square** | **F Value** | **Prob > F** |
|---|---|---|---|---|---|
| Model | 205.85 | 8 | 25.73 | 35.20 | < 0.0001 |
| significant | | | | | |
| *A* | *16.69* | *2* | *8.34* | *11.42* | *0.0034* |
| *B* | *36.52* | *2* | *18.26* | *24.98* | *0.0002* |
| *AB* | *152.64* | *4* | *38.16* | *52.21* | *< 0.0001* |
| Pure Error | 6.58 | 9 | 0.73 | | |
| Cor Total | 212.43 | 17 | | | |

The Model F-value of 35.20 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, AB 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. | 0.85 | R-Squared | 0.9690 |
| Mean | 58.64 | Adj R-Squared | 0.9415 |
| C.V. | 1.46 | Pred R-Squared | 0.8761 |
| PRESS | 26.31 | Adeq Precision | 17.554 |

The "Pred R-Squared" of 0.8761 is in reasonable agreement with the "Adj R-Squared" of 0.9415.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 17.554 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 | 58.64 | 1 | 0.20 | 58.18 | 59.10 |
| A[1] | -0.62 | 1 | 0.28 | -1.26 | 0.028 |
| A[2] | 1.36 | 1 | 0.28 | 0.72 | 2.00 |
| B[1] | -1.79 | 1 | 0.28 | -2.43 | -1.14 |
| B[2] | 0.086 | 1 | 0.28 | -0.56 | 0.73 |
| A[1]B[1] | 1.80 | 1 | 0.40 | 0.89 | 2.71 |
| A[2]B[1] | -4.60 | 1 | 0.40 | -5.51 | -3.68 |
| A[1]B[2] | 1.86 | 1 | 0.40 | 0.95 | 2.77 |
| A[2]B[2] | 2.07 | 1 | 0.40 | 1.16 | 2.98 |

**Final Equation in Terms of Coded Factors:**

Kinematic Viscosity @40 =+58.64-0.62 * A[1]+1.36 * A[2]-1.79 * B[1]+0.086 * B[2]+1.80 * A[1]B[1]-4.60 * A[2]B[1] +1.86 * A[1]B[2]+2.07 * A[2]B[2]

# APPENDIX-B

## B-1 Diagnostic Plots

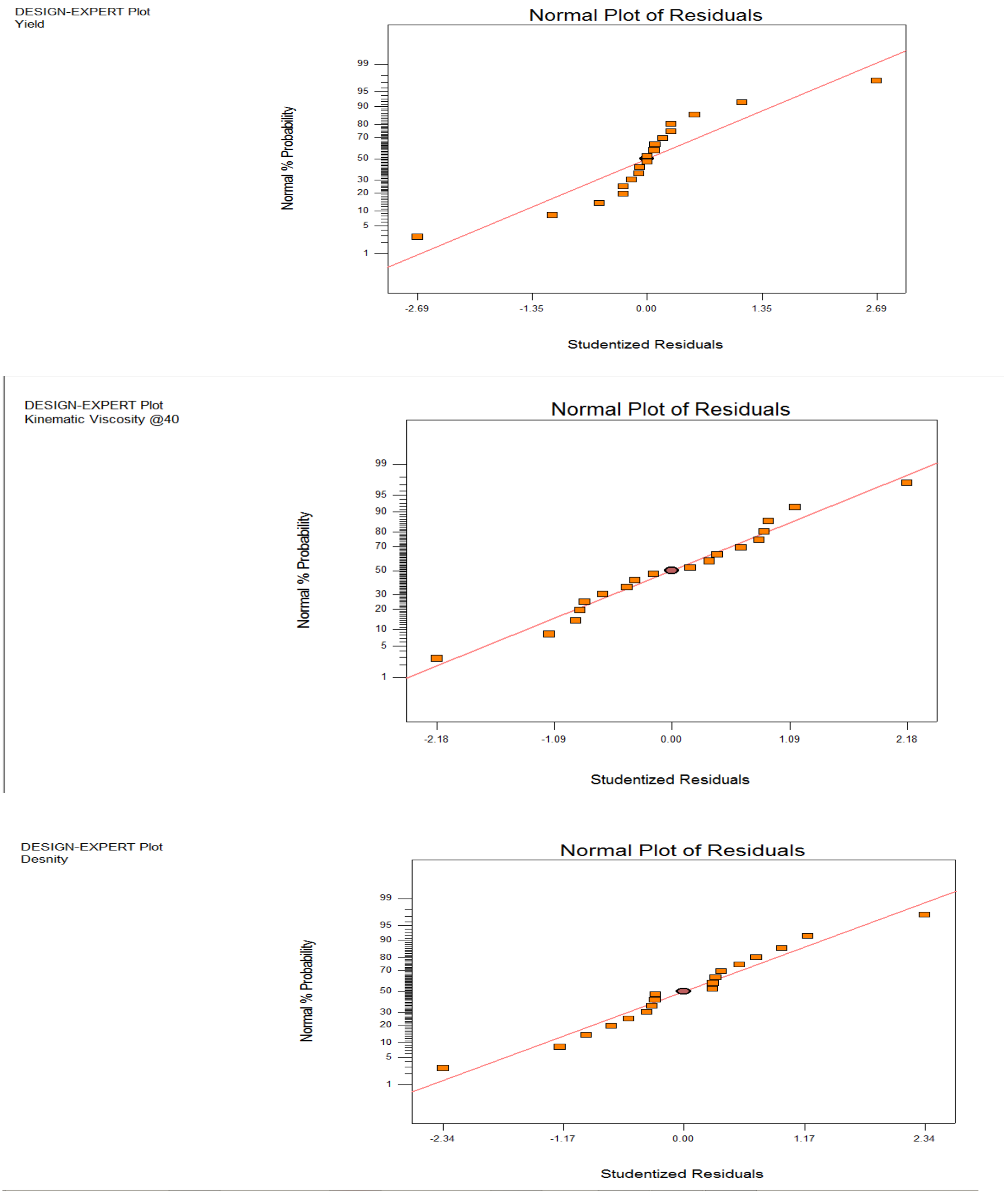


Figure B-1: Normal Plot of residuals

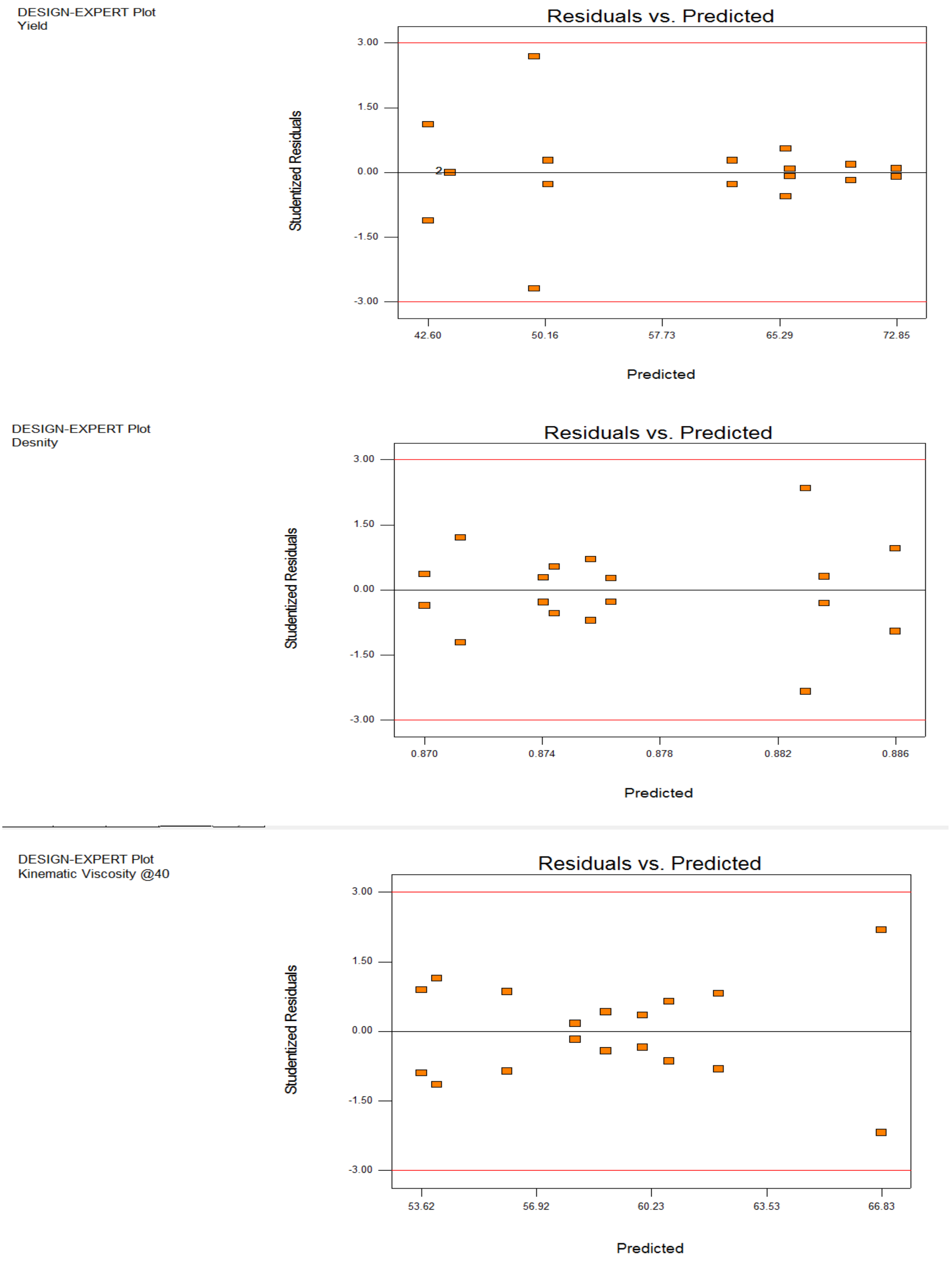


Figure B-2 : Plot of Residuals Vs. Predicted

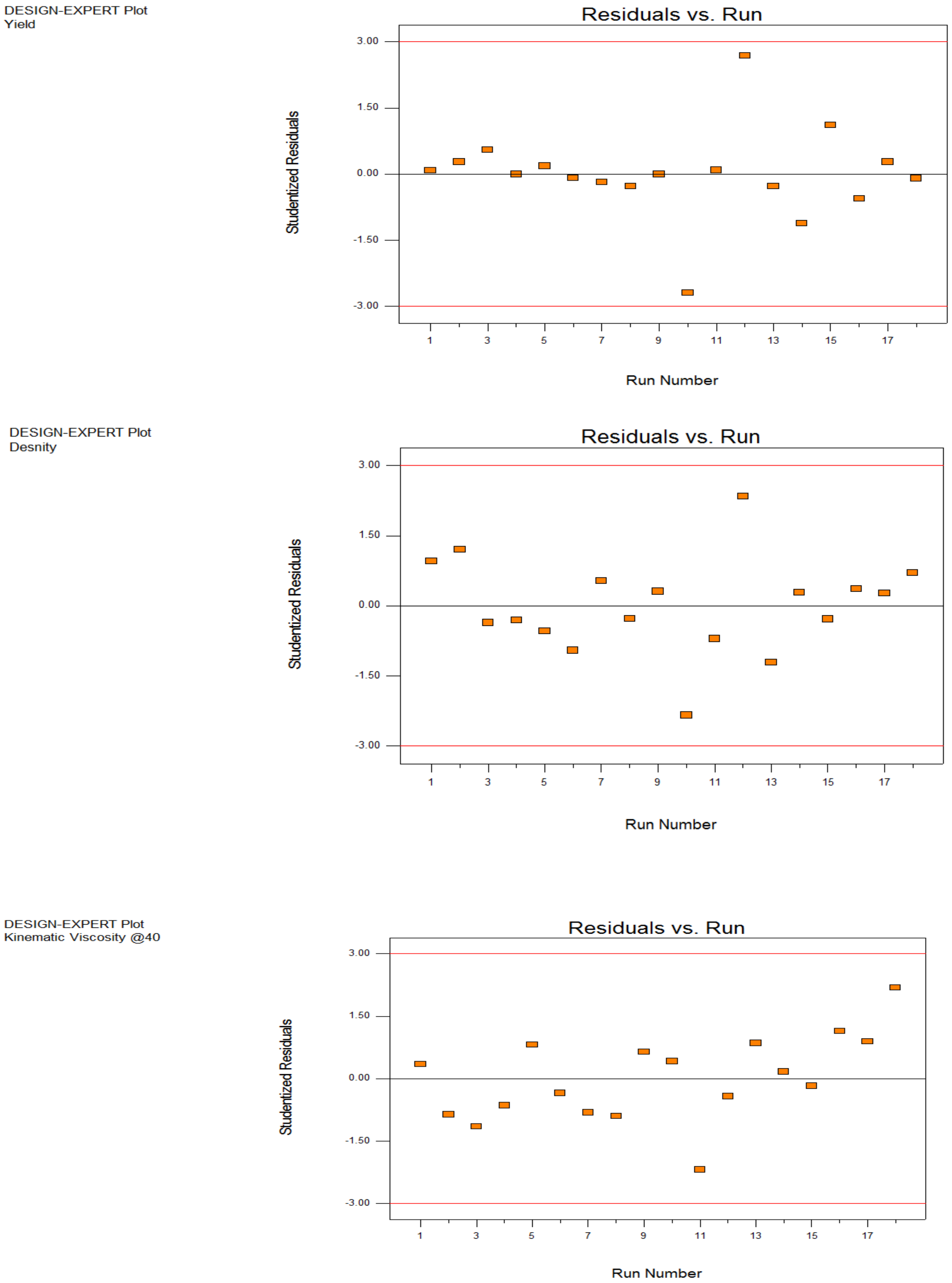
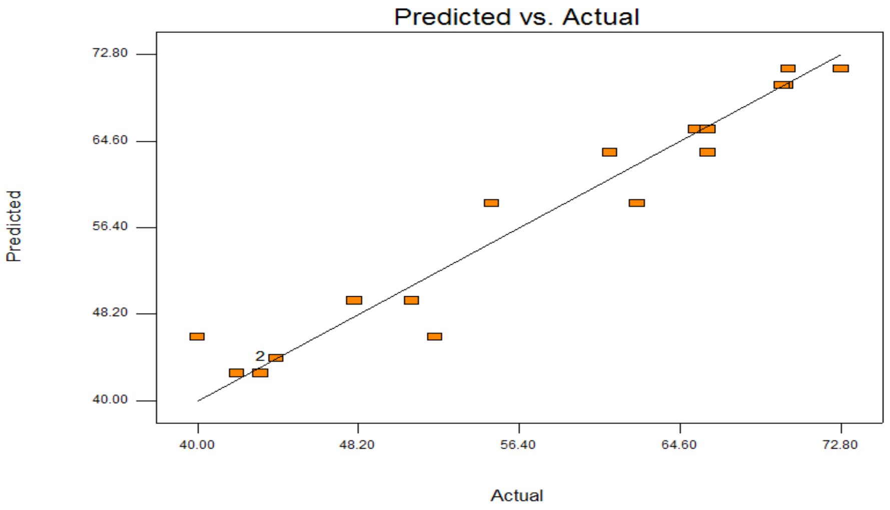
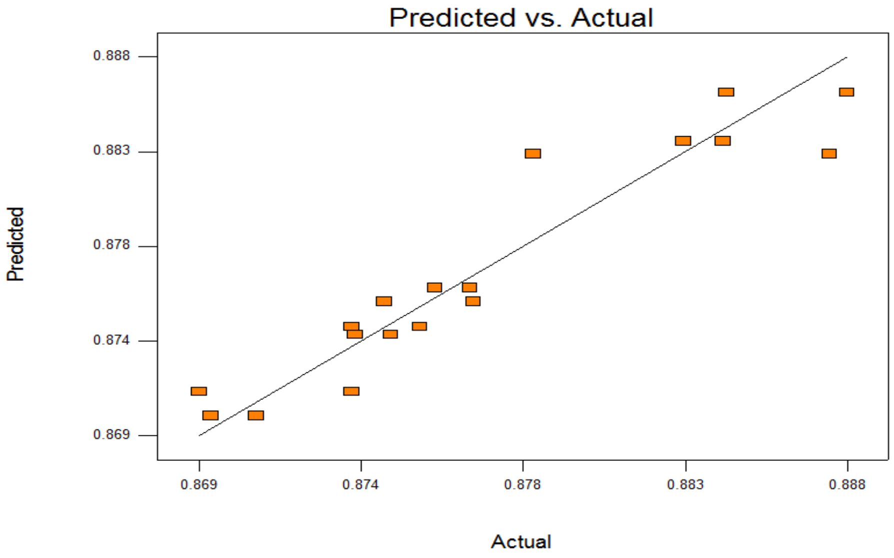


Figure B-3: Plot of externally studentized residual

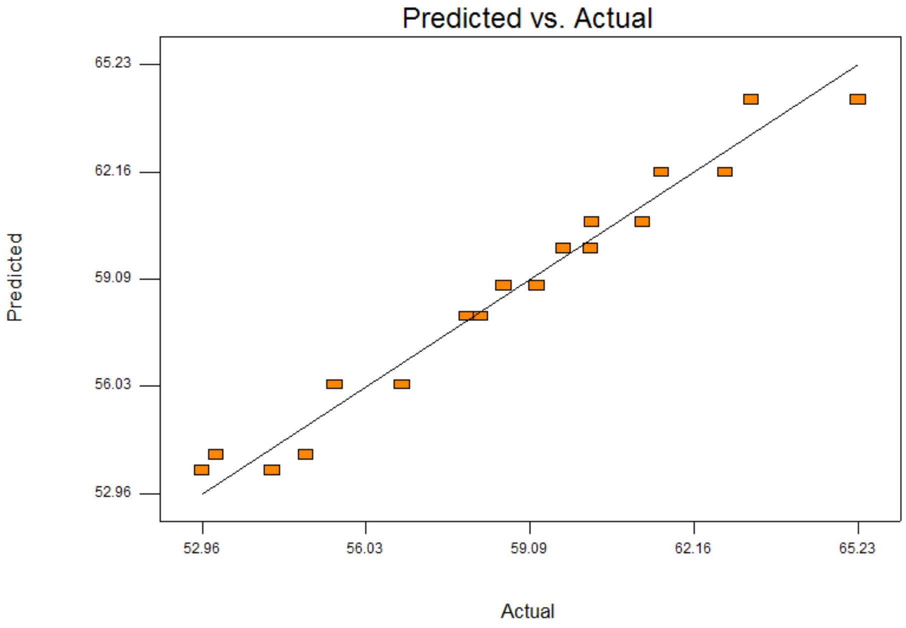
DESIGN-EXPERT Plot
Yield



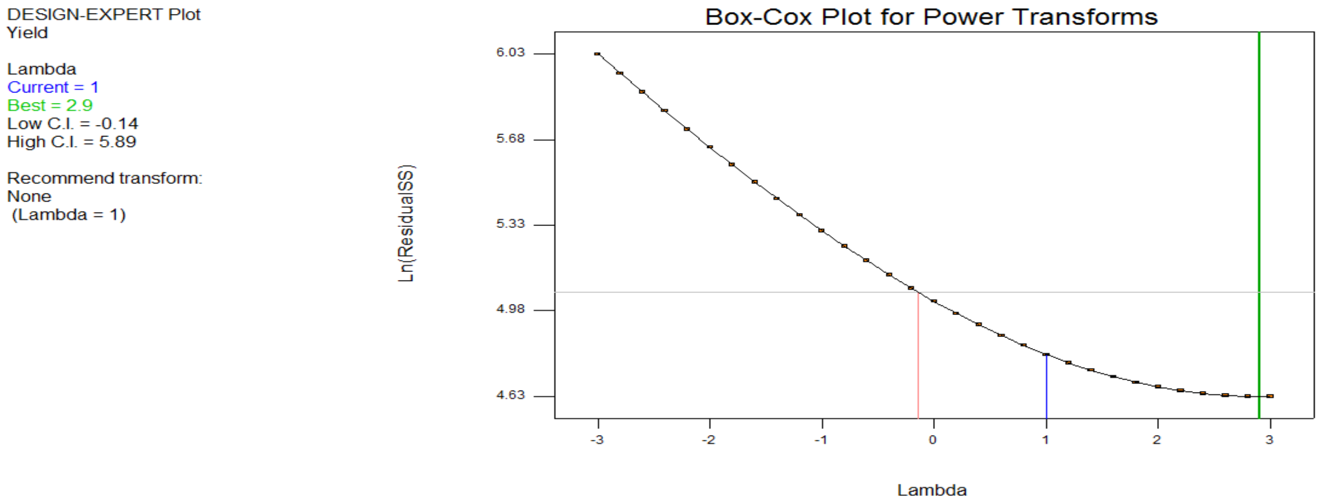
DESIGN-EXPERT Plot
Desnity



DESIGN-EXPERT Plot
Kinematic Viscosity @40



FigureB-4: Plot of Predicted vs. Actual values



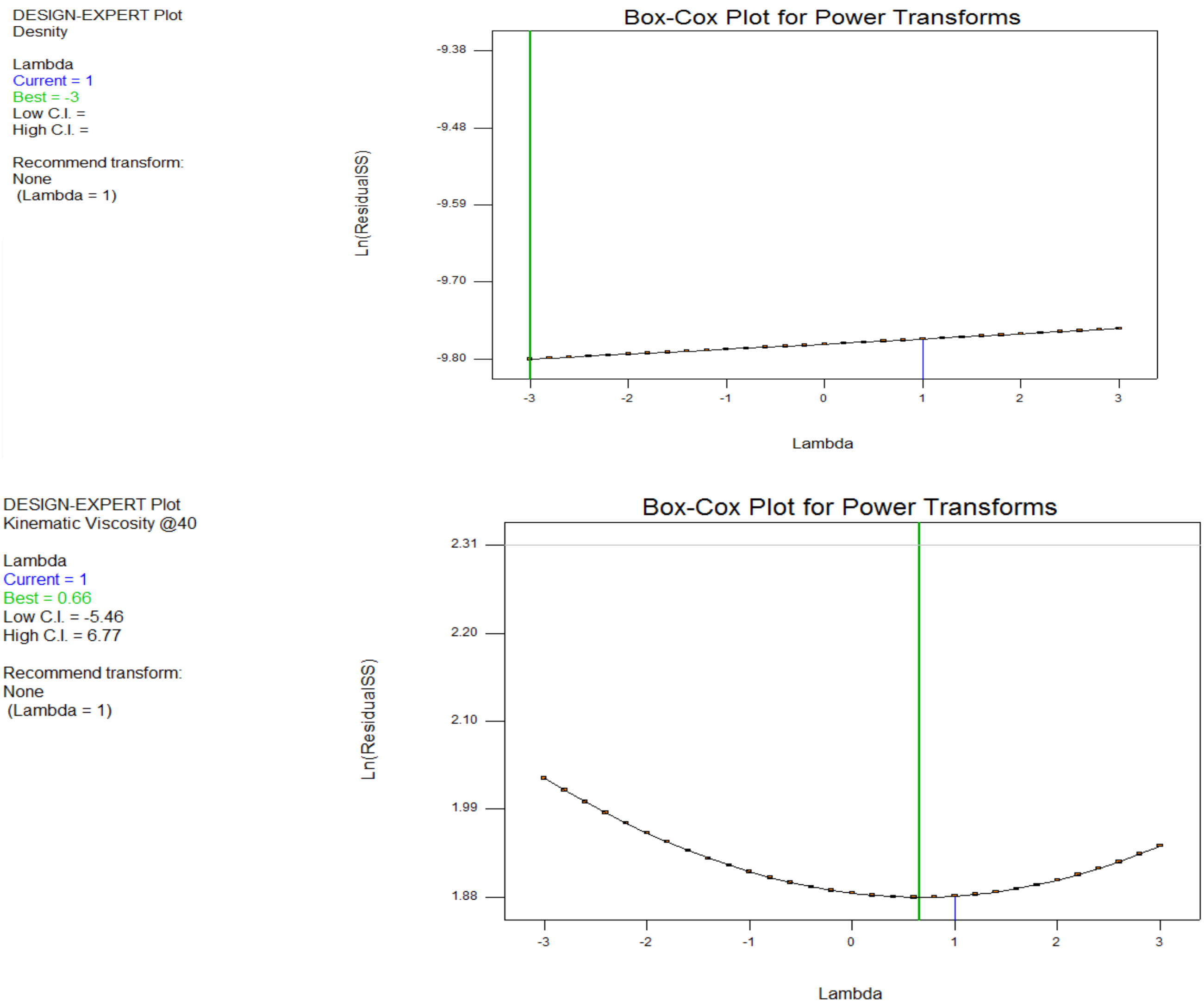


Figure B-5: Box-Cox plot for power transforms

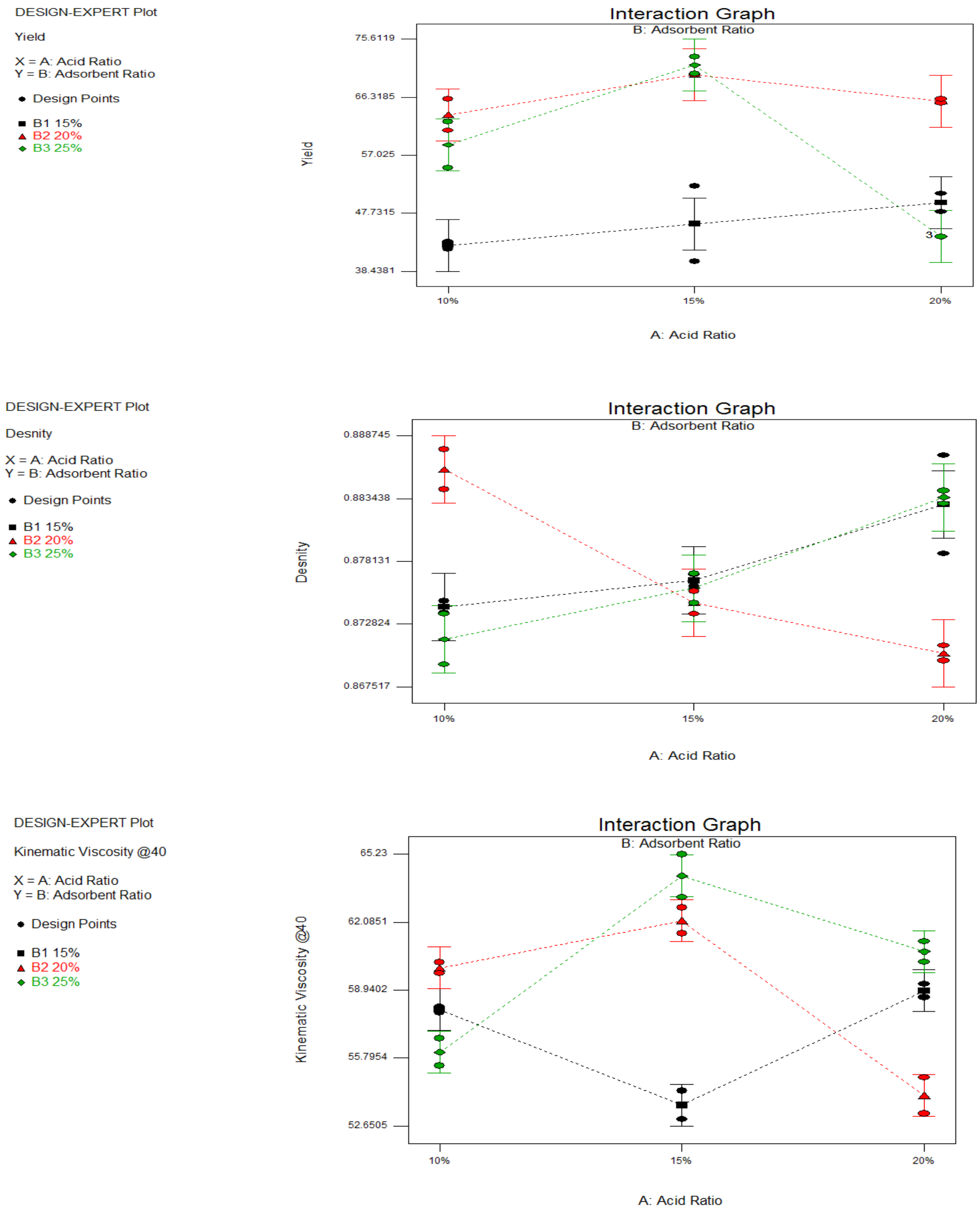


Figure B-6 Model graph for the different responses

# APPENDIX- C

## C1-Experimental Design and Analysis of Data for Quartz 5000-20W-50

**Response1 : Yield**

**ANOVA for Selected Factorial Model**

**Analysis of variance table [Partial sum of squares]**

| **Source** | **Sum of Squares** | **DF** | **Mean Square** | **F Value** | **Prob > F** | |
|---|---|---|---|---|---|---|
| Model | 1038.44 | 8 | 129.81 | 12.910. | 0004 | significant |
| *A* | *294.78* | *2* | *147.39* | *14.66* | *0.0015* | |
| *B* | *152.44* | *2* | *76.22* | *7.58* | *0.0118* | |
| *AB* | *591.22* | *4* | *147.81* | *14.70* | *0.0006* | |
| Pure Error | 90.50 | 9 | 10.06 | | | |
| Cor Total | 1128.94 | 17 | | | | |

The Model F-value of 12.91 implies the model is significant. There is only a 0.04% 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, AB 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. | 3.17 | R-Squared | 0.9198 |
| Mean | 60.06 | Adj R-Squared | 0.8486 |
| C.V. | 5.28 | Pred R-Squared | 0.6793 |
| PRESS | 362.00 | Adeq Precision | 10.703 |

The "Pred R-Squared" of 0.6793 is in reasonable agreement with the "Adj R-Squared" of 0.8486."Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 10.703 indicates an adequate signal. This model can be used to navigate the design space.

| | Coefficient | | Standard | 95% CI | 95% | CI |
|---|---|---|---|---|---|---|
| **Term** | **Estimate** | **DF** | **Error** | **Low** | **High** | |
| Intercept | 60.06 | 1 | 0.75 | 58.36 | 61.75 | |
| A[1] | -0.72 | 1 | 1.06 | -3.11 | 1.67 | |
| A[2] | 5.28 | 1 | 1.06 | 2.89 | 7.67 | |
| B[1] | -3.89 | 1 | 1.06 | -6.28 | -1.50 | |
| B[2] | 0.78 | 1 | 1.06 | -1.61 | 3.17 | |
| A[1]B[1] | -6.44 | 1 | 1.49 | -9.83 | -3.06 | |
| A[2]B[1] | -2.94 | 1 | 1.49 | -6.33 | 0.44 | |
| A[1]B[2] | 0.39 | 1 | 1.49 | -2.99 | 3.77 | |
| A[2]B[2] | -1.11 | 1 | 1.49 | -4.49 | 2.27 | |

**Final Equation in Terms of Coded Factors:**

Yield =+60.06-0.72 * A[1]+5.28 * A[2]-3.89 * B[1]+0.78 * B[2]-6.44 * A[1]B[1]-2.94 *A[2]B[1]+0.39 * A[1]B[2]-1.11 * A[2]B[2]

**Response 2: Density**

**ANOVA for Selected Factorial Model**

**Analysis of variance table [Partial sum of squares]**

| Source | Sum of Squares | DF | Mean Square | F Value | Prob > F | |
|---|---|---|---|---|---|---|
| Model | 2.550E-004 | 8 | 3.187E-006 | 6.34 | 0.0060 | significant |
| *A* | *1.949E-004* | *2* | *9.744E-005* | 19.38 | *0.0005* | |
| *B* | *2.058E-006* | *2* | *1.029E-006* | *0.2* | *0.8187* | |
| *AB* | *5.805E-005* | *4* | 1.451*E-005* | *2.89* | *0.0860* | |
| Pure Error | 4.526E-005 | 9 | | | | 5.029E-006 |
| Cor Total | 3.003E-004 | 17 | | | | |

The "Model F-value" of 6.34 implies the model is not significant relative to the noise. There is a 0.6 % 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. | 2.243E-003 | R-Squared | 0.8493 |
| Mean | 0.89 | Adj R-Squared | 0.7153 |
| C.V. | 0.25 | Pred R-Squared | 0.3970 |
| PRESS | 1.810E-004 | Adeq Precision | 7.126 |

The "Pred R-Squared" of 0.3970is not close to the"Adeq Precision" of 0.7153 as one might normally excpect. This may indicate a large block effect or a possible problem with your model and/or ddta. Things to consider are model reduction, response transformation, outliers, etc
‘ Adeq precision’ measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 7.126 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 | 4.826E-004 | 0.89 | 0.89 |
| A[1] | 3.111E-004 | 1 | 6.825E-004 | -1.233E-003 | 1.855E-003 |
| A[2] | -3.222E-004 | 1 | 6.825E-004 | -1.866E-003 | 1.222E-003 |
| B[1] | 6.944E-004 | 1 | 6.825E-004 | -8.496E-004 | 2.238E-003 |
| B[2] | 6.111E-005 | 1 | 6.825E-004 | -1.483E-003 | 1.605E-003 |
| A[1]B[1] | -1.028E-003 | 1 | 9.653E-004 | -3.211E-003 | 1.156E-003 |
| A[2]B[1] | 1.156E-003 | 1 | 9.653E-004 | -1.028E-003 | 3.339E-003 |
| A[1]B[2] | 8.556E-004 | 1 | 9.653E-004 | -1.328E-003 | 3.039E-003 |
| A[2]B[2] | 4.889E-004 | 1 | 9.653E-004 | -1.695E-003 | 2.672E-003 |

**Final Equation in Terms of Coded Factors:**

Density =+0.89-4.522E-003* A[1]+1.311E-003*A[2]-2.222E-004* B[1]-2.5556E-004* B[2]+2.2222E-003 * A[1]B[1]-6.111E-004 * A[2]B[1]+2.556E-004 *A[1]B[2]-2.078E-004 * A[2]B[2]

**Response 3:** **Kinematic Viscosity @ 40**

**ANOVA for Selected Factorial Model**

**Analysis of variance table [Partial sum of squares]**

| **Source** | **Sum of Squares** | **DF** | **Mean Square** | **F Value** | **Prob > F** | |
|---|---|---|---|---|---|---|
| Model | 161.09 | 8 | 20.14 | 7.93 | 0.0027 | significant |
| *A* | *123.70* | *2* | *61.85* | *24.35* | *0.0002* | |
| *B* | *11.92* | *2* | *5.96* | *2.35* | *0.1513* | |
| *AB* | *25.47* | *4* | *6.37* | *2.51* | *0.1160* | |
| Pure Error | 22.86 | 9 | 2.54 | | | |
| Cor Total | 183.95 | 17 | | | | |

The Model F-value of 7.93 implies the model is significant. There is only a 0.27% 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. | 1.59 | R-Squared | 0.8757 |
| Mean | 104.94 | Adj R-Squared | 0.7653 |
| C.V. | 1.52 | Pred R-Squared | 0.5029 |
| PRESS | 91.44 | Adeq Precision | 9.069 |

The "Pred R-Squared" of 0.5029 is not as close to the "Adj R-Squared" of 0.7653 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 9.069 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 | 104.94 | 1 | 0.38 | 104.09 | 105.79 |
| A[1] | -3.70 | 1 | 0.53 | -4.91 | -2.50 |
| A[2] | 1.99 | 1 | 0.53 | 0.79 | 3.19 |
| B[1] | -0.42 | 1 | 0.53 | -1.62 | 0.78 |
| B[2] | -0.72 | 1 | 0.53 | -1.92 | 0.48 |
| A[1]B[1] | 1.24 | 1 | 0.75 | -0.46 | 2.94 |
| A[2]B[1] | -2.01 | 1 | 0.75 | -3.71 | -0.31 |
| A[1]B[2] | -0.91 | 1 | 0.75 | -2.61 | 0.79 |
| A[2]B[2] | 0.24 | 1 | 0.75 | -1.46 | 1.94 |

**Final Equation in Terms of Coded Factors:**

Kinematic Viscosity @ 40 =+104.94-3.70 * A[1]+1.99 * A[2]-0.42 * B[1]-0.72 * B[2]+1.24 * A[1]B[1]-2.01 * A[2]B[1]-0.91 * A[1]B[2]+0.24 * A[2]B[2]

# APPENDIX D

## D 1: Diagnostic Plots

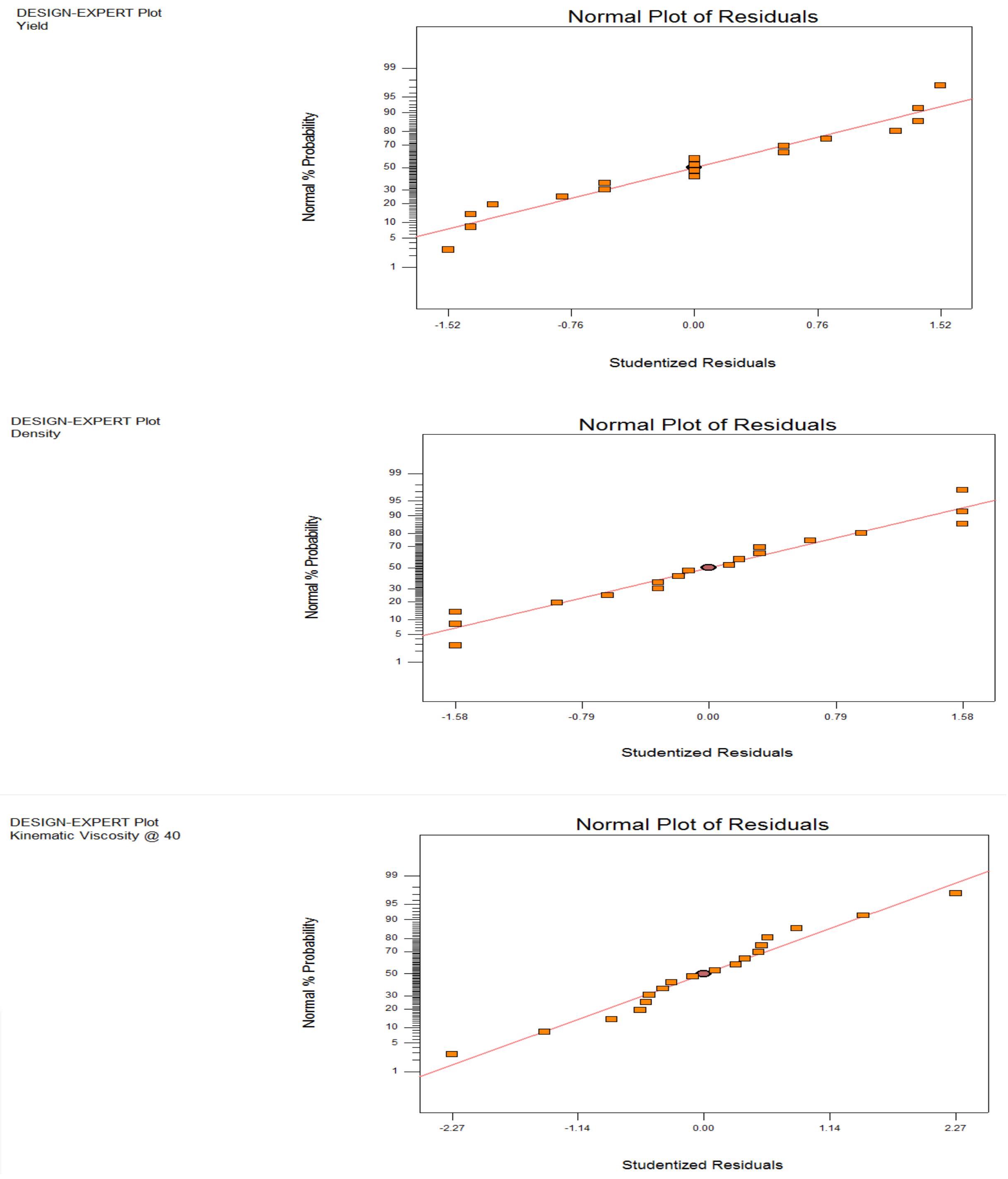
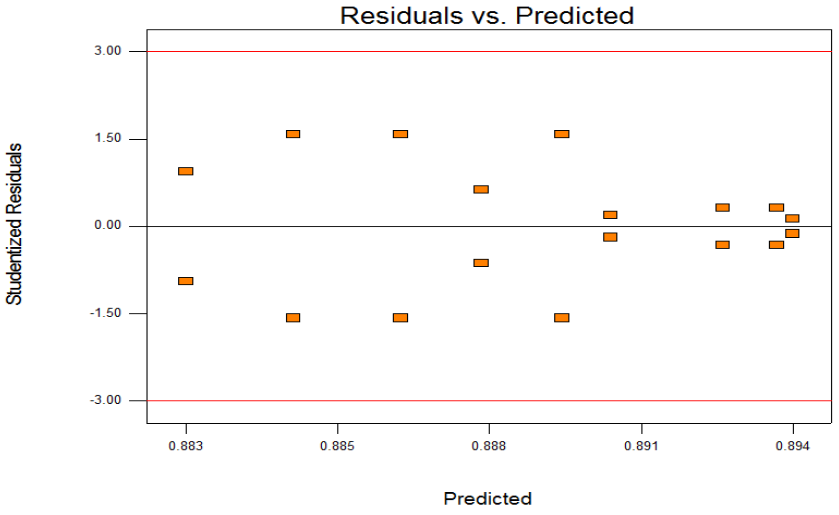
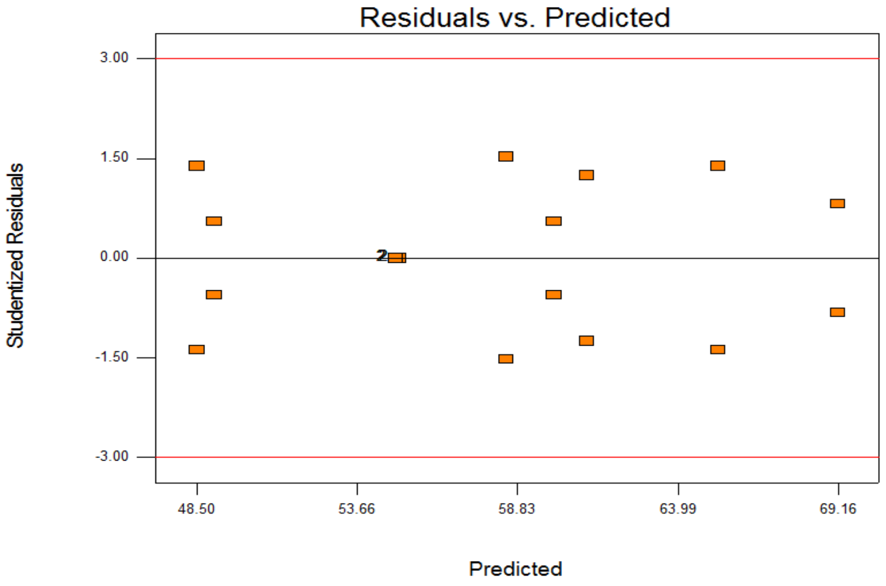


Figure D-1: Normal Plot of residuals

DESIGN-EXPERT Plot
Density



DESIGN-EXPERT Plot
Yield



DESIGN-EXPERT Plot
Kinematic Viscosity @ 40

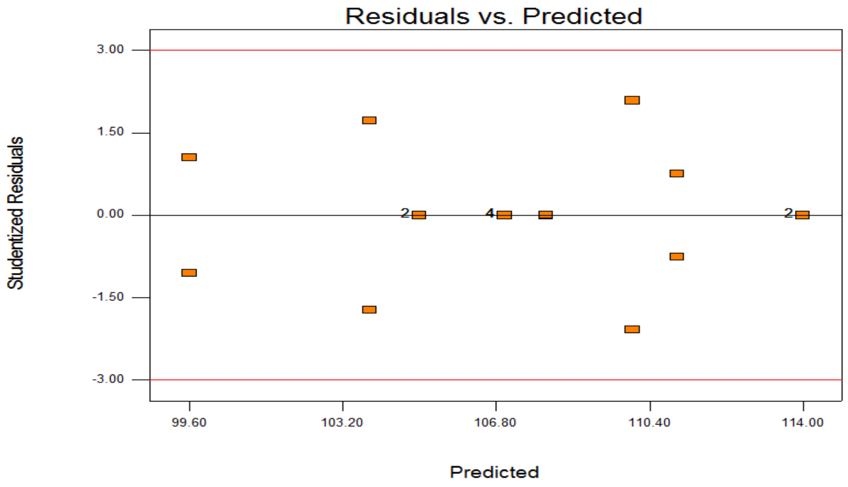


Figure D-2: Plot of Residual Vs. Predicted

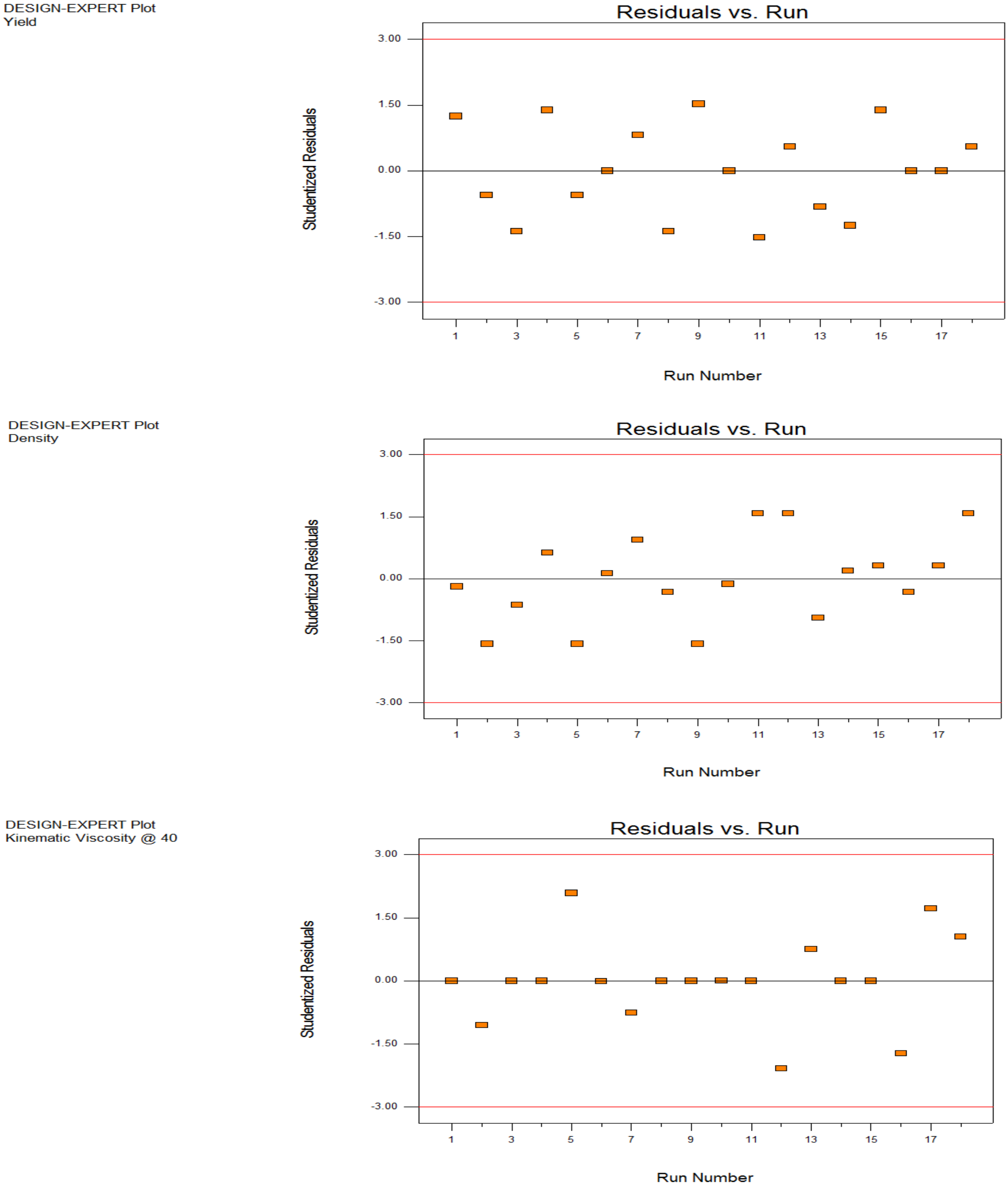
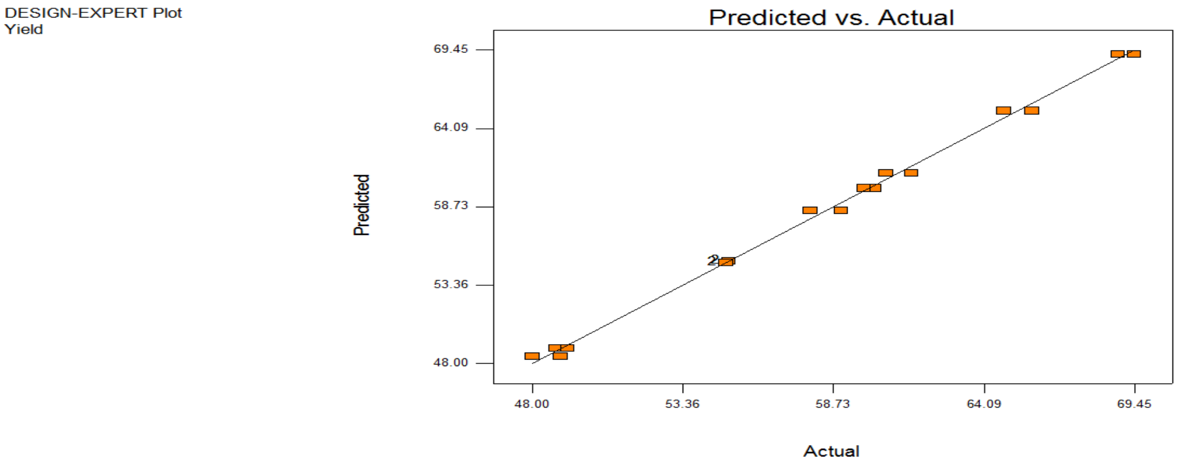
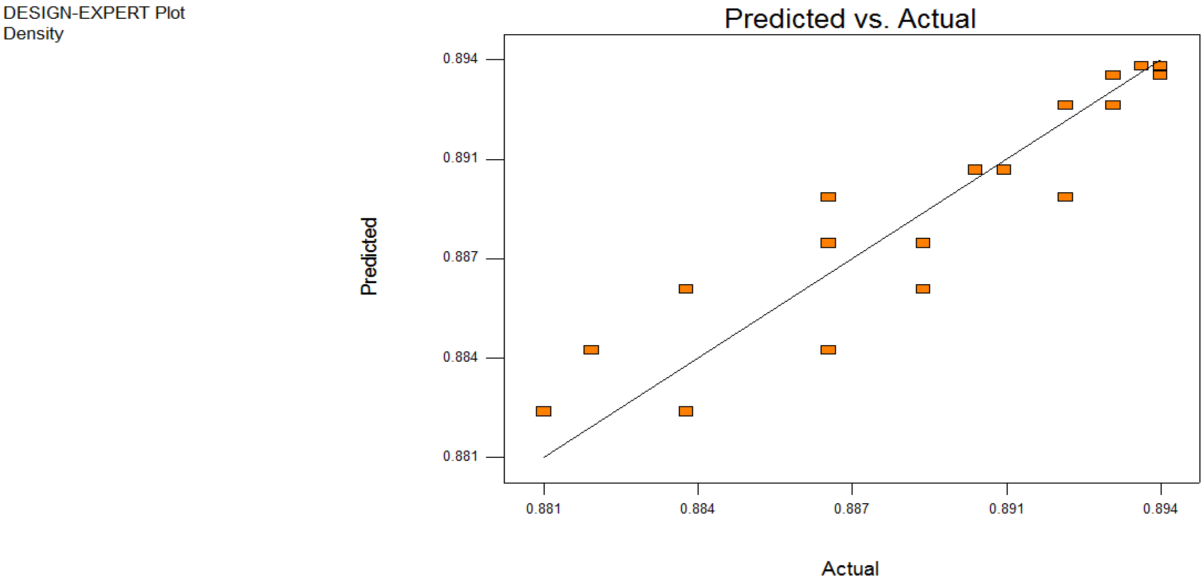


Figure D-3: Plot of Residual Vs. Run


DESIGN-EXPERT Plot
Yield
Predicted vs. Actual
Predicted
Actual
69.45
64.09
58.73
53.36
48.00
48.00
53.36
58.73
64.09
69.45
2


DESIGN-EXPERT Plot
Density
Predicted vs. Actual
Predicted
Actual
0.894
0.891
0.887
0.884
0.881
0.881
0.884
0.887
0.891
0.894

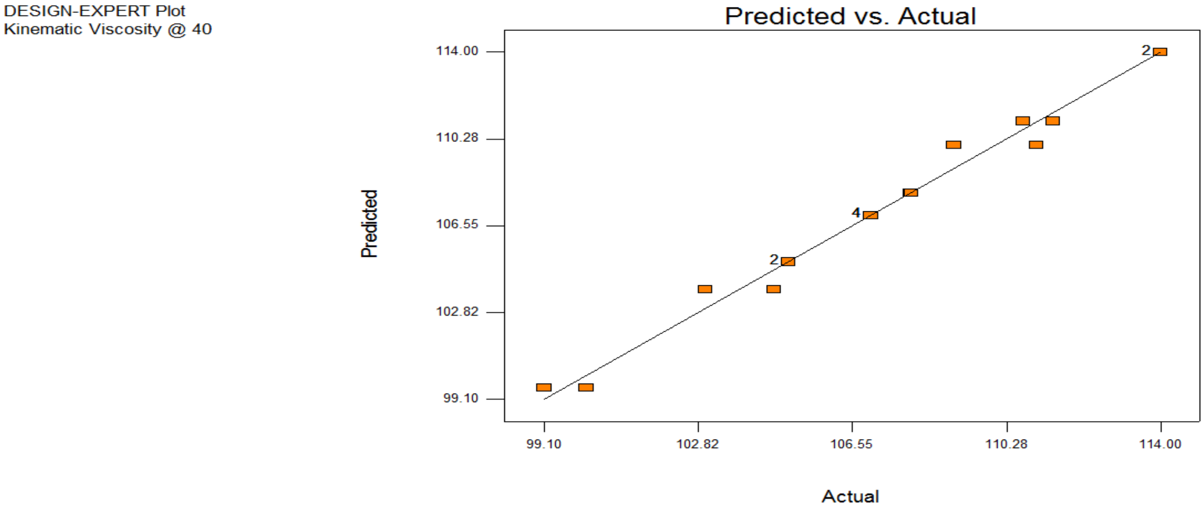

DESIGN-EXPERT Plot
Kinematic Viscosity @ 40
Predicted vs. Actual
Predicted
Actual
114.00
110.28
106.55
102.82
99.10
99.10
102.82
106.55
110.28
114.00
2
4
2

Figure D-4: Plot of Actual Vs. Predicted

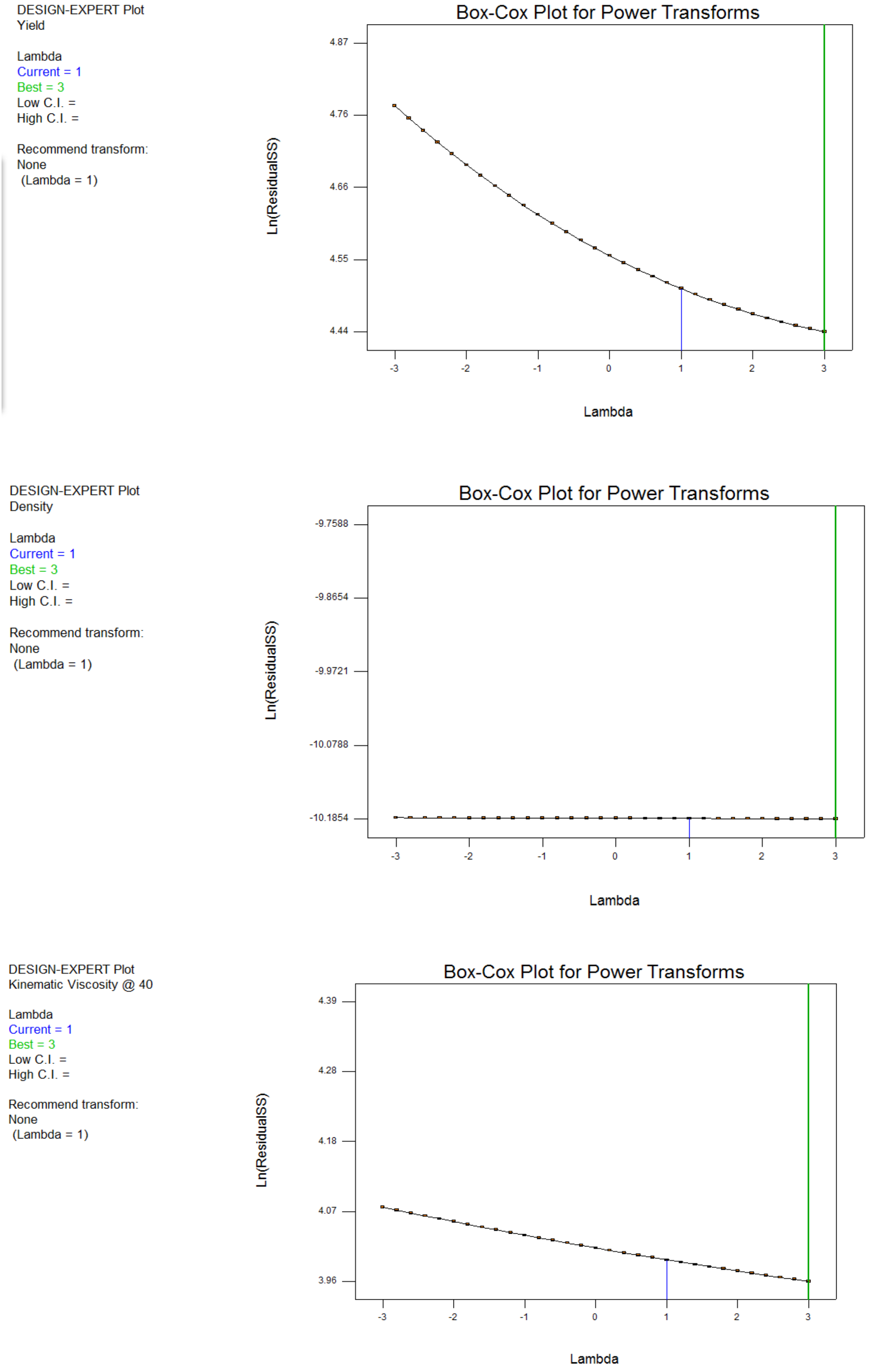


Figure D-5: Plot of Box- cox for power transforms.

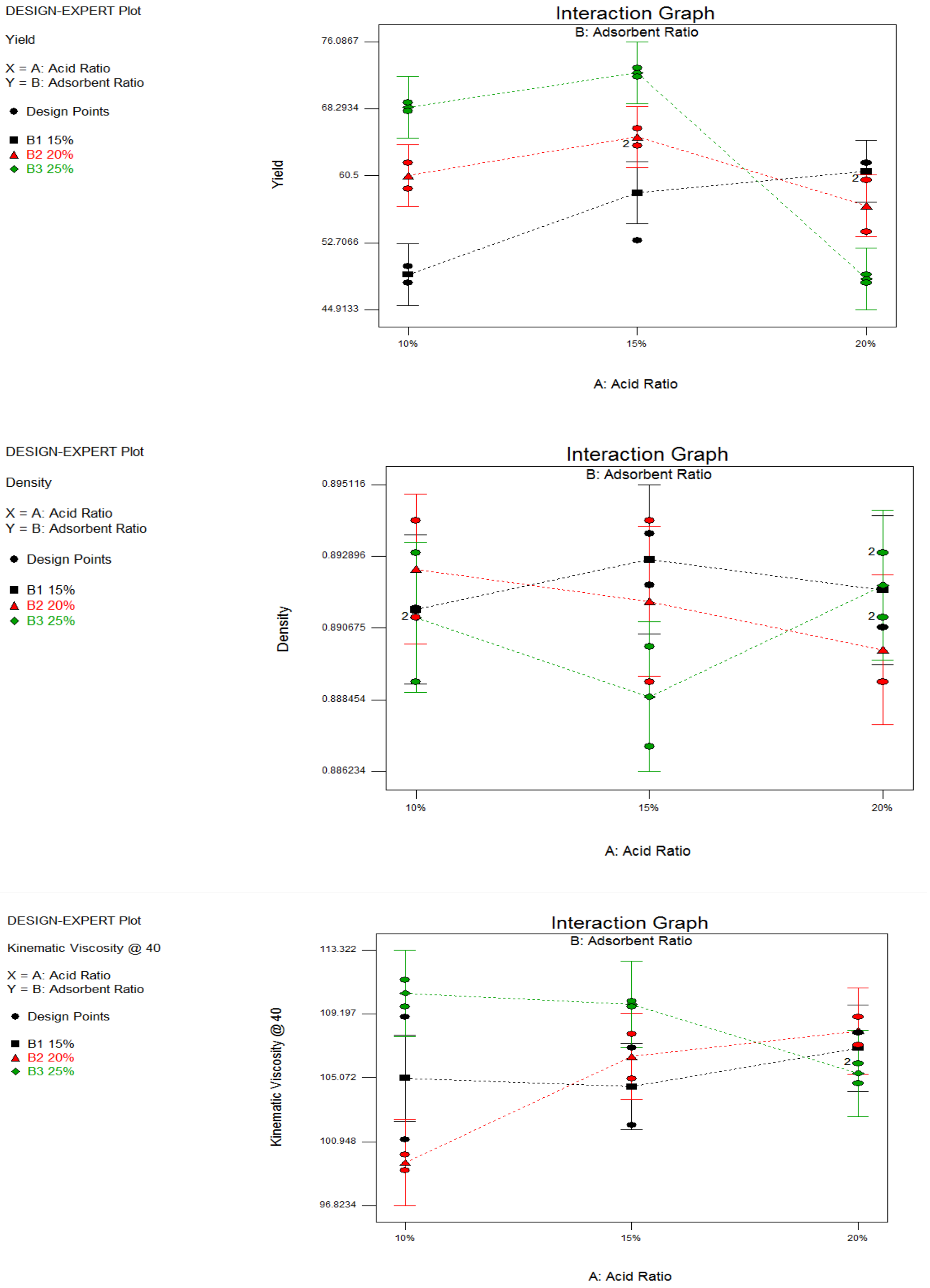


Figure D-6: Plot of Interaction Graph

# ANNEX

## 1- Statistical Analysis for Rubia and Quartz

### 1.1 Statistical Analysis for Rubia

ANOVA and model fitting results of experimental data showed that amount of acid had the strongest effect on the yield (p-value = 0.0038), kinematic viscosity (p-value =0.0034) while it doesn't have any effect on density. Adsorbent ratio also had significant effect on yield (p-value < 0.0001)and kinematic viscosity (p-value=0.0002) of recovered oil but not on density.

Values of "Prob > F" less than 0.0500 indicate model terms are significant.In this case AB are significant model terms.  Values greater than 0.1000 indicate the model terms are not significant.  From this it can be concluded that both acid ratio and adsorbent ratio have significant effect on the overall ANOVA and model fitting .

**Table annex1: Analysis of variance results summary for Rubia Tir 7400.**

| **Response 1 : Yield** | | | | | |
|---|---|---|---|---|---|
| Source | Sum of squares | Df | Mean square | F- value | p- value (prob>F) |
| Model | 2098.01 | 8 | 262.25 | 19.37 | <0.0001- Significant |
| A- Acid Ratio | 297.94 | 2 | 148.97 | 11.00 | 0.0038 |
| B- Adsorbent Ratio | 1254.02 | 2 | 627.01 | 46.31 | <0.0001 |
| AB | 546.04 | 4 | 136.51 | 10.08 | 0.0022 |
| Pure Error | 121.85 | 9 | 13.54 | | |
| Cor Total | 22219.86 | 17 | | | |
| **Response 2: Density** | | | | | |
| Model | 4.902E-004 | 8 | 6.12E-005 | 9.7 | 0.0013 – Significant |
| A | 3.235E-005 | 2 | 1.618E005 | 2.56 | 0.1318 |
| B | 3.505E-006 | 2 | 1.752E-006 | 0.28 | 0.764 |
| AB | 4.544E-004 | 4 | 1.136E-004 | 17.98 | 0.0003 |
| Pure Error | 5.687E-005 | 9 | 6.319E-006 | | |
| Cor Total | 5.471E-004 | 17 | | | |
| **Response:3- Kinematic viscosity @ 40°C** | | | | | |
| Model | 205.85 | 8 | 25.73 | 35.20 | <0.0001- significant |
| A | 16.69 | 2 | 8.34 | 11.42 | 0.0034 |
| B | 36.52 | 2 | 18.26 | 24.98 | 0.0002 |
| AB | 152.64 | 4 | 38.16 | 52.21 | <0.0001 |
| Pure Error | 6.58 | 9 | .073 | | |
| Cor Total | 212.43 | 17 | | | |

## 2- Statistical Analysis for Quartz 5000-20W-50

ANOVA and model fitting results of experimental data showed that amount of acid had the strongest effect on the yield (p-value = 0.0015), kinematic viscosity (p-value =0.0027) and density (p-value=0.0005). Adsorbent ratio also had significant effect on yield (p-value= 0.0118)and kinematic viscosity (p-value=0.0002) and density (p-value=0.8187) adsorbent ratio has no significant effect on recovered oil's density.

Values of "Prob > F" less than 0.0500 indicate model terms are significant.In this case AB are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. From this it can be concluded that both acid ratio and adsorbent ratio have no effect over density. Acid ratio (p-value=0.8682) and Adsorbent ratio (p-value= 0.4971) which showes insignificany for ANOVA and model fitting.

**Table annex 2: Analysis of variance results summary for Quartz 5000-20W-50.**

| **Response 1 : Yield** | | | | | |
|---|---|---|---|---|---|
| **Source** | **Sum of squares** | **Df** | **Mean square** | **F- value** | **p- value (prob>F)** |
| Model | 1038.44 | 8 | 129.81 | 12.910 | **0.0004- significant** |
| A- Acid Ratio | 294.78 | 2 | 147.39 | 14.66 | 0.0015 |
| B- Adsorbent Ratio | 152.44 | 2 | 76.22 | 7.58 | 0.0118 |
| AB | 591.22 | 4 | 147.81 | 14.7 | 0.0006 |
| Pure Error | 90.50 | 9 | 10.06 | | |
| Cor Total | 1128.94 | 17 | | | |
| **Response 2: Density** | | | | | |
| Model | 2.550 E-004 | 8 | 3.187E-005 | 6.34 | **0.0060 –Significant** |
| A | 1.949E-004 | 2 | 9.744E-005 | 19.38 | 0.0005 |
| B | 2.058E-006 | 2 | 1.029E-006 | 0.2 | 0.8187 |
| AB | 5.805E-005 | 4 | 1.451E-005 | 2.89 | 0.086 |
| Pure Error | 4.526E-005 | 9 | 5.028E-006 | | |
| Cor Total | 3.003E-004 | 17 | | | |
| Response:3- Kinematic viscosity @ 40 | | | | | |
| Model | 161.09 | 8 | 20.14 | 7.93 | **0.0027- significant** |
| A | 123.70 | 2 | 61.85 | 24.35 | 0.0002 |
| B | 11.92 | 2 | 5.96 | 2.35 | 0.1513 |
| AB | 25.47 | 4 | 6.37 | 2.51 | 0.1160 |
| Pure Error | 22.86 | 9 | 2.54 | | |
| Cor Total | 183.95 | 17 | | | |

## 4. 3- Optimization of variance for Rubia Tir 7400 15W-40

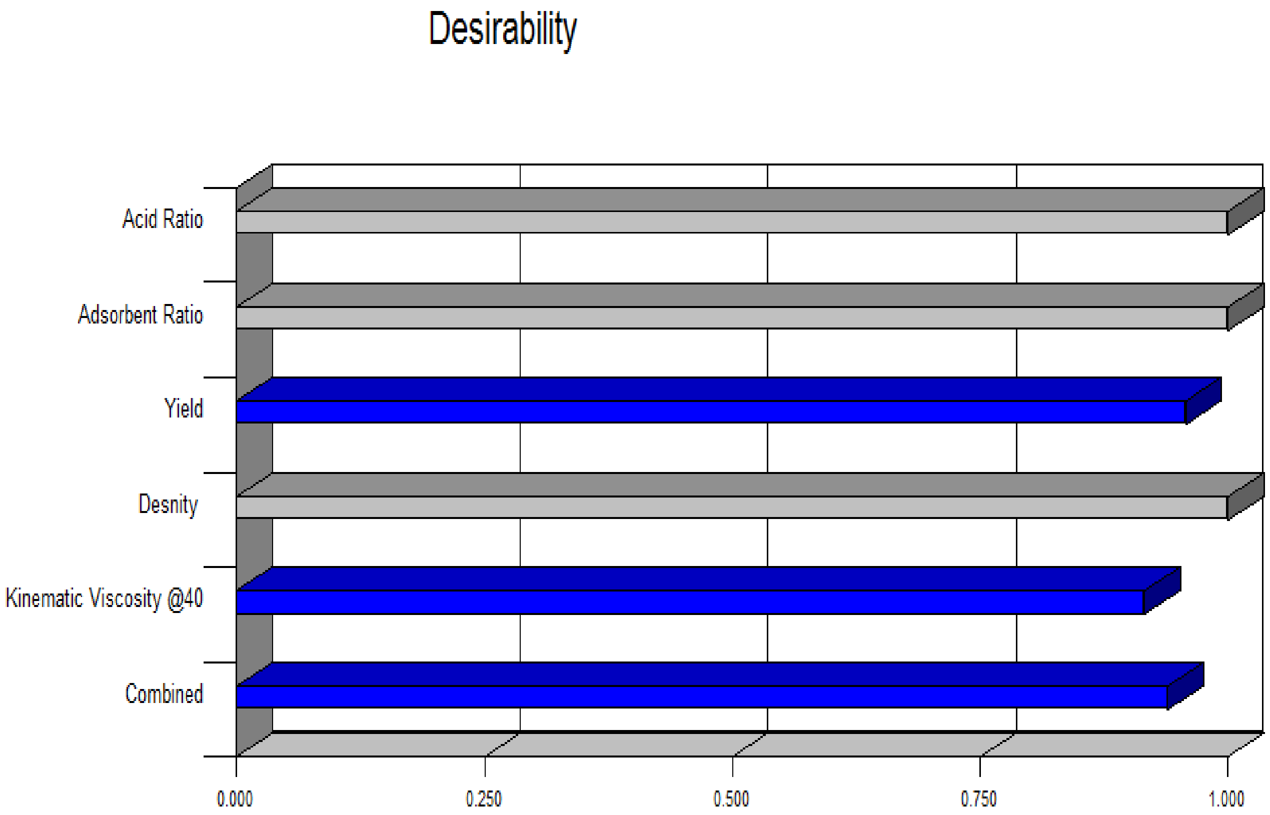
Table annex 3 optimization of variance for Rubia Tir 7400

| **Name** | **Goal** | **Lower limit** | **Upper Limit** | **Lower weight** | **Upper weight** | **Importance** |
|---|---|---|---|---|---|---|
| Acid Ratio | Is in range | 10% | 20% | 1 | 1 | 3 |
| Adsorbent Ratio | Is in range | 15% | 25% | 1 | 1 | 3 |
| Yield | Maximize | 40 | 72.8 | 1 | 1 | 4 |
| Density | Is in range | 0.8694 | 0.887594 | 1 | 1 | 3 |
| Kinematic Viscosity | Maximize | 52.96 | 65.23 | 1 | 1 | 3 |

| **Sol #** | **Acid Ratio** | **Adsorbent Ratio** | **Yield** | **Density** | **Kin. Viscosity** | **Desirability** |
|---|---|---|---|---|---|---|
| **1** | **15** | **25** | **71.45** | **0.87585** | **64.229** | **0.941= Selected** |
| 2 | 15 | 20 | 69.9 | 0.874641 | 62.153 | 0.838 |
| 3 | 10 | 20 | 63.5 | 0.885902 | 59.96 | 0.65 |
| 4 | 10 | 25 | 58.7 | 0.87154 | 56.01 | 0.403 |
| 5 | 20 | 15 | 49.45 | 0.88294 | 58.91 | 0.36 |
| 6 | 20 | 20 | 65.7 | 0.87036 | 54.01 | 0.309 |
| 7 | 20 | 25 | 44 | 0.88355 | 60.720 | 0.247 |
| 8 | 10 | 15 | 42.6 | 0.87428 | 58.034 | 0.161 |
| 9 | 15 | 15 | 46.05 | 0.87651 | 53.617 | 0.109 |

The combination of Run 11 and Run 18 with acid ratio of 15% and adsorbent ratio of 25% were selected as an optimum operating condition for used oil recovery.

With maximum desirability of 0.941 while the response factors gave an average result of 71.45%, 0.87585 and 64.229Cst, for yield, density and kinematic viscosity @40 respectively.


Desirability
Acid Ratio
Adsorbent Ratio
Yield
Desnity
Kinematic Viscosity @40
Combined
0.000
0.250
0.500
0.750
1.000

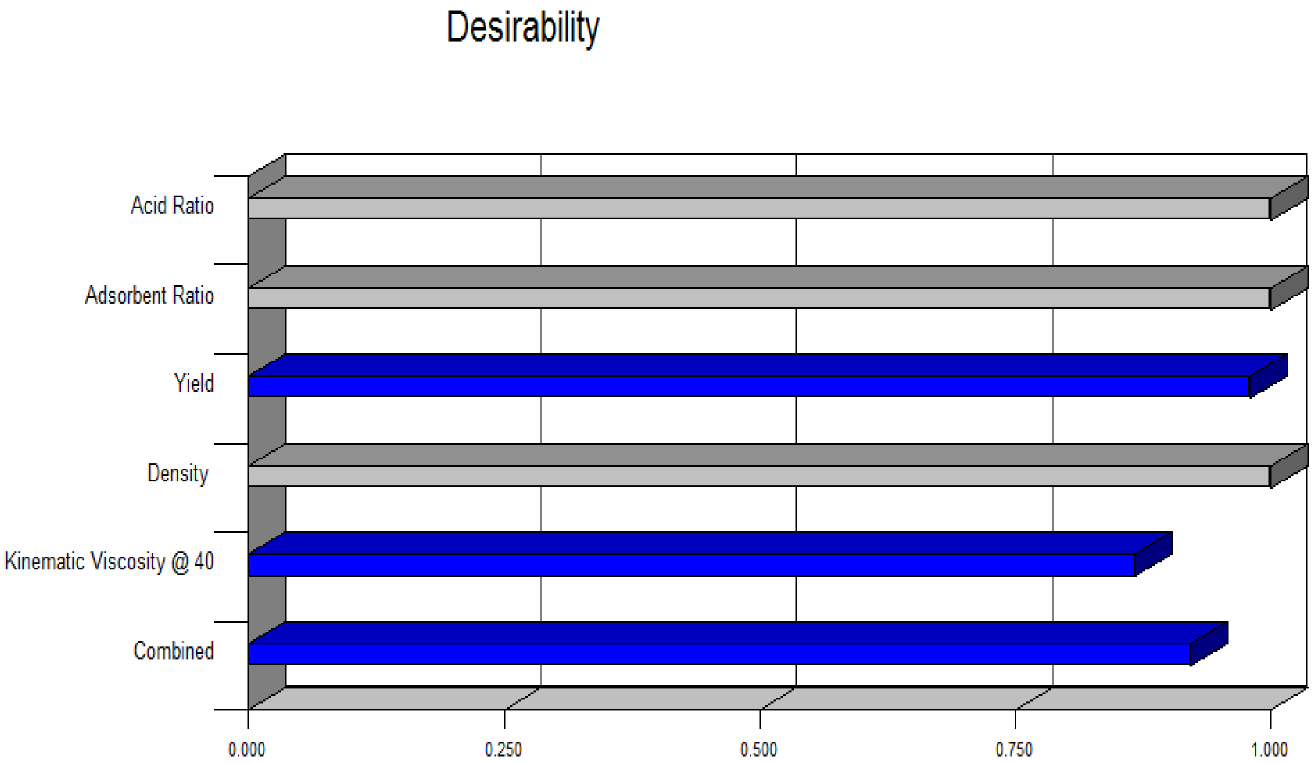
### 4- Optimization of variance for Quartz 5000-20W-50

**Table annex 4 optimization of variance for quartz 5000-20W-50**

| Name | Goal | Lower limit | Upper Limit | Lower weight | Upper weight | Importance |
|---|---|---|---|---|---|---|
| Acid Ratio | Is in range | 10% | 20% | 1 | 1 | 3 |
| Adsorbent Ratio | Is in range | 15% | 25% | 1 | 1 | 3 |
| Yield | Maximize | 48 | 73 | 1 | 1 | 3 |
| Density | Is in range | 0.887 | 0.894 | 1 | 1 | 3 |
| Kinematic Viscosity | Maximize | 99.1 | 111.4 | 1 | 1 | 3 |

| Sol # | Acid Ratio | Adsorbent Ratio | Yield | Density | Kin. Viscosity | Desirability |
|---|---|---|---|---|---|---|
| 1 | 15 | 25 | 72.5 | 0.88855 | 109.825 | 0.924=Selected |
| 2 | 10 | 25 | 68.5 | 0.891 | 110.54 | 0.873 |
| 3 | 15 | 20 | 65 | 0.8915 | 106.45 | 0.637 |
| 4 | 20 | 15 | 61 | 0.89185 | 107 | 0.578 |
| 5 | 20 | 20 | 57 | 0.89 | 108.095 | 0.513 |
| 6 | 15 | 15 | 58.5 | 0.8928 | 104.5 | 0.429 |
| 7 | 10 | 20 | 60.5 | 0.8925 | 99.605 | 0.143 |
| 8 | 10 | 15 | 49 | 0.89125 | 105.05 | 0.139 |
| 9 | 20 | 25 | 48.5 | 0.892 | 105.355 | 0.101 |

The combination of Run 16 and Run 17 with acid ratio of 15% and adsorbent ratio of 25% were selected as an optimum operating condition for used oil recovery. With maximum desirability of 0.924 while the response factors gave an average result of 72.5%, 0.88855 and 109.825 Cst, for yield, density and kinematic viscosity @40 respectively.


Desirability
Acid Ratio
Adsorbent Ratio
Yield
Density
Kinematic Viscosity @ 40
Combined
0.000
0.250
0.500
0.750
1.000