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REFINING OF USED MOTOR OIL USING SOLVENT EXTRACTION

A Thesis Submitted to the Graduate Studies of Addis Ababa University in Partial Fulfillment of the Degree of Masters of Science in Chemical Engineering (process engineering)

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DEDICATION

I would like to dedicate this thesis to my beloved country.

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ABSTRACT

Used lubricating motor oil is a high pollutant material that requires responsible management. It may cause damage to the environment when dumped into the ground or into water streams including sewers. This may result in groundwater and soil contamination. Recycling of such contaminated materials will be beneficial in reducing lubricating motor oil costs. In addition, it will have a significant positive impact on the environment.

Used oil can be refined to yield base oils that are blended into lubricating products, thus reducing the consumption of virgin oils. Refining restores the physical and chemical properties of lubricating oil so that it can go back to its original and intended use.

This thesis work investigates refining of used lubricating motor oil using solvent extraction method. The laboratory experiment was based on a full factorial design and two categorical factors with two levels were nominated which were solvent to used oil ratio (4:1&6:1) and solvent type (2-Propanol and n-Butanol). First used lubricating motor oil, of two varieties, namely TOTAL Rubia and TOTAL Quartz was collected from TOTAL Ethiopia oil company gas stations and characterized for important properties and contaminates. Then by applying appropriate treatment, i.e. pretreating, dehydration, vacuum distillation, solvent extraction and distillation for solvent recovery, the base oil was obtained. The refined base oil was then characterized and compared with the used and virgin oil.

The type of solvent used and the mixing ratio applied for different runs has shown significant effects on the yield of recovered oil. 2-Propanol solvent with mixing ratio of 6:1 gave the best result. A Maximum yield of 72% was obtained for Rubia Tir 7400 using 2-Propanol solvent and mixing ratio of 6:1, whereas minimum recovery yield of 55% was obtained using n-Butanol and 4:1 mixing ratio. For Quartz 20W-50 a maximum yield of 73.4 was obtained using 2-Propanol solvent and mixing ratio of 6:1 whereas minimum recovery yield of 50% was obtained using n-Butanol and 4:1 mixing ratio. The metal contaminants and chlorine are considerably reduced in the base oils for both lubricants.

So it can be concluded that used lubricating motor oil can be refined using solvent extraction method and reduces environmental contaminations and decreases foreign currency.

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ACRONYMS

ASTM	American Society for Testing and Material
API	American Petroleum Institute
DIYers	Do-It-Yourselfers
EPA	Environmental Protection Agency
GC	Gas Chromatography
IS	Infrared Spectroscopy
ISO	International Organization for Standardization
KTI	Kinetics Technology International
LPG	Liquid Petroleum Gas
MEK	Methyl Ethyl Ketone
MRS	Magnetic Resonance Spectroscopy
MS	Mass Spectroscopy
OEM	Original Equipment Manufacturer
PAH	Polycyclic Aromatic Hydrocarbons
PAN	poly Acrylo Nitrile
PES	Poly Ether Sulphone
PCB’S	Poly ChlorinateBiphenyls
PVDF	Poly Vinylidene Fluoride
SAE	Society of Automotive Engineers

INTRODUCTION

1.1 BACKGROUND

Used motor oil is a high pollutant material that requires responsible management. Used motor oil may cause damage to the environment when dumped into the ground or into water streams including sewers. This may result in groundwater and soil contamination. Recycling of such contaminated materials will be beneficial in reducing motor oil costs. In addition, it will have a significant positive impact on the environment. The conventional methods of recycling of used motor oil either requires a high technology such as vacuum distillation, solvent extraction or the use of toxic materials such as sulfuric acid.

Lubricant oils have been used primarily for reducing friction between moving parts of various machinery or equipment, minimize material wear, improve the efficiency of equipment /machinery and for fuel and energy savings. Access to lubricants is essential to any modern society and not only does lubrication reduce friction and wear by interposition of a thin liquid film between moving surfaces, but it also removes heat, keeps equipment clean, and prevents corrosion. One of its important applications includes gasoline and diesel engine oils. Used lubricating oil refers to the engine oil, transmission oil, hydraulic and cutting oils after use. It is also refers to the degradation of the fresh lubricating components that become contaminated by metals, ash, carbon residue, water, varnish, gums, and other contaminating materials, in addition to asphaltic compounds which result from the bearing surface of the engines. These oils must be changed and removed from the automobile after a few thousand kilometers of driving because of stress from serious deterioration in service. (Ihan Hamawand, 2013)

The amount of used lubricating oils that is collected annually in Ethiopia is very large. This large amount of used motor oils has a significant impact on both economic and environmental aspects. They cost millions of dollars/birr to manufacture and represent a high pollutant material when disposed off. If discharged into the land, water or even burnt as a low grade fuel, this may cause serious pollution problems because they release harmful metals and other pollutants into the environment. A recommended solution for this issue is the recovery of the lubricating base oil from the used oil. Recycling processes using nontoxic and cost effective materials can be an optimum solution.

1.2 STATEMENT OF THE PROBLEM

Used oil is refined to yield base oils that are blended into lubricating products, thus reducing the consumption of virgin oils. Refining restores the physical and chemical properties of lubricating oil so that it can go back to its original and intended use. Used oil contains 70 to 75 percent lubricant base oil and less energy is required to produce the same amount of base stock from used oil than from crude oil.

Refining technologies two decades ago used low-yield acid/clay processes that generated large quantities of acid muds with high levels of sulfur, metals and metalloids that posed waste disposal problems. Today’s processes can produce high-quality base oils comparable to lubricants derived from crude oil. Current refining technologies generally involve vacuum distillation of the dehydrated waste oil, followed by extraction and/or hydro-treatment of the distilled stocks.

In our country, Ethiopia, recycling the used motor oil is not practiced. Instead some are sold for factories as a burning material and for construction companies in order to lubricate the panel to protect from rust and corrosion, and some are wasted into ground and river. But if it is recycled it benefits the country economically and environmentally. So in order to recycle and refine the used motor oil it is necessary to study, investigate, characterize and compare the property and composition of refined base oil, used motor oil and virgin base oil.

1.3 OBJECTIVE

1.3.1 General Objective

The general objective of this research is to refine and recycle used motor oil using solvent extraction method.

1.3.2 Specific Objective

- Characterization of used motor oil.
- Treatment of used motor oil using solvent extraction.
- Characterization of the main parameters of treated motor oil such as density & specific gravity, viscosity, viscosity index, flash point and metal content.
- Optimization of the process conditions.
- Comparison of solvent type.
- Comparison of the refined motor oil with the untreated used motor oil and the virgin oil.

1.3.3 Significance

This study is very significant for our country at all. Because it solves environmental pollution due to waste motor oil released to the ground and river, and also from factory gas emission that use waste motor oil as a furnace oil. Used oil will be refined to yield base oils that can be blended into lubricating products, thus reducing the consumption of virgin oils.

LITERATURE REVIEW

2.1 INTRODUCTION TO LUBRICATING OIL

- **The Origins of Oil**

Oil is a primary energy resource in developed nations. Although advances in modern technology have historically permitted the extraction of crude oil from regions previously considered inaccessible, the world oil resources and reserves are a limited natural resource. (A limited natural resource is one of finite quantity or with an extended life cycle which requires specific physical conditions to permit its regeneration. (Gary, 1990)

Current theory holds that oil was formed from the bodies of millions of marine plants and animals, especially plankton. As they died, they slowly drifted to the bottom of the shallow seas and were covered with inorganic sediments. After the bodies of these organisms decayed, they were compressed by the weight of overlying materials and heated by the geological activity of the earth. This process caused the remains of these organisms to undergo chemical changes. Very slowly, crude oil and gas were formed. Once it was formed, the oil then moved through the layers of sedimentary rock until it became confined by nonporous layers forming oil traps. The crude oil we use today is obtained by drilling wells into these traps or pockets. Oil is often found in conjunction with natural gas. This lighter weight material is generally removed from drilling sites first. Once the crude oil has been extracted from the ground, it can be separated into different components at an oil refinery.(Gary, 1990)

- **Exploration**

As geologists explore possible locations for oil, they look for certain changes in the layers and make-up of the rock. Geologists identify likely areas in which oil may be found by creating vibrations using vibration mechanisms or even sonar. The resulting sound waves are measured as they move through the rock by sensitive instruments called seismophones. Seismophones are instruments similar to those used to detect earthquakes. Graphs of the differential rates of sound movement have been keyed to oil pockets or traps. Based on these indicator patterns, the geologist recommends where test wells should be drilled.

Some of the test wells are productive wells. In the old days, wells used to be called gushers because the process of piercing the oil trap released pressure built up in the trap through the ages. The oil then shot through the top of the well. Today, specialized valves prevent this explosive release. Hence, the loss of natural gas and crude oil is reduced as is pollution caused by oil spills around the drilling operations. This practice is both cost effective for the oil companies and environmentally sound.

Once oil has been discovered, multiple wells are sunk in the vicinity of the test well to determine the size of the oil supply. Samples are taken and the relative quality of the oil is determined. If the size of the oil supply is large and development of the resource is considered to be cost effective, additional wells are drilled into the trap. Some of the oil and natural gas discovered is under enough pressure to flow upward unassisted. The remaining oil must be pumped from the pocket. Steam and other chemicals may be injected into the wells to help force the more tightly bound oil out of the enclosing pocket. Once crude oil is extracted from the ground, it is sent to an oil refinery where it is processed into different products.

- **Separation of Crude Oil**

Crude oil is a mixture of many chemical compounds. At the refinery, it is separated into several components. The first part of this process is called fractionating. During the fractionating process, the oil is heated in a tall tower called distillation. This causes molecules of different sizes and chemical characteristics to separate from each other. The lightest components rise to the top of the tower. These are called light ends and will be further processed to become solvents and fuels for automobiles and airplanes. The heaviest and most complex of the crude oil components go on to become greases and asphaltic materials. The parts of the crude oil that are a little lighter than greases are used as lubricants. Once separated, chemicals are added depending on the oil's intended use. The oil is then packaged and marketed.

One of the products we are most familiar with is engine lubrication oil. It has several functions. Oil lubricates moving parts, thus reducing friction and, aiding in cooling the engine. Oil also cleans the cylinder and, at the same time, creates a seal between the piston rings and the cylinder wall so that when a spark ignites the fuel in the cylinder, the force is directed down to the arm on the crankshaft and does not escape past the cylinder walls.

During normal engine operation, friction causes abrasion of metal surfaces. This produces superfine particles and other debris that find their way into the oil. To remove this material, oil is filtered as it works its way through the engine. Throughout this process, oil is exposed to extremely high temperatures (approximately 250 degrees F.). This high heat chemically breaks down the oil. As the oil breaks down, its effectiveness in reducing wear and tear on the engine is Slowly lost, and dirt and contaminants further hinder its effectiveness. This is why auto manufacturers suggest the oil should be drained out and replaced with new oil on a regular basis. To prolong the life in today's high performance (and high temperature) engines, a number of materials are added to the refined oil such as detergents, dilutants and special additives to ensure proper lubrication and flow. These additives figure heavily in the pollution caused by improper disposal of used engine oil.(Gary, 1990)

2.1.1 Lubricating Oil

Petroleum products are essentially composed of hydrocarbons, i.e. compounds containing exclusively carbon and hydrogen. The simplest hydrocarbon molecule is methane, CH_4. This basic molecule is the main constituent of natural gas. It can be extended with the addition of more carbon and hydrogen atoms, usually forming into longer chains. Four carbon atoms in a chain forms butane, one of the main constituents of LPG. The atoms may also form side chains of the main chain, or form into ring structures such as the benzene ring. Lubricating oils are just extensions of these basic hydrocarbon structures, containing from 20 to 70 carbon atoms per molecule, often in an extremely complex arrangement of straight chains, side chains and five and six membered ring structures.

The lubricating oil molecules can be divided into three broad groups:

Paraffinic*:* Predominantly straight chain, tend to be waxy, have a high pour point and good viscosity/temperature stability.

Naphthenic*:* Straight chains with a high proportion of five and to a lesser extent six membered ring structures. Tend to have a low pour point. For this reason they are used as refrigeration oils. They are highly carcinogenic and are little used in engine oil. Dominion Oil treats used refrigerator oils separately from the main plant. As refrigerator oils do not come in contact with products of combustion they are much cleaner than engine oils.

Aromatic*:* Straight chains with six membered ring benzene structures.

In practice, no sharp distinction exists between these various groupings as many lubricating oil molecules are a combination, to varying degrees, of the different types of hydrocarbons. The main point to bear in mind is that these molecules are extremely stable. Lubricating oil molecules never wear out - all that happens is that the additives in the oil wear out or deplete and need replacing.

The lubricating oil fraction is very stable and involatile. To heat the lubricating oil to the temperature required for distillation will actually decompose the oil, so the diesel and lube oil fractionation is carried out under vacuum to reduce the effective boiling point of these products. Oil which will normally boil at 500^oC will boil at 300^oC under the very high vacuum used. Boiling ranges are as follows:

Gasoline: - 40 – 190 ^oC

Kerosene:- 190 – 260 ^oC

Diesel:- 260 – 330 ^{o}C

Lube oil:- 330 – 400 ^{o}C under vacuum

The very heavy components of the crude (i.e. tars) will not distill even under a vacuum and remain as bottoms or residue. The lubricating oil fraction must then be further refined before being suitable for use. The oil is dewaxed by cooling; asphalts, aromatics and resins are removed by solvent extraction and colored molecules are removed by hydro-treating, or treatment with activated earths. The base oil molecular type (i.e. paraffinic, naphthenic) must then be blended to provide the desired properties of color, oxidation stability, viscosity characteristics and additive response. Only then can the additives be blended into the base oils to produce the high quality lubricants available today.(Layzell, 2009)

2.2 USED MOTOR OIL

As motor oil is used in automobile engines, it picks up a number of additional components from engine wear. These include iron and steel particles, copper, lead, zinc, barium, cadmium, (two highly toxic metals), sulfur, water, dirt and ash. Because of the additives and contaminants, used motor oil disposal can be more environmentally damaging than crude oil pollution. These materials may cause both short and long term effects if they are allowed to enter the environment through our waterways or soil. Engines leak oil if not properly maintained and repaired. This represents a significant addition to the improper disposal of oil. One may have noticed the darkened center areas on road lanes. This darkening is due to the oil and other lubricants that have leaked out of the engines of cars and trucks. When it rains, much of this oil washes onto the soil surface and then into a water system. Once motor oil is drained from an engine, it is no longer clean, as it has picked up metals, dirt particulates and other chemicals during engine operation. This lubricating oil is now classified as used oil. (Gary, 1990)

2.2.1 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 used 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.

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 vapor 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. Flash point is determined by Cleveland open cup apparatus method. The oil is taken in the open cup and heated. The temperature at which the vapor given out by the heating oil catches fire momentarily when exposed to the ignition source is noted as flash point temperature.(Shri Kannan C, 2014)

Metal contents

Calcium: Used as a detergent and dispersant additive to maintain suspension of particulate matter, along with maintaining a reserve alkalinity. Concentration levels vary greatly depending on oil brand.

Zinc: Another anti-wear, anti-oxidant, and corrosion inhibitor additive also commonly found in bearing alloys. Concentration levels vary greatly depending on oil brand.

Chromium: The source of chromium wear metals is almost always from piston rings, which are used to form a tight seal between the moving piston and stationary cylinder wall. These rings have to reliably create a tight seal between the piston and the cylinder wall while travelling at up to 4,000+ feet per second and dealing with peak pressures of over 2,000 psi (136 Bar) depending on the engine design and usage.

Lead: Lead is a soft, sacrificial wear metal used on surfaces such as bearings. Lead based Babbitt alloys. Commonly found in main crankshaft journal bearings and contaminated fuels. Other sources include leaded fuels and gasoline octane improvers.

Copper: Copper is widely used due to its high ductility and thermal conductivity. It is mainly utilized in bushings and bearings such as: crankshaft journal bearings, connecting rod bearings, camshaft bushings, piston wrist pin bushings, thrust washers, and even heat exchangers (oil coolers).

Iron: This is the only wear metal that accurately and linearly increases with the length of time the oil has been in service. It has many sources inside of an engine, most commonly coming from cylinder liners, camshaft lobes, crankshaft journals, and oil pumps.

Nickel: Though not very widely used anymore, Nickel can be found in certain alloys of steel for internal engine parts, and also is used as a coating on bearings.

Magnesium: Also used as a detergent and dispersant additive to maintain suspension of particulate matter, and occasionally used in certain alloys of steel. Concentration levels vary greatly depending on oil brand.

Molybdenum: This is most commonly used as an anti-wear/anti-scuff additive and has an effect commonly called “Moly plating” where over time, a thin and microscopic layer of Molybdenum tends to form between contact surfaces, thereby creating a lower coefficient of friction between the two parts. Concentration levels of Molybdenum vary greatly depending on the formulation of each specific oil brand, and viscosity. (http://www.bobistheoilguy.com/engine-oil-analysis/, June 7, 2016).

2.2.2 Uses of used Motor Oil

Outlets for used oil

Until today used oil is utilized for a number of applications. Some of them can be tolerated other are environmentally unacceptable.

- The first and best option for the disposal of used oil is to return the oil back to the producer. Particular in industrialized countries there are collection schemes for waste oil in place. The oil producer themselves know best what to do with the waste oil and can secure an environmentally friendly method for disposal or recycling. A big portion of the collected waste oil is re-refined on a large scale in refineries similar to those for crude oil.
- Also environmentally acceptable is the use of oil waste as fuel in cement and lime kilns, in brick works or metallurgical furnaces. Due to the high combustion temperature and the absorption properties of cement, lime and clay, hazardous hydrocarbons are destroyed while heavy metals, sulphur and chlorides are absorbed. Additionally, modern plants are normally equipped with sophisticated gas cleaning systems, which minimize possible air pollution effects.
- Mainly in developing countries, used engine oil is often utilized as fuel for diverse small scale applications. Apart from its use in foundries, traditional brick and lime kilns, in asphalt-producing vehicles, the oil is also used in traditional bakeries as well. In these cases, the waste oil is often blended with black oil (tar oil, bunker oil) (e.g. bakeries), charcoal/ mineral coal powder (lime kilns) or rubber pieces from used tyres (asphalt-producing vehicles).
- There are some reports as well, which state that unrefined waste oil can be mixed in small quantities to the diesel fuel of diesel engines.
- Another simple method to make use of waste engine oil is the production of grease. In many developing countries there are local small scale soap making units. To produce grease, waste oil is added to the ready soap (as long the soap is still warm and soft) in a composition of 20% soap to 80% waste oil. The mixture is stirred for some while until it forms the typical greasy consistency. The amount of oil determines the viscosity of the final grease. It is obvious that due to a minor quality of oil, the final grease is also of minor quality, but, nevertheless, sufficient for

many low scale applications. Apart from the use of waste oil as fuel or for the production of grease some other "traditional" applications are known:

- In many African countries, where all wooden structures are endangered by termites and other wood eating insects, old engine oil is used as a timber protecting agent. Fence posts, for example, are soaked in used oil to make them resistant against termite attack.(Dr.Ing Heino Vest, 2000)

2.2.2.1 Use of used Oil as Fuel for Heating and Energy Generation

Waste oil can as well be used for heating or energy production. As it is practiced in many developing countries waste oil is a cheap fuel for many heating purposes. Depending on the composition and the impurities of the waste oil the off-gas produced by this operation may be very dirty and hazardous. Therefore, the current practice in these countries is not environmentally sound and can be hazardous for people living nearby. In case the off-gas is properly cleaned waste oil can be used for heating and energy production. In industrialized countries, there are a number of companies offering special designed waste oil burners. Incinerator for waste oil which is attached with off-gas heat exchanger supply steam to small steam turbines or steam motors for electrical energy generation.(Dr.Ing Heino Vest, 2000)

2.2.2.2 Utilization of used Oil as Fuel for Diesel Engines

One striking idea for the utilization of waste engine oil is its use as fuel in diesel engines. In principle, waste oil can be used in diesel engines, although there are a number of limitations. Suitable engines for the use of waste oil are the big, slow moving stationary diesel aggregates used for power generation or those used as ship engine. Particularly engines which take residual fuel for combustion will run on waste oil too. When using waste oil as fuel, the major limitation is the content of additives in the oil. These additives often reach the amount of 10% of the oil and mainly consist of Ca-based organic compounds. During the combustion of the oil in a diesel engine the additives generate a considerable amount of ash. This ash will partly melt under the working temperature of the engine (400 to 550 °C) and will be deposited at the discharge valves or in the turbo-supercharger. This may lead to the destruction of the valves and to a clogged turbo-supercharger. Used lubrication oil also contains paraffin. If it is mixed with residual fuel, the paraffin may support a segregation of the residual fuel, leading to the formation of a sludge of long-chained hydrocarbons, which will settle at the fuel tank bottom.

In principle, there are two possibilities to overcome these problems. First, all additives are removed by an appropriate refining step. After the removal the refined waste oil can be used without any limitations (in concentration of up to 100%). In this case it is advisable not to mix the refined waste oil with diesel or residual fuel in order to avoid the segregation of the fuel.

In the case that the additives are not removed, only some 3% to 5% of waste oil may be added to the ordinary fuel. Some engine manufacturing companies suggests to limit the Ca-content to 100 mg/kg and to make sure that the limits of the ISO 8217 (quality standard of residual fuel) are not exceeded. A preliminary mechanical cleaning step using a centrifuge is recommended as well to remove the suspended matters. When using waste oil as fuel, the engine has to be supervised carefully. By increasing the amount of waste oil slowly, it will be possible to investigate the right percentage of waste oil in the fuel, in order to make sure that no damage is done to the engine. In general, there is no modification of the engine necessary and due to minor percentages of waste oil in the fuel, there is no significant change in the off-gas composition. (Dr.Ing Heino Vest, 2000)

2.2.2.3 Use Of Used Oil For Refining To Yield Base Oil

Used oil can be re-refined into base lube oil. Lube oil is a premium substance that can be re-refined and reused again and again. In general, water and dissolved low boiling point organic are removed by atmospheric or moderate vacuum distillation. Lube oil is then recovered and fractionated by distillation. Light ends byproducts are commonly used for plant combustion fuels. Diesel fraction and gas oil fractions can be recovered as high quality byproducts after further advanced treatment. Residual streams from distillation can be used by asphalt industry as an asphalt flux to produce roofing asphalt, paving asphalt, insulating materials, and other asphalt based products.

2.2.3 Contaminants in Used Motor Oil

Lubricating oil becomes unfit for further use for two main reasons: accumulation of contaminants in the oil and chemical changes in the oil. The main contaminants are listed below.

- **Combustion products**

Water: Fuel burns to CO_2 and H_2O. For every liter of fuel burnt, a liter of water is produced. This normally passes out through the exhaust when the engine is hot, but when cold it can run down and collect in the oil. This leads to sludge formation and rust.

Soot and carbon: These make the oil go black. They form as the result of incomplete combustion, especially during warm-up with a rich mixture.

Lead: Tetraethyl lead, which used to be used as an anti-knock agent in petrol, passes into the oil. Typical used engine oil may have contained up to 2% lead, but today any lead comes from bearing wear and is likely to be in the 2 - 12 ppm range.

Fuel: Unburnt gasoline or diesel can pass into the lubricant, again especially during start-up.

- **Abrasives**

Road dust: This passes into the engine through the air-cleaner (Composed of small particles of silicates).

Wear metals: Iron, calcium, zinc, copper and aluminum and other released due to normal engine wear.

- **Chemical products**

Oxidation products: Some of the oil molecules, at elevated temperatures, will oxidize to form complex and corrosive organic acids.

2.2.4 Impact of Improper Disposal of Used Motor Oil

According to EPA, just one quart of used oil is able to 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.

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. (Tchobanoglous, 1993)

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

2.2.4.1 Environmental Issues

Oil, in any form, is potentially harmful to the environment. Post-studies of oil spills indicate that it takes up to twenty years for an aquatic environment to return to a healthy condition. Once it has been used by industry or the DIYers, it has even more potential for environmental damage.

In an aquatic community oil residue tends to settle on the bottom, coating the substrate and whatever organisms live there. When poured on the ground, oil can rapidly migrate through the soil. In both instances bacteria, plants, invertebrates and vertebrates experience physiological stress.

Oil film on water can reduce the penetration of light into the water and, consequently, reduce the rate of photosynthesis. When photosynthesis is reduced, oxygen production is also reduced. The oil film may also inhibit the movement of oxygen from the air through the surface of the water. The reduction of dissolved oxygen in the water stresses animals living in the water. Oil can clog respiratory (breathing) mechanisms and even be incorporated into the tissues of these organisms. These substances in the tissues of these organisms make them unfit for human consumption and therein contribute to economic loss. If not incorporated in a human food source, the contaminants may be passed along the food chain, thereby contributing to environmental degradation. Some of the substances found in both virgin crude and refined oil can affect the nervous system of living things. This reduces their ability to find food or reproduce. Some of the compounds (on the light end) evaporate into the air and/or dissolve into the water. Many of these lighter compounds are known as carcinogens and/or mutagens. Microscopically, oil compounds impinge on algae’s, bacteria and plankton, the basis of the aquatic food chain. Larger organisms such as mammals and birds are the most dramatic victims of oil pollution because of their visibility and emotional appeal to humans. Feathers and fur become coated with oil and lose their ability to control body temperature. Death results from exposure or ingestion of the oil compounds via grooming. In soil, oil can rapidly percolate through the sand grains and create similar problems for soil microbes and macroscopic invertebrates. Eventually this oil may make its way into the water table or into a water body such as a lake.

Used oil is a valuable resource. One definition for pollution is a resource out of place, and used oil certainly fits that description. The potential impact on our environment depends on how we manage this resource to make sure it is not out of place.

To summarize, pollution can be defined as a resource in the wrong place or one that has not been completely used. Improper disposal of used oil is a source of significant pollution. The potential impact on our water and environment is serious. (Gary, 1990)

2.2.4.2 Economic Impact of Disposal Methods

The environmentally sound way to dispose of used motor oil is to recycle. It also makes sense from a purely economic standpoint. For example, if used oil is reprocessed into boiler fuel, a net savings of $0.65 per gallon could be realized. If the oil is re-refined into lubricating oil for vehicular use, a net savings of $1.50 per gallon could be realized. The energy saved by collecting and recycling used motor oil can also help reduce our dependence on foreign oil imports. Although crude oil prices fluctuate from year to year, valuable energy resources can be conserved by the use of fuel oil made from reclaimed motor oil. (Gary, 1990)

2.2.5 Solution For The Problem

2.2.5.1 Reclaiming

At the used oil-reprocessing center, the uncontaminated used oil is slowly heated. This separates small amounts of water from the oil. The water produced during this process is released to a wastewater treatment plant. Next, the oil is filtered and resold for use by various industries. One of the most frequent applications of this reclaimed oil in the southeast is to fuel the high temperature furnaces used to melt asphalt for road construction. It is also used in drying ovens for mined clay in the production of landfill liner, cat litter, and cement. Many other options exist for reclaimed oil, including waste to energy power plants.

2.2.5.2 Refining

The oil may also be sent to a re-refiner. Used oil produced in several countries are reprocessed using fractionating techniques very similar to those used in the refining of virgin crude. The big difference is that in fractionating used oil, fewer types of products are formed. The main products of re-refining are diesel fuel, high and low quality lubricants and heavy fuel oils used in industrial burners. During the re-refining process, hazardous materials are separated out of the oil resource and sent to hazardous waste treatment, storage or disposal facilities. Technology is progressing to restore the additives and reconstitute the oil to its original lubrication specifications.

2.3 REFINING TECHNOLOGIES

2.3.1 Technological Review

Recycling processes using nontoxic and cost effective materials can be an optimum solution. Acid-clay has been used as a recycling method for used motor oil for a long time. This method has many disadvantages; it also produces large quantity of pollutants, is unable to treat modern multi-grade oils and it is difficult to remove asphaltic impurities. (Fox, 2007)

Membrane technology is another method for regeneration of used lubricating oils. In this method three types of polymer hollow fiber membranes [polyethersulphone(PES), polyvinylidene fluoride (PVDF), and polyacrylonitrile(PAN)] were used for recycling the used motor oils. The process is carried out at 40 °C and 0.1MPa pressure. The process is a continuous operation as it removes metal particles and dusts from used motor oil and improves the recovered oils liquidity and flash point. Despite the above mentioned advantages, the expensive membranes may get damaged and fouled by large particles. (Dang, 1997)

Vacuum distillation and hydrogenation are two other methods that can be used for recycling used engine oil. The Kinetics Technology International (KTI) process is a combination of vacuum distillation and hydro-finishing. This method removes most of the contaminants from the waste oil. The process starts with atmospheric distillation to eliminate water and light hydrocarbons. This is then followed by vacuum distillation at a temperature of 250 °C. The final stage is hydrogenation of the products to eliminate the sulphur, nitrogen and oxygenated compounds. This stage is also used to improve the color and odor of the oil. The product can be of quality standard with a yield of approximately 82% and minimized polluting by-products.(Havemann, 16-18 October 1978)

Solvent extraction has replaced acid treatment as the method of choice for improving the oxidative stability and viscosity/temperature characteristics of base oils. The solvent selectively dissolves the undesired aromatic components (the extract), leaving the desirable saturated components, especially alkanes, as a separate phase (the raffinate).(Ihan Hamawand, 2013)

In one study a mixture of methyl ethyl ketone (MEK) and 2-propanol was used as an extracting material for recycling used motor oils. Although the oil resulting from this process is comparable to that produced by the acid-clay method, its cost is high. Expensive solvents and vacuum distillation are required to carry out this method. Recently propane was used as a solvent. Propane is capable of dissolving paraffinic or waxy material and intermediately dissolved oxygenated material.(Mohammad Shakirullah, 2006)

2.3.2 Comparison of Available Technologies

It is possible to categorize waste oil re-refining technologies under three main titles. These technologies are: 1- Acid-Clay Process, 2- Hydro-processing, 3- Solvent Extraction. The main criteria for the comparison of these methods are mentioned below and the advantages and disadvantages of each method are listed under subtitles.

Acid-Clay Method is no more a widely preferred method due to the additional hazardous waste (spent clay and acid sludge) generated during the process and the risks of contact with strong acids. Therefore, it is possible to claim that Hydro-processing and Solvent Extraction methods are the only acceptable technologies in present-day conditions.

When the available methods are compared in terms of initial investment costs, Solvent Extraction process requires a relatively small-scale investment. However, depending upon the technology adopted, the total cost might be higher than Hydro-processing due to the operating costs to make up for the solvent loss. On the other hand, when compared to Hydro-processing, catalyst is not required in Solvent Extraction. Moreover, it is not necessary to establish a hydrogen gas supply facility in this method and it poses a smaller risk concerning operation safety.

When the available methods are compared in terms of the qualities of the feedstock required to obtain the intended product, it is observed that in order to obtain Group II/II+ oil in Solvent Extraction method, the feedstock that will be processed needs to be a homogeneous mixture. Therefore the quality of the base oil produced with this technology is directly related to the feedstock. In this respect, despite the higher investment cost of Hydro-processing technology, it is advantageous because of the Group II quality product output it produces independent of the quality and source of the feedstock. The major drawback of Hydro-processing in this regard is that the catalyst used is sensitive to the quality of the feedstock. For example, using low quality oils, such as industrial waste oils, as feedstock might shorten the catalyst life.

Another point that should be considered is that the facilities all around the world using the same technology and have similar product outputs are able to reduce cost of the OEM tests by exchanging their stocks of different feedstock between each other. Companies like Puralube and CEP try this approach in the facilities around the world that use their technologies and therefore have a significant advantage in the base oil market.(PETDER, 2012)

2.3.2.1 Acid Clay Method

Features

- Low capital investment. Makes it most cost effective for small and tiny scale plants.
- No advanced instruments, no skilled operators required.
- This is a proven technology that worked for many years worldwide.

Drawbacks

- Causes Environmental pollution due to generation of acid sludge and acid gas emission. Disposal of acid sludge is a problem.
- High operation costs, continuous clay consumption, disposal cost of spent clay. The process requires high temperatures
- Very high clay consumption, low yield, inconsistent quality. (High viscosity, API Group I Base Oil),
- The sulphur and PAHs in the oil cannot be separated, the contaminants in the oil remain in the base oil.
- Gives Lower yield due to loss of oil in sludge as well as clay since higher dosage of clay is required.
- Life span of the equipment used in acidic environment is reduced.

2.3.2.2 Hydro-processing Methods

Features

- Product quality and yield are high (API Group II Base Oil),
- PBC and Chloride can be eliminated efficiently
- PNA can be eliminated efficiently at high pressure and temperature

Drawbacks

- The process requires high pressure, high temperature and hydrogen usage
- It requires high safety standards, H_2S and HCl can be generated during the process
- Investment cost and operational costs are high, operational efficiency is low

- A separate facility needs to be established on the field in order to provide hydrogen to the process continuously
- Expensive catalysts are required

2.3.2.3 Solvent Extraction Methods

Features

- "API Group II/II+ Base Oil" can be produced based on the quality of the waste oil,
- Toxic Polyaromatic Hydrocarbons (PAH) and PNA can be completely eliminated,
- All of the synthetic base oil compounds like PAO / hydrocarbon oils are preserved,
- The process is carried out under lower pressure and temperature compared to other technologies,
- The process has high product operational efficiency,
- Small quantities of waste and contaminants are generated, waste disposal cost is low.

Drawbacks

- The product quality is dependent upon the waste oil mixture used as feedstock. High quality feedstock is required for high quality Group II, Group II+ base oil. In hydro processing, with hydrogen saturation, the product quality is not dependent on the quality of the feedstock.
- Based on the waste oil used, the solvent costs can be high.(PETDER, 2012)

2.3.3 Research Related to Refined Oil

M. Alves dos Reis (1991) developed a solution of potassium hydroxide in 2-propanol and a hydrocarbon, which segregates organic sludge from waste oils. The operation of re-refining waste lubricating oils by treatment with an organic solvent which dissolves base oil and flocculates the major part of additives and particulate matter is intended to substitute the classical reaction with sulfuric acid, which generates an acid sludge and creates difficult disposal problems. Upon separation with this technique, the sludge may be used as a component of asphalts, or better, as a component of offset inks, consequently increasing the value of waste oils.

Armstrong and Strigner (1982) conducted a field test and laboratory analysis program to evaluate the comparative performance characteristics of a virgin and an acid/clay re- refined API-SE/SAE 20W-40 automotive engine lubricating oil. Eight new police patrol cars (four on virgin and 4 on re-refined oil) were run in normal operation for 100,000 km (about 62,500 miles) with an oil change interval of 5,000 km (3,125 miles). Inspection of the engine components showed that there were no oil related problems with any of the vehicles. In general, both oils operated satisfactorily and were considered substantially equivalent.

Brinkman and Dickson (1995) suggested that used oils are an excellent example of a high-volume recyclable commodity that can be turned from waste into valuable products. The degree of hazard posed by improper management of used oils as related to the contaminants typically found in waste oil is debated. Samples for this study were taken at every step in a used oil management system, including there-refining process. Concentrations of chlorinated solvents, metals (Cd, Cr, and Pb), and polynuclear aromatics were compared for each step in the used oil management program and with past studies.

Brinkman, Dickson, and Wilkinson (1995) processed approximately 225,000 gallons of used oil contaminated with polychlorinated biphenyls (PCB's) through a full-scale re-refinery using vacuum distillation hydro-treatment technology. The catalytic reaction with hydrogen not only destroyed the PCB's but also generated useful petroleum products, including lubricating oil. Testing of the used oil feed as well as all intermediates, by-products, and products allowed for the monitoring of the fate of the PCB's and demonstrated their destruction. The important advantage of the hydrogenation reaction chemistry is pointed out and the fact that the chemistry involved in the catalytic destruction of PCB's is well documented.

Brinkman and San Julian (1993) site several options for the recycling of wastes from off-highway operations. Parts can be cleaned with solvents that are recycled over and over, on a regular schedule and possibly not be considered as hazardous waste. Recycling used oil might involve ensuring that the waste oil goes to are-refiner and using re-refined lubricants. Reclamation and reuse are good options for antifreeze and segregated industrial solvents. Brinkman and San Julian suggest that even for more complex wastes, including oil filters and mixed liquid wastes, there are opportunities to reclaim the recyclable solvent and metallic portions of the waste, while blending the remainder for cement kiln fuel. Thus, in the end, almost nothing is left for land disposal. This technique not only satisfies waste minimization requirements, but also eliminates long-term liability for future environmental releases from the disposal site.

Brinkman (1991) indicates that recent technology enhancements and Safety-Kleen's marketing decisions to significantly increase volume throughput have combined to produce the next generation of used oil refineries. With a feedstock capacity of75 million gallons per year, the first of these units, which is in full production in East Chicago, Ind., is believed to be the largest used oil refinery in the world. The primary factor which allowed Safety-Kleen to construct this large facility is the potential use of an existing collection system within its industrial solvent servicing business. Brinkman emphasizes the importance of properly handling the used oil resource.

Brinkman (1987) reviews several re-refining process configuration options and notes the recent resurgence of used lubricating oil re-refining due largely to the availability and active promotion of the many new and varied technologies. Even though a recent annotated bibliography provides abstracts for 266 publications on new processes and over 1,200 abstracts on used oil recycling in general that were released since 1970, Brinkman reviews a selected few process schemes that have advanced to commercialization. Several of these schemes have been implemented and the selection process to determine which general approaches seem most commercially viable has begun to converge. Brinkman indicates that due to the maturing of the technology, only a few variations of one generic process, thin film evaporators, have accounted for most plants built in the late 1970's and early 1980's.(Jesse C. Jones, 1995)

2.4 REFINING PROCESS USING SOLVENT EXTRACTION

2.4.1 The Need to Refine Used Oil

Used oil has always been refined in the past on large-scale basis by the big oil producing companies. By applying highly complex processes and plants (e.g. solvent treatment-distillation-finishing re-refining process, distillation hydro-finishing refining process, high temperature distilling process) they are able to produce a high-quality lubrication oil from former oil waste. During times when the price for crude oil was high or in isolated economies the refining of used oil made economic sense. In times when the price for crude oil is low the economic advantage of used oil refining diminished. Nevertheless a reasonable amount of oil waste is constantly generated, last but not least by the numerous motor vehicles populating the streets world-wide. Industrialized countries with a great number of cement factories, metallurgical plants or incinerators may be able to use oil waste as fuel for the different combustion processes. Small or less dense populated countries, particularly in developing countries, often have not this opportunity. Additionally the infrastructure for used oil collection and disposal is not sufficiently established. This results in an indiscriminate and improper disposal of oil waste wherever the waste oil is generated. To fill the gap between the refining and/or re-use of oil waste in big industrial plants on one side and an indiscriminate disposal of waste oil somewhere in the bush or backyard on the other, there is a need for small-scale processing plants which produce new products and minimize the amount of waste. Obviously small scale recycling processes might not be able to achieve an oil product of high quality, but particularly in developing countries, there are numerous applications for minor quality lubrication oils in the small scale industry sector as well. At least small scale oil recycling offers an opportunity to create jobs and income, makes use of waste oil as raw material, decreases the amount of waste to dispose of and improves the environmental situation in preventing an indiscriminate disposal of used oil.(Jesse C. Jones, 1995)

2.4.2 Refining Using Solvent Extraction

The used lubricating oil refining process commonly used today includes three distillation stages, followed by a solvent extraction process. The distillation stages (dehydration, fuel stripping, and vacuum distillation) produce distilled oil, fuel, and asphalt extender products. The distilled oil is then goes to solvent extraction to yield finished base oils

The main processes that are taking place are as follows.

- **pretreatment**

The used lubricating oil contains different types of solid materials, so first it must be removed. Used motor lubricating oil is stored for several days to allow large suspended particles to settle under gravity. This means there is a need to perform a pretreatment process such as settling or filtration using vacuum filter. Therefore the used oil is settled or filtered.

- **Dehydration**

Then after the pretreatment of the used oil, it must be dehydrated in order to remove the water in the used oil. The oil is heated in a heating mantle at a temperature of 120-140^{o}c to remove the water that has been mixed into it.

- **Diesel Stripping**

The dehydrated used oil is then fed continuously into a vacuum distillation for fractionation at a temperature of above 240^{o}c. Lighter oils boil off first and are removed. Other heavier components will do not boil in the conditions used.

Light fuel oil: The light fuel oil produced at a temperature of 140°C. The light fuel oil can be used as fuel source for heating.

Lubricating oil: At 240°C the lubricating oil fraction is obtained.

Residue: The remaining oil at this temperature (240°C) contains the dirt, degraded additives, metal wear parts and combustion products like carbon and is collected as residue. The residue is in the form similar to that of tar, which can be used as a construction material.

- **Extraction, Distillation And Condensation**

A liquid extraction process then removes any aromatic components from the oil. By this stage, the oil is similar to virgin base oil.

Solvent extraction: solvent such as n-Butanol and 2-Propanol are selective aromatic solvents employed in the solvent extraction process. The lubricating oil fraction obtained by vacuum distillation will be mixed by agitation with the solvent in an appropriate ratio. The lubricating oil and solvent mixture will be allowed to settle in the separation flask for four hours.

The aromatic content and degraded additives present in the lubricating oil fraction are settle at the bottom and the lubricating oil fraction and solvent mixture layer forms at the top. The lubricating oil produced at this stage is similar to that of the base lubricating oil.

- **Mixing And Finishing**

It is then tested, appropriate additives are added and the oil is ready to be reused.

Additives adding: Additives are added to the lubricating oil produced from the above sequential process to further improve the properties and to make them eligible for use in automobile engines. ZincDialkyl Dithiosulphate or other common additive is added to the lubricating oil while heating. The heating and mixing ensures the complete mixing of the additive with the lubricating oil. The lubricating oil produced at this stage is tested weather it is identical to the commercially available lubricating oil.(Shri Kannan C, 2014)

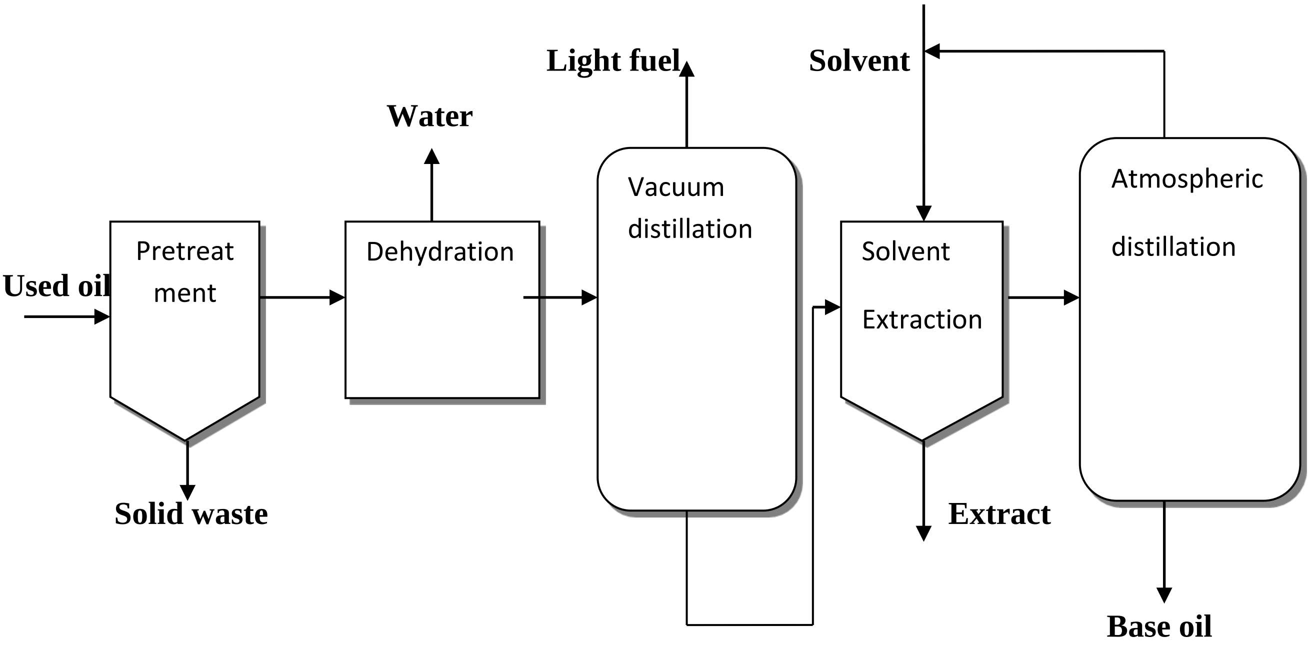


Figure 2.1:- process flow diagram

MATERIALS AND METHODS

3.1 MATERIALS

For this research different equipment and chemicals were used. The sample used oil for this experiment was collected from TOTAL Ethiopia oil company gas stations, when the cars changed their motor oil after use of thousands of kilometer. Other equipment and chemical were from Addis Ababa institute of technology laboratory and some chemicals were purchased from private chemical suppliers. The different kinds of chemical and equipment are listed below with their use.

Table 3.1: List of Equipment and chemicals for the experiment

Items	use
➢ Equipment	
Oil drum (plastic bottle)	Sample collection
Glass & plastic Beakers	Sample and product handling
Distillation flask	Holding sample for distillation
Condenser	Cooling the vapor
Heating mantle	Heating the sample
Measuring cylinder	Measure the sample and chemical
Mixer	Mixing the samples with solvent
Thermometer	Measuring temperature
Vibro Viscometer	Measuring viscosity
Picnometer	Measuring density
Atomic absorption	Measuring metals
➢ Chemicals	
2-propanol (99.5%)	Solvent for extraction
n-butanol (99.5)	Solvent for extraction

➢ Auxiliary materials	
Gloves	Safety
Mouth mask	Safety
Eye glass	Safety
Cleaning materials (kerosene, detergents, water, sponge)	Cleaning the equipment and working area
Aluminum foil	Covering the sample beakers
Stationary materials(Masking tape, marker)	Labeling sample

3.2 METHODES

The methodology that was used to perform this research is through laboratory experiment. Here, in this research, solvent extraction method was selected. The general experimental procedure follows three basic steps which are:

1) Characterization of used motor oil
2) Treatment of the used motor oil
3) Characterization of treated oil

3.2.1 Characterization of Used Motor Oil

As it has been seen the used motor oil has different contaminants. In order to refine these oil, the compositions it had should be known. Then comparison should be done with the new virgin oil, in order to know how much the magnitude and composition is different. Then the treatment process will follow. In the characterization Density, Viscosity, Viscosity index, Flash point and metal content analysis had been performed for adequate characterization of the sample. Some of these tests also give clues of the different sources of contaminations. The full characterization of the used oil will be covered in the next chapter. Below is the characterized result of two types of virgin oils which is obtained from TOTAL Ethiopia Oil Company.

Table 3.2:- Characterization of TOTAL RUBIA TIR 7400 15W-40 & TOTAL QUARTZ 5000 20W-50 virgin oil

Test	Unit	Method	Value	
			Rubia	Quartz
Density @15 °C	Kg/m^3	ASTM D1298	888	892.1
K. viscosity @ 40 °C	mm^2/s	ASTM D445	98.7	176.4
K. viscosity @ 100 °C	mm^2/s	ASTM D445	13.4	19.1
Viscosity index	-	ASTM D2270	136	123
Flash point	°C	ASTM D92	236	240

(source: TOTAL Ethiopia Oil company)

3.2.1.1 Density And Specific Gravity (ASTM D1298)

The level of impurities in the used oil is indicated by the density and specific gravity. The density and 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. Using the measuring device which is called picnometer, the density will be measured. First the dry picnometer was measured using digital mass balance (model EP214C) and 50ml of used motor oil was added to the 50ml size picnometer. The combined mass of oil and picnometer was measured. The difference is the mass of the oil and dividing by 50ml gives the density of the used oil.

$$\rho = \frac{m(p+o)-mp}{Vo} \qquad 3.1$$

Where :- m (p+o) is the combined mass of picnometer and used oil
mp is mass of picnometer
Vo is volume of used oil which is 50ml

3.2.1.2 Viscosity (ASTM D445)

The kinematic viscosity of oil is calculated by dividing the dynamic viscosity to density. The dynamic viscosity is found by using vibro-viscometer (model SV-10), a viscosity measuring equipment. First the used oil sample was heated at a temperature of 100 and 40 ^{o} C, then the heated sample was poured to the vibro-viscometer cup and the vibro-viscometer tip was inserted into the sample and a reading was taken.

$$K.V = \frac{\mu}{\rho} \qquad 3.2$$

Where :- K.V is the kinematic viscosity
μ is the dynamic(absolute) viscosity and
ρ is the density of the oil

3.2.1.3 Viscosity Index (ASTM D2270)

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. The viscosity index calculator (Viscopedia) was used from internet online system.

3.2.1.4 Flash Point (ASTM D92)

Flash point is determined by Cleveland open cup apparatus method. The oil is taken in the open cup and heated. The temperature at which the vapor given out by the heating oil catches fire momentarily when exposed to the ignition source is noted as flash point temperature.

3.2.1.5 Metal content (ASTM D92)

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 (listed in the table 4.1) 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.

3.2.2 Treatment of Used Motor Oil Procedure

The first step in doing this experiment is pretreatment of the used oil following is dehydration to remove waters and some light fuels. Then the vacuum distillation will follow. After cooling, the mixing of solvent with used oil will succeed. Finally the solvent recovery will follow. The full procedure is discussed below.

Step 1:- pretreatment

The used motor oil contains different types of solid materials, so first it must be removed, therefore the used oil was settled for one day in the plastic bottle (oil drum) and then it was poured into the beakers for dehydration.

Figure 3.1 collecting and settling the used motor oil

Step 2 - Dehydration

Then after pretreatment of the used oil, a sample with 300ml of used oil was measured using beaker with size of 1000ml and it was dehydrated at about 140^{o}c for 1 hour using heating mantle and controlling the temperature by thermometer. Here the water and some of the light fuels were separated.

Figure 3.2 dehydration

Step 3 – vacuum distillation

The dehydrated used oil was then fed continuously into a vacuum distillation with a vacuum pressure of 20 mmHg and at a temperature of 250^{0}c for fractionation. Light fuels boil off first and were removed. Other heavier components do not boil in the conditions used. The distillation process was continued until last drop of condensed light fuel was seen.

Light fuel oil: The light fuel oil is produced, which can be used as a burning fuel.

Figure 3.3:- vacuum distillation

Step 4 – Solvent Extraction

Solvent such as n-Butanol and 2-propanol are a selective aromatic solvents employed in the solvent extraction process. By preparing two beakers with size of 2000ml mixing was started with one beaker for n-Butanol with used oil and the other beaker for 2-propanol with used oil. The lubricating oil fraction obtained by vacuum distillation was mixed by agitation at a speed of 1200 rpm with n-Butanol and 2-propanol in an appropriate with different solvent to oil ratio (6:1 and 4:1). Then the lubricating oil and solvent mixture was left to settle in the separation flask for 72 hours.

The aromatic content and degraded additives present in the lubricating oil fraction is settled at the bottom, and the lubricating oil fraction and solvent mixture layer forms at the top. Then separating the mixture from the sludge and recovering the solvent using atmospheric distillation was followed.

Figure 3.4:- mixing and settling

Figure 3.5:- after settling

Step 5:- Distillation and Condensation

The mixture of solvent and oil was distilled to recover the solvent. At the boiling point of n-Butanol and 2-propanol (i.e. 118^0c and 83.5^0c respectively) the distillation process was performed and the condensed solvent was collected by the flask. The final product, which is the base oil, is obtained finally and left to cool at room temperature. The final products were collected using glass flasks and sent for characterization.

Figure 3.6 solvent recovering using distillation

3.2.3 Characterization of Treated Oil

The product that had been found from the experiment was collected in the glass flask. Before characterizing the whole parameters or properties, it should be selected the best sample from the performed experiment. The choice was based on physical analysis. This are

- Yield
- Kinematic viscosity @ 40 ^oC
- Density

The product with best value of the above test was chosen and further characterization and analysis is performed like viscosity @ 100 ^oC, viscosity index, flash point and metal contents.

3.3 EXPERIMENTAL DESIGN

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

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

3.3.1 Experimental Factors

The experimental factors which were investigated in this study were selected based on their influential rank in affecting used oil recovery ability of the solvent extraction process and availability of required facility that allow monitoring and controlling.

Two categorical factors were nominated for the laboratory experiment. These are solvent-to-used oil sample ratio and solvent type. As described in the previous chapter and as the treatment name itself indicates, solvent-to-used oil sample ratio and solvent type have significant influence on the effectiveness of the refining method.

Both solvent-to-used oil sample ratio and solvent type were varied in two levels. The experimental factors and their corresponding levels are listed in the table below. Both the Rubia and Quartz experimental factors are the same only the difference is the raw used oil that is Rubia and Quartz used oil.

Table 3.3:- Experimental factors and corresponding levels

Solvent : used oil	**Solvent type**	
	n-Butanol	**2-Propanol**
4:1	Run 1	Run 2
6:1	Run 3	Run 4

As represented in the table above, four runs are required to complete the overall factorial combination of both factors and their respective test levels for each of the Rubia used oil and Quartz used oil. But a duplicate of each run was performed to minimize experimental errors. The total experimental runs and randomization of the practical experiment is presented in the results and discussion section.

RESULT AND DISCUSSION

4.1 CHARACTERIZATION OF USED MOTOR OIL

In this section the characterization of used motor oil is performed and the results of the treated oil is also characterized and then compared with each other and with the virgin oil. The characterized result for used Rubia and Quartz lubricant is listed in the table below.

Table 4.1:- Characterized Rubia and Quartz Used oil sample

Properties	Rubia Used motor oil	Quartz Used motor oil
Flash Point °C	170	167.8
Kinematic Viscosity@ 40 °C (cSt)	102.21	180.4
Kinematic Viscosity@ 100 °C (cSt)	13.8	24
Viscosity Index	135.9	163.195
Density (g/ml)	0.946268	0.948340
Metal Contents (ppm)		
➢ Ca	175.06	201.6
➢ Zn	105.89	105.83
➢ As	<0.5	<0.50
➢ Cd	0.46	<0.20
➢ Cr	0	0.01
➢ Pb	0.03	0.03
➢ Cu	42.17	12.84
➢ Fe	283.48	583.39
➢ Ni	0.53	0.48
➢ Mg	9.35	8.36
➢ Mo	52.56	74.76

As it can be seen from the above table the property of the used oil is different from the virgin oil which is because of degradation during the working time of the engine. As indicated in the table, Flash point is the minimum temperature at which the vapor 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. Increased density and viscosity parameters show possible oxidation and polymerization products dissolved and suspended in the used oil. Finally metal contents show contamination from engine parts wearing.

4.2 THE PHYSICAL ANALYSIS OF TREATED OIL

As it is seen in the previous chapter the used oil was treated by a solvent extraction method and a product was collected. The result of physical analysis of the product is listed in the table below.

Table 4.2:- Result from physical analysis of treated Rubia oil

Std	Run	Block	Solvent:used oil	Solvent type	Yield (%)	K.Viscosity @40 °C (cSt)	K.Viscosity @100°C (cSt)	Density (g/ml)
5	1	Block 1	4:1	n-Butanol	55	46.4	5.8	0.8697
3	2	Block 1	6:1	2-propanol	71	69.7	9.2	0.8715
6	3	Block 1	4:1	n-Butanol	55	46.4	5.8	0.8697
7	4	Block 1	6:1	n-Butanol	64	58	7.9	0.8701
8	5	Block 1	6:1	n-Butanol	65	58	7.9	0.8701
4	6	Block 1	4:1	2-Propanol	60	62.1	7.1	0.8701
1	7	Block 1	6:1	2-Propanol	72	70	9.2	0.8715
2	8	Block 1	4:1	2-Propanol	62	62.1	7.1	0.8701

Table 4.3:- Result from physical analysis of treated Quartz oil

Std	Run	Block	Solvent: used oil	Solvent type	Yield (%)	K.Viscosity @40 °C (cSt)	K.Viscosity @100 °C (cSt)	Density (g/ml)
6	1	Block 1	4:1	n-Butanol	50	76	9.7	0.8731
5	2	Block 1	4:1	n-Butanol	51.8	74.6	9.2	0.8706
8	3	Block 1	6:1	n-Butanol	60.9	89	12.3	0.8869
3	4	Block 1	6:1	2-propanol	73.4	96.3	13.9	0.8834
7	5	Block 1	6:1	n-Butanol	61.7	87.6	11.8	0.8861
1	6	Block 1	4:1	2-Propanol	56.2	84	11.1	0.8795
4	7	Block 1	6:1	2-Propanol	72.6	98	14.7	0.8846
2	8	Block 1	4:1	2-Propanol	58.4	81.9	10.7	0.8701

From the analysis of the above table, it is observed that the maximum and minimum yield is 72% and 55% respectively for the Rubia and 73.4% and 50% for Quartz treated oil. The maximum kinematic viscosity at 40 ^{o} C is 70 cSt and a minimum of 46.4 cSt for Rubia treated oil with density of 0.8715 and 0.8697g/ml respectively While that of Quartz has maximum at 98 cSt with density of 0.8846g/ml and minimum at 74.4 cSt with a density of 0.8706g/ml.

4.3 EFFECTS OF EXPERIMENTAL FACTORS ON THE RESULT

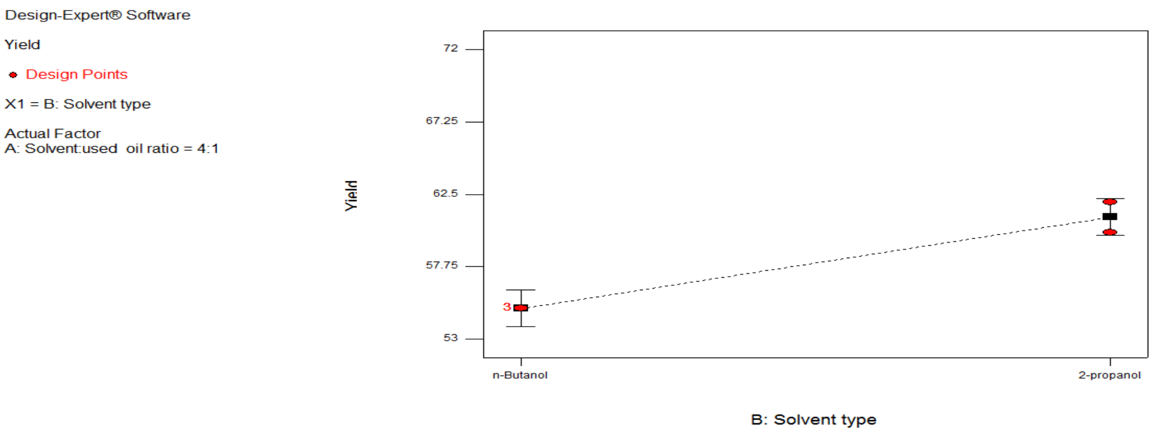
The type of solvent used and the mixing ratio applied for different runs has shown significant effects on the yield of recovered oil as considered separately and interacting. Density and viscosity are also influenced with different intensity as the type and amount of the experimental factors are varied.

4.3.1 Effect of Solvent Type

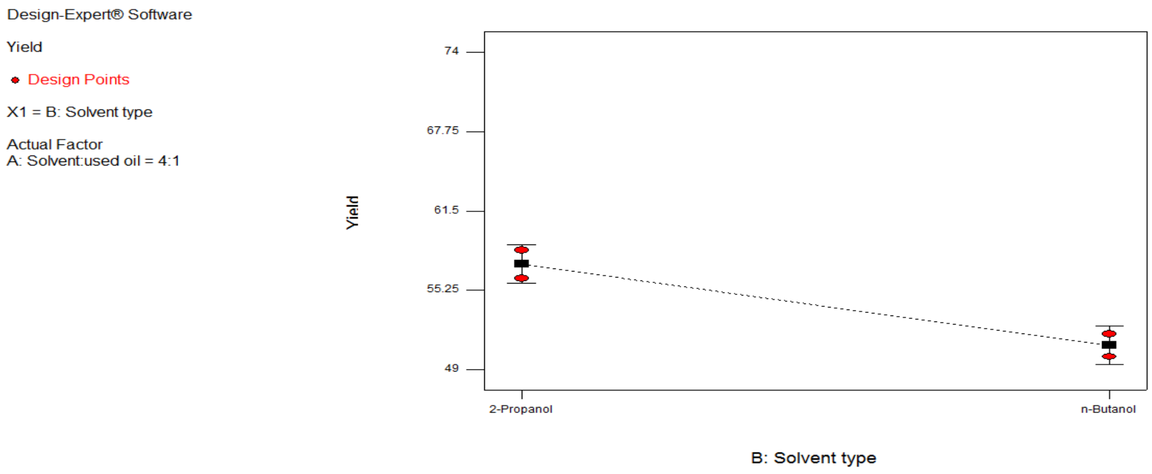
From the experimental result, as it shown in the table 4.2&4.3, the types of solvent have significant effect on the properties of the treated oil such as yield, kinematic viscosity and the density.

4.3.1.1 Effect of Solvent Type on Yield

The amount (percentage) of yield which was acquired from the experiment by varying the type of solvent was different, even keeping the solvent to used oil ratio constant. The yield of both Rubia and Quartz was not the same. The yield with solvent type 2-Propanol was higher than that of n-Butanol. As it is shown in the table 4.4 the yield is different for the two solvent type while the mixing ratio is constant, that is at a ratio of 4:1 the yield using 2-Propanol was 61% for Rubia and 57.3% for quartz while that of n-Butanol is 55% for Rubia and 50.9% for Quartz. The same thing is observed for a ratio of 6:1 which is 71.5% for Rubia and 73% for Quartz using 2-Propanol and 64.5% for Rubia 61.9% for Quartz using n-Butanol respectively. As it is shown in the figure 4.1, the yield increase with the solvent type from n-Butanol to 2-Propanol and its more significant in the Rubia oil.



(a)

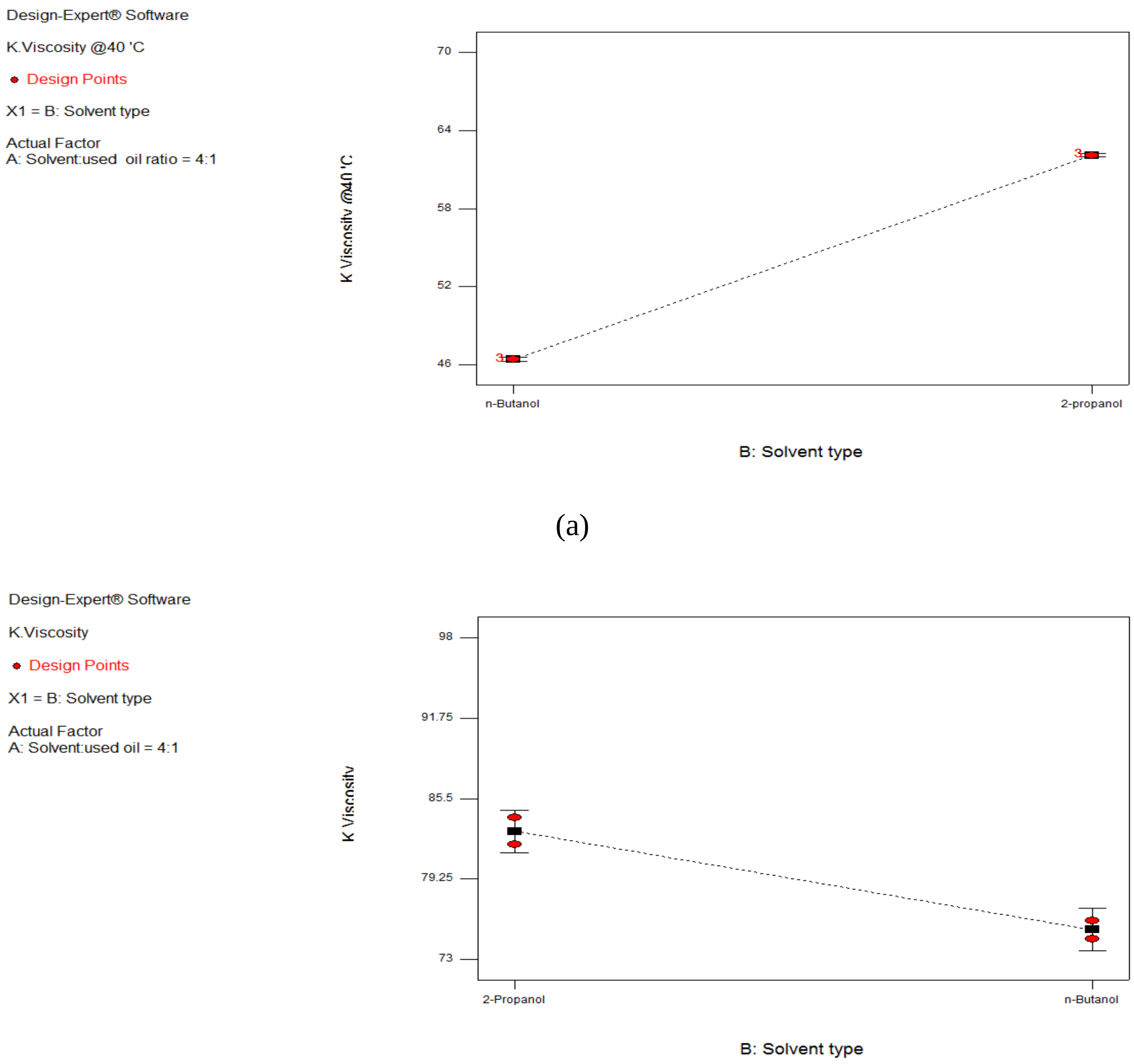


(b)

Figure 4.1 Effect of solvent type on yield for (a) Rubia and (b) Quartz

4.3.1.2 Effect of Solvent Type on Kinematic Viscosity

The kinematic viscosity of the used motor oil is large as it is shown in the table 4.1, this is because of contaminants and degraded materials. When the treatment was performed it was decreased from 102.21 and 180.4 cSt to lower value as it was shown in table 4.2&4.3. When the treated Rubia and Quartz oil was seen there is a difference between the used, treated and virgin oil. For example, the kinematic viscosity of treated oil at 40 ^{o}C becomes in the range of 46.4 to 70 cSt for Rubia and 74.6 to 98 cSt for Quartz. This shows the degraded materials and impurities are removed. Here the solvent type also influence the kinematic viscosity at 40 ^{o}C, as it is shown in table 4.4, that is at mixing ratio of 4:1 the average kinematic viscosity of treated oil is 46.4 cSt using n-Butanol and 62.1 cSt using 2-Propanol. Also if the mixing ratio is increased the kinematic viscosity with solvent type of 2-Propanol is 69.9 cSt while that of n-Butanol is 58 cSt. When the treated Quartz oil is seen, by the same reason like that of Rubia, the average kinematic viscosity at 40 ^{o}C was increased from n-Butanol to 2-Propanol solvent type, i.e. 75.3 to 83 cSt and 88.3 to 97.2 cSt at mixing ratio of 4:1&6:1respectively. Below is the figure which supports the above idea. As solvent type goes from n-Butanol to 2-Propanol the K.viscosity increased.



(a)

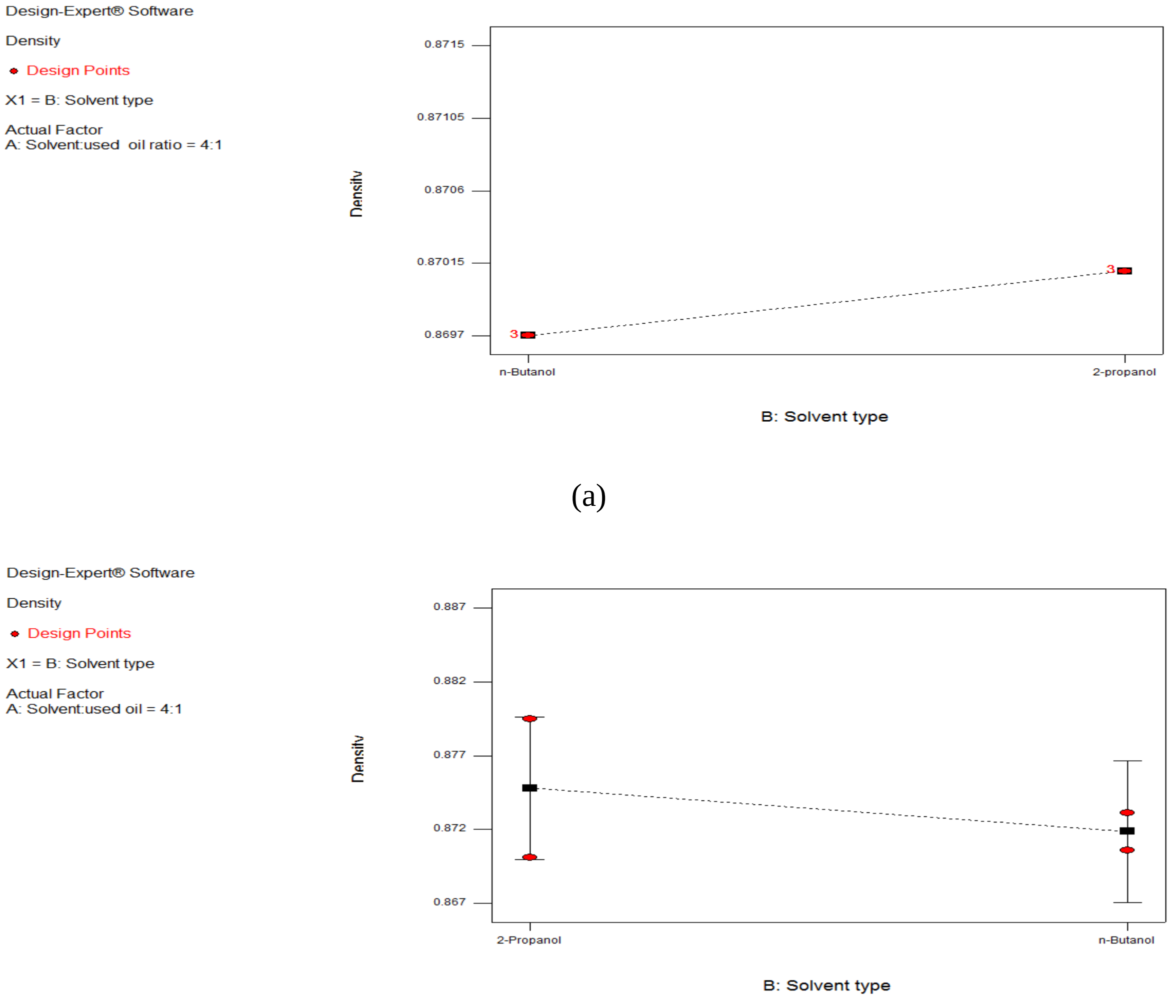
(b)

Figure 4.2 Effect of solvent type on K.viscosity for (a) Rubia and (b) Quartz

4.3.1.3 Effect of Solvent Type on Density

The density of the used oil is higher than that of the virgin oil and the treated oil. As it was shown in the table 4.2 and 4.3, the density of the treated Rubia oil ranges between 0.8697 to 0.8715 g/ml while that of treated Quartz oil ranges between 0.8701 to 0.8869 g/ml. Here also the type of solvent used has some effect even if it is small. At a mixing ratio of 4:1 when n-Butanol is used the density becomes 0.8697 and the 2-Propanol is 0.8701g/ml, at a mixing ratio of 6:1 the density is 0.8701 for n-Butanol and 0.8715 g/ml for 2-Propanol in the case of Rubia oil, and it is

0.8719 for n-Butanol and 0.8778 g/ml for 2-Propanol at mixing ratio of 4:1 and 0.8865 for n-Butanol and 0.8840 g/ml for 2-Propanol at mixing ratio of 6:1 in the case of Quartz. Generally, Theses shows that the density of treated Rubia oil is increased by using 2-Propanol instead of n-Butanol. But when the treated Quartz oil is seen, the density has little difference with mixing ratio, i.e. for the mixing ratio of 4:1 the 2-Propanol is higher but for mixing ratio of 6:1 n-Butanol is higher. Below is the comparison table for the effect of solvent type by keeping the mixing ratio constant. The above statement is supported by the following figure.



(a)

(b)

Figure 4.3 Effect of solvent type on density for (a) Rubia and (b) Quartz

Table 4.4:- Effect of solvent type

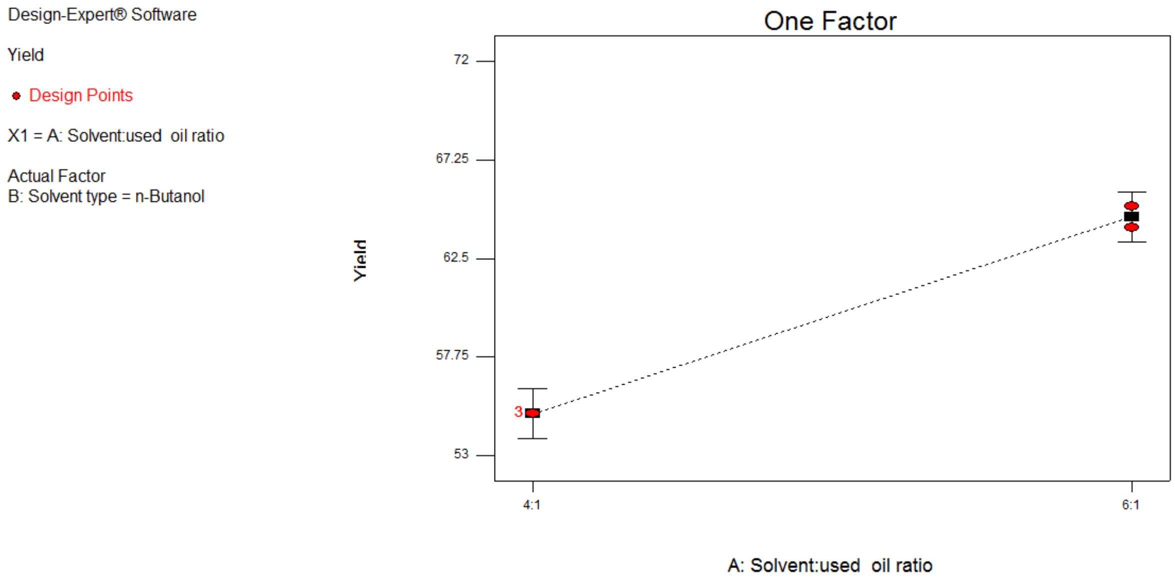
	Solvent type	Solvent: used oil	Avg Yield (%)	K.Viscosity @40 °C (cSt)	K.Viscosity @100 °C (cSt)	Density (g/ml)
RUBIA	n-Butanol	4:1	55	46.4	5.8	0.8697
	2-Propanol	4:1	61	62.1	7.1	0.8701
	n-Butanol	6:1	64.5	58	7.9	0.8701
	2-propanol	6:1	71.5	69.9	9.2	0.8715
QUARTZ	n-Butanol	4:1	50.9	75.3	9.5	0.8719
	2-Propanol	4:1	57.3	83	10.9	0.8778
	n-Butanol	6:1	61.3	88.3	12.1	0.8865
	2-Propanol	6:1	73	97.2	14.3	0.8840

4.3.2 Effect of Mixing Ratio (Solvent to Used Oil Ratio)

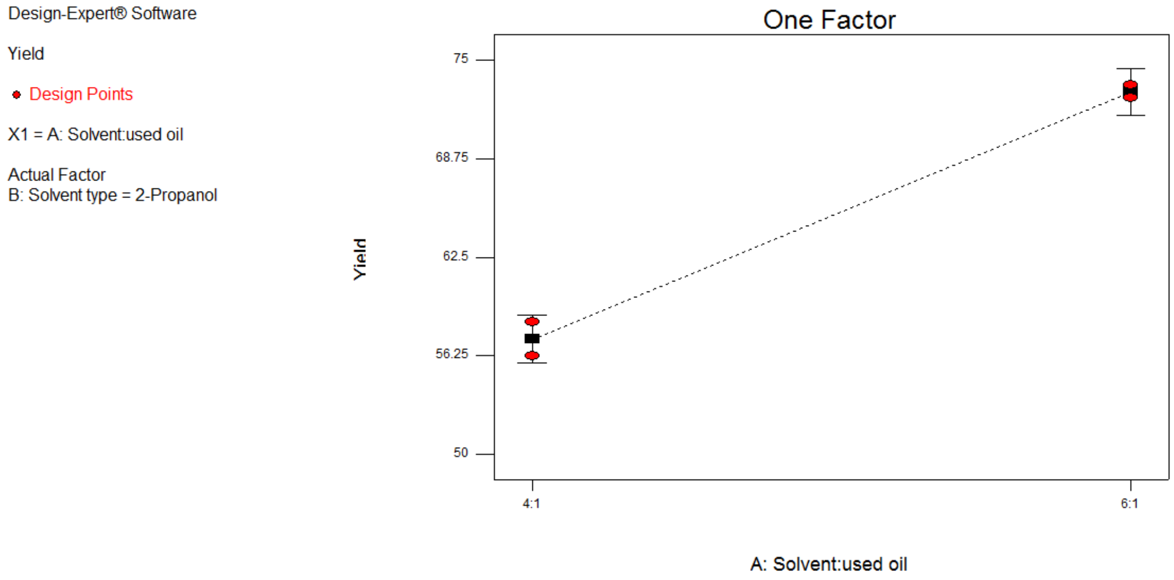
As it is seen from the experimental result, which is shown in the table 4.2&4.3, the mixing ratio i.e. solvent:used oil ratio have an effect on the properties of the treated oil such as yield, kinematic viscosity and the density.

4.3.2.1 Effect of Mixing Ratio (Solvent to Used Oil Ratio) on Yield

The amount (percentage) of yield which is acquired from the experiment by varying the mixing ratio is different even keeping the solvent type constant. The yield of both Rubia and Quartz is not the same. The yield with mixing ratio of 6:1 is higher than that of 4:1. As it shown in the table 4.5 the yield is increasing while the solvent type is constant, that is with the solvent type of n-Butanol the yield at a ratio of 6:1 is 64.5% while that of 4:1 is 55% and using 2-Propanol the 6:1ratio is71.5% while that of 4:1 is 61%. The same thing is observed for a solvent type of 2-Propanol for Rubia, and for Quartz using n-Butanol, the yield at a mixing ratio of 6:1 is 61.3% and 50.9% for mixing ratio of 4:1. And using that of 2-Propanol with a ratio of 6:1 is 73 and for a ratio of 4:1 is 57.3. The following figure shows this fact, as solvent to used oil ratio increased the yield is also increased. Particularly the treated Quartz shows a large increase.



(a)

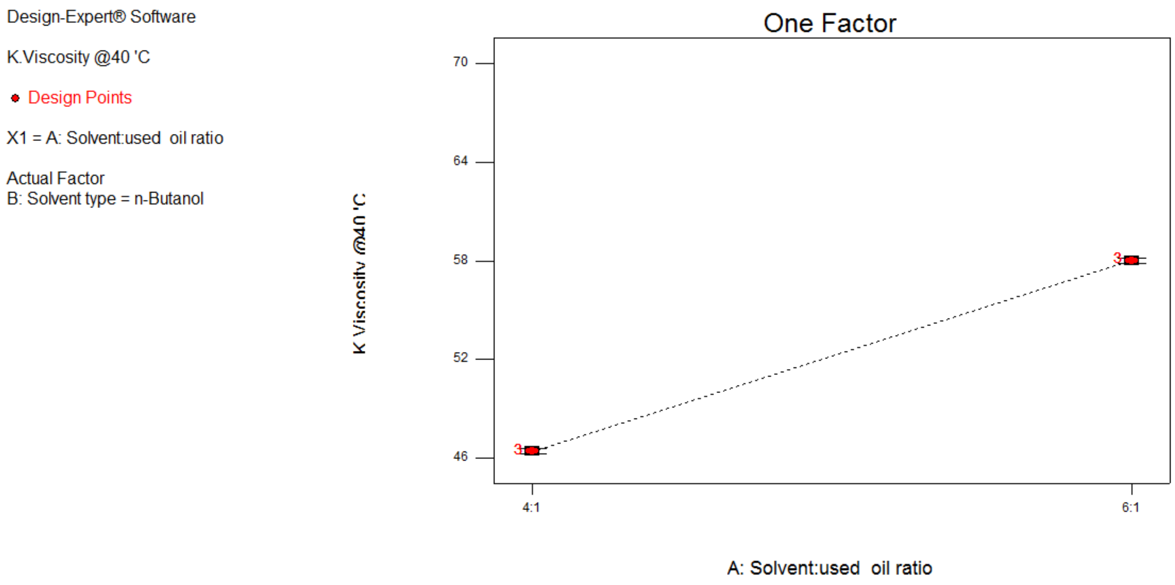


(b)

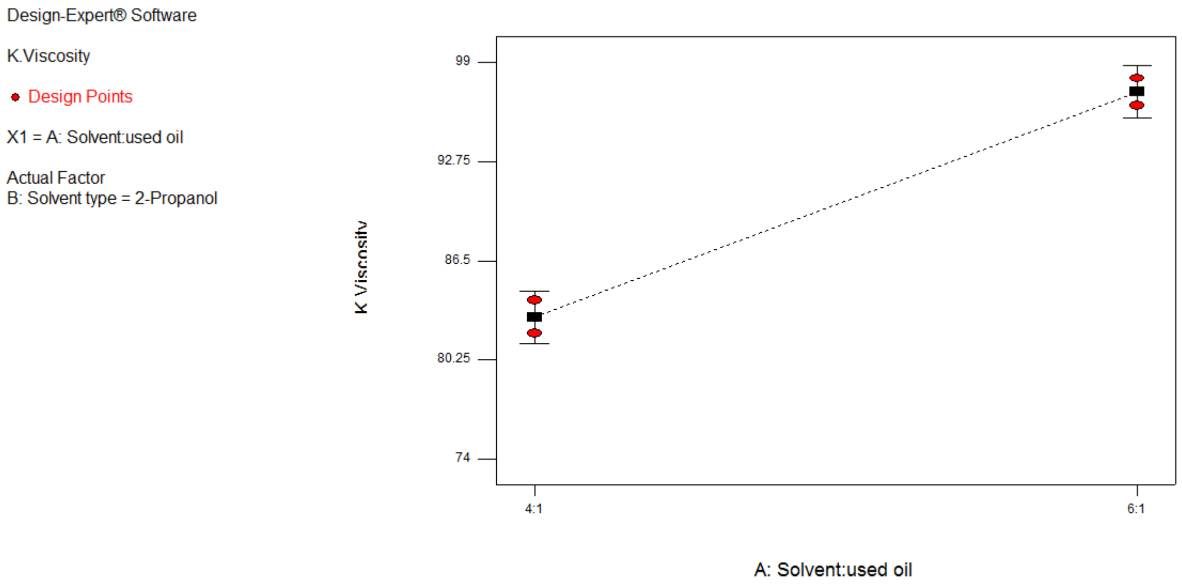
Figure 4.4 Effect of solvent : used oil ratio on yield for (a) Rubia and (b) Quartz

4.3.2.2 Effect of Mixing Ratio (Solvent to Used Oil Ratio) on Kinematic Viscosity

The kinematic viscosity of the treated oil is influenced by mixing ratio. As indicated in the table 4.3, the kinematic viscosity of the treated oil at 40 ^{o}C becomes in the range of 46.4 to 70 cSt for Rubia and 74.6 to 98 cSt for Quartz. This shows the degraded materials and impurities are removed. Here fixing the solvent type constant, the average kinematic viscosity at 40 ^{o}C for the treated Rubia oil, as it is shown in table 4.5, with solvent type of n-Butanol is 46.4 cSt at a mixing ratio of 4:1 and increased to 58 cSt at a 6:1 mixing ratio. And with the solvent type of 2-Propanol it is 62.1 cSt at mixing ratio of 4:1 and increased to 70 cSt at 6:1 mixing ratio. The same thing is observed for treated Quartz oil i.e. using n-Butanol it is 75.3 cSt at 4:1 mixing ratio and increased to 88.3 cSt at 6:1 mixing ratio, and with 2-Propanol it is 83 cSt at mixing ratio of 4:1 and increased to 97.2 cSt for a mixing ratio of 6:1. The kinematic viscosity is increased with the mixing ratio, as the above statement and the figure 4.5 below shows.



(a)

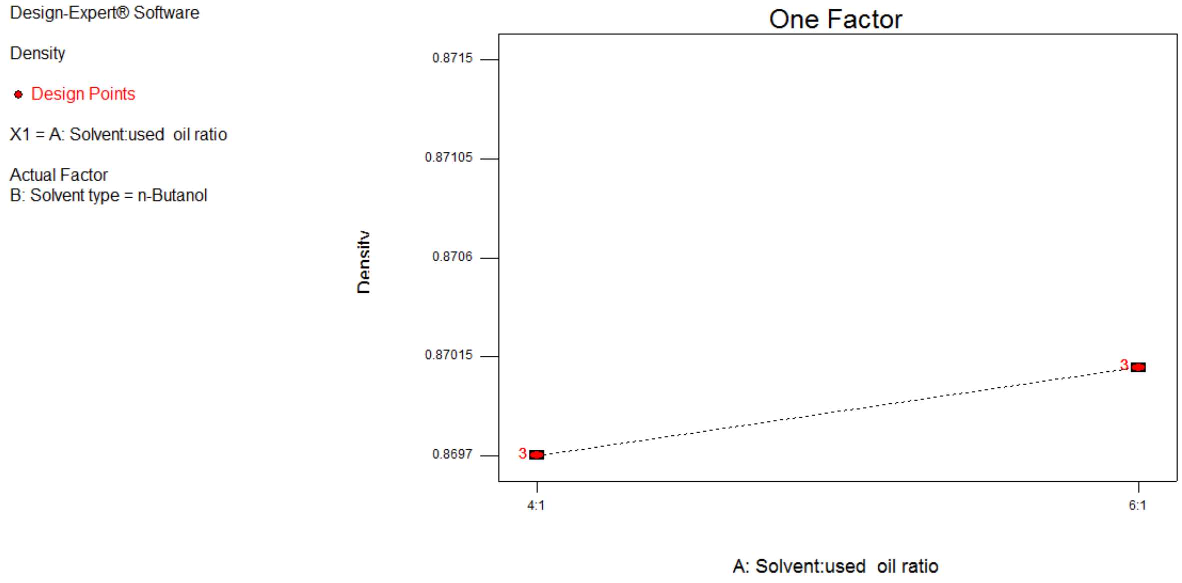


(b)

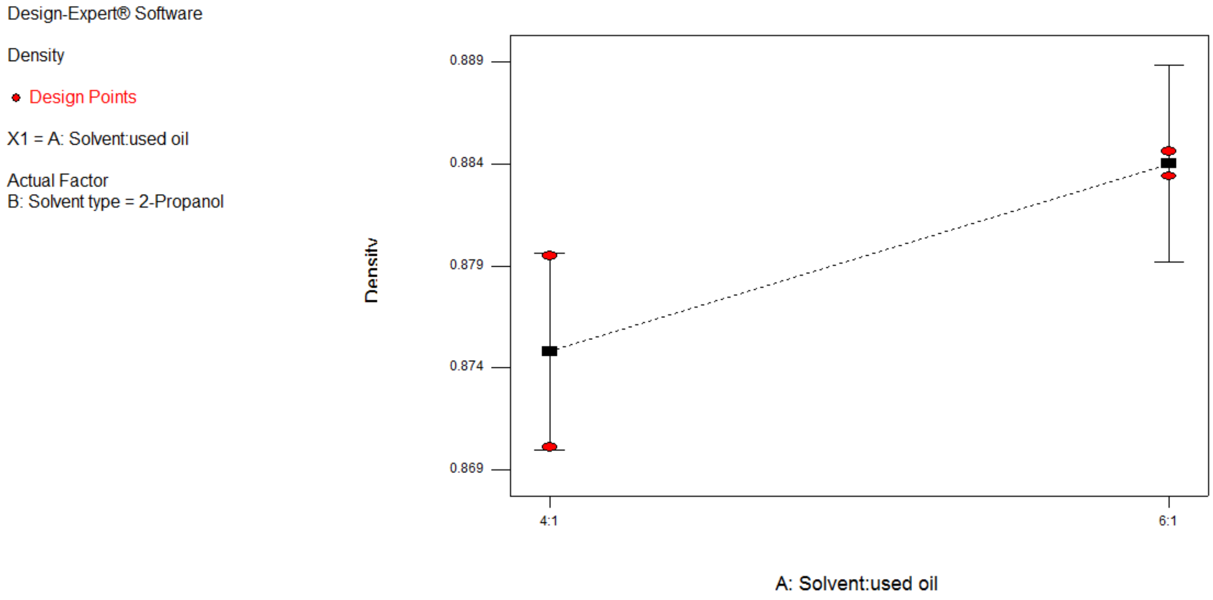
Figure 4.5 Effect of solvent : used oil ratio on K.viscosity for (a) Rubia and (b) Quartz

4.3.2.3 Effect of Mixing Ratio (Solvent to Used Oil Ratio) on Density

As it was mentioned previously, the density of the used oil is higher than that of the virgin oil and the treated oil. As it was shown in the table 4.2&4.3, the density of the treated Rubia oil ranges between 0.8697 to 0.8715 g/ml while that of treated Quartz oil ranges between 0.8701 to 0.8869 g/ml. Here also the mixing ratio has some effect even if it is small. When a mixing ratio of the treated Rubia oil increased from 4:1 to 6:1, the average density also increased from 0.8697 to 0.8701 g/ml in n-Butanol and from 0.8701 to 0.8715 g/ml in 2-propanol. And the average density of treated Quartz oil also increased from 0.8719 to 0.8865 g/ml in n-Butanol and from 0.8778 to 0.8840 g/ml in 2- Propanol. Generally, Theses shows that the density of treated Rubia and Quartz oil is increased when the mixing ratio increases. Below is the comparison table for the effect of mixing ratio by keeping the solvent type constant. As the figure supporting the above arguments, as the mixing ratio increase the density also increases.



(a)



(b)

Figure 4.6 Effect of solvent : used oil ratio on density for (a) Rubia and (b) Quartz

Table 4.5:- Effect of mixing ratio (solvent : used oil ratio)

	Solvent: used oil	Solvent type	Yield (%)	K.Viscosity @40 °C (cSt)	K.Viscosity @100 °C (cSt)	Density (g/ml)
RUBIA	4:1	n-Butanol	55	46.4	5.8	0.8697
	6:1	n-Butanol	64.5	58	7.9	0.8701
	4:1	2-Propanol	61	62.1	7.1	0.8701
	6:1	2-propanol	71.5	69.9	9.2	0.8715
QUARTZ	4:1	n-Butanol	50.9	75.3	9.5	0.8719
	6:1	n-Butanol	61.3	88.3	12.1	0.8865
	4:1	2-Propanol	57.3	83	10.9	0.8778
	6:1	2-Propanol	73	97.2	14.3	0.8840

4.3.3 Statistical Analysis

Analyzing statistical results for treated Rubia oil, ANOVA and model fitting results of experimental data from Table 4-6 it can be that Mixing ratio (i.e. solvent : used oil ratio) had the strongest effect on the yield (p-value < 0.0001) , kinematic viscosity (p-value < 0.0001) and density (p-value < 0.0001) of treated oil. Solvent type also had significant effect on yield (p-value < 0.0004), kinematic viscosity (p-value < 0.0001) and density (p-value < 0.0001) of treated oil.

For the case of treated Quartz oil ANOVA and model fitting results of experimental data (Table4-7) showed that Mixing ratio (i.e. solvent : used oil ratio) had the strongest effect on the yield (p-value < 0.0001) , kinematic viscosity (p-value < 0.0001) and density (p-value < 0.0083) of treated oil. Solvent type also had significant effect on yield (p-value < 0.0003) and kinematic viscosity (p-value < 0.0006) but not on density (p-value < 0.9315) of treated oil. For model terms (experimental factors) to be influentially significant each of the terms need to have a p-value less than 0.05 or at least less than 0.10. And the other diagnostics and model graph were shown in the appendices A.

Table 4.6 ANOVA for treated Rubia oil

Response 1: Yield
ANOVA for selected factorial model

Source	**Sum of Squares**	**df**	**Mean Square**	**F value**	**P- value Prob > F**
Model	285.00	3	95.00	162.67	0.0002 **Significant**
A-solvent:used oil ratio	200.00	1	200.00	266.67	< 0.0001
B-solvent type	84.50	1	84.50	112.67	0.0004
AB- interaction	0.50	1	0.50	0.67	0.4601
Pure Error	3.00	4	0.75		
Cor Total	288.00	7			

Response 2: Kinematic Viscosity @ 40 °C
ANOVA for selected factorial model

Source	**Sum of Squares**	**df**	**Mean Square**	**F- value**	**P- value (Prob > F)**
Model	574.12	3	191.37	17011.07	< 0.0001 **Significant**
A- solvent:used oil ratio	187.21	1	187.21	16641.00	< 0.0001
B- solvent type	379.50	1	379.50	33733.44	< 0.0001
AB- interaction	7.41	1	7.41	658.78	< 0.0001
Pure Error	0.045	4	0.011		
Cor Total	574.17	7			

Response 3: Density
ANOVA for selected factorial model

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**P- value Prob > F**
Model	3.740E-006	3	1.247E-006	6.366E+007	< 0.0001 **Significant**
A- solvent:used oil ratio	1.620E-006	1	1.620E-006	6.366E+007	< 0.0001
B- solvent type	1.620E-006	1	1.620E-006	6.366E+007	< 0.0001
AB- interaction	5.000E-007	1	5.000E-007	6.366E+007	< 0.0001
Pure Error	0.000	4	0.000		
Cor Total	3.740E-006	7			

Table 4.7 ANOVA for treated Quartz oil

Response 1: Yield
ANOVA for selected factorial model

Source	Sum of Squares	df	Mean Square	F Value	P- value (Prob > F)
Model	518.46	3	172.82	147.71	0.0001 **Significant**
A-solvent:used oil ratio	340.61	1	340.61	291.12	< 0.0001
B-solvent type	163.81	1	163.81	140.00	< 0.0003
AB- interaction	14.05	1	14.05	12.00	0.0257
Pure Error	4.68	4	1.17		
Cor Total	523.13	7			

Response 2: Kinematic Viscosity @ 40 °C
ANOVA for selected factorial model

Source	Sum of Squares	df	Mean Square	F-Value	P- value (Prob > F)
Model	506.76	3	168.92	120.44	0.0002 **Significant**
A- solvent:used oil ratio	369.92	1	369.92	263.76	< 0.0001
B- solvent type	136.13	1	136.13	97.06	0.0006
AB- interaction	0.72	1	0.72	0.51	0.5133
Pure Error	5.61	4	1.40		
Cor Total	512.38	7			

Response 3: Density
ANOVA for selected factorial model

Source	Sum of Squares	df	Mean Square	F Value	P- value Prob > F
Model	2.994E-004	3	9.979E-005	8.26	0.0345 **Significant**
A- solvent:used oil ratio	2.844E-004	1	2.844E-004	23.53	0.0083
B- solvent type	1.012E-007	1	1.012E-007	8.377E-003	0.9315
AB- interaction	1.485E-005	1	1.485E-005	1.23	0.3298
Pure Error	4.834E-005	4	1.209E-005		
Cor Total	3.477E-004	7			

4.4 OPTIMIZATION OF THE YIELD OF THE TREATED OIL

The objective here was to obtain maximum yield in the given interval of the investigated independent variables. Using design expert software the maximum yield of treated Rubia oil was achieved at the combination of the second level of the first factor (6:1) and the second level of the second factor (2-propanol) and the desirability equal to 0.982. The second highest yield obtained at the combination of the second level of the first factor (6:1) and the first level of the second factor (n-Butanol) and the desirability equal to 0.524. Also the maximum yield of treated Quartz oil was achieved at the combination of the second level of the first factor (6:1) and the second level of the second factor (2-propanol) and the desirability equal to 0.985. The second highest yield obtained at the combination of the second level of the first factor (6:1) and the first level of the second factor (n-Butanol) and the desirability equal to 0.575. The table below shows the optimization result for both Rubia and Quartz treated oil.

Table 4.8:- Numerical optimization solution for treated Rubia oil

Constraints

Name	Goal	Lower limit	Upper Limit	Lower weight	Upper weight	Importance
Solvent:used oil ratio	Is in range	4:1	6:1	1	1	3
Solvent type	Is in range	n-Butanol	2-Propanol	1	1	3
Yield	maximize	55	72	1	1	5
K.Viscosity @40 'C	minimize	46.4	70	1	1	5
Density	Is in range	0.8697	0.8715	1	1	5

Solutions for 4 combinations of categoric factor levels

Number	**Solvent:used oil ratio**	**Solvent type**	**Yield**	**K.Viscosity @40 ^oC**	**Density**	**Desirability**
1	6:1	2-propanol	71.5	69.85	0.8715	0.982 Selected
2	6:1	n-Butanol	64.5	58	0.8701	0.524
3	4:1	2-propanol	61	62.1	0.8701	0.485

Table 4.9:- Numerical optimization solution for treated Quartz oil

Constraints

Name	Goal	Lower limit	Upper Limit	Lower weight	Upper weight	Importance
Solvent:used oil ratio	Is in range	4:1	6:1	1	1	3
Solvent type	Is in range	2-Propanol	n-Butanol	1	1	3
Yield	maximize	50	73.4	1	1	5
K.Viscosity @40 'C	minimize	74.6	98	1	1	5
Density	Is in range	0.8701	0.8869	1	1	5

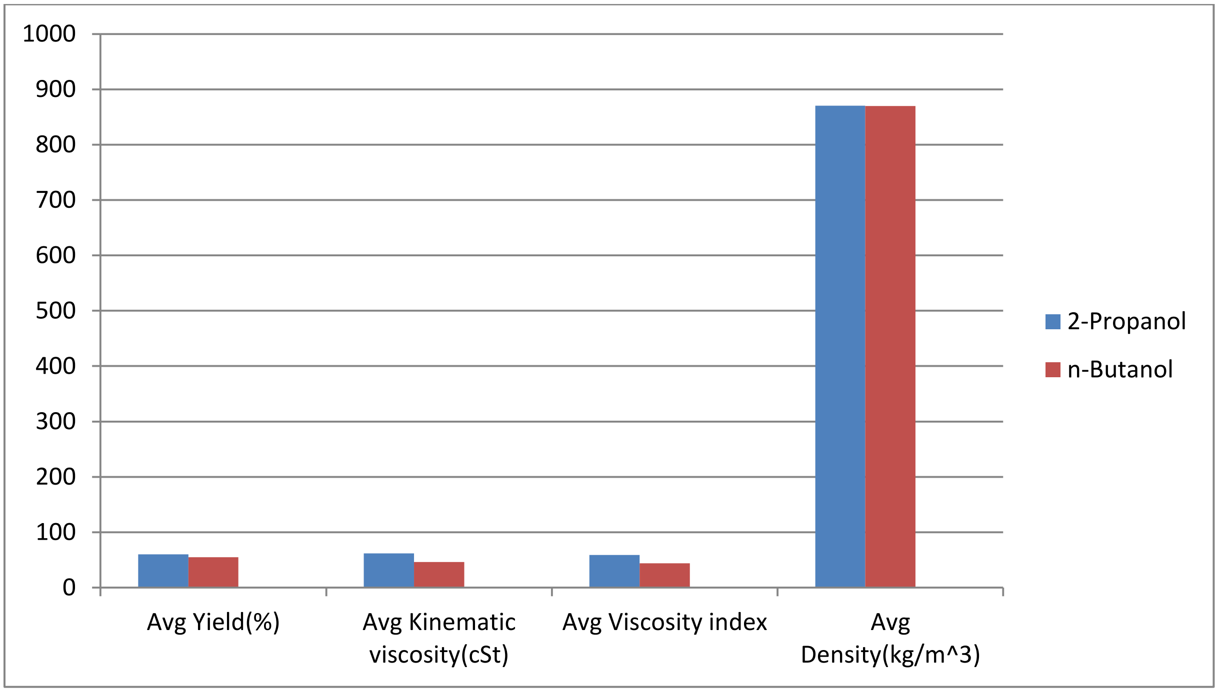
Solutions for 4 combinations of categoric factor levels

Number	**Solvent:used oil ratio**	**Solvent type**	**Yield**	**K.Viscosity @40 ^{o}C**	**Density**	**Desirability**
1	6:1	2-propanol	73	97.15	0.884	0.973 Selected
2	6:1	n-Butanol	61.3	88.3	0.8865	0.532
3	4:1	2-propanol	57.3	82.95	0.8748	0.334

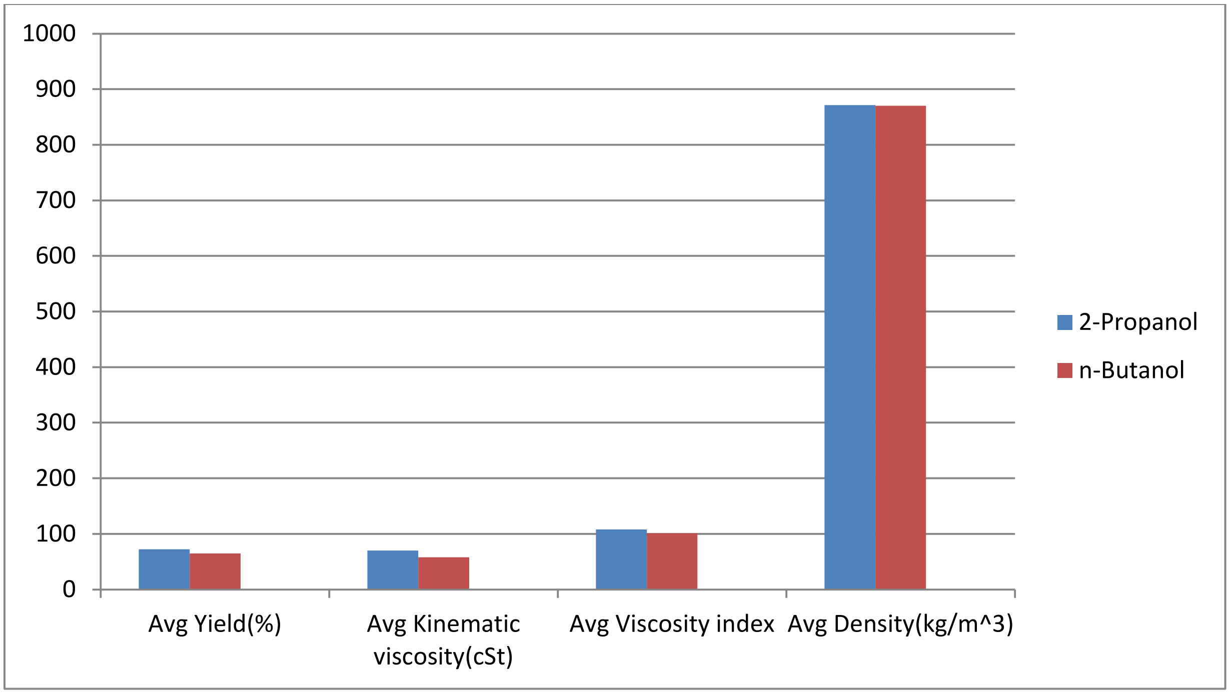
4.5 COMPARISON OF SOLVENT TYPE

As it is indicated from the previous section the type of solvent is one of the influencing factors in refining the used oil treatment process. Here in this study 2-propanol (isopropyl alcohol) and n-Butanol was used.

As it was shown in the result, when the 2-propanol was used the product of the treatment process gives better result in terms of the yield, kinematic viscosity and density. This shows that the solvent 2-propanol is a best choice than that of n-Butanol. Even when the color is compared, the 2-propanol solvent gives better color than n-Butanol. The Figure Below shows the comparison between the two solvent type in the property of the oil at different mixing ratio.

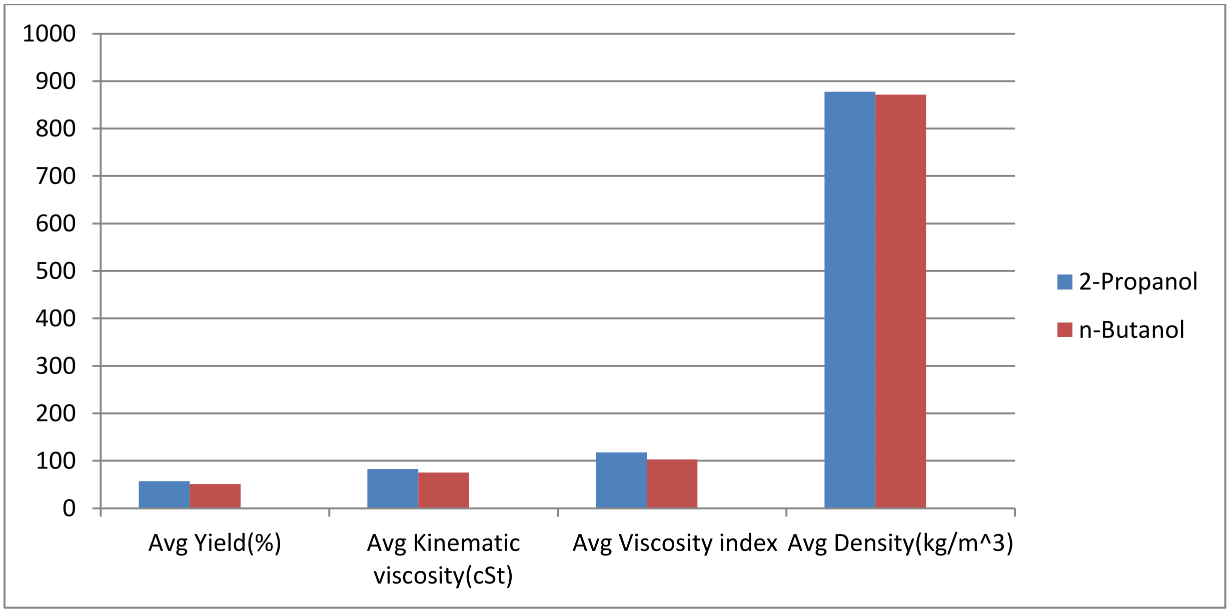


(a)

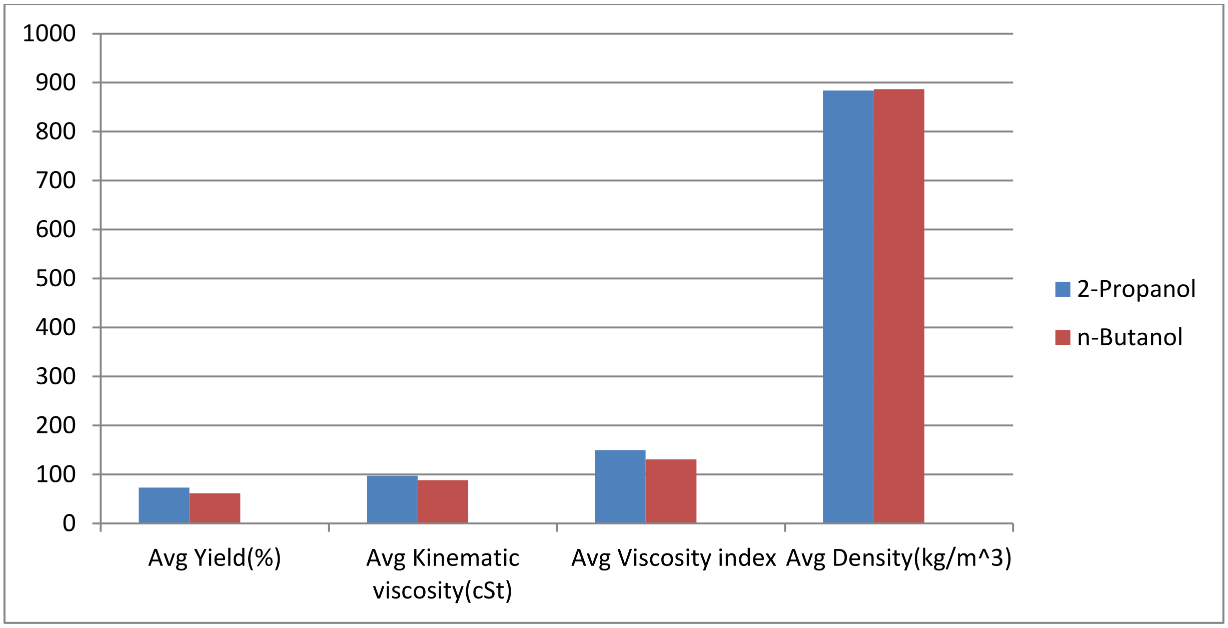


(b)

Figure 4.9 comparison of solvent type of Rubia treated oil @ mixing ratio a) 4:1 and b) 6:1



(a)



(b)

Figure 4.10 comparison of solvent type of Quartz treated oil @ mixing ratio a)4:1 and b)6:1

4.6 CHARACTERIZATION OF OTHER PROPERTIES OF TREATED OIL

Using the optimization result summary, the base oil obtained from the selected experimental run is further analyzed to fully describe its properties. Flash point, kinematic viscosity@ 100 °C, viscosity index (VI) and metal contents are the additional characteristics tested. This characterization helps to explain the quality improvement of the treated base oil as compared to the properties of the used oil sample.

The flash points of the treated oil is 218°C for both the Rubia and Quartz oil which is one of the parameter used in comparing properties of the oil.

The kinematic viscosity @ 100 °C of the treated Rubia oil is 9.2 cSt and that of treated quartz oil is 13.9 cSt which is found by using a solvent type of 2-Propanol and mixing ratio of 6:1. The kinematic viscosity @ 100°C of others experimental runs are shown in table 4.2 and 4.3.

The viscosity index of the two variety of the optimized oil, which is found using 2-Propanol with mixing ratio of 6:1, is 107.424 and 145.442 for Rubia and Quartz treated oil respectively. The viscosity index of others experimental runs are listed in the Appendix B.

The amount of metals that present in the treated oil is also listed in the table below (table 4.10) which is analyzed by using atomic absorption spectrophotometry. Each metal have different value and it is also compared with the used oil to know how much it is decreased and with the virgin oil to know by how much it differs.

Table 4.10 Characterized property of treated oil

Properties	Rubia treated base oil	Quartz treated base oil
Flash Point °C	218	
Kinematic Viscosity@ 40 °C (cSt)	69.85	97.15
Kinematic Viscosity@ 100 °C (cSt)	9.2	13.9
Viscosity Index	107.424	145.442
Density (g/ml)	0.8715	0.884
Metal Contents (ppm)		
➢ Ca	<1.00	<1.00
➢ Zn	8.5074	2.79
➢ As	<0.1	<0.20
➢ Cd	0.4	<0.20
➢ Cr	<0.50	<0.01
➢ Pb	<0.01	<0.01
➢ Cu	2.24	0.6
➢ Fe	7.61	8.77
➢ Ni	0.42	0.23
➢ Mg	2.842	6.5
➢ Mo	1.57	6.62

4.7 COMPARISON OF TREATED OIL WITH THE USED AND VIRGIN OIL

As it had been seen from the previous discussion, the amount of different parameter of the treated oil has a value of which different from the used oil. Now in this section the treated oil was compared with the used oil and that of virgin oil.

The flash points of the treated oil is 218°C which is far better than the used oil, which is 170 and 167.8 °C for Rubia and Quartz respectively, and slightly lower than the virgin oil 236 and 240°C(Total Oil Company Specification). As stated in previous sections, the decrease in value of flash point for the used oil could be as result of the presence of light ends of oils. In essence, after undergoing combustion and oxidation at high temperature of the combustion engine, the additive breaks down into component parts, which include some light ends. The decrease in flash point for the used oil, may also be as a result of fuel dilution; that is, for an engine with bad piston rings. The flash point has greatly improved but not as good as the fresh oil because the additives are not added. Nevertheless, the flash point is within acceptable range according to the ASTM D 4304 reference standard i.e.it should be greater than 180°C.

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

The density of the used oil is higher than virgin oil and the treated one. The results of Rubia and Quartz virgin oil are 0.888&0.8921 g/ml (Total Oil Company Specification) and used oils are 0.946268 and 0.948340 g/ml respectively, while the treated oil has 0.8715 and 0.884 g/ml for Rubia and Quartz oil respectively. The treatment has approximately restored the oils density to that of the fresh oil.

The metal that is found in the used oil as a result of contamination and degradation was lowered during the treatment process. As it is shown in the table 4.11&4.12 all of the metal content in the used oil is reduced greatly.

Table 4.11 Comparison of characterized property of Rubia oil

Properties	Used motor oil	treated base oil	Virgin oil
Flash Point °C	170	218	236
Kinematic Viscosity@ 40 °C (cSt)	102.21	69.85	98.7
Kinematic Viscosity@ 100 °C (cSt)	13.8	9.2	13.4
Viscosity Index	135.9	107.424	136
Density (g/ml)	0.946268	0.8715	0.888
Metal Contents (ppm)			
➢ Ca	175.06	<1.00	
➢ Zn	105.89	8.50	
➢ As	<0.50	<0.10	
➢ Cd	0.46	0.40	
➢ Cr	<1.00	<0.50	
➢ Pb	0.03	<0.01	
➢ Cu	42.17	2.24	
➢ Fe	283.48	7.61	
➢ Ni	0.53	0.42	
➢ Mg	9.35	2.842	
➢ Mo	52.56	1.57	

Table 4.12 Comparison of characterized property of Quartz oil

Properties	used motor oil	treated base oil	Virgin oil
Flash Point °C	167.8	218	240
Kinematic Viscosity@ 40 °C (cSt)	180.4	97.15	176.4
Kinematic Viscosity@ 100 °C (cSt)	24	13.9	19.1
Viscosity Index	163.195	145.442	123
Density (g/ml)	0.948340	0.884	0.8921
Metal Contents (ppm)			
➢ Ca	201.6	<1.00	
➢ Zn	105.83	2.79	
➢ As	<0.50	<0.20	
➢ Cd	<0.20	<0.20	
➢ Cr	0.01	<0.01	
➢ Pb	0.03	<0.01	
➢ Cu	12.84	0.6	
➢ Fe	583.39	8.77	
➢ Ni	0.48	0.23	
➢ Mg	8.36	6.5	
➢ Mo	74.76	6.62	

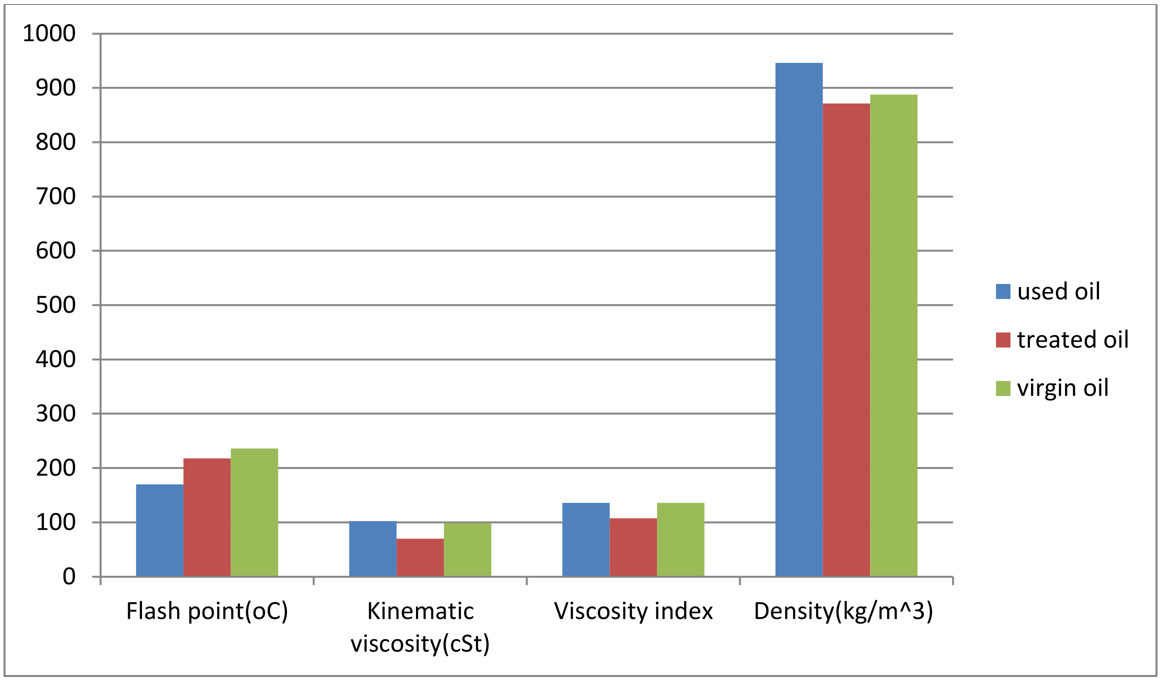


Figure 4.7 comparison of properties between Rubia used, treated and virgin oil.

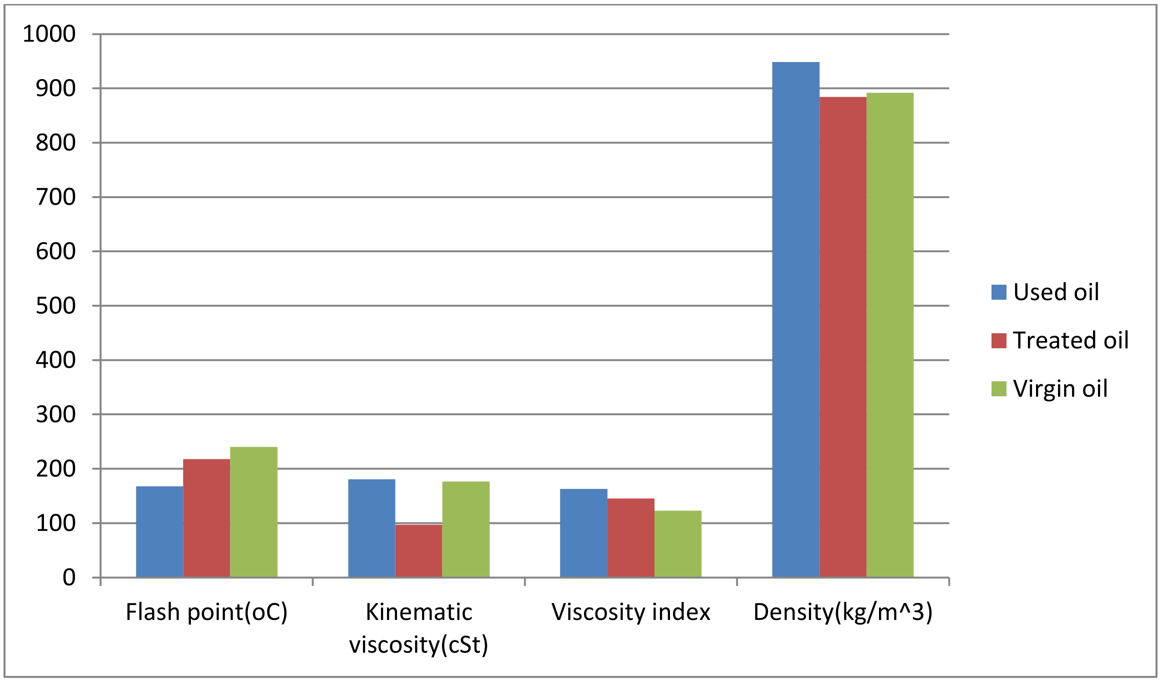


Figure 4.8 comparison of properties between Quartz used, treated and virgin oil.

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

Used motor oil is a high pollutant material that requires responsible management. Used motor oil cause damage to the environment when dumped into the ground or into water streams including sewers. This results in groundwater and soil contamination. Recycling of such contaminated materials is beneficial in reducing motor oil costs. In addition, it has a significant positive impact on the environment. A solution for this issue is the recovery of the lubricating base oil from the used oil. Recycling processes using nontoxic and cost effective materials is an optimum solution.

This research started from characterizing the used motor oil in order to know that how much the virgin oil degraded and loses its property. Results of used oil characterization showed the kinematic viscosity, density, flash point and metal content had a value which is much differ from the virgin oil. The viscosity and density increased because of contamination and degradation, the flash point was decreased as a result of light ends to a value of 170 and 168.7^{o}C. The metal content also increased. Also the color was changed to black as a result of carbon and soot.

The type of solvent used and the ratio applied for different runs has shown significant effects on the yield of recovered oil as considered separately and interacting. Density and viscosity are also influenced with different intensity as the type and amount of the experimental factors are varied. It was observed that the maximum and minimum yield is 72&73.4% and 55&50% respectively for Rubia and Quartz treated oil. The maximum kinematic viscosity at 40 ^{o} C is 70 cSt and a minimum of 46.4 cSt for Rubia treated oil with density of 0.8715 and 0.8697g/ml respectively While that of Quartz is maximum at 98 cSt with density of 0.8846g/ml and minimum at 76 cSt with a density of 0.8731g/ml. then it is concluded that the mixing ratio of 6:1 with type of solvent of 2-Propanol gives a best result. The other properties of the oil were also characterized and gave a good result as it was compared with the used oil. Also the solvent type was compared with each other and 2-Propanol was the best one.

Generally conclusion can be drawn from the experiment that the mixing ratio of 6:1 with 2-Propanol is the best result and as the ratio increase, economically, the yield and purity will be maximized and increased.

5.2 RECOMMENDATION

As this thesis implies, the refining of the used motor oil is mandatory, environmentally and economically, to reduce the environmental pollution and to decrease foreign currency. In order to do this, a deep investigation of this project is needed. Here, it is recommended the following important points.

- The amount of used oil that is collected from stations or garages in the Ethiopia, Mechanism of separating the types of used oils (Quartz, Rubia…) that are going to be collected.
- Carful and deep investigation of the contents of used motor oil such as metal content, water content ash content, carbon residue and others. And other properties such as flash point, cloud point, fire point, pour point, viscosity, density and others.
- Studying another refining technology is also important to compare and evaluate the efficiency, the cost and the hazardous of the technology.
- Controlling parameters other than the one which is discussed in this research work must be performed to see their effect. Such parameters are temperature, pressure, mixing time, mixing speed, setting time and time taken by each process.
- Investigation of other solvent type is also recommended to study the effective absorbability with economically. Also the byproduct and the waste need analysis and study.
- Finally demonstration of the laboratory experiment by adding additives should be done in order to compare the refined oil with the virgin oil.

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APPENDICIES

APPENDIX A:- EXPERIMENTAL DESIGN AND DATA ANALYSIS

A.1 Analysis of Variance (ANOVA)

A.1.1 ANOVA for treated Rubia oil

Response 1 Yield

ANOVA for selected factorial model

Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	285.00	3	95.00	126.67	0.0002	significant
A-Solvent:used oil ratio	200.00	1	200.00	266.67	< 0.0001	
B-Solvent type	84.50	1	84.50	112.67	0.0004	
AB	0.50	1	0.50	0.67	0.4601	
Pure Error	3.00	4	0.75			
Cor Total	288.00	7				

The Model F-value of 126.67 implies the model is significant. There is only a 0.02% chance that a "Model F-Value" this large could occur due to noise.

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

Std. Dev.	0.87	R-Squared	0.9896
Mean	63.00	Adj R-Squared	0.9818
C.V. %	1.37	Pred R-Squared	0.9583
PRESS	12.00	Adeq Precision	26.944

The "Pred R-Squared" of 0.9583 is in reasonable agreement with the "Adj R-Squared" of 0.9818.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 26.944 indicates an adequate signal.This model can be used to navigate the design space.

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	63.00	1	0.31	62.15	63.85	
A-Solvent:used oil ratio	5.00	1	0.31	4.15	5.85	1.00
B-Solvent type	3.25	1	0.31	2.40	4.10	1.00
AB	0.25	1	0.31	-0.60	1.10	1.00

Final Equation in Terms of Coded Factors:

$$\text{Yield} = + 63.00 + 5.00 * A + 3.25 * B + 0.25 * A * B$$

Final Equation in Terms of Actual Factors:

Solvent:used oil ratio	4:1
Solvent type	n-Butanol
Yield	= +55.00000

Solvent:used oil ratio	6:1
Solvent type	n-Butanol
Yield	= +64.50000

Solvent:used oil ratio	4:1
Solvent type	2-propanol
Yield	= +61.00000

Solvent:used oil ratio	6:1
Solvent type	2-propanol
Yield	= +71.50000

Response 2 K.Viscosity @40 'C

ANOVA for selected factorial model

Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	574.12	3	191.37	17011.07	< 0.0001	significant
A-Solvent:used oil ratio	187.21	1	187.21	16641.00	< 0.0001	
B-Solvent type	379.50	1	379.50	33733.44	< 0.0001	
AB	7.41	1	7.41	658.78	< 0.0001	
Pure Error	0.045	4	0.011			
Cor Total	574.17	7				

The Model F-value of 17011.07 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.	0.11	R-Squared	0.9999
Mean	59.09	Adj R-Squared	0.9999
C.V. %	0.18	Pred R-Squared	0.9997
PRESS	0.18	Adeq Precision	312.667

The "Pred R-Squared" of 0.9997 is in reasonable agreement with the "Adj R-Squared" of 0.9999.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 312.667 indicates an adequate signal. This model can be used to navigate the design space.

Factor	**Coefficient Estimate**	**df**	**Standard Error**	**95% CI Low**	**95% CI High**	**VIF**
Intercept	59.09	1	0.037	58.98	59.19	
A-Solvent:used oil ratio	4.84	1	0.037	4.73	4.94	1.00
B-Solvent type	6.89	1	0.037	6.78	6.99	1.00
AB-0.96	1	0.037	-1.07	-0.86	1.00	

Final Equation in Terms of Coded Factors:

K.Viscosity @40 'C = + 59.09 + 4.84 * A + 6.89 * B - 0.96 * A * B

Final Equation in Terms of Actual Factors:

Solvent:used oil ratio 4:1
Solvent type n-Butanol
K.Viscosity @40 'C = +46.40000

Solvent:used oil ratio 6:1
Solvent type n-Butanol
K.Viscosity @40 'C = +58.00000

Solvent:used oil ratio 4:1
Solvent type 2-propanol
K.Viscosity @40 'C = +62.10000

Solvent:used oil ratio 6:1
Solvent type 2-propanol
K.Viscosity @40 'C = +69.85000

Response 3 Density

ANOVA for selected factorial model

Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	3.740E-006	3	1.247E-006	6.366E+007	< 0.0001	significant
A-Solvent:used oil ratio	1.620E-006	1	1.620E-006	6.366E+007	< 0.0001	
B-Solvent type	1.620E-006	1	1.620E-006	6.366E+007	< 0.0001	
AB	5.000E-007	1	5.000E-007	6.366E+007	< 0.0001	
Pure Error	0.000	4	0.000			
Cor Total	3.740E-006	7				

The Model F-value of 63660000.00 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.	0.000	R-Squared	1.0000
Mean	0.87	Adj R-Squared	1.0000
C.V. %	0.000	Pred R-Squared	1.0000
PRESS	0.000	Adeq Precision	

The "Pred R-Squared" of 1.0000 is in reasonable agreement with the "Adj R-Squared" of 1.0000.

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	0.87	1				
A-Solvent:used oil ratio	4.500E-004	1				1.00
B-Solvent type	4.500E-004	1				1.00
AB	2.500E-004	1				1.00

Final Equation in Terms of Coded Factors:

$$\text{Density} = +\,0.87 + 4.500\text{E-}004 * A + 4.500\text{E-}004 * B + 2.500\text{E-}004 * A * B$$

Final Equation in Terms of Actual Factors:

Solvent:used oil ratio	4:1
Solvent type	n-Butanol
Density	= +0.86970

Solvent:used oil ratio	6:1
Solvent type	n-Butanol
Density	= +0.87010

Solvent:used oil ratio	4:1
Solvent type	2-propanol
Density	= +0.87010

A.1.1 ANOVA for treated Quartz oil

Response 1 Yield

ANOVA for selected factorial model

Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	518.46	3	172.82	147.71	0.0001	significant
A-Solvent:used oil	340.61	1	340.61	291.12	< 0.0001	
B-Solvent type	163.81	1	163.81	140.00	0.0003	
AB	14.05	1	14.05	12.00	0.0257	
Pure Error	4.68	4	1.17			
Cor Total	523.13	7				

The Model F-value of 147.71 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.	1.08	R-Squared	0.9911
Mean	60.63	Adj R-Squared	0.9843
C.V. %	1.78	Pred R-Squared	0.9642
PRESS	18.72	Adeq Precision	28.894

The "Pred R-Squared" of 0.9642 is in reasonable agreement with the "Adj R-Squared" of 0.9843.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 28.894 indicates an adequate signal. This model can be used to navigate the design space.

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	60.62	1	0.38	59.56	61.69	
A-Solvent:used oil	6.53	1	0.38	5.46	7.59	1.00
B-Solvent type	-4.52	1	0.38	-5.59	-3.46	1.00
AB	-1.33	1	0.38	-2.39	-0.26	1.00

Final Equation in Terms of Coded Factors:

$$\text{Yield} = +60.62 + 6.53 * A - 4.52 * B - 1.33 * A * B$$

Final Equation in Terms of Actual Factors:

Solvent:used oil	4:1
Solvent type	2-Propanol
Yield	= +57.30000

Solvent:used oil	6:1
Solvent type	2-Propanol
Yield	= +73.00000

Solvent:used oil	4:1
Solvent type	n-Butanol
Yield	= +50.90000

Solvent:used oil	6:1
Solvent type	n-Butanol
Yield	= +61.30000

Response 2 K.Viscosity

ANOVA for selected factorial model

Analysis of variance table [Partial sum of squares - Type III]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	506.76	3	168.92	120.44	0.0002	significant
A-Solvent:used oil	369.92	1	369.92	263.76	< 0.0001	
B-Solvent type	136.13	1	136.13	97.06	0.0006	
AB	0.72	1	0.72	0.51	0.5133	
Pure Error	5.61	4	1.40			
Cor Total	512.38	7				

The Model F-value of 120.44 implies the model is significant. There is only a 0.02% chance that a "Model F-Value" this large could occur due to noise.

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

Std. Dev.	1.18	R-Squared	0.9891
Mean	85.92	Adj R-Squared	0.9808
C.V. %	1.38	Pred R-Squared	0.9562
PRESS	22.44	Adeq Precision	26.092

The "Pred R-Squared" of 0.9562 is in reasonable agreement with the "Adj R-Squared" of 0.9808.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 26.092 indicates an adequate signal. This model can be used to navigate the design space.

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	85.93	1	0.42	84.76	87.09	
A-Solvent:used oil	6.80	1	0.42	5.64	7.96	1.00
B-Solvent type	-4.13	1	0.42	-5.29	-2.96	1.00
AB	-0.30	1	0.42	-1.46	0.86	1.00

Final Equation in Terms of Coded Factors:

K.Viscosity = + 85.93+ 6.80 * A - 4.13 * B - 0.30 * A * B

Final Equation in Terms of Actual Factors:

Solvent:used oil	4:1
Solvent type	2-Propanol
K.Viscosity	= +82.95000

Solvent:used oil	6:1
Solvent type	2-Propanol
K.Viscosity	= +97.15000

Solvent:used oil	4:1
Solvent type	n-Butanol
K.Viscosity	= +75.30000

Solvent:used oil	6:1
Solvent type	n-Butanol
K.Viscosity	= +88.30000

Response 3 Density

ANOVA for selected factorial model

Analysis of variance table [Partial sum of squares - Type III]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	2.994E-004	3	9.979E-005	8.26	0.0345	significant
A-Solvent:used oil	2.844E-004	1	2.844E-004	23.53	0.0083	
B-Solvent type	1.012E-007	1	1.012E-007	8.377E-003	0.9315	
AB	1.485E-005	1	1.485E-005	1.23	0.3298	
Pure Error	4.834E-005	4	1.209E-005			
Cor Total	3.477E-004	7				

The Model F-value of 8.26 implies the model is significant. There is only
a 3.45% 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.	3.477E-003	R-Squared	0.8610
Mean	0.88	Adj R-Squared	0.7567
C.V. %	0.40	Pred R-Squared	0.4438
PRESS	1.934E-004	Adeq Precision	5.959

The "Pred R-Squared" of 0.4438 is not as close to the "Adj R-Squared" of 0.7567 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 5.959 indicates an adequate signal. This model can be used to navigate the design space.

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	0.88	1	1.229E-003	0.88	0.88	
A-Solvent:used oil	5.963E-003	1	1.229E-003	2.550E-003	9.375E-003	1.00
B-Solvent type	-1.125E-004	1	1.229E-003	-3.525E-003	3.300E-003	1.00
AB	1.362E-003	1	1.229E-003	-2.050E-003	4.775E-003	1.00

Final Equation in Terms of Coded Factors:

Density = + 0.88 + 5.963E-003 * A - 1.125E-004 * B + 1.362E-003 * A * B

Final Equation in Terms of Actual Factors:

Solvent:used oil	4:1
Solvent type	2-Propanol
Density	= +0.87480

Solvent:used oil	6:1
Solvent type	2-Propanol
Density	= +0.88400

Solvent:used oil	4:1
Solvent type	n-Butanol
Density	= +0.87185

Solvent:used oil	6:1
Solvent type	n-Butanol
Density	= +0.88650

A.2 Optimization

A.2.1 Optimization solution for treated rubia oil

Constraints

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
Solvent:used oil ratio	**is in range**	**4:1**	**6:1**	**1**	**1**	**3**
Solvent type	**is in range**	**n-Butanol**	**2-propanol**	**1**	**1**	**3**
Yield	**maximize**	**55**	**72**	**1**	**1**	**5**
K.Viscosity @40 'C	**minimize**	**46.4**	**70**	**1**	**1**	**5**
Density	**is in range**	**0.8697**	**0.8715**	**1**	**1**	**5**

Solutions for 4 combinations of categoric factor levels

Number	Solvent:used oil ratio	Solvent type	Yield	K.Viscosity @40 'C	Density	Desirability	
1	6:1	2-propanol	71.5	69.85	0.8715	0.982	Selected
2	6:1	n-Butanol	64.5	58	0.8701	0.524	
3	4:1	2-propanol	61	62.1	0.8701	0.485	

3 Solutions found

Number of Starting Points: 4 for 4 combinations of categoric factor levels

Solvent:used oil ratio	Solvent type
4:1	n-Butanol
6:1	n-Butanol
4:1	2-propanol
6:1	2-propanol

A.2.1 Optimization solution for treated Quartz oil

Constraints

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
Solvent:used oil	**is in range**	**4:1**	**6:1**	**1**	**1**	**3**
Solvent type	**is in range**	**2-Propanol**	**n-Butanol**	**1**	**1**	**3**
Yield	**maximize**	**50**	**73.4**	**1**	**1**	**5**
K.Viscosity @40 'C	**minimize**	**74.6**	**98**	**1**	**1**	**5**
Density	**is in range**	**0.8701**	**0.8869**	**1**	**1**	**3**

Solutions for 4 combinations of categoric factor levels

Number	Solvent:used oil	Solvent type	Yield	K.Viscosity @40 'C	Density	Desirability	
1	6:1	2-Propanol	73	97.15	0.884	0.973	Selected
2	6:1	n-Butanol	61.3	88.3	0.8865	0.532	
3	4:1	2-Propanol	57.3	82.95	0.8748	0.334	

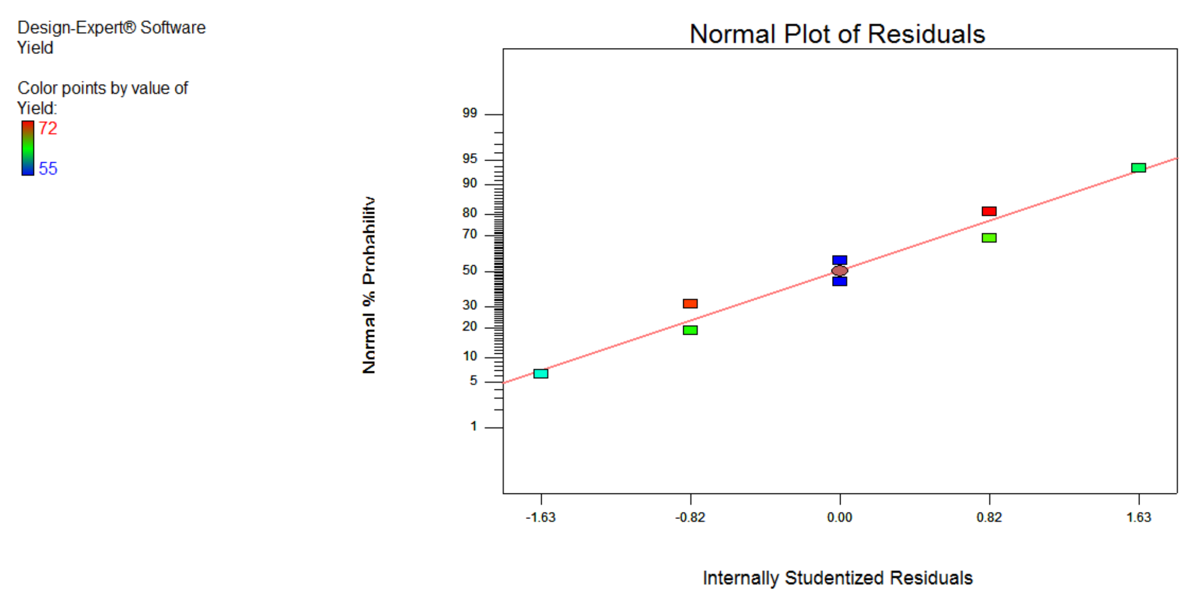
3 Solutions found

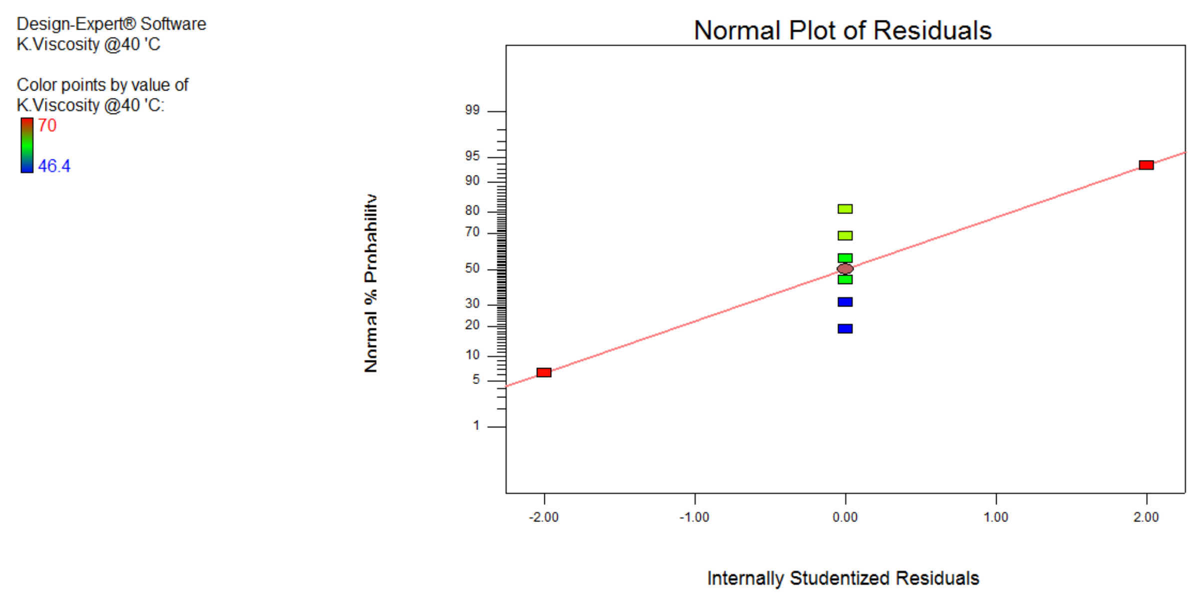
Number of Starting Points: 4 for 4 combinations of categoric factor levels

Solvent:used oil	Solvent type
4:1	2-Propanol
6:1	n-Butanol
4:1	n-Butanol
6:1	2-Propanol

A.3 Diagnostic plots

A.3.1 Diagnostic plots of treated Rubia oil





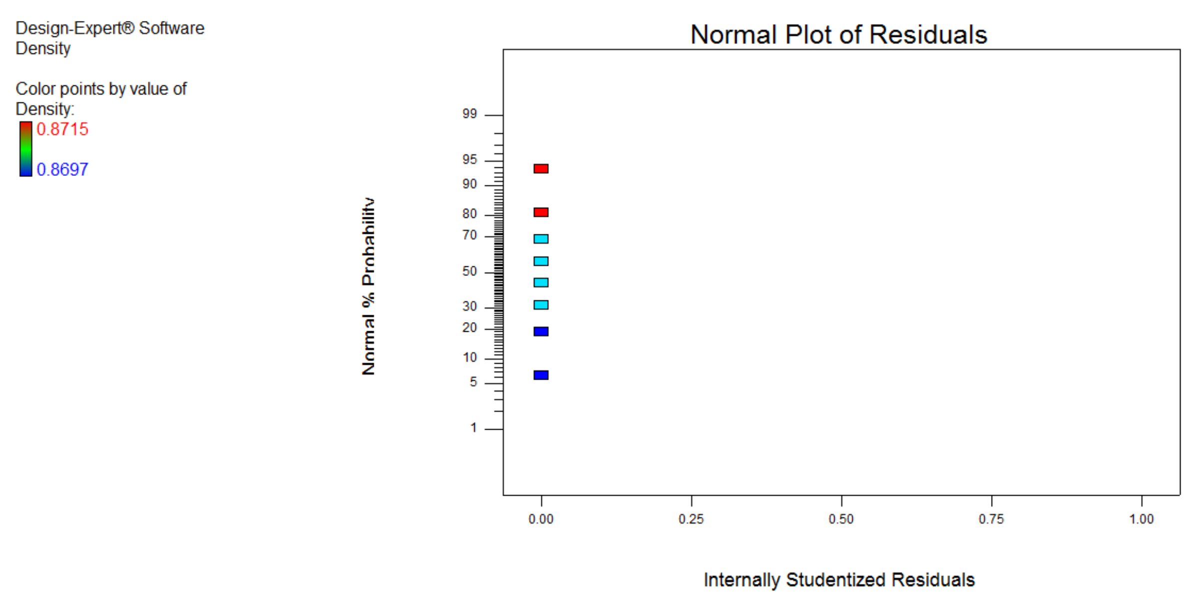
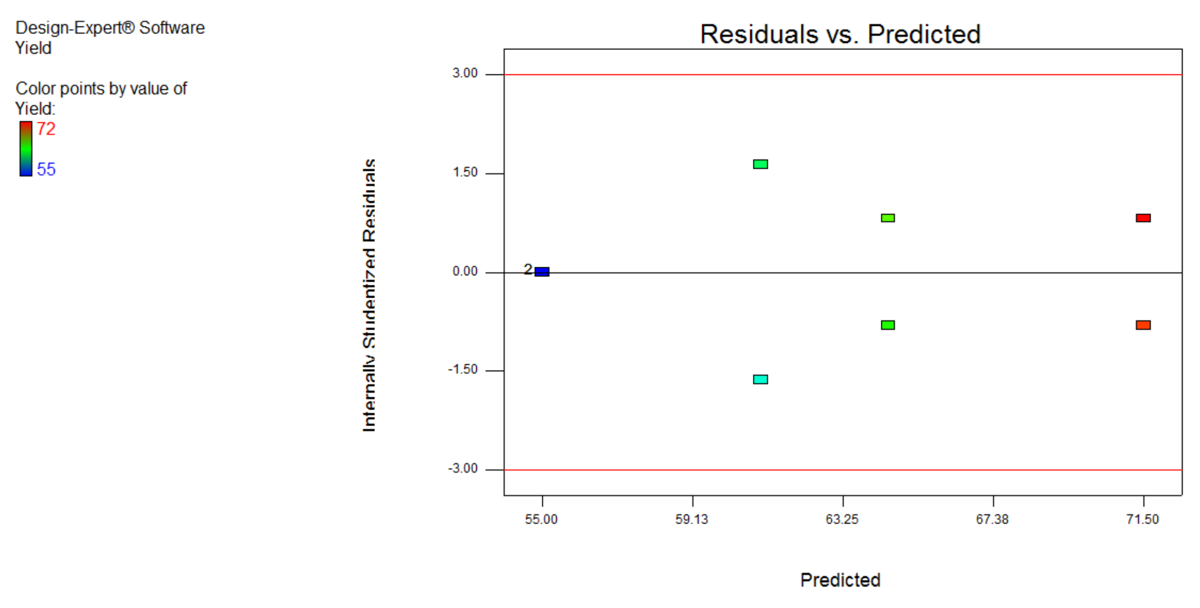


Figure A.3.1.1 Rubia Normal plots of residuals



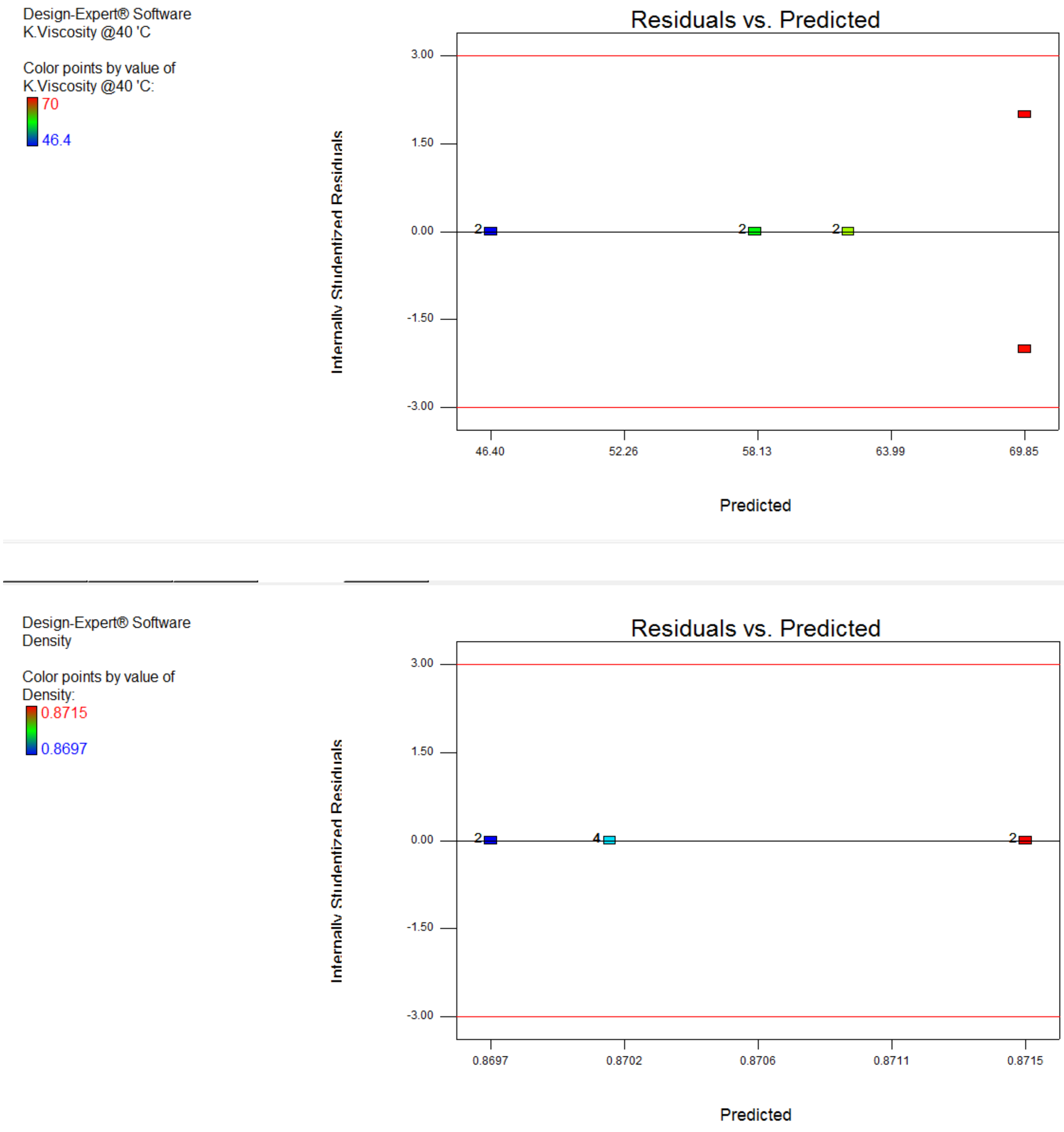
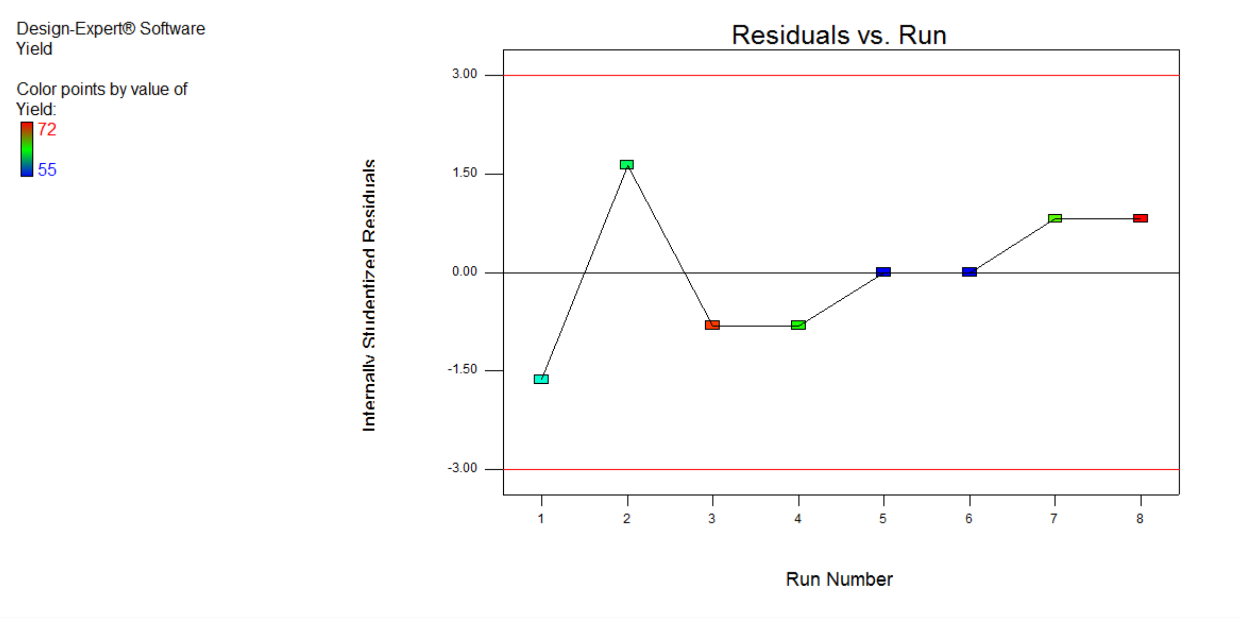
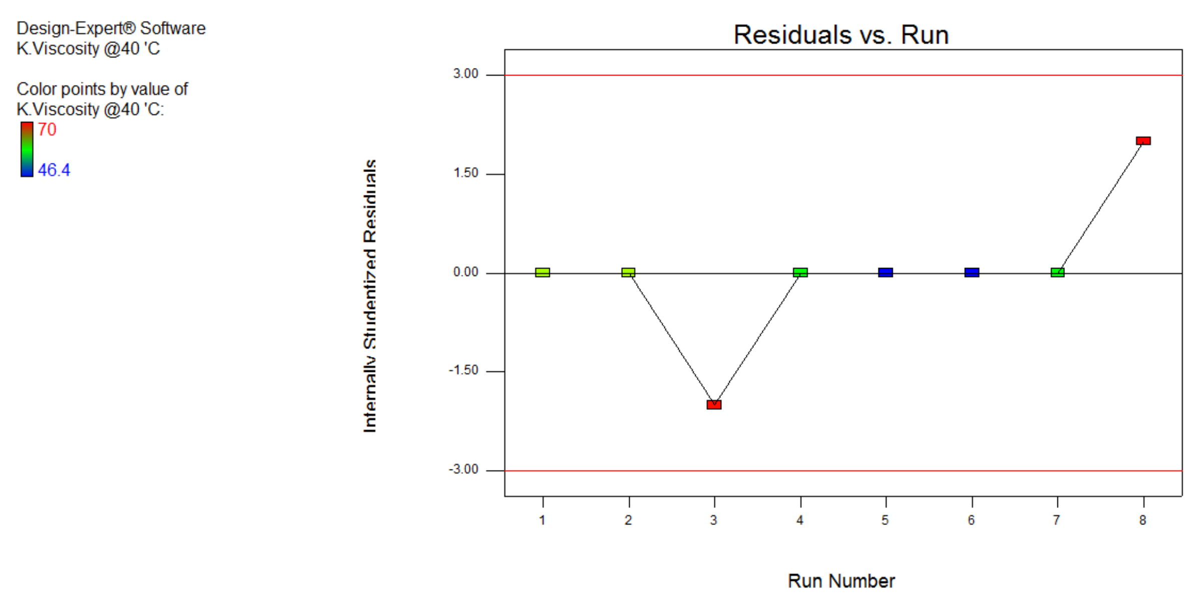


Figure A.3.1.2 Rubia Residuals Vs predicted


Design-Expert® Software
Yield
Color points by value of
Yield:
72
55
Residuals vs. Run
Internally Studentized Residuals
3.00
1.50
0.00
-1.50
-3.00
1
2
3
4
5
6
7
8
Run Number


Design-Expert® Software
K.Viscosity @40 'C
Color points by value of
K.Viscosity @40 'C:
70
46.4
Residuals vs. Run
Internally Studentized Residuals
3.00
1.50
0.00
-1.50
-3.00
1
2
3
4
5
6
7
8
Run Number

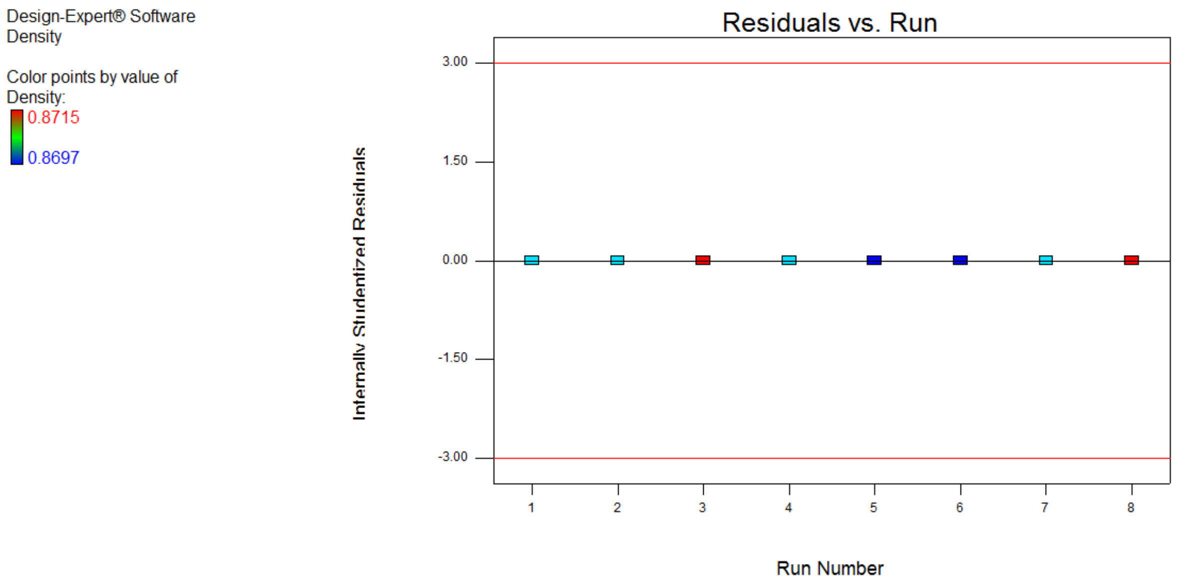
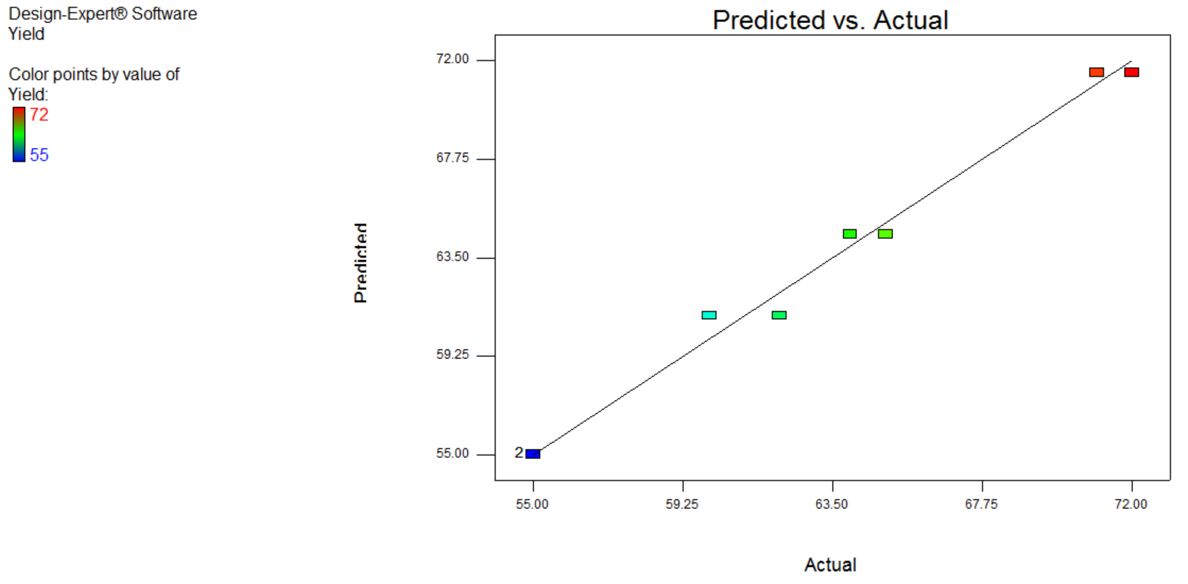
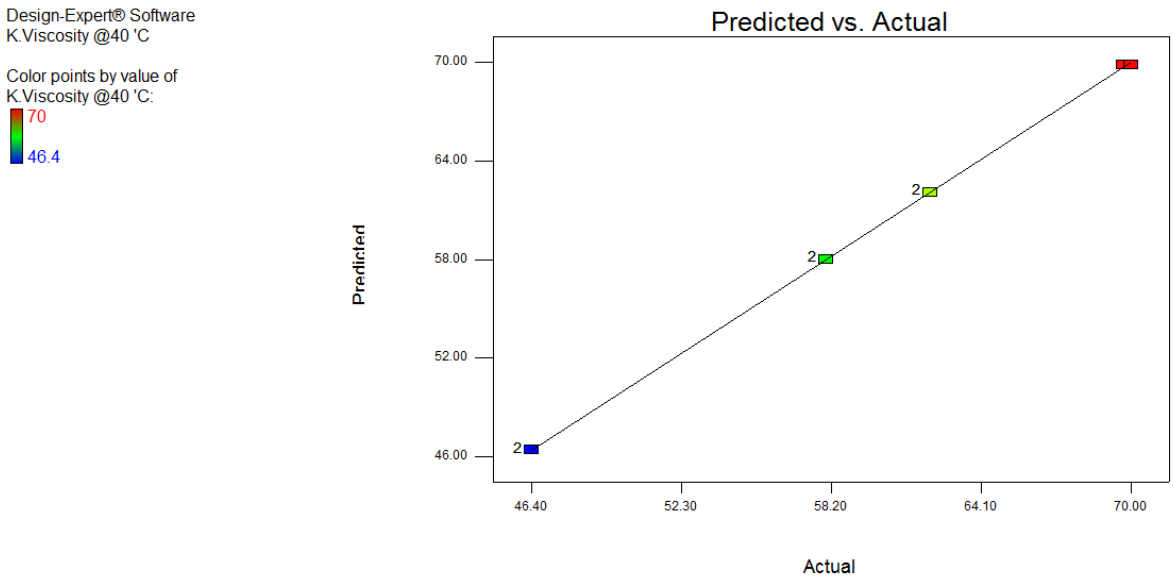


Figure A.3.1.3 Rubia Residuals Vs. Run





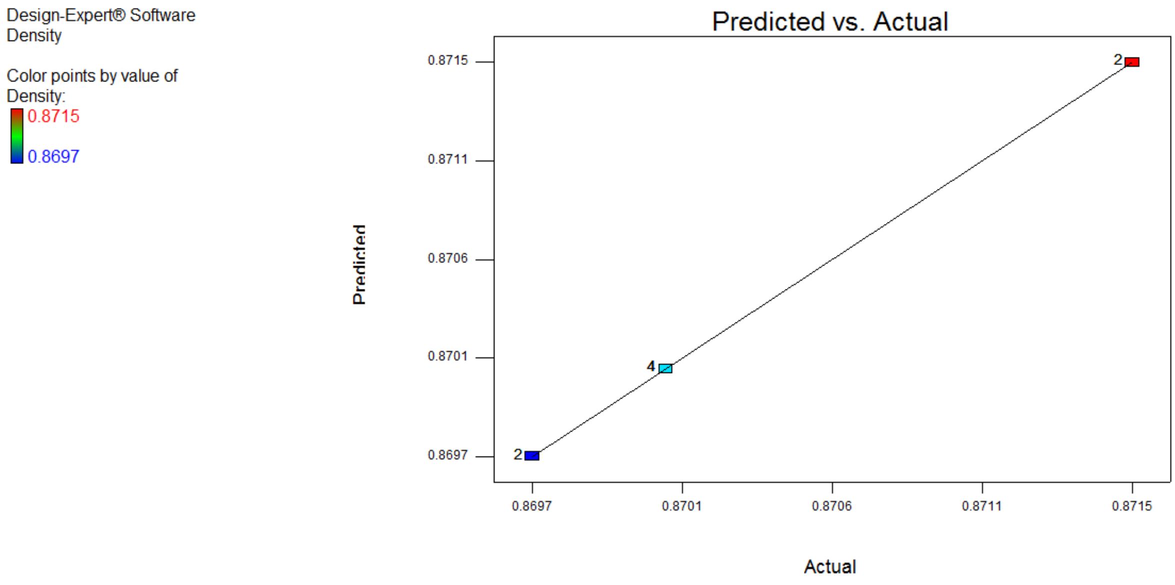
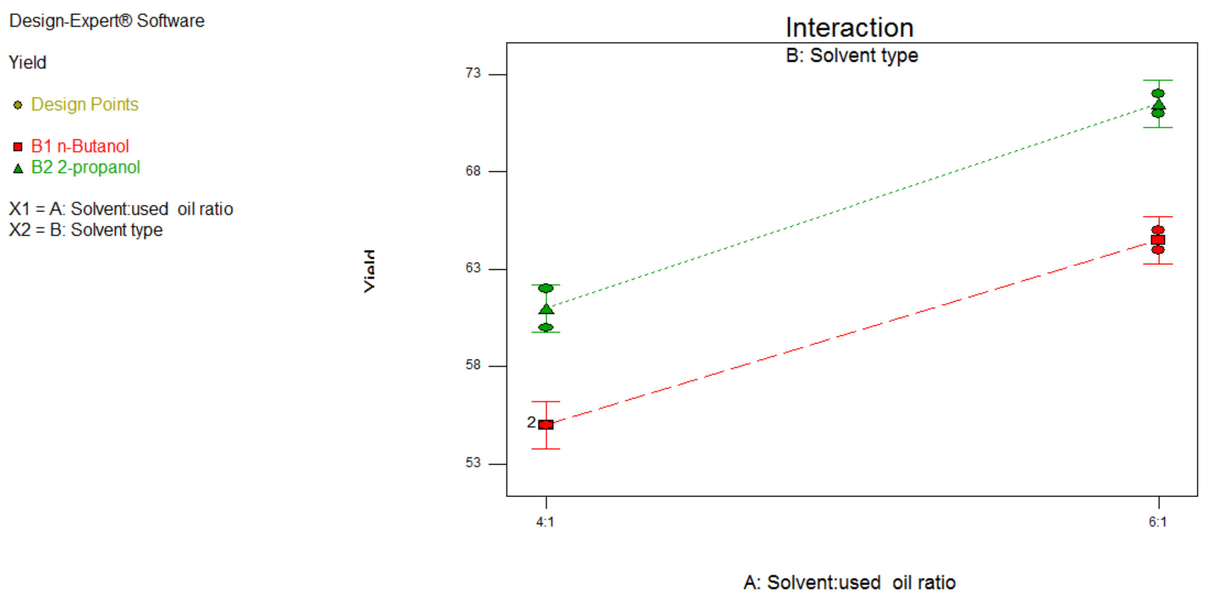
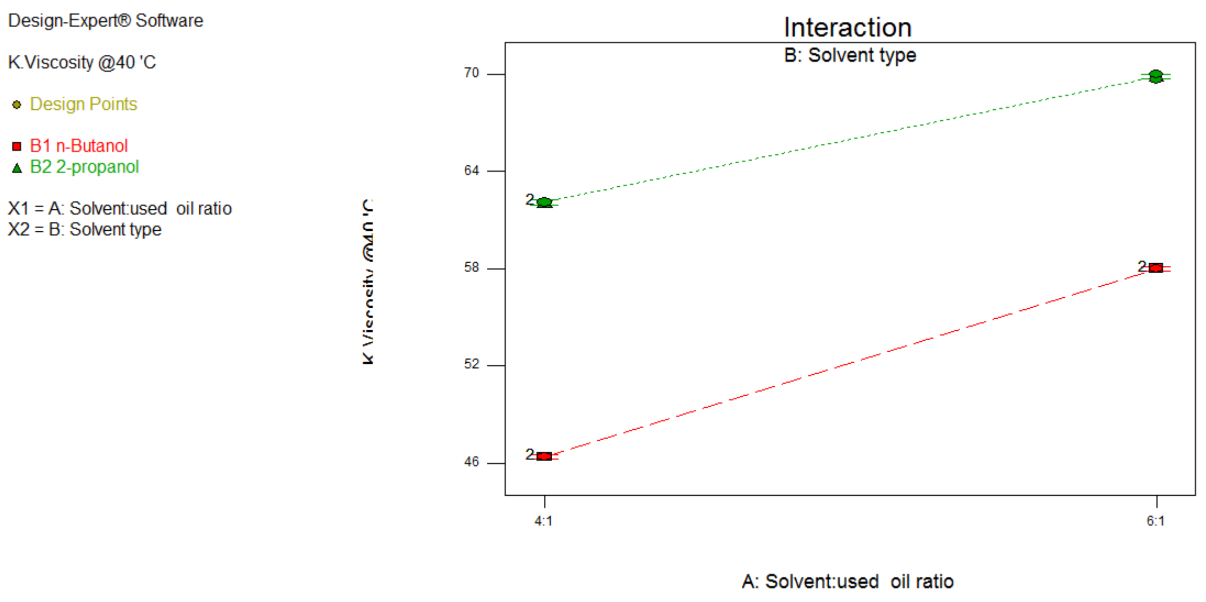


Figure A.3.1.4 Rubia Predicted Vs. Actual


Design-Expert® Software
Yield
● Design Points
■ B1 n-Butanol
▲ B2 2-propanol
X1 = A: Solvent:used oil ratio
X2 = B: Solvent type
Interaction
B: Solvent type
Yield
73
68
63
58
53
2
4:1
6:1
A: Solvent:used oil ratio


Design-Expert® Software
K.Viscosity @40 'C
● Design Points
■ B1 n-Butanol
▲ B2 2-propanol
X1 = A: Solvent:used oil ratio
X2 = B: Solvent type
Interaction
B: Solvent type
70
64
58
52
46
2
2
2
4:1
6:1
A: Solvent:used oil ratio

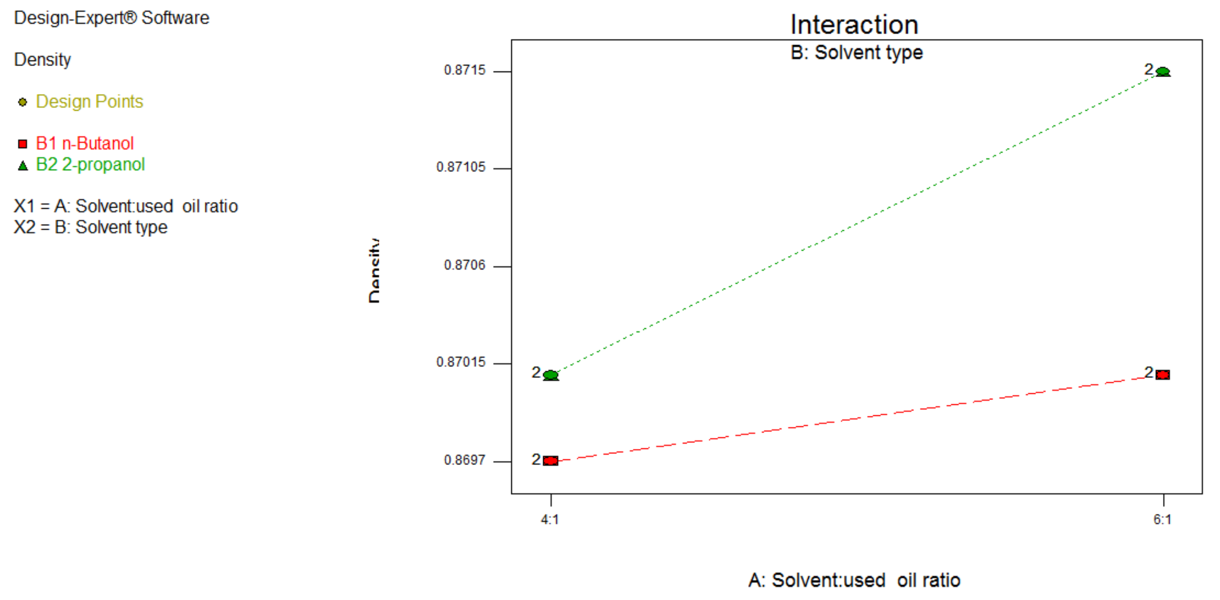
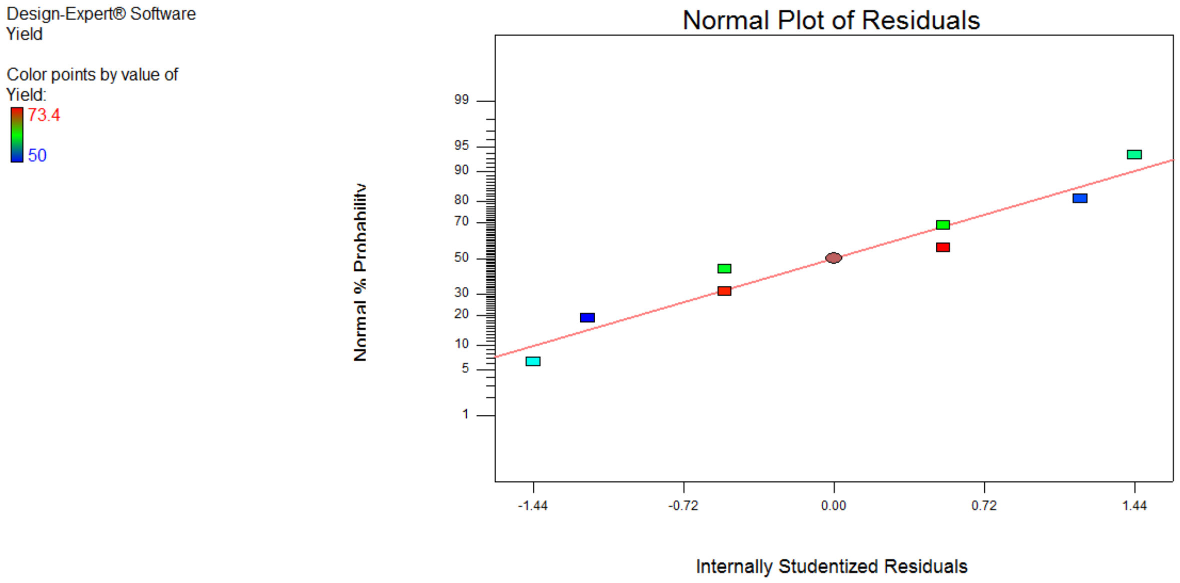
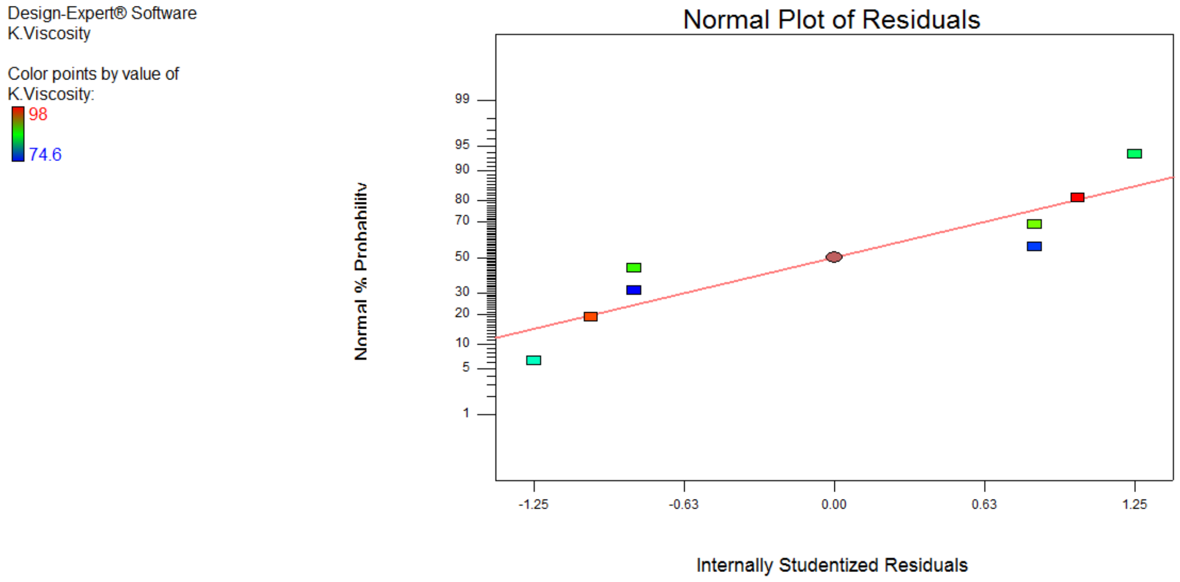
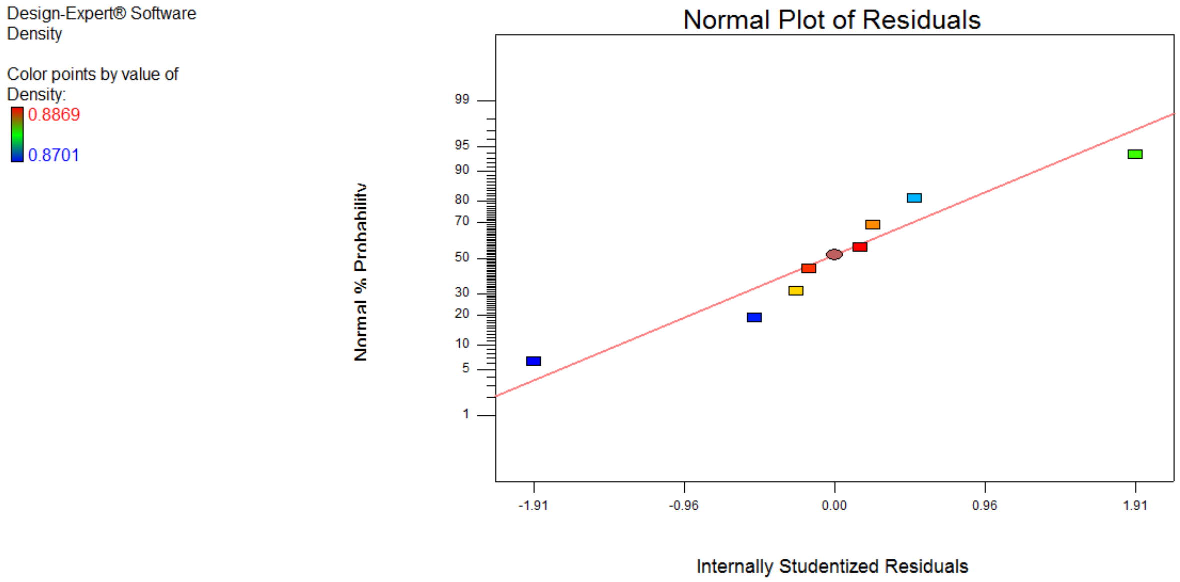


Figure A.3.1.5 Rubia Interaction

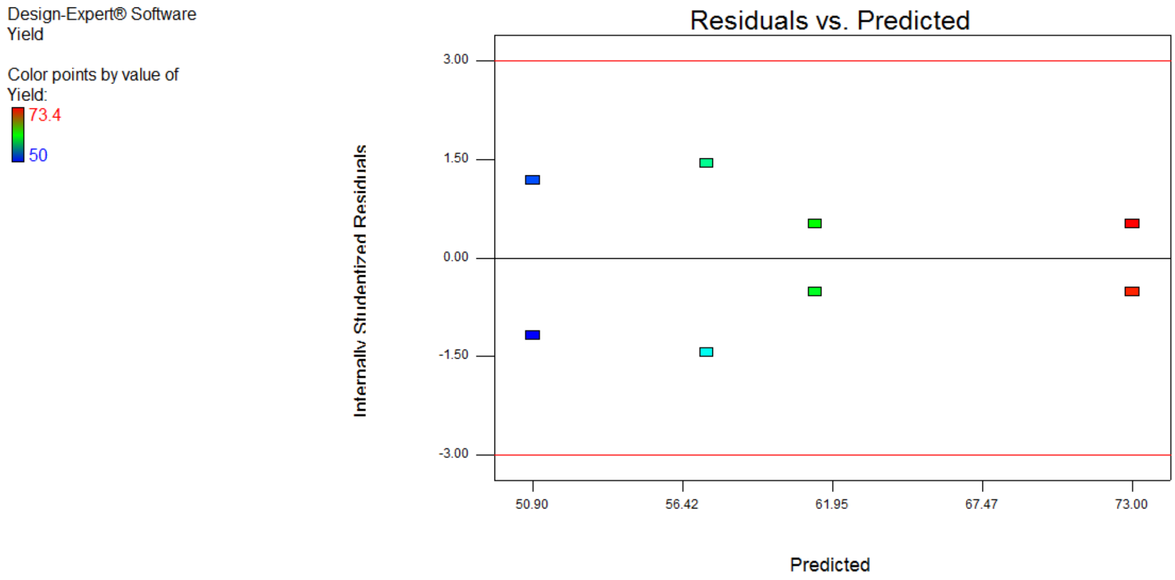
A.3.2 Diagnostic plots of treated Quartz oil







Figures A.3.2.1 Quartz Normal plots of residuals



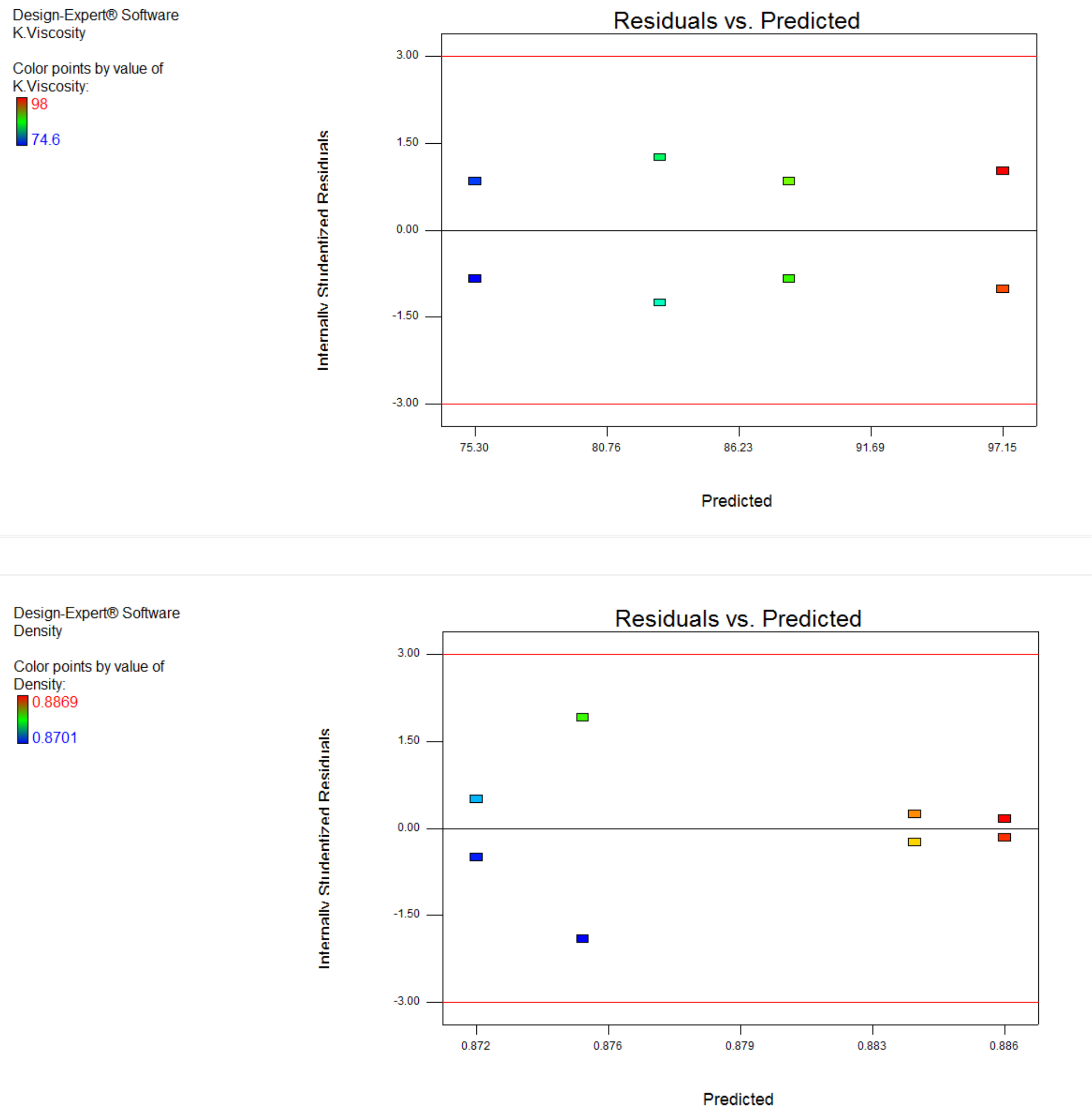
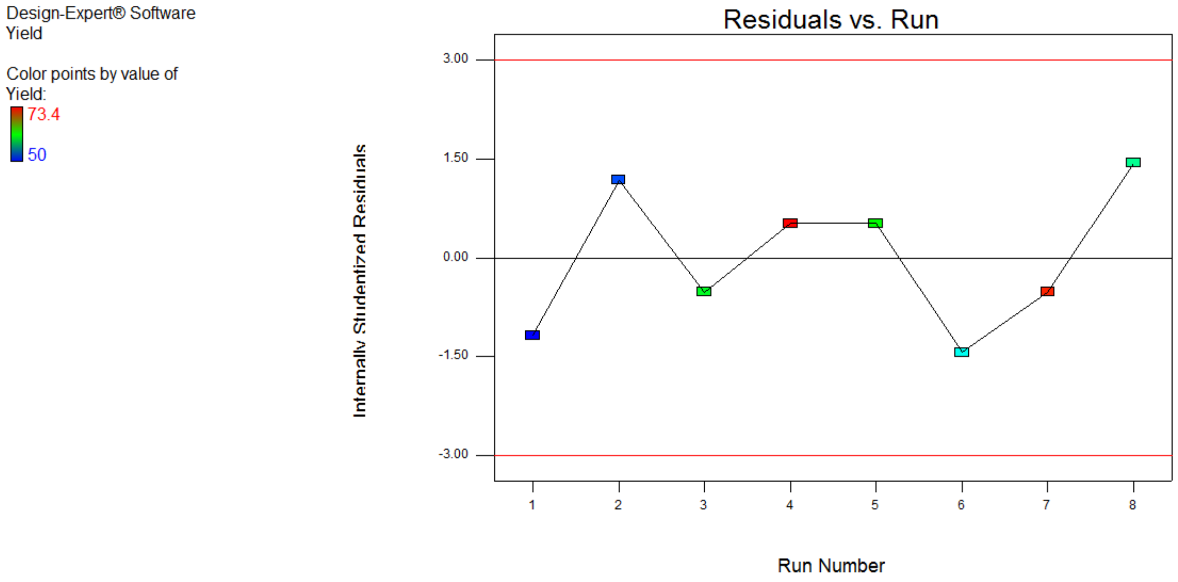
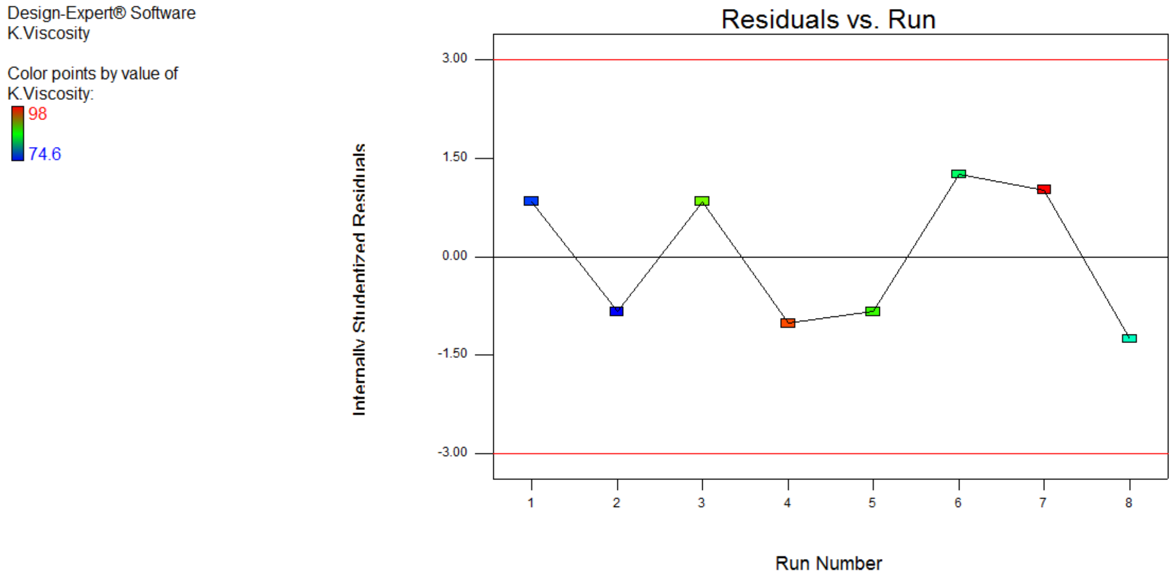


Figure A.3.2.2 Quartz Residuals Vs. Predicted


Design-Expert® Software
Yield
Color points by value of
Yield:
73.4
50
Residuals vs. Run
Internally Studentized Residuals
3.00
1.50
0.00
-1.50
-3.00
1
2
3
4
5
6
7
8
Run Number


Design-Expert® Software
K.Viscosity
Color points by value of
K.Viscosity:
98
74.6
Residuals vs. Run
Internally Studentized Residuals
3.00
1.50
0.00
-1.50
-3.00
1
2
3
4
5
6
7
8
Run Number

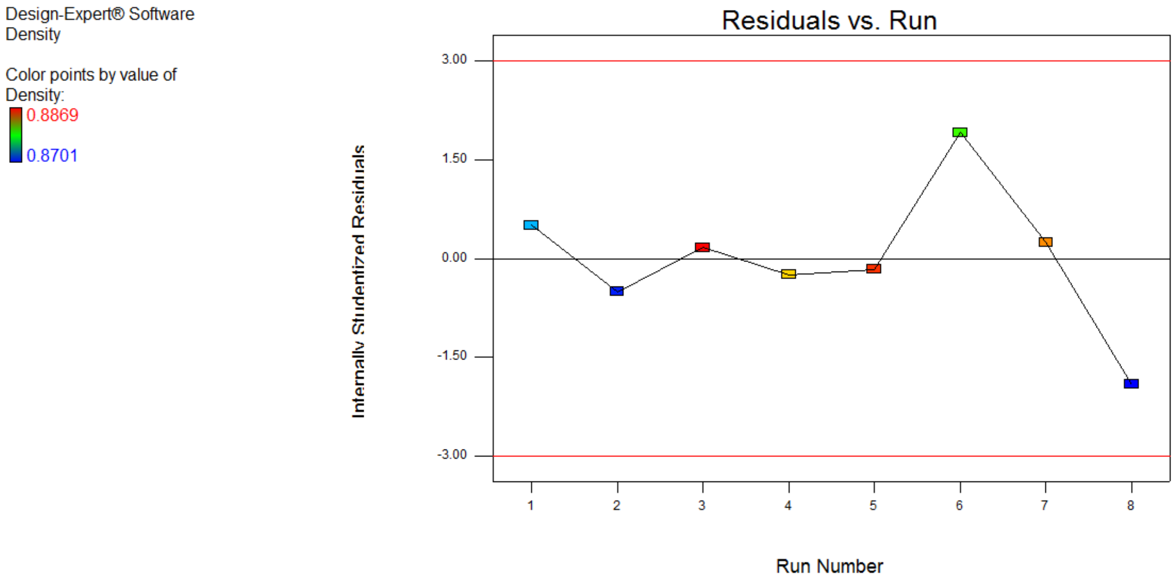
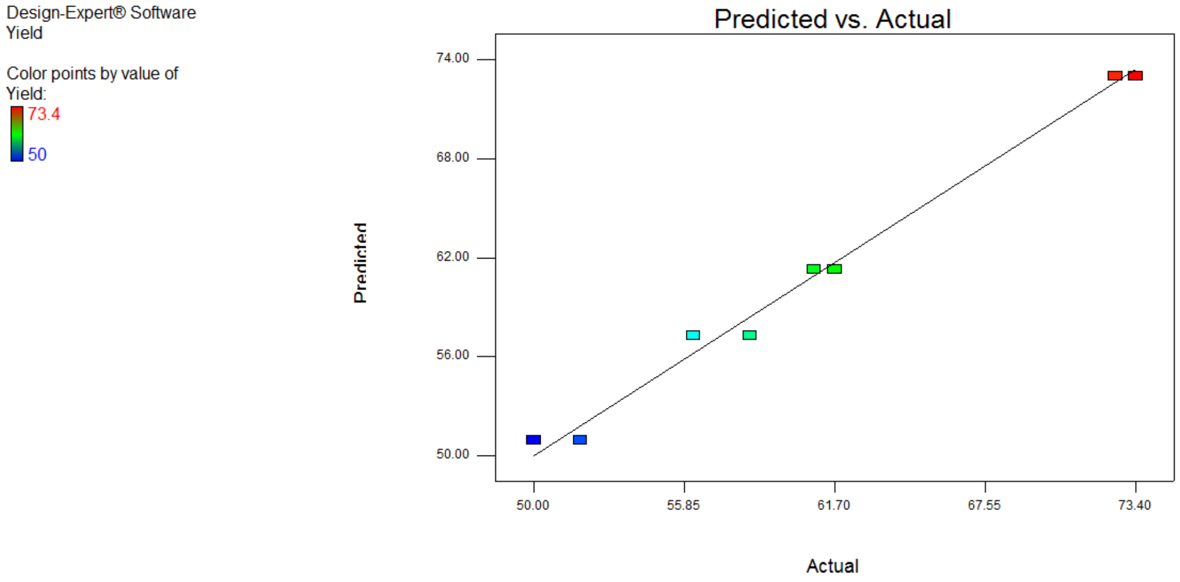


Figure A.3.2.3 Quartz Residuals Vs. Run



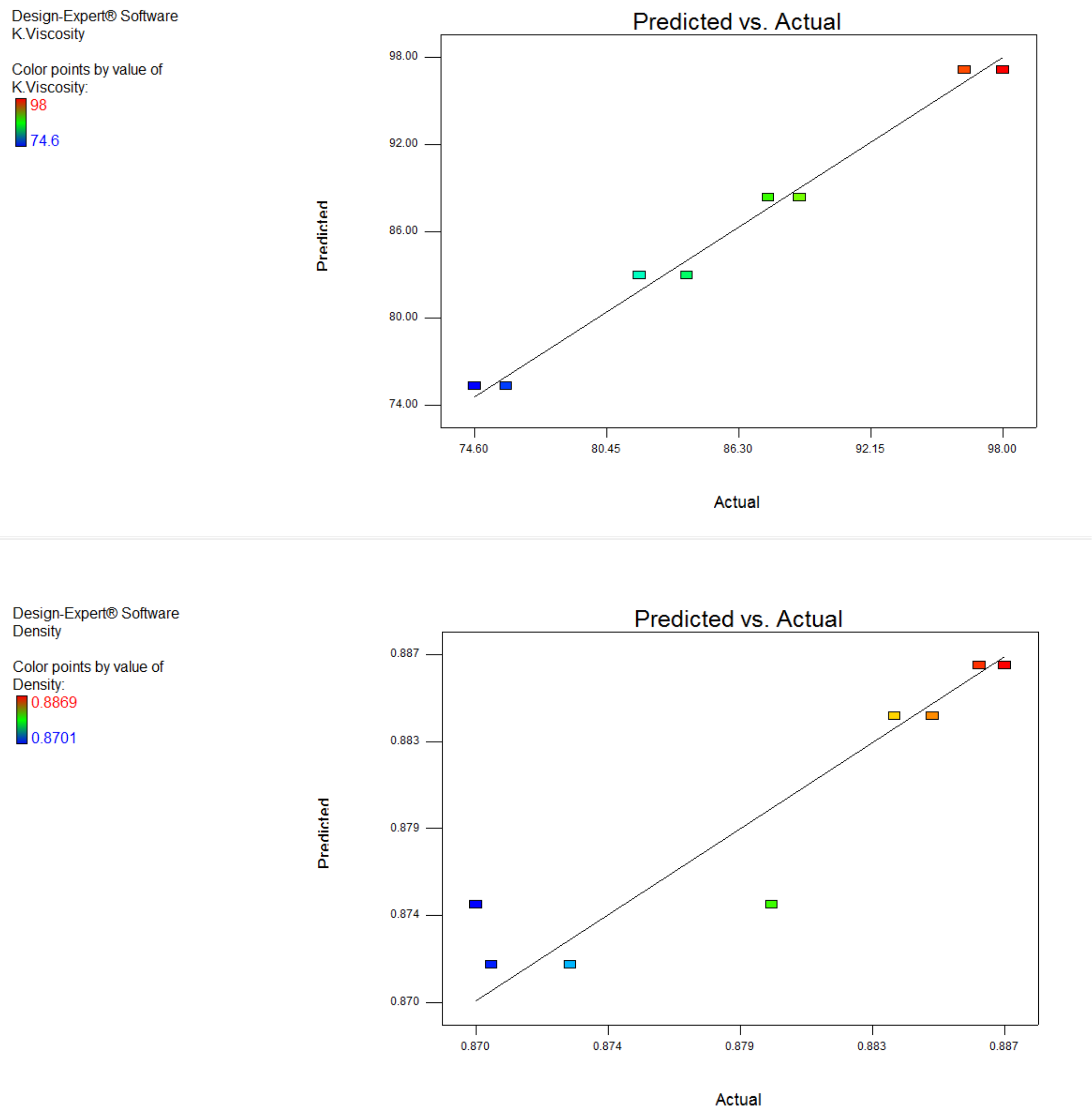
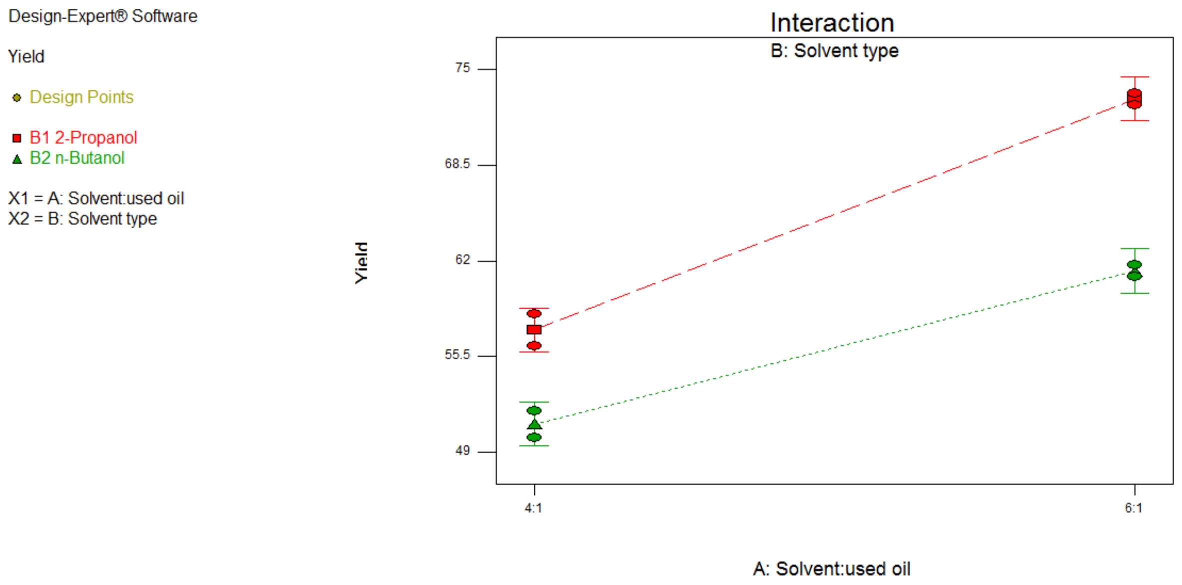
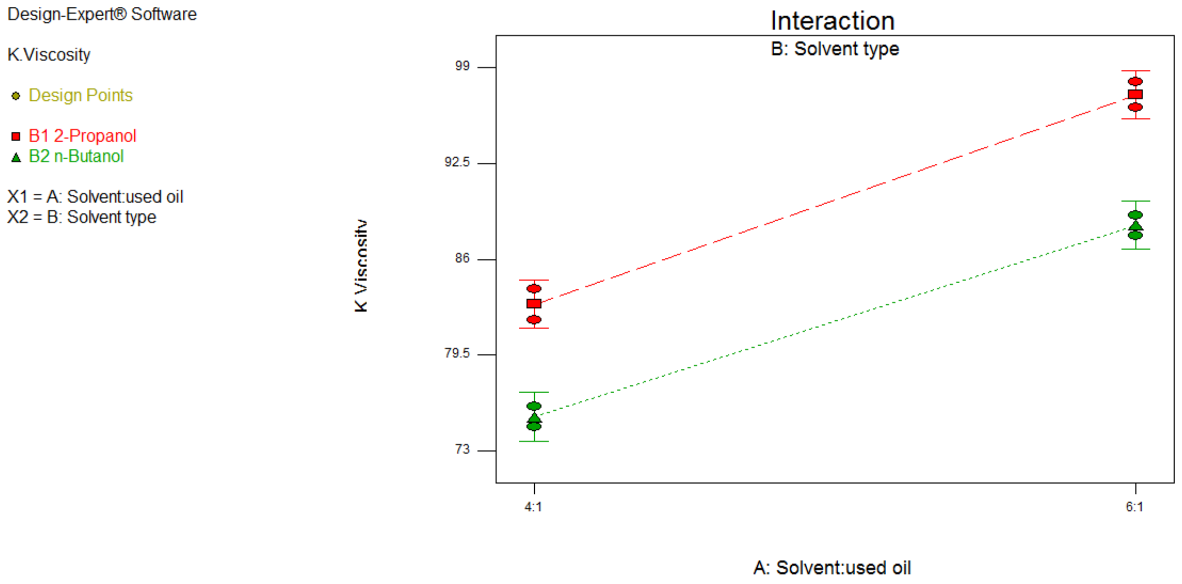


Figure A.3.2.4 Quartz Predicted Vs Actual


Design-Expert® Software
Yield
Design Points
B1 2-Propanol
B2 n-Butanol
X1 = A: Solvent:used oil
X2 = B: Solvent type
Interaction
B: Solvent type
Yield
75
68.5
62
55.5
49
4:1
6:1
A: Solvent:used oil


Design-Expert® Software
K.Viscosity
Design Points
B1 2-Propanol
B2 n-Butanol
X1 = A: Solvent:used oil
X2 = B: Solvent type
Interaction
B: Solvent type
K Viscosity
99
92.5
86
79.5
73
4:1
6:1
A: Solvent:used oil

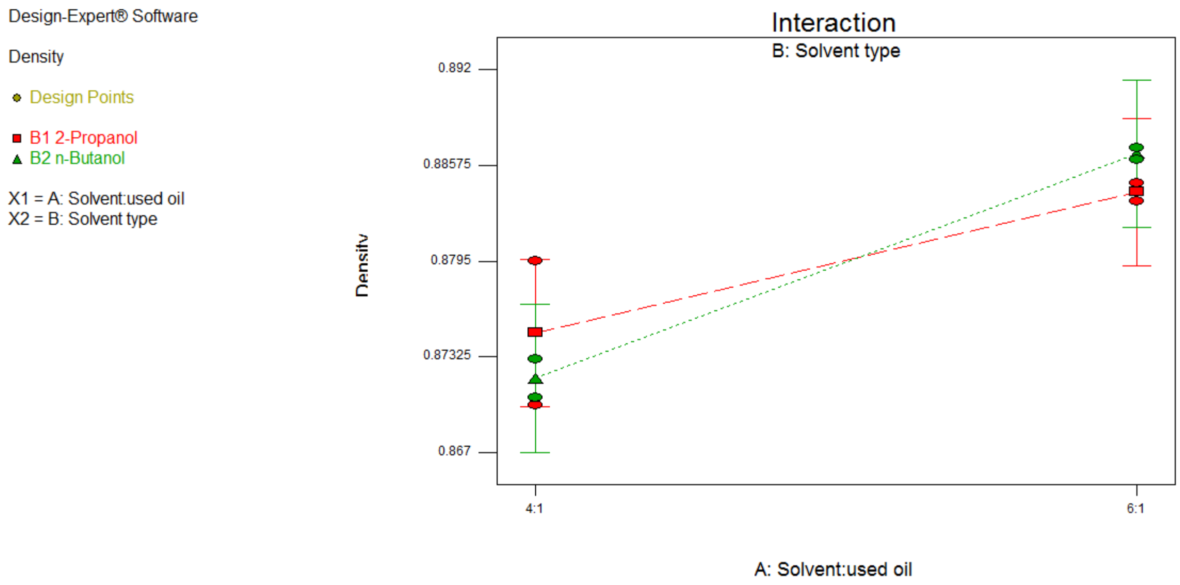


Figure A.3.2.5 Quartz Interaction

APPENDIX B : DATA'S AND CALCULATIONS

Viscosity index using viscopedia

Table B-1:- Characterization of treated Rubia oil

Std	Run	Block	Solvent: used oil	Solvent type	Yield (%)	K.Viscosity @40 °C (cSt)	K.Viscosity @100 °C (cSt)	Density (g/ml)	VI
5	1	Block 1	4:1	n-Butanol	55	46.4	5.8	0.8697	44.163
3	2	Block 1	6:1	2-propanol	71	69.7	9.2	0.8715	107.753
6	3	Block 1	4:1	n-Butanol	55	46.4	5.8	0.8697	44.163
7	4	Block 1	6:1	n-Butanol	64	58	7.9	0.8701	101.209
8	5	Block 1	6:1	n-Butanol	65	58	7.9	0.8701	101.209
4	6	Block 1	4:1	2-Propanol	60	62.1	7.1	0.8701	59.236
1	7	Block 1	6:1	2-Propanol	72	70	9.2	0.8715	107.096
2	8	Block 1	4:1	2-Propanol	62	62.1	7.1	0.8701	59.236

Table B-2:- Characterization of treated Quartz oil

Std	Run	Block	Solvent: used oil	Solvent type	Yield (%)	K.Viscosity @40 °C (cSt)	K.Viscosity @100 °C (cSt)	Density (g/ml)	VI
6	1	Block 1	4:1	n-Butanol	50	76	9.7	0.8731	106.1
5	2	Block 1	4:1	n-Butanol	51.8	74.6	9.2	0.8706	97.838
8	3	Block 1	6:1	n-Butanol	60.9	89	12.3	0.8869	132.838
3	4	Block 1	6:1	2-propanol	73.4	96.3	13.9	0.8834	146.873
7	5	Block 1	6:1	n-Butanol	61.7	87.6	11.8	0.8861	126.344
1	6	Block 1	4:1	2-Propanol	56.2	84	11.1	0.8795	119.77
4	7	Block 1	6:1	2-Propanol	72.6	98	14.7	0.8846	156.122
2	8	Block 1	4:1	2-Propanol	58.4	81.9	10.7	0.8701	115.735