

بسم الله الرحمن الرحيم

SUDAN UNIVERSITY OF SCIENCE AND TECHNOLOGY
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Development and Improvement of Diesel Oil Characteristics for
Varied Petrochemical Industries Applications

تطوير وتحسين خواص الديزل لتطبيقات صناعية بتروكيميائية متعددة

A Thesis Submitted in Fulfillment of the Requirements of the
Degree of Master of Science in Chemistry

By

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إستهلال

بسم الله الرحمن الرحيم

"ويري الذين أوتوا العلم الذي أنزل إليك من ربك هو
الحق و يهدي الي صراط العزيز الحميد "

(سورة سبأ الآية رقم 6)

صدق الله العظيم

Dedication

This thesis is dedicated to:

*Souls of my parents, my beloved family my wife and children,
my brothers and sisters.*

Acknowledgement

Firstly, praise to Al-mighty Allah for having given me the ability to complete this thesis.

My sincere gratitude goes to, Dr. Elfatih Ahmed Hassan for his continuous support of my study and related research, for his follow up, patience, motivation, and immense knowledge and guidance and help throughout the course of my study.

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Gratefully, I thank my colleague, whom I consider as my elder brother, Dr. Yousry Eltoukhee, who introduced me to this area of research, for the endless support. He was never tired or hesitant to give advice and technical support, which credited for any successful results obtained in this research output. I would like to express.

Abstract

The presence of aromatics in fuel deters ultra-low sulfur fuel production. Consequently the researcher's interest has involved the de-aromatization of fuels. Dearomatization would ultimately improve the quality of the fuels in terms of density, cetane number, viscosity etc. In this study, solvent extraction was adopted to de-aromatize a feedstock sample of 20.1 % aromatic and 166 ppm sulfur using acetonitrile. The extraction was performed at low temperatures 25, 35 and 45 °C and ambient atmospheric pressure. The aromatic contents were determined via HPLC, while ASTM methods were employed to determine other parameters. The results showed 72 % minimum yield, 8.6 % aromatic content, 58 - 64 cetane index, 73.2 ppm sulfur content, 5.4 viscosity, RI 1.4535, aniline point 82.15, specific gravity 0.824 – 0.812 with API 40.32 – 42.88 and flash point 70 – 78 °C, which reflects a significant improvement to the characteristics of the feedstock where these parameters were: aromatic content 20.1%, cetane index 54.4, sulphur content 166 ppm, RI 1.4581, aniline point 76C, specific gravity@15 0.824 Kg/m³, with API 40.28 and flash point 68C.

مستخلص

أن وجود المواد العطرية في الوقود يثبط من إنتاج وقود منخفض الكبريت. وبالتالي فإن اهتمام الباحث قد شمل العمل على تقليل وازالة المواد العطرية للوقود. نتيجة لإزالة المواد العطرية ، تتحسن جودة الوقود من حيث الكثافة ورقم السيتان واللزوجة وما إلى ذلك. في هذا العمل ، تم اعتماد استخراج المذيبات لإزالة المواد العطرية من عينة المادة الخام والتي تحتوي على 20.1 % من المركبات العطرية و 166 جزء من المليون نسبة كبريت باستخدام الأسيتونيتريل. تم إجراء استخلاص في درجات حرارة منخفضة 25 و 35 و 45 درجة مئوية والضغط الجوي المحيط. تم تحديد المحتويات العطرية عبر HPLC ، في حين تم استخدام طرق ASTM في تحديد المعلومات الأخرى. أظهرت النتائج 72 % كحد ادنى من العائد المنتج ، 8.6 % محتوى عطريات ، ومؤشر 58-64 سيتان ، 73.2 جزء في المليون محتوى الكبريت ، 5.4 لزوجة ، RI 1.4535 ، نقطة أنيلين 82.15 ، كثافة 0.812 - 0.824 مع API 40.32 - 42.88 ونقطة وميض 70 - 78 ° C ، وهو ما يعكس تحسنا ملحوظا في خصائص المواد الأولية حيث كانت هذه النتائج: المحتوى العطري 20.1 % ، مؤشر سنتان 54.4 ، محتوى الكبريت 166 جزء في المليون ، RI 1.4581 ، نقطة الأنيلين 76°C ، الثقل النوعي @ 15 0.824 Kg/m³ ، مع API 40.28 ونقطة وميض C68.

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List of Abbreviations

HPLC	High Performance Liquid Chromatography
PPM	Parts per million
RI	Refractive Index
Sp.gr	Specific gravity
ASTM	American Society for Testing and Materials
API	American Petroleum Institute
PAH	Poly Aromatic Hydrocarbons
DEG	Di-Ethylene Glycol
MEG	Mono Ethylene Glycol
DMSO	Di Methyl Sulfoxide
SO_x	Sulfoxide(s)
NO_x	Nitroxide(s)
CO_x	Carboxide(s)
LPG	Liquid Petroleum Gas
VGO	Vacuum Gas Oil
FCC	Fuel Catalytic Cracking
LCO	Light Cycle Oil
MMF	Mono Methyl Formamide
DMF	Di Methyl Formamide
HDS	Hydro-De-Sulphurization
PFD	Production Flow Diagram
EDXRF	Energy Dispersive X-ray Fluorescence
MAHs	Mono Aromatic Hydrocarbons
DAHs	Di Aromatic Hydrocarbons
T+Ahs	Total Aromatic Hydrocarbons
Cst	CentiStoke
PNA	Paraffin's Naphtha's Aromatics
IBP	Initial Boiling point
FBP	Final Boiling Point.
UV	Ultra Violet
CI	Cetane Index
CN	Cetane Number
EPA	Environmental Protection Agency
FTIR	Fourier Transform Infra Red

CHAPTER ONE

Introduction and Literature Review

1.1: INTRODUCTION:

Diesel fuel is a petroleum product with a density between 820 to 950 grams per liter (g/l). It is, slightly heavier than the density of gasoline (Simetric. Co. UK) which is between 710 to 740 grams per liter. The average empirical formula for diesel fuel lies in the range of $C_{10}H_{22}$ to $C_{15}H_{32}$. Diesel fuel is primarily a blend of 75% aliphatic hydrocarbon and 25% aromatic hydrocarbons (Speight, et al. 2002). Aliphatic hydrocarbons consist of paraffins (alkanes), naphthalenes (cycloalkanes). While aromatic hydrocarbons include alkyl benzene and olefins (styrene Polycyclic aromatic hydrocarbons (PAH), these are aromatic hydrocarbons that contain one or more “benzene” ring structures. PAH have a greater density than aliphatic hydrocarbon and generate more soot on burning. Of these emissions, pollutants such as sulfur dioxide will cause devastating environmental hazards; some unregulated pollutants are even mutagenic in the Ames test.

Aromatic compounds are the key chemicals in petrochemical and chemical industry; they are basic raw ingredients for many intermediate and fine chemicals. Aromatics are extracted from hydrocarbon feed stocks where it remains as a mixture of aromatic and aliphatic compounds. Aromatic compounds extracted from hydrocarbon feed stocks are useful in the oil industry. The separation of aromatics from aliphatic mixtures is an extremely challenging task in oil industry. Conventional separation routes for aromatics and aliphatic hydrocarbon mixtures are liquid-liquid extraction. Liquid-liquid separation process is commonly advantageous in terms of less cost and energy requirement. The commercial acetonitrile solvents used for aromatic separation. There are others several solvents can be for liquid-liquid extraction such as Di ethylene glycol (DEG), Mono ethanol glycol (MEG), N-Methyl-2-pyrrolidone (NMP), Di methyl sulfoxide (DMSO).

The main goal of solvent extraction is to upgrade diesel as (finished product) by eradicating unsaturated, aromatic hydrocarbons. The solvent extraction protocol by acetonitrile removes aromatics, naphthenes, paraffin and impurities product diesel by dissolution. The diesel after its standards specification are measured is then mixed with acetonitrile in different weight ratios followed by agitation, settling and separation process proceeds and finally a whole analysis for the specifications for both raffinate and extract is carried out. In one type of process, the feedstock is washed with a plenty of water in which the substances to be removed are readily soluble than in the desired resultant product. Whereas, in another process, a selected solvent is measured at deferent temperatures to study the effect of heat.

The changes in diesel fuel specifications can be expected to lower some of the total aromatic hydrocarbons. The positive impact of improvement is reflected by the decrease in aromatic hydrocarbons content and increase in cetane index. The decrement in the diesel aromatic hydrocarbons content will dramatically upgrade the level of tolerance required for other petrochemicals industries, and at the same time can yield high solvency-power solvent as an additional product when using extract as feed for other production line.

Various physical and chemical processes are employed to produce high yields of valuable products such as petroleum gas, gasoline, jet and diesel fuels and wax. Such processes include distillation, extraction, reforming, hydrogenation, cracking and blending are adopted in modern refineries. About 70–80% of refining products are gasoline, diesel and non-transportation fuels [1] .As dieselization of automotives is becoming a global target, the relative ratio of diesel in fuel products is estimated to rise

unceasingly .For instance, in China the diesel to gasoline utilization ratio had increased 55% between 1995 and 2009, with an expected ratio of 74% by 2020 [2] . Usually diesel is produced by fluid catalytic cracking and coke units. Such products has high sulfur contents (≈ 2.5 wt. %), elevated level of aromatics and polyaromatics, a very low cetane number (≈ 20), and a high density [1]. A substantial level of air pollution was attributed to the combustion of such diesel fuels. Adverse environmental and human health defects result from gaseous pollutants (SO_x , NO_x , CO_x), unburned hydrocarbons including polycyclic aromatic hydrocarbons (PAHs) and carbonaceous particulates present in diesel exhaust [3, 4] . Therefore, considerable attention is to be paid to the diesel fuel processing chemistry. Recently, solvent extraction is employed for the production of less aromatic and ultra-low sulfur wide boiling range raffinates as starting materials for various petrochemical industries [5].

Development and improvement of uncut primary petroleum products to harvest high quality products is becoming a significant research priority. Diesel oil obtained as a distillate of petroleum refining cuts within 200- 370°C temperature range finds great international demand. Recently industrial regulations are imposing additional stringent specifications in diesel applications in chemicals and industrial oils. Consequently, to improve the quality requirements of diesel various technical procedures such as catalytic, hydrogenation, reforming and extraction are employed.

Solvent treating is an extensively adopted method of petroleum products refining besides being a host of other refinery stocks. As distillation (fractionation) splits up petroleum products into collections by virtue of their boiling-point ranges only, impurities may still linger. Such impurities comprise of organic compounds containing sulfur, nitrogen, and oxygen; inorganic salts and dissolved metals as well as soluble salts that already exist in the crude feedstock. Moreover, kerosene and distillates may contain amounts of aromatics and naphthenes. Furthermore, Diesel oil may contain kerosene and related lighter cuts. Solvent refining procedures including solvent extraction usually eliminate these unwanted products at intermediate refining phases or just before transporting the product for storage.

1.2 Literature review

1.2.1 Diesel Fuel:

Diesel fuel is a vital factor for keeping the world economy moving. Its importance ranges from consumer goods transport around the world, generation of electric power, increased efficiency on farms. Thus, diesel fuel plays a dynamic role in strengthening the global economy and the standard of living. The major uses of diesel fuel are:

1.2.1.1 On-road transportation

1.2.1.2 Farming

1.2.1.3 Rail transportation

1.2.1.4 Off-road uses (e.g., mining, construction, and logging)

1.2.1.5 Electric power generation

1.2.1.6 Military transportation

1.2.2 Diesel Fuel Refining and Chemistry:

Diesel fuel is obtained from petroleum crude oils which are composed predominantly of the paraffinic, naphthenic and aromatic hydrocarbons classes. Each class contains a very broad range of molecular weights. Coming out of the ground, crude oil can be as thin and light-colored as apple cider or as thick and black as melted tar. Thin crude oils have relatively low densities and thus, high API gravities. In the U.S., light crudes are called high-gravity crude oils; conversely, thick and heavy crude oils with relatively high densities are low-gravity crude oils. Outside of the U.S. the terminology “light crude” refers to a low-density crude oil and “heavy crude” to a high-density crude oil[6]. Refining is the procedure of altering crude oil into high value products. The most significant are transportation fuels: gasoline, jet fuel, and diesel fuel. Other products

include liquefied petroleum gas (LPG), heating fuel, lubricating oil, wax, and asphalt. High-gravity crude oils contain more of the lighter products such as gasoline, generally, have lower sulfur and nitrogen contents, which make them easier to refine. However, modern refining processes are capable of turning low-gravity crude oils into high value products. Refining low-gravity crude oils requires more complex and expensive processing equipment, more processing steps, and more energy; therefore, costs is more. The price difference between high-gravity and low-gravity crude oils, reflects a portion of the refining cost difference.

1.2.3 REFINING PROCESSES[6]

Today's refinery is a complex combination of interdependent processes, the output of a fascinating intertwining of advances in chemistry, engineering, and metallurgy. These processes can be divided into three basic categories:

1.2.3.1 Separation processes: The feed is separated into two or more components based on a physical property, usually boiling point. These processes do not otherwise change the feedstock. The most common separation process in a refinery is distillation.

1.2.3.2 Upgrading processes: These processes improve the quality of a material chemical reactions to remove compounds present in trace amounts that give the material an undesirable quality. Otherwise the bulk properties of the feedstock are not changed. The most commonly used upgrading process for diesel fuel is hydro-treating to remove sulfur. Hydro-processing (hydrogen treating process) is a generic term for a series of processes that use hydrogen with an appropriate catalyst[8]to remove undesired components from a refinery stream. The processes run the gamut from mild conditions that remove reactive. In distillation terminology, the terms "light" and "heavy" are used for "lower boiling" and "higher boiling." They do not refer to the density of materials; although, generally, a lower boiling material is also less dense than a high boiling material. Methane and ethane are often present in crude oil as it comes out of the ground. These lightest compounds are removed before the crude oil is transported by pipeline or tanker. A catalyst is a material that accelerates or otherwise facilitates a chemical reaction without undergoing a permanent chemical change itself. Compounds like olefins, some sulfur, nitrogen and

oxygen compounds (hydro-finishing), are subjected to more severe conditions that saturate aromatic rings and remove almost all sulfur and nitrogen compounds (hydro-treating).

1.2.3.3 Conversion processes: These processes essentially modify the molecular structure of the feedstock, usually by “cracking” large molecules into small ones (e.g., catalytic cracking and hydrocracking). Hydrocarbons with higher boiling points (the larger molecules in the distillation bottoms) can be broken down (cracked) into lower boiling hydrocarbons by subjecting them to very high temperatures. The discovery of this process (thermal cracking) offered a way to correct the mismatch between supply and demand. Since 1913, thermal cracking has been used to increase gasoline production. Although by today’s standards, the quality and performance of these earlier cracked products was low, they were sufficient for the engines of the day.

Eventually heat was supplemented by a catalyst, transforming thermal cracking into catalytic cracking. Catalytic cracking produces higher quality products than thermal cracking. There are many variations on catalytic cracking, but fluid catalytic cracking (FCC) is probably the most widely used conversion process, worldwide. Most of the liquid product from FCC eventually goes into gasoline; however, one product stream, light cycle oil (LCO), is often blended into diesel fuel. Before blending, LCO undergoes subsequent hydro-treating to lower sulfur content which makes the LCO more stable and suitable for adding to diesel fuel. To meet the 15 ppm sulfur requirement, LCO undergoes subsequent hydro-treating to lower sulfur content.

Hydrocracking is another major conversion process. It is similar to catalytic cracking because it uses a catalyst, but the reactions take place under a high pressure of hydrogen. The primary feed to the hydrocracking unit is VGO. During hydrocracking, large VGO molecules are cracked into smaller molecules by either cleaving carbon-carbon bonds or by plucking out sulfur and nitrogen atoms from -carbon-sulfur-carbon- and -carbon-nitrogen-carbon- molecular linkages. Because of the high hydrogen pressure used in hydro-treating, hydrogen is added to the fragmented molecular ends formed by either

cleaving carbon-carbon bonds or by extracting sulfur and nitrogen linkage atoms; in addition, rings of some aromatic compounds are saturated with hydrogen during the hydrocracking process. Kerosene and diesel form a large percentage of the product from a hydrocracker. These products are nearly void of sulfur and nitrogen and are enriched in hydrogen.

1.2.4 Distillation:

Distillation is by far the most important and widely used separation process in a petroleum refinery. In large part, petroleum products are classified in accordance to their boiling range, and distillation is the process used to separate crude oil or other wide boiling range mixtures into products with narrower boiling ranges. Crude oil is made up of many thousands of components from light gases that boil below ambient temperature, to very heavy materials that cannot be distilled even at temperatures above 550°C[7].

In crude petroleum distillation, hot oil is pumped into a distillation column and the lightest hydrocarbons present, usually propane and butane, rise to the top of the column and are removed. Since gasoline is a little heavier, it does not rise quite so high and is drawn off from the side of the column. Kerosene and diesel, the next heavier products, are drawn off at successively lower points on the column. The products that are obtained directly from crude oil distillation are called straight-run products (e.g., straight-run diesel). The material that is too heavy to vaporize under atmospheric distillation conditions is removed from the bottom of the column (atmospheric bottoms).

The atmospheric bottoms can be fractionated further by a second distillation carried out under reduced pressure. The lower pressure in the distillation column allows some of the heavier components to be vaporized and collected. This process is called vacuum distillation; the overhead product is called vacuum gas oil (VGO), and the bottoms product is called vacuum residue.

Due to the distillation profile of the typical crude, refining by distillation alone has not been able to meet market demand for light fuel products since the early 1900s. It yields too much heavy products and not enough light products. In addition, the quality of light

products produced by distillation alone is often poor. The petroleum refiner uses the upgrading and conversion processes to match the barrel to the market

1.2.5 ABOUT HYDROCARBONS:

Hydrocarbons are organic compounds composed entirely of carbon and hydrogen atoms. There are four major classes of hydrocarbons: paraffins, naphthenes, olefins, and aromatics. Each class is a family of individual hydrocarbon molecules that share a common structural feature, but differ in size (number of carbon atoms) or geometry. The classes also differ in the ratio of hydrogen to carbon atoms and in the way the carbon atoms are bonded to each other.

1.2.5.1 Paraffins:

Paraffins have the general formula C_nH_{2n+2} (Fig.1.1), where “n” is the number of carbon atoms (carbon number) in the molecule. There are two subclasses of paraffins: normal paraffins and isoparaffins.

Normal paraffins have carbon atoms linked to form chain-like molecules, with each carbon – except those at the ends – bonded to two others, one on either side. Isoparaffins have a similar carbon backbone, but they also have one or more carbons branching off from the backbone. Normal decane and 2,4-dimethyloctane have the same chemical formula, $C_{10}H_{22}$, but different chemical and physical properties. Compounds like this, with the same chemical formula but a different arrangement of atoms, are called structural isomers.

1.2.5.2 Naphthenes:

Naphthenes⁴ have some of their carbon atoms arranged in a ring. The naphthenes in diesel fuel have rings of five or six carbons. Sometimes two or more rings are fused together, with some carbons shared by adjacent rings. Naphthenes with one ring have the general formula C_nH_{2n} (Fig1.2)

1.2.5.3 Olefins are similar to paraffins but have fewer hydrogen atoms and contain at least one double bond between a pair of carbon atoms. Olefins rarely occur in crude oil; they

are formed by certain refinery processes. Like paraffins, olefins with four or more carbons can exist as structural isomers. Olefins with one double bond have the general formula C_nH_{2n} , the same as naphthenes.

Paraffin and ISO Paraffin

$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3, CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

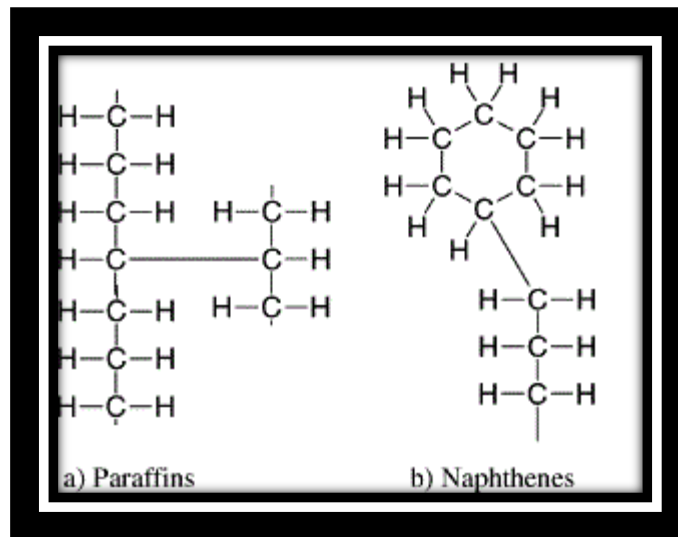


Fig 1.1: An example for Paraffins and Naphthenes structure

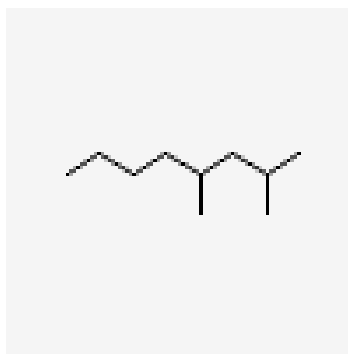


Fig 1.2: 2,4-Dimethyloctane $C_{10}H_{22}$

1.2.6 Refining Technologies:

Different refining approaches have been used for sulfur and aromatic content of diesel fuel. The conventional hydrotreating technology which is the most popular one has the drawbacks of using catalysts, H₂S formation, high operational expenses and less aromatics and sulfur removal [9]. Adsorption technology through efficient and economic measures has the rapid sorbent overloading problem. Recently solvent extraction is employed in the purification of various petroleum derived fuels. Generally, in this procedure sulfur and aromatics containing feedstock is mixed with a suitable solvent where the desirable components (sulfur and aromatics) get into the solvent phase due to their higher selectivity or polarity [9]. The solvent-feedstock mixture is then fed into a separator in which the two separated phases, i.e. raffinate and extract are obtained. To improve the efficiency of the process, the solvent should meet the following criteria: high hydrocarbon extraction capacity, partial miscibility with the hydrocarbon feed stream, high selectivity for aromatic hydrocarbons, non-corrosiveness to the equipment at operating conditions, complete stability under operating conditions, easy recoverability from the hydrocarbon products, has boiling temperature different from that of the extractable compounds and low cost [9]. Various solvents such as monomethyl formamide (MMF), dimethylformamide (DMF) [10, 11], diethylene glycol (DEG), mixtures of methyl and ethyl carbamates [12] and methanol-water [9][13] were employed along with others. Aromatics were extracted from the diesel fraction with acetonitrile at 30°C (acetonitrile : feed = 3 : 1 [14], from atmospheric gasoil with acetonitrile and dimethylacetamide (DMA) at 30°C (acetonitrile or DMA : feed = 5 : 1. The performance of acetonitrile was found to surpass that of ethanol and methanol in extraction of oxidized

sulfur-containing compounds of kerosene [15]. Acetonitrile does not form azeotropic mixtures with C₉ arenes but forms them with saturated C₉–C₁₀ hydrocarbons [16].

1.2.7 Some of De aromatization and Sulfur removal technologies:

1.2.7.1Hydrotreating:

Hydrotreating[17], formally known as hydrodesulphurization (HDS), is a chemical process chemical used on natural gas and refined petroleum. The aim of this process is to decrease the amount of sulfur in the petroleum by increasing the amount of hydrogen in the product. This is done for a variety of reasons, such as decreasing the environment impact when these petroleum products are used, and to keep the reforming units that process the petroleum from being poisoned. Most of the sulfur produced annually comes from this process. The environment is the main reason for reducing the sulfur, another reason is because a lower sulfur amount provides a higher-quality fuel. The smell and color of the fuel also is better when the sulfur is reduced. Another reason is to help the longevity of the parts involved in processing the fuel. When fuel is processed, it goes through a catalytic reforming unit that is able to enhance the octane rating of the fuel. Catalytic reforming units are made of noble metals, primarily platinum and rhenium. While both metals are resistant to corrosion, slight amounts of sulfur poison these metals and make them useless in octane enhancement.

In hydrotreating, hydrogen is introduced into a mixture to increase the overall hydrogen count Fig 1.3. Petroleum undergoes what is specifically called hydrogenolysis. This is when the carbon and sulfur bond contained within petroleum is split, and a hydrogen atom is linked to both the carbon and the sulfur atom. Through this process, the sulfur can be removed from the petroleum until it reaches an acceptable level.

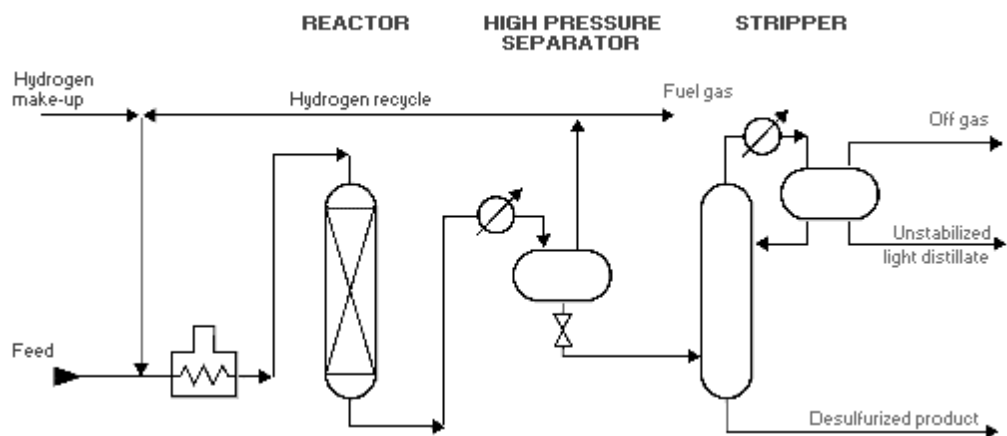


Fig. 1.3 PFD scheme of hydrotreating unit

Benefits of effective hydrotreating are:

- Major Benefit - Removal of Sulphur, improving Diesel Cetane Number from Aromatic & Coker Distillates.
- Associated benefit - Removal of Nitrogen through denitrification
- Olefin Saturation
- Aromatic Saturation
- Removal of metals such as iron, nickel, vanadium etc

1.2.7.2 HYDROCRACKING

Hydrocracking [18] is another major conversion process Fig 1.4. It is similar to catalytic cracking because it uses a catalyst, but the reactions take place under a high pressure of hydrogen. The primary feed to the hydrocracking unit is VGO. During hydrocracking, large VGO molecules are cracked into smaller molecules by either cleaving carbon-carbon bonds or by plucking out sulfur and nitrogen atoms from -carbon-sulfur-carbon- and -carbon-nitrogen-carbon- molecular linkages. Because of the high hydrogen pressure used in hydrotreating, hydrogen is added to the fragmented molecular ends formed by either cleaving carbon-carbon bonds or by extracting sulfur and nitrogen linkage atoms; in addition, rings of some aromatic compounds are saturated with hydrogen during the

hydrocracking process. The cracking is usually promoted by acid sites on Zeolites (Silica –alumina). Kerosene and diesel form a large percentage of the product from a hydrocracker. These products are nearly void of sulfur and nitrogen and are enriched in hydrogen. Therefore the process accomplishes hydrotreating + breaking up of bigger diesel range molecules into lower-boiling low sulphur Diesel at Temp up to 425 OC and pressure up to 200 bar. Hydrogenation is promoted by Palladium, Molybdenum or Tungsten sulphides. Hydrocracking is very flexible but consumes more H₂ and very expensive.

The benefits of hydrocracking can be summarized as:

- As Refinery margins improve with the processing of cheaper heavier Crudes,
- Hydrocracking is becoming more popular due to an increasing demand on diesel vehicles for cleaner air.
- Upgrading low-grade diesel and cycle oil into high value Diesel and other lighter products.

The main drawback of hydrotreating it cannot achieve target sulphur reduction for the full diesel range.

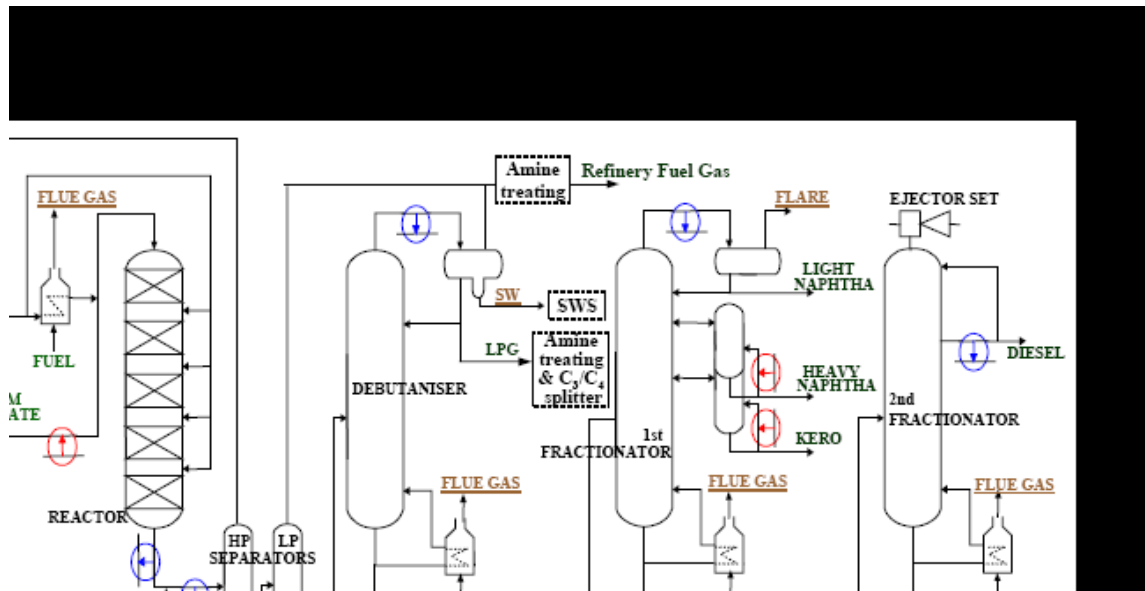


Fig. 1.4 PFD scheme of hydrocracking unit

1.2.8 Theoretical background of test methods:

1.2.8.1 Flash point:

Flash point measures the tendency of the specimen to form a flammable mixture with air under controlled laboratory conditions. It is only one of a number of properties that shall be considered in assessing the overall flammability hazard of a material. Flash point is used in shipping and safety regulations to define flammable and combustible materials. One should consult the particular regulation involved for precise definitions of these classes. Flash point can indicate the possible presence of highly volatile and flammable materials in a relatively nonvolatile or nonflammable material. For example, an abnormally low flash point on a sample of kerosene can indicate gasoline contamination.

1.2.8.2 Distillation

The boiling point of a liquid is defined as the temperature at which the vapor escaping from the surface of the liquid has a pressure equal to the pressure existing above the liquid [19] boiling point of the used oil was determined with the help of an adequately calibrated thermometer by taking the temperature of the oil on heating, immediately physical boiling was observed Fig 1.5.



Fig 1.5 Kohler Distillation Unit

1.2.8.3 Aniline Point:

The aniline point is defined as the lowest temperature at which equal volumes of aniline ($C_6H_5NH_2$) and oil have complete miscibility. The value gives estimation for the aromatic compounds content in the oil. This is because the miscibility of aniline, which is also an aromatic compound, indicates the existence of similar (i.e. aromatic) compounds in the oil. The aniline point is inversely proportional to the aromatics content. In brief, 4 ml of aniline and 4 ml of the sample are placed into the test tube. Stopper was placed into the test tube and a thermometer was inserted, making sure the bulb didn't touch the sides or bottom of the tube. The tube was heated slowly while stirring the mixture (by moving the thermometer up and down) until complete miscibility (the mixture becomes clear) was attained Fig 1.6. The tube was removed from heat source and stirring was continued until mixture becomes cloudy. The thermometer temperature at cloud point was reported as the aniline point in °C.



Fig 1.6 Tanaka Aniline Point Tester

1.2.8.4 POUR POINT:

The pour point of petroleum is an index of the lowest temperature at which oil will flow under specified conditions [20]. The pour point was determined according to ASTM D-5853 using petrotest cloud and pour point Fig.1.7. The samples were poured into a test jar to the level marked and heated to a temperature of at least 20°C above the expected sample's pour point. The test jar was instantly closed with a cork carrying the high cloud and pour thermometer. As soon as the test specimen reached the required temperature, the cork carrying thermometer was removed and the specimen was gently stirred using a spatula, afterwards the cork carrying thermometer was put back in place. The test jar was then cooled by using a succession of baths at lower temperatures. Cooling media of possible use in these baths include, (ice and water down to 10°C, crushed ice and salt down to -12°C, ice calcium chloride down to -23°C, solid carbon-dioxide and petrol down to - 57 °C). The appearances of the test specimen were observed at different temperature intervals expressed in positive or negative multiples of 3°C when movement was still observed, the test jar was instantaneously returned to the water bath within the time of 3 s. The removal and replacement procedure was continued until no movement in the test jar was observed when held in a horizontal position for 5 s. This value of temperature was then recorded as the pour point temperature.



Fig 1.7 petrotest cloud and pour point tester

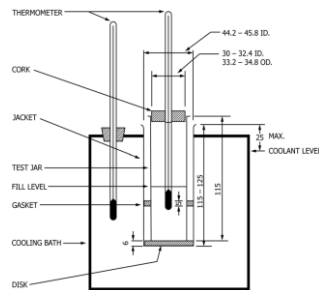


Fig 1.8 Assembly of cloud & pour point test

1.2.8.5 Specific Gravity and API[21]

A small volume (approximately 1 to 2 mL) of liquid sample is introduced into an oscillating sample tube and the change in oscillating frequency caused by the change in the mass of the tube is used in conjunction with calibration data to determine the density, relative density, or API Gravity of the sample. Both manual and automated injection techniques are described.

The specific gravity and density of the oil were determined using a 25 ml specific gravity bottle and a weighing balance. A clean empty bottle was weighted and then filled with the sample and reweighted again. The mass of the oil was the difference between these

two masses. Likewise, the bottle was filled with distilled water and weighed. The density and specific gravity were determined using the formulae:

$$\text{Density} = \text{Mass of Oil} / \text{Volume of Oil} \quad \dots\dots\dots (1.1)$$

$$\text{Specific Gravity} = \text{Mass of 25ml Oil} / \text{Mass of 25ml Water} \quad \dots\dots\dots (1.2)$$

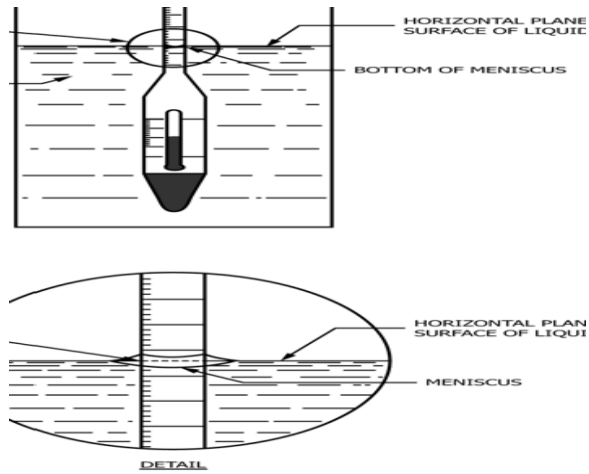


Fig 1.9 Hydrometer scale reading



Fig 1.10 Kem Densitymeter

1.2.8.6 REFRACTIVE INDEX

Refractive index is the ratio of the velocity of light (of specific wavelength) in air to its velocity in the substance under examination. It is a fundamental physical property that can be used in conjunction with other properties to characterize pure hydrocarbons and their mixtures.

The refractive index was measured according to ASTM-D1218 using a Bausch and Lomb precision refractometer Fig 1.11 and monochromatic light. It was ensured that the prism faces were cleaned and dry. The prism temperature was checked and was ensured that it was within 0.1°C of the desired temperature. The prism assembly was unlocked and 2 drops of the used oil sample was placed on the prism face after which it was locked. The light source was then turned on and a temperature equilibration time of 3 min was allowed. A close observation of the field consisting of light and dark positions was then made with the help of the eye piece. The instrument was adjusted so that the boundary between the lines and the position of the feed was as sharp as possible.



Fig 1.11 Kruss Refractometer

1.2.8.7 Sulfur Content:

The determination of sulfur content by the energy dispersive X-ray fluorescence analysis (5) was performed by means of the energy-dispersive X-ray fluorescence analyzer regakuthe50 kV X-ray tube Fig 1.12 with a palladium cathode and a proportional argon detector is built in the apparatus. During the analyses, the apparatus was calibrated up to the sulfur content of 0.2 %. Instruments of the last generation permit the determination of samples containing a very low and a very high amount of sulfur. The calibration of the instrument LAB-X 3000 is usually practiced within the range was of 0.05—5 % for samples containing a high amount of sulfur (e.g. fuel oils) and for those containing a low amount of sulfur either within the ranges of 10—1000 ppm or 10—5000 ppm, for instance for Diesel fuels. This method is used for the determination of total sulfur in petroleum and petroleum products that are single-phase and either liquid at ambient conditions, liquefiable with moderate heat, or soluble in hydrocarbon solvents. These materials can include diesel fuel, jet fuel, kerosene, other distillate oil, naphtha, residual oil, lubricating base oil, hydraulic oil, crude oil, unleaded gasoline, gasohol, biodiesel and similar petroleum products.



Fig 1.12Regaku, EDXRF

1.2.8.8 Aromatic content :

Mono-aromatic hydrocarbons (MAHs) were determined using HPLC Fig 1.13 in this test method, compounds that have a longer retention time on the specified polar column than the majority of non-aromatic hydrocarbons but a shorter retention time than the majority of DAHs.

Di-aromatic hydrocarbons (DAHs), compounds that have a longer retention time on the specified polar column than the majority of mono-aromatic hydrocarbons, but a shorter retention time than the majority of tri+-aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (POLY-AHs), in this method, sum of the di-aromatic hydrocarbons and tri+-aromatic hydrocarbons

Total aromatic hydrocarbons, in this test method, sum of the MAHs, DAHs, and T+AHs.

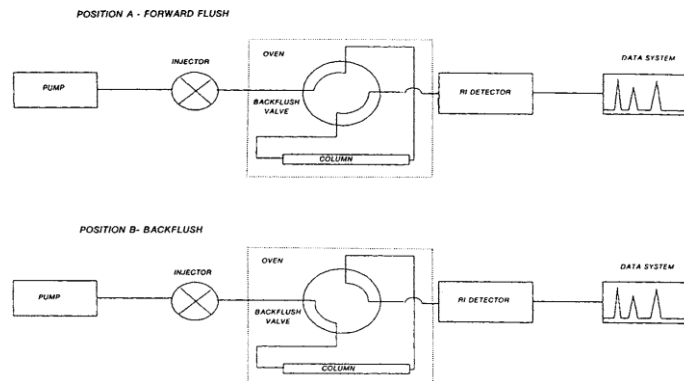


Fig 1.13 work flow of HPLC

1.2.8.9 Cetane Number and Cetane Index:

Cetane number is determined at constant speed in a pre-combustion chamber type compression ignition test engine. The relationship of test engine performance to full scale, variable speed, and variable load engines is not completely understood

Cetane number is a physico-chemical factor linked to burning of fuel in the engine. This parameter measures the ignition quality of a fuel and it directly affects both ignition and operation with load. Ignition quality is evaluated by quantifying the ignition delay, which is the period between injection and beginning of combustion of a fuel. Thus, a fuel with a high cetane number has a short ignition delay and starts to burn soon after it is injected in an engine [22]. The cetane number test is performed in a mono-cylindrical engine, where fuel ignition delay is paralleled with the delay of a mixture of cetane and alpha-methylnaphthalene with known cetane number, in accordance with ASTM-D613 [23]. A four variables equation, including density at 15 °C and distillation temperatures equivalent to 10%, 50% and 90% of recovered volume, is used to calculate the cetane index. $CCI = 45.2 + 0.0892 T_{10N} + (0.131 + 0.901B)T_{50N} + (0.0523 - 0.420B)T_{90N}$

$$+ 0.00049 (T_{10N}^2 - T_{90N}^2) + 107B + 60B^2 \quad (1.4)$$

$$\text{where } T_{10N} = T_{10} - 215, T_{50N} = T_{50} - 260, T_{90N} = T_{90} - 310, B = [e^{3.5(D-0.85)}] \quad (1.5)$$

1.2.8.10 Viscosity

The viscosity of the feedstock was measured according to the ASTM D-445. This test method specifies a procedure for the determination of the kinematic viscosity, “v” of liquid petroleum products, by recording the time for the volume of liquid to flow under gravity through a calibrated glass capillary U-tube viscometer Fig1.14. The samples were charged into the viscometer, after which the viscometer was immersed in an oil bath attained at a constant temperature of 25, 35 and 45°C. After thermal equilibrium between the sample and bath temperature was established, the sample was dragged and the time for oil flow between the two levels in the capillary tube was recorded. Generally,

viscosity is related to time of flow of a fixed volume of the test sample through a given capillary viscometer. The kinematic viscosity was then calculated by applying the formula:

$$v = kxt \quad (1.6)$$

Where: “k” is a constant factor for the calibrated viscometer. “t” is the time taken by the oil to flow through the viscometer in seconds. “v” is the kinematic viscosity measured in mm²/s (centistoke cSt).



Fig 1.14 kinematic viscosity bath

1.2.9 RESERCH OBJECTIVE:

- 1** To perform solvent extraction of diesel utilizing Acetonitrile.
- 2** To determine physicals and chemicals properties of diesel before and after acetonitrile extraction.
- 3** To determine and detect Total Aromatic hydrocarbons in the treated diesel by HPLC.
- 4** To determine sulfur content in the treated diesel.
- 5** To achieve high quality of diesel by correlating the aromatic hydrocarbons percentage and cetane index with extraction efficiency.

CHAPTER TWO

Materials and Methods

Materials and Methods

2.1 Materials

2.1.1 Feedstock Sample has been collect from the market as representative sample which produced from Aramco refineries. No treatment has been done to the sample.

2.2 Methods

The different tests were carried out for samples having stock solution to acetonitrile ratios ranging from 1:1 up to 1:5 and at 25, 35 and 45 °C using the standard ASTM methods [24].

2.2.1 The IBP, FBP/ Distillation Kohler distillation-K45100

The method ASTM D86Distillation (IBP, FBP) was adopted where 100-mL specimen of the sample is distilled under prescribed conditions for the group 4 using Kohler distillation-K45100 Fig2.5, and observations are made of the temperatures at which various percentages are recovered and/or the percentages recovered at specified temperatures in which the sample falls. The distillation is performed in a laboratory batch distillation unit at ambient pressure under conditions that are designed to provide approximately one theoretical plate fractionation. Systematic observations of temperature readings and volumes of condensate are made (IBP, 10%, 20%,.....FBP), depending on the needs of the user of the data. The volume of the residue and the losses are recorded.

2.2.2 Aromatic Content:

Through the ASTM D6591methodand HPLC Agilent- MODEL INFINITY 1260, (Detector :UV/RI COLUMN: amino column C18 stationary phase dimethyl-n-octadecylsilane/ (>99.995% SiO₂), mobile phase: n-heptane 99.9) was employed for aromatics content estimation Fig2.13. Between 0.9 and 1.1 g (weighed to the nearest

0.001 g) of sample was taken in a 10-mL volumetric flask, and made up to the mark with heptane. It was thoroughly shaken to mix and allowed to stand for 10 minute then 1.0 to 1.0 ml was sampled in a glass vial from which 10 μ mL was injected to the system to start mon- di- and poly-aromatics data collection.

2.2.3 Flash point

For flash point the ASTM D93 Pensky-Martens Closed Cup Apparatus was followed using petro test closed cup –PMA 4. 75 ml of test specimens was taken in the test cup and the test cover was placed on the test cup and assembled into the apparatus for applying heat. The heat was applied as indicated by the temperature measuring device, increases 5 to 6°C/minute. The test flame was lighted, and adjusted to a diameter of 3.2 to 4.8 mm. Then, the ignition source was apply when the temperature of the test specimen attained $23 \pm 5^\circ\text{C}$ before expected flash point until flash point of sample was observed.

2.2.4 Total sulfur:

EDXRF Rigaku model NEX-CG Fig 2.12 was used for total sulfur content determination as per ASTM D4294. Here, 4 g of sample was weighted in plastic cup sealed with myler film covered with cap and placed in x-ray chamber after turning on x-ray source(50 W, 50 kV X-ray tube.) and aging x-ray tube for 10min then allowed for 30min instrument warm up. The resultant excited characteristic X radiation was measured, and the accumulated count was compared with counts from previously prepared calibration samples to obtain the sulfur concentration in mass % and/or mg/kg. A minimum of three groups of calibration samples were required to span the concentration range: 0.0 to 0.1 mass %, 0.1 to 1.0 mass %, and 1.0 to 5.0 mass % sulfur.

2.2.5 Aniline point

Tanaka-model aap-6 aniline point tester Fig 2.6 was used to determine the aniline point adopting the ASTM D611 method. 10 mL of aniline and 10 mL of the dried sample were delivered into the test tube fitted with stirrer and thermometer (the center the thermometer in the test tube so that the immersion mark is at the liquid level, making sure that the thermometer bulb does not touch the side of the tube). The test tube was fitted in the jacket tube. The mixture was rapidly stirred using a 50-mm (2-in.) stroke, avoiding the introduction of air bubbles. Heat was directly applied to the jacket tube and the temperature was adjusted to rise at a rate of 1 to 3°C/minute. The heating was then reduced until complete miscibility is obtained. Then the stirring was continued and the mixture was allowed to cool at a rate of 0.5 to 1.0°C/minute. Cooling was further continue to a temperature of 1 to 2°C below the first appearance of turbidity. The aniline point was specified as the temperature at which the mixture suddenly becomes cloudy throughout. The average of three reading was considered as the final aniline point.

2.2.6 Refractive Index

Using the ASTM D1218 method the refractive index was determined via akruSS-Refractometer- model DR6000 (**Fig 2.11**), one to two drops of the sample were placed on the lower prism face. The prism assembly was closed and locked. The light source was turned on and allowed for three minutes for temperature to equilibrate then the refractive index reading on the scale was recorded.

2.2.7 Specific gravity @ 15, API, D4052kem density meter (DA-640)

This density/specific gravity meter (**Fig 2.10**) measures density of liquid or gaseous sample with precision in a short span of time, 2 mL of sample was introduced into an

oscillating sample tube and the change in oscillating frequency caused by the change in the mass of the tube is used in conjunction with calibration data to determine the density, relative density, or API Gravity of the sample..

CHAPTER THREE

Results and Discussion

3.0 Results and Discussion:

Air-pollution harms caused by the combustion of fuels such as gasoline and diesel are aggravated with the growing number of automobiles. It is known that air-pollution primarily results from the sulfur and aromatics found in diesel fuel. Sulfur which can be reduced by desulfurization and the aromatic components which affect specifications and cetane number are environmental pollution sources. However, there are restrictive problems with the use of diesel fuels. Recently the relationship between aromatic components and physical properties and cetane number of diesel fuels produced by hydrocracking process of heavy fractions has become a most subject of research [25]. To verify the effect of acetonitrile extraction, the parameters of the starting diesel feedstock are presented in Table 3.1.

Table 3.1: Characteristics of the feedstock

Parameter	IBP – FBP	Flash point	Total Sulfur content	Total Aromatic content	CI	Specific Gravity @ 15	API	Pour point	Aniline point	RI	Viscosity @ 20 C
Value	177 – 366	68 C	166 ppm	20.1 %	54.4	0.824	40.28	- 21 C	76 C	1.4581	5.01

3.1 Extraction:

After extraction with the different ratios of diesel to solvent (1:1 – 1:5), the following percentage yields were obtained (Fig. 3.1).

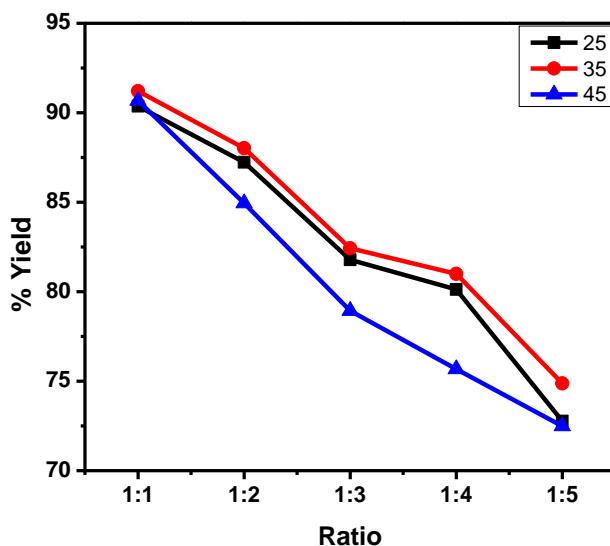


Fig. 3.1: The percentage yield at the experimental parameters.

The percentage yield Fig 3.1 data clearly shows a relative decrease following the solvent ratio increase with a maximum loss of about 25% at the highest working temperature of 45°C and maximum ratio. This level of yield exceeds the values previously reported by Gaile *et al.*[26]. Moreover the extraction is conducted at low temperature and ambient pressure, thus reducing the drawbacks related to harsh conditions extraction.

3.2 Aromatic contents

The mono-, di- and poly aromatic hydrocarbons obtained from HPLC analysis are listed in Table 3.2. The total aromatic contents of the raffinate are displayed in Fig. 3.2. A significant drop can be observed as the aromatic content falls from 20.1 to 8.6%. This result is comparable with the specifications wet by US EPA (35%), US CARB (10– 20%) and EU (15%)[27]. The aromatics removal achieved in this work exceeds the 14.0 to 8.51% [28]and 29.0 to 11.0% reported earlier[29]. It had been reported that, as the acetonitrile : feed ratio increased, the aromatics recovery increases and their concentration

in the raffinate is reduced [28]. The reduction of aromatic can improve the ignition quality which was reported to reduce and hence increase emissions as the aromatic content increases [30]. A number of previous studies [31-33] revealed that the application of noble metal catalysts was a potential route for dearomatization. But, the main disadvantage of this route, however, is the conventional catalyst systems of sulphur and nitrogen sensitivity[31]. Therefore, the findings of this work exhibit a convenient route for dearomatization under mild conditions.

Table 3.2 :Mono (MAH), Di (DAH) and Poly (PAH) Aromatic Hydrocarbons from HPLC analysis

Ratio		1:1	1:2	1:3	1:4	1:5
25°C						
MAH		13.0521	11.4878	10.4899	9.5390	8.5508
DAH		0.7166	0.5178	0.4192	0.3460	0.3014
PAH		0.1412	0.0965	0.0708	0.0633	0.0668
Total		13.9100	12.1022	10.9800	9.9483	8.9190
35°C						
MAH		12.8208	11.3787	9.7411	8.8942	8.4382
DAH		0.6052	0.4499	0.3732	0.3120	0.2494
PAH		0.1145	0.0689	0.0911	0.0543	0.0411
Total		13.5405	11.8975	10.2054	9.2606	8.7288
45°C						
MAH		12.4109	10.9341	9.6975	8.7551	8.2749
DAH		0.6010	0.4563	0.3464	0.3142	0.2572
PAH		0.1006	0.0763	0.0000	0.0619	0.0599
Total		13.1125	11.4668	10.0439	9.1312	8.5920

* Feedstock: MAH = 19.6, DAH = 0.3, PAH = 0.21, **Total** = 20.1.

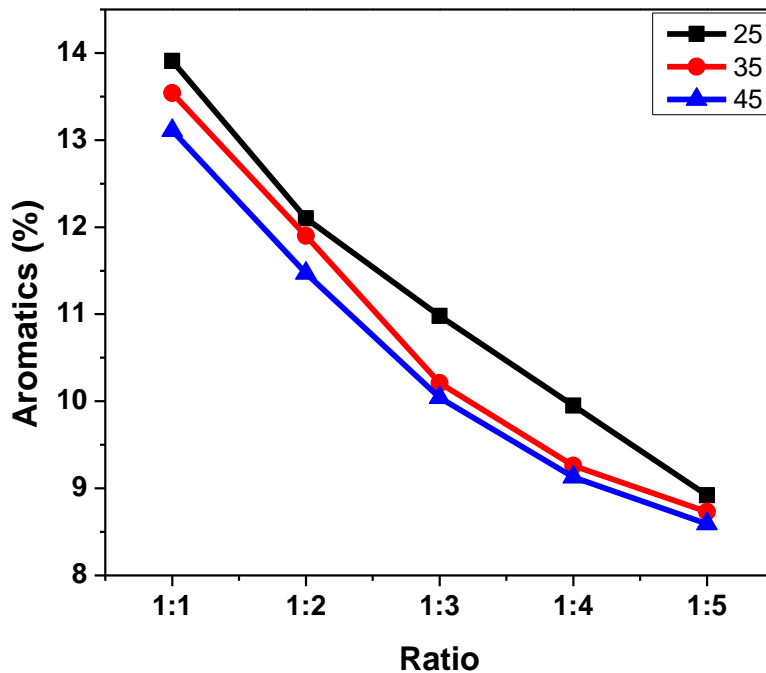


Fig. 3.2: The total aromatics content of raffinate.

From the data it can be seen that the PAHs was reduced by $\approx 50\%$ which has a positive impact to the environment due to the high toxicity of PAHs [34]. Moreover such low value of PAHs qualifies the product for other than industrial fuel applications.

3.3 Sulfur content

The Fig. 3.3 raffinate sulfur contents in demonstrated shows the 166 ppm sulfur content of the feedstock has been considerably lowered as a result of extraction to 73 ppm at 45°C and 1:5 ratio. The results achieved in this study are far better than that reported by Ramirez-Verduzco[35], who extracted sulfur from 320 ppm diesel feedstock using butyrolactone, DMF, 2-ethoxyethanol and MeCN to obtain 180, 130, 180 and 220 ppm respectively. Hydrotreating is common process used to reduce the sulfur content of diesel fuels. On the other hand, aromatic content reduction is achievable using a hydrotreating process that requires much higher operating pressures than those used to reduce sulfur, as mild hydrotreating which is used to reduce fuel sulfur typically has little effect on the total aromatic content [36]. In comparison the extraction process adopted in

this work has achieved both aromatics and sulfur reduction under mild condition. This implies the potential of extraction for simultaneous removal of aromatics and sulfur compounds from the feed.

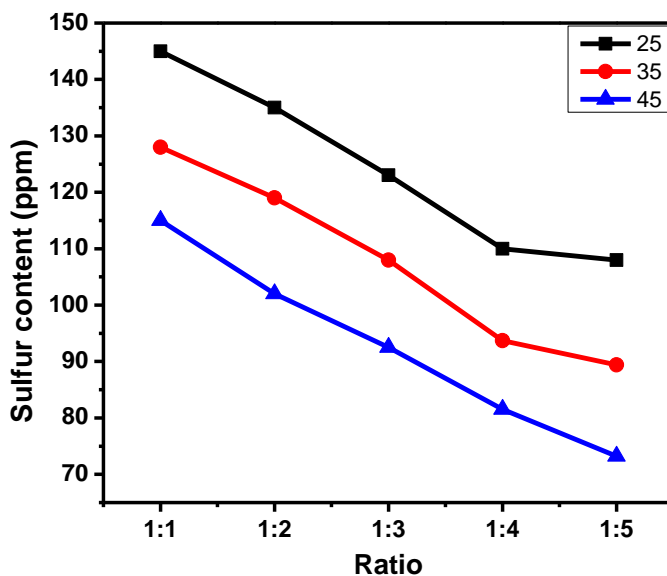


Fig. 3.3: The sulfur content of raffinate.

3.4 Aniline point

The increase of aniline point with the increase of the solvent ratio is shown in Fig. 3.4. This finding connotes the removal of aromatics from the feedstock along with the enhancement of the naphthenic and paraffinic characteristics of diesel [37]. Moreover the range of aniline point reported in this work agrees well with the range reported for diesel products [37]. The proportional increase in aniline point with the ratio of solvent evidently reflects the efficient reduction of the aromatics content of the feedstock after extraction [Fig. 3.2].

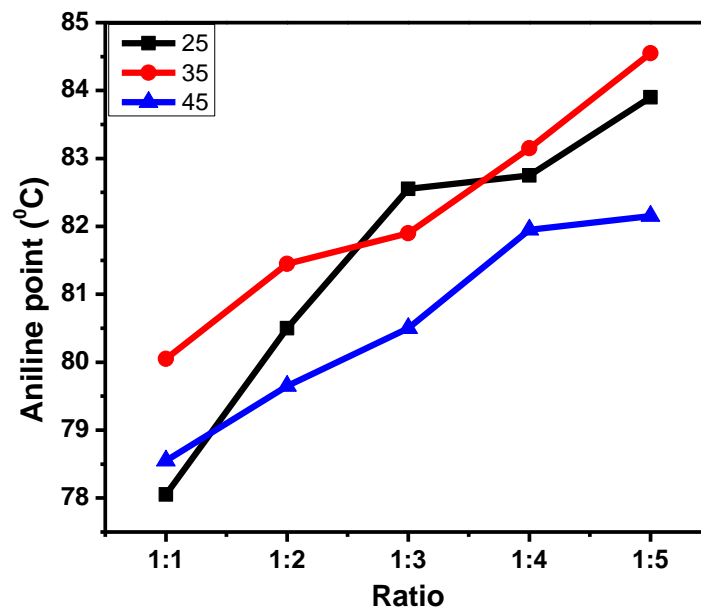


Fig. 3.4: The aniline of raffinate at different temperature and ratios.

The aniline point increases with the increment of solvent to feedstock ratio and the rise in temperature. It can also be inversely related with the decrease in aromatics contents (Fig. 3.4).

3.5 Cetane index

The calculated cetane index as a function of solvent ratio is given in Fig. 3.5. The prominent increase of CI clearly indicates an improvement of auto-ignition properties of the diesel as well as its cetane number [38]. This result confirms the strong correlation between the increasing CI with the decreasing aromatic contents [39] after extraction. The data is in consistency with the SHARAFUTDINOV *et al.* who derived analogous correlation between aromatics reduction and the CI increment [40]. The increase in cetane index leads to reduction of particulates [39] and NO_x [41] in exhaust gases generated in diesel engines. Thus, by this method we could obtain a raffinate with high cetane number satisfying the short ignition delay required for diesel engines [22].

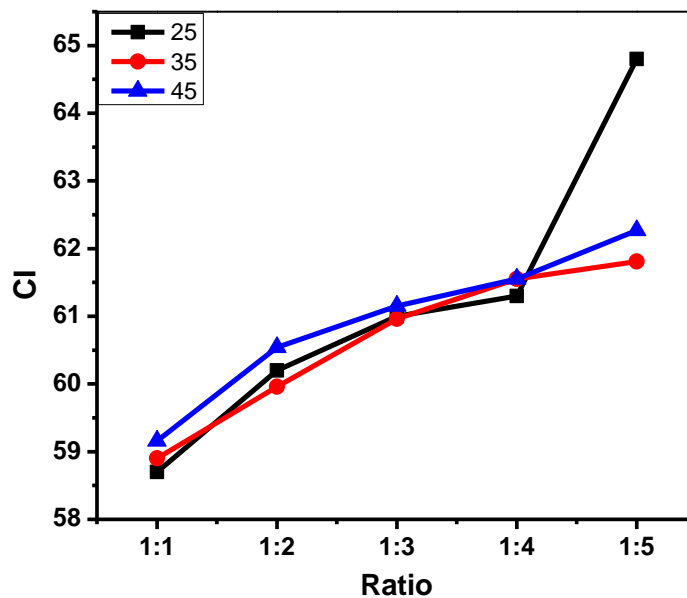


Fig. 3.5: The cetane index of raffinate at different temperatures and ratios.

3.6 Boling point range (IBP-FBP)

The boiling range as IBP and FBP for the raffinate at different temperature and oil to solvent ration are given in Table 3.3. The results show that applying different acetonitrile ratios didn't alter the diesel specification matrix from the ASTM method D975. This indicates that the diesel still maintains its quality and composition aftersolvent extraction.

Table 3.3: IBP and FBP for the raffinate at different temperatures

solvent: diesel ratios

Raio	25°C		35°C		45°C	
	IBP	FBP	IBP	FBP	IBP	FBP
1:1	186.4	369.4	181.2	369.2	177.2	371.2
1:2	186.7	369.6	184.2	369.8	177.2	371.7
1:3	196.4	373.3	184.3	369.8	179.4	372.8
1:4	189.6	373.6	188.8	371.5	189.6	372.5
1:5	195.8	373.6	194.8	372.2	189.7	372.5

3.7 Kinematic viscosity

Fig. 3.6 shows the variation of the kinematic viscosity with both the extraction temperature and feedstock: solvent ratio. The kinematic viscosity increase with the extraction temperature while its increase of solvent ratio may be attributed to the removal of aromatics as indicated in Fig. 3.2.

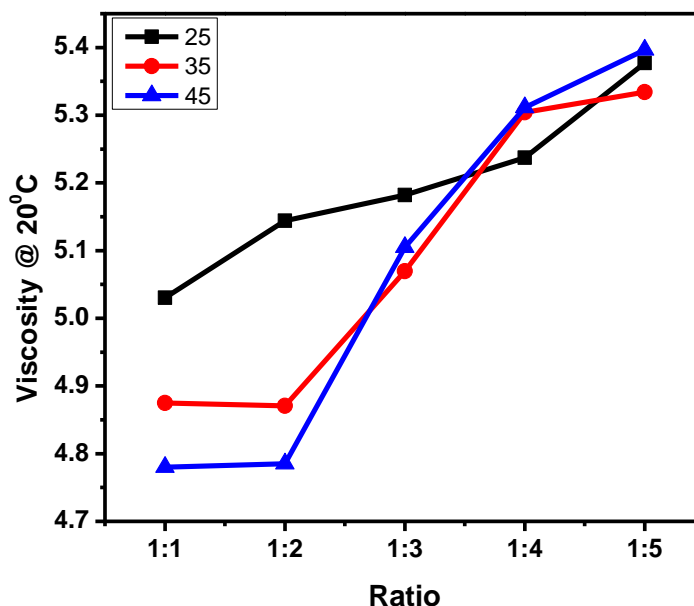


Fig. 3.6: Variation kinematic viscosity of raffinate with different temperatures and solvent ratios.

3.8 Refractive index

Refractive index (RI) values as a function of extraction temperature and feedstock: solvent ratio is illustrated in Fig. 3.7. The RI decreases with both parameters. The refractive index plot shows reciprocal relation with the aromatic content and cetane index [25] as can be seen in Figs. 3.2 and 3.4).

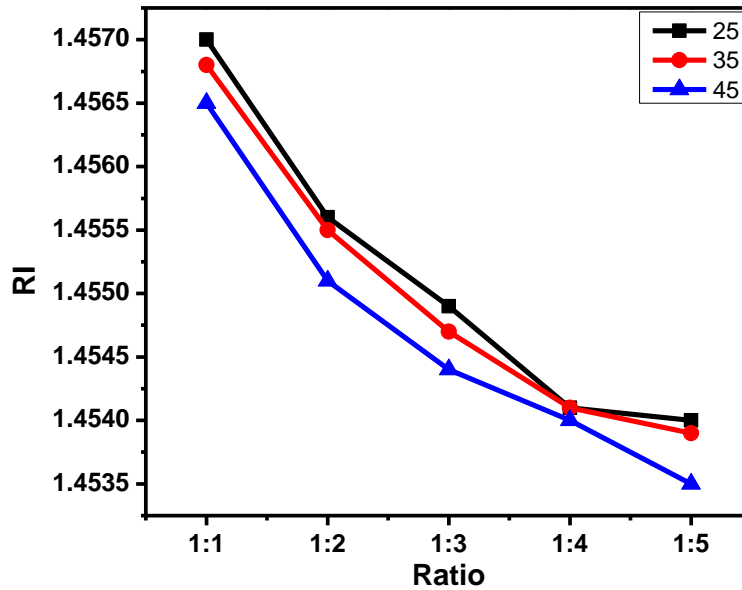


Fig. 3.7: The variation of raffinate refractive index with temperatures and solvent ratios.

The relation between the gross heat of combustion and the refractive index could be represented by the following formula:

$$H = 93.116 - 32.239 n \quad 3.1$$

Where H represents the gross heat of combustion in kPa and n represents the refractive index of diesel fuel [25]. The decrease in the refractive index shown in Fig. 3.7 may indicate that the heat of combustion of the raffinate will be higher as a result of increasing

the ratio and temperature at the extraction. The variation of cetane numbers with the refractive indices can be determined by the 2nd order polynomial fitting method:

$$CN=4.2799 \times 10^4 - 5.7558 \times 10^4 \times n + 1.9374 \times 10^4 \times n^2 \times 3.2$$

This relation shows an increase in CN with the decrease in the refractive index. Therefore, the increase in cetane numbers with the solvent ratio of distillate mixture (Fig.3.5) can be correlated with the decrease in the refractive indices (Fig. 3.7).

3.9 The specific gravity

The decrease in specific gravity as a function of extraction temperature and feedstock: solvent ratio is indicated in Fig. 3.8. The specific gravity has inverse relation with CI change and direct relation with diesel aromatic contents. Due to the high density of aromatics their removal will obviously results in lower specific gravity diesel.

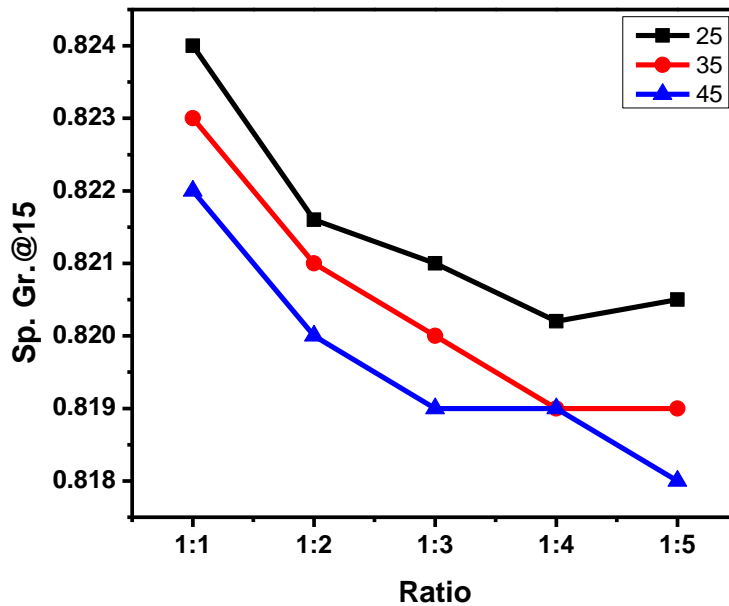


Fig. 3.8: The specific gravity of raffinate at different temperatures and ratios.

3.10 (API)

The API plot in Fig. 3.9 shows values greater than 40° indicating a light feedstock [42].

The diagram also shows the normal inverse relation with the Specific gravity.

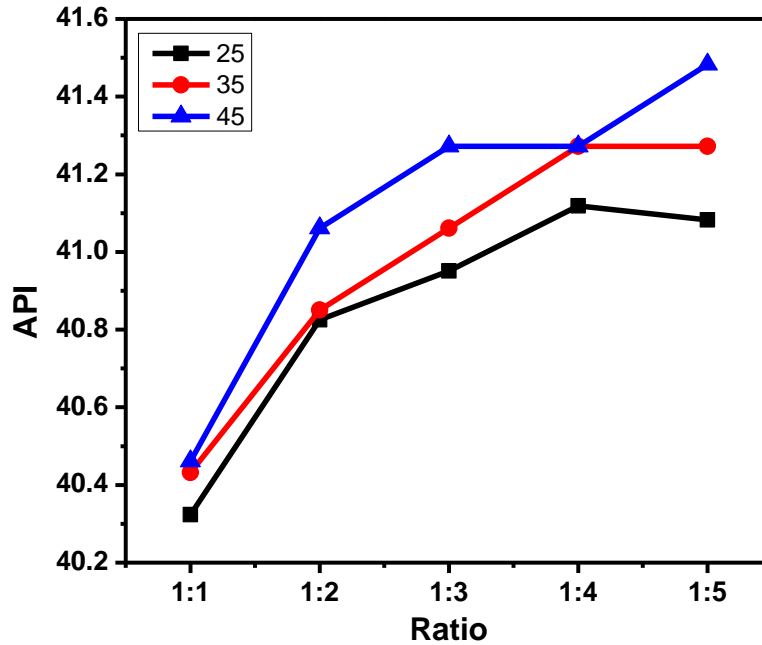


Fig. 3.9: The API of raffinate at different temperatures and ratios

3.11 Flash point

The flash point (Fig. 3.10) shows a general trend of increasing value with the decrease of aromatics. The low flash point at 45°C can be attributed to the evaporation loss at such relatively high temperature.

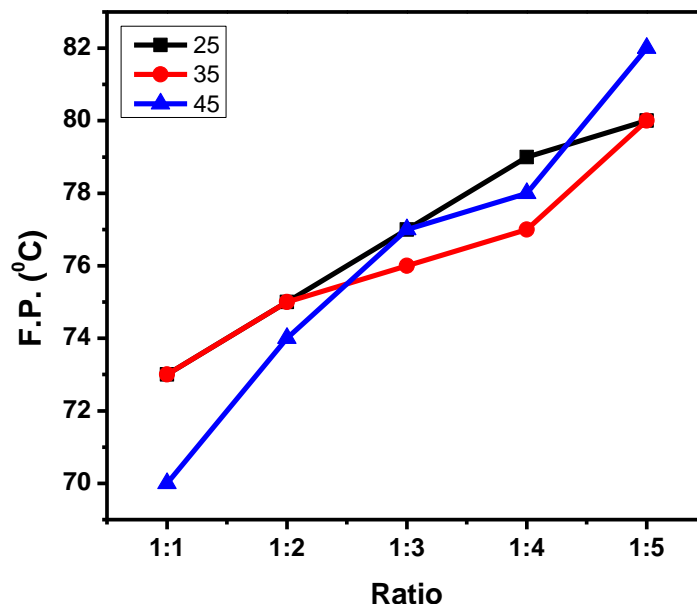


Fig. 3.10: The flash point of raffinate at different temperatures and ratios.

As previously reported a diesel is suitable for use when the flash point value is above 38 °C [43]. Thus the raffinate obtained in this work is an excellent candidate for use as fuel. When the fuel parameters of this work are contrasted with the US EPA[44] Europe[45], Korea[46] , China[46] and WWFC [47] diesel specifications, a great similarity can be drawn. This is of course a clear indication of the effectiveness of the extraction followed in this study. Moreover, this extraction was carried at room temperature to avoid the high cost, long residence time and harsh operating conditions applied by other refining methods.

The physicochemical parameters of the obtained raffinate can be utilized (as a point of maximizing its value) as a base feed stock for other types of solvents, white spirit [ASTM D-235], transformers oils [ASTM D-3487 and light hydraulic oil.

Lastly, the extract obtained after the treatment is considered as a high solvency product for different petrochemical industries. Table 3.4 shows the flash point and aromatic contents of the extract.

Table 3.4: Flash point and aromatic contents of the extract

Ratio	1:1	1:2	1:3	1:4	1:5
25°C					
Flash Point (°C)	79	80	81	81	82
Aromatic Contents (%)	57.4	56.8	52	48	44.5
35°C					
Flash Point (°C)	85	85	87	89	90
Aromatic Contents (%)	61	60.7	60	58.1	56.7
45°C					
Flash Point (°C)	84	86	88	89	88
Aromatic Contents (%)	55.2	53	52	51.1	50

3.12FTIR analysis:

The FTIR spectra of the (1:1, @ 25°C) and (1:5 @ 45°C) are shown in Fig. 3.11. The bands at 2900 cm^{-1} , 1600 - 1500 cm^{-1} and 900–700 cm^{-1} typical of aromatics [48] are observable at the FTIR spectra of the samples at different solvent ratios and temperature. All absorption peaks for the arenes of the raffinate have nearly disappeared. The skeletal C=C vibrations in aromatic rings caused another two bands at about 1460 cm^{-1} [49]. The peak at 3402 cm^{-1} is ascribed to the hydroxyl group (–OH) flex vibration. And 1192 cm^{-1} is the (C–O) flex vibration peak which did not exist in diesel explaining that the hydroxyl group in diesel may come from the absorption of moisture from air. The peaks at 2923 cm^{-1} , 2858 cm^{-1} , 1580 cm^{-1} , 1372 cm^{-1} and 711 cm^{-1} are ascribed to the methylene group (–CH₂) antisymmetric vibration, methenyl group (–CH) symmetric vibration, the alkyne group (–C≡C–), the alkene hydrocarbon group (–C = C–), and the (C–H) bending vibration [50]. The reduction in the peaks intensity and/or shift in the peaks is an indication of aromatics reduction supporting the data obtained in Table 3.2 [51].

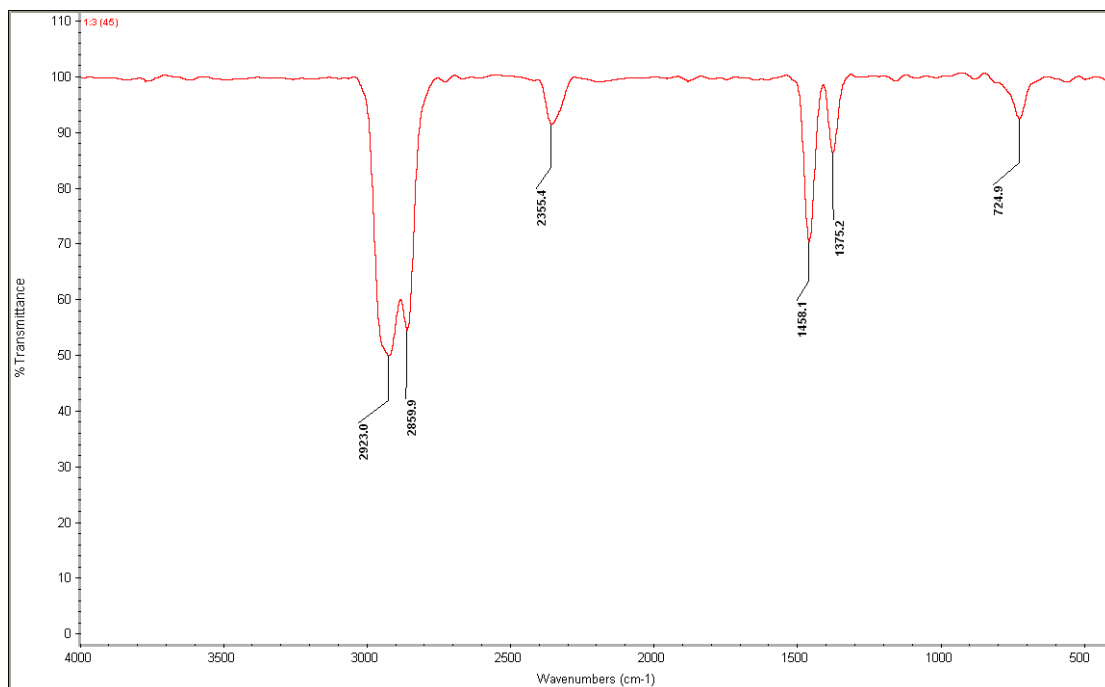
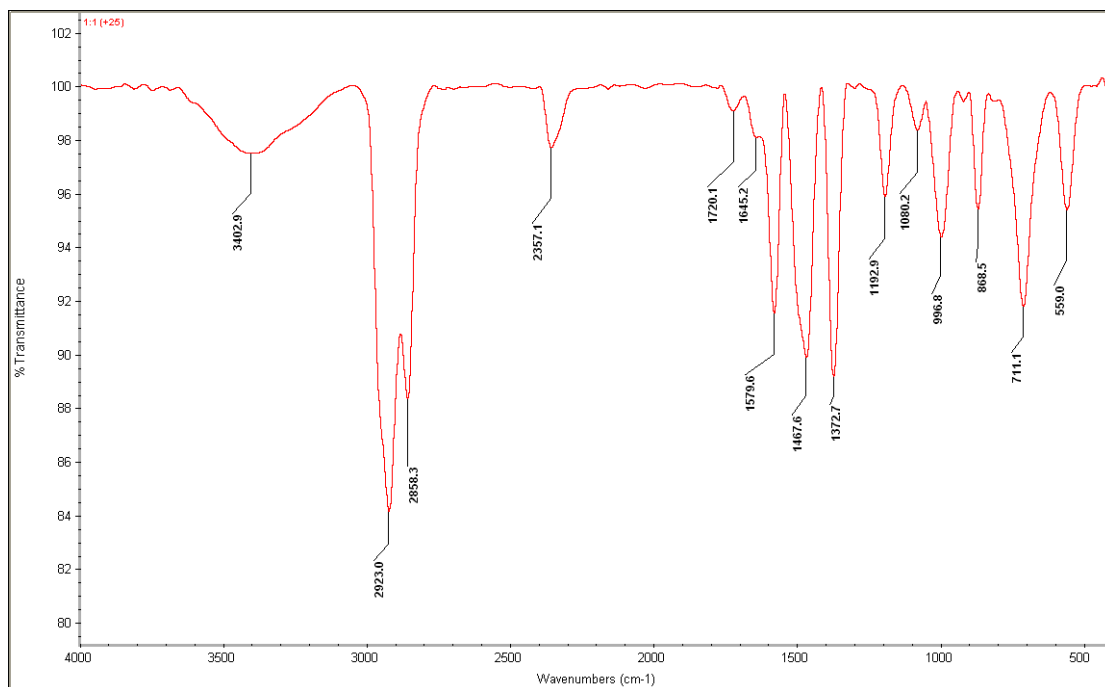


Fig. 3.11: FTIR spectra of (1:1, 25) and (1:5, 45) samples

CONCLUSIONS

To achieve the goal of obtaining environmentally less harmful petroleum product with improved qualities this research was carried out. In this work,

We proposed a simple and effective extraction procedure for feedstock of diesel using acetonitrile extract with varying solvent to feed stock ratios at low temperature and ambient pressure.

The increase of the solvent to feed stock ratio has decreased the raffinate yield and enhanced its quality in terms of less total aromatic and sulfur contents along with improved diesel index.

A range of physicochemical raffinate parameters were investigated via ASTM methods, while the aromatics were determined using the HPLC technique.

The results revealed a raffinate with marvelous characteristics of product. That abides with the stringent environmental regulations for petroleum products. An extracted product (Raffinate) with low aromatics, low sulfur, high cetane index, high aniline point and high flash point was achieved.

In contrast to others, the proposed method presents undeniable advantages such as simplicity, low operation cost, high extraction efficiency at a relatively short extraction time under mild conditions.

The extract obtained after the treatment is considered as a high solvency product for different petrochemical industries

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