

Comparative Studies of Diesel Fuel Properties with Biodiesel and Recycled Diesel

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Abstract— This research investigated the comparative studies of diesel fuel properties with renewable diesel and recycled diesel. Nowadays the disposal of used engine oil and used cooking oil are major problem due to the ecological pollution. Both are discarded into the ground or landfills which neither protects the environment nor conserves its resource value. Recycling of used motor oil and used cooking oil can produce more valuable products which can be reused again without any pollution. The main objective of this research is to focus on the development of an alternative method that is ecofriendly and produces good quality renewable fuels and to compare the properties of diesel fuel with renewable diesels like Bio diesel and recycled diesel. In this study the method used to re-refining used motor oil is acid treatment, vacuum distillation followed by activated charcoal treatment. By using trans-esterification process we can change the used cooking oil as a fuel called Biodiesel. After the effective preparation of the diesel fuel samples from the above methods it's blended with fresh diesel called Blended diesel. This paper gives a brief review about the properties of all the diesels derived from used engine oil, used cooking oil and blended diesels were analyzed and compared with the fresh diesel properties.

Index Terms— Biofuel, Re-refining of used motor oil, Renewable fuels, Trans esterification.

I. INTRODUCTION

IN recent years, lessening of fossil fuel sources, increasing of demand and cost of petroleum based fuels, and ecological hazards as a result of burning of them have encouraged researchers to investigate possibility of using alternative fuels instead of the fossil fuels. They have stated that it is necessary to reduce consumption of the petro fuels due to the negative effects on human life by producing alternative renewable fuels. As known fossil energy sources have been exhausted rapidly nowadays, it is predicted that fossil fuel sources will be depleted in

the near future. According to some studies, it is estimated that crude oil will last only for roughly 80 more years, gaseous fuels for about 150 years, and coal

for 230 years. Therefore, scientists and researchers all over the world are now working hard to discover new sources of energy for the future, and also try to develop new technologies that allow recycling or reusing waste material as a source of energy(4). Municipal and industrial wastes that contain high heat value, such as waste plastics oil (WPO),

waste cooking oil (WCO), and waste lubricating oil (WLO) are considered efficient feed stocks for energy production in a Waste-to-Energy regimen.

Diesel, the main petrol derivative energy resource, is a hydrocarbon mixture of hundreds of different molecules containing from 7 to 20 carbon molecules, including decane, tetradecane, hexadecane, butyl cyclohexane, naphthalene, etc. Renewable energy sources like biodiesel, re-recycled diesel offers an alternative energy source in place of petroleum diesel that is renewable and more environmentally favorable. Biodiesel is defined as a mono alkyl ester, commonly a methyl or an ethyl derivative, prepared from a vegetable oil or an animal fat with a carbon chain that contains from 10 to 20 carbons. It is renewable, biodegradable and oxygenated. Although many researches pointed out that it might help to reduce greenhouse gas emissions, stimulate sustainable rural development, and improve income distribution, there still exist some resistances for using it. The chemistry behind the conversion of this process is, most vegetable oils are composed of a specific category of organic compounds called triglycerides (TG). The most common derivatives of TG's (or fatty acids) for fuels are fatty acid methyl esters (FAME) formed by Trans esterification of the TG with methanol in presence of a catalyst.

The lubricating oils or engine oils are used in all automobile engines for lubrication with effective functioning of the machine by reducing friction. After a certain period of time these used engine oils are taken out. During lubrication about 20% of the lubricating oil is spent and the rest 80% remain as such with some impurities. Thus a huge quantity of used engine oil is left and wastage from different transport sectors every day. Utilization of the diesel and gasoline-like fuels produced from the waste lubricant oils, and blending of the produced fuels with gasoline or turpentine decrease consumption of petroleum based fuels, protecting environment from toxic and hazardous chemicals. It also saves of foreign exchange, reduces greenhouse gas emissions and enhances regional development especially in developing countries. Used engine oil are easily found from bus & trucks garages and provide diesel fuel from the purifying certain processes such as clay-acid treatment and solvent extraction method.

II. MATERIALS AND METHODS

A. Equipment used

Manual distillation setup, Vacuum pump, Conical/ Round bottom flask, Beaker, Buchner Funnel, Density meter, Ostwald Viscometer, Sulfur content Analyzer, Thermometer, Flash Point Tester, Muffle furnace, Magnetic stirrer setup,

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Hot plate, KF Titration apparatus.

B. Sample Preparation Sample 1 (Diesel)

The Diesel fuel is collected from a local ADNOC gas station sharjah, UAE. It was 4 litres and pale green color.

C. Sample 2 (Recycled Diesel) Collection of used lube oil Sample

The used lubricating oil is collected from a local automobile four wheeler service station in Sharjah, UAE. The used oil was obtained from a Saloon car, whose oil has been used for 3 month and half respectively. Three liters of used oil was collected for the samples and the basic specifications are density 0.871 kg/L, color dark brown, kinematic viscosity 44 cSt @ 40oC, flash point 141, and the water content 3.8%.

D. Reagents used:

98% Sulphuric Acid, Sodium Hydroxide, Charcoal

E. Experimental Procedure

Filtration of the used oil was carried out to remove impurities such as sand, metal chips, micro impurities that contaminated the lube oil. This was done using a vacuum pump, Buchner funnel, and a filter paper. Add 8% (based on the weight of oil) 98% H₂SO₄ to the filtered oil and stirring well for 20 minutes using magnetic stirrer. After one hour settling time, remove bottom sludge (black asphalt) then add 8% of NaOH to neutralize the oil. Then the oil is subjected to vacuum distillation by the distillation apparatus. After dehydration, the Diesel fractions are collected carefully in to a separate beaker which is light brown in color. Then it is allowed to pass through a chamber of charcoal packed surface under gravity flow (12). The resulted light yellow color diesel is Recycled diesel. The Schematic for the production of RC diesel from used lube oil in figure-1

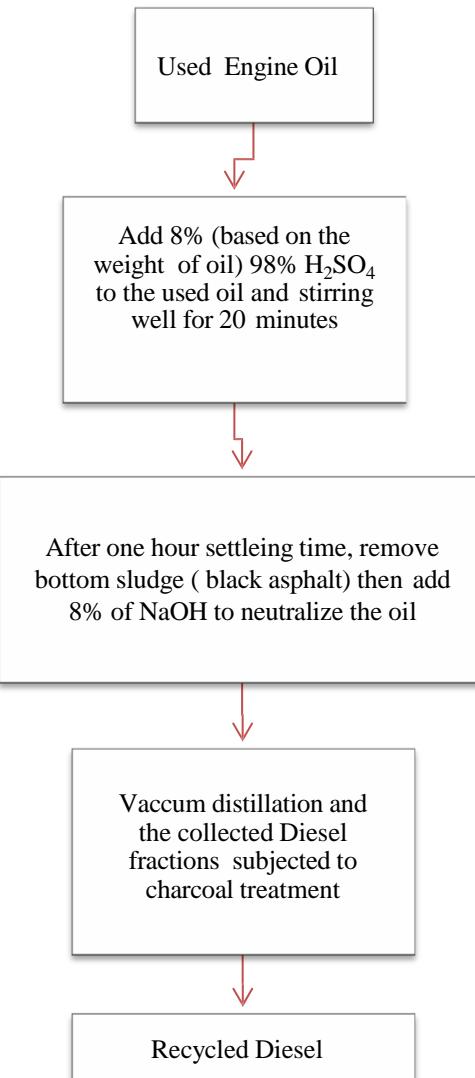


Figure 1 - The Schematic process diagram for the Production of diesel from used lube oil

Sample 3 (Biodiesel)

Collection of used Cooking oil Sample

The used cooking oil was collected from a labor camp kitchen in sharjah, UAE. It's sunflower oil, yellow in color, kinematic viscosity 33.9 cSt @ 40oC, flash point 174oC, Density 0.916 kg/L, manufactured date March 2015 and origin from India. It was cooked two times for frying wheat food and three liters of this sample taken for the production of biodiesel and analysis.

Reagents used:

Methanol and Sodium Hydroxide

Experimental Procedure

Filtration of the used cooking sunflower oil was carried out to remove impurities such as food pieces, burned carbon chips, food related micro impurities that contaminated in the cooking oil. This was done using a vacuum pump, Buchner funnel, and a filter paper. Add 10g of NaOH pellets to 400ml of the Methanol in to a separate beaker and agitate until the pellets are dissolved. Add this methoxide lye solution to 2 liters of used cooking oil which is filtered before.

Add a magnetic stirring bar to the mixture and place the

beaker on the hot plate. Heat the mixture to 60-65°C and agitate for 90 minutes with continuous stirring.

Pour the total mixture in to a separating funnel and allow separating for 4 hours. It's separated in to two layers, the top layer is methyl esters, that Biodiesel and the down layer is glycerol. Separate the top layer and washed with water, the resulted pale yellow color diesel is Biodiesel. The Schematic for the production of Biodiesel from used cooking oil in figure-2

Sample 4 (R20) and Sample 5 (B20)

Sample 4 & 5 are blended samples, which is prepared by mixing the renewable diesels with fresh diesel. R20 is the blended sample which is prepared by 80% fresh diesel mixed with 20% of Recycled diesel (Sample 2). In same B20 is also the blended sample which is prepared by 80% fresh diesel mixed with 20% of Biodiesel (Sample 3).

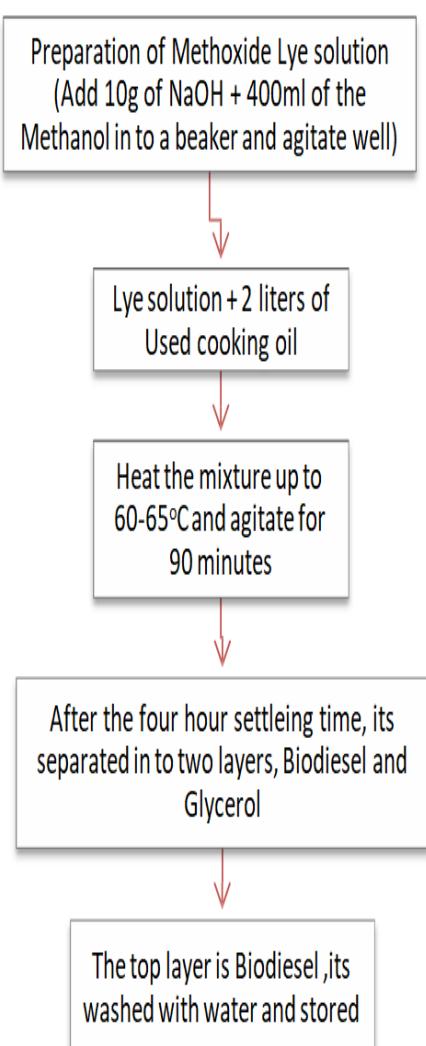


Figure 2- the Schematic process diagram for the Production of Biodiesel from used cooking oil

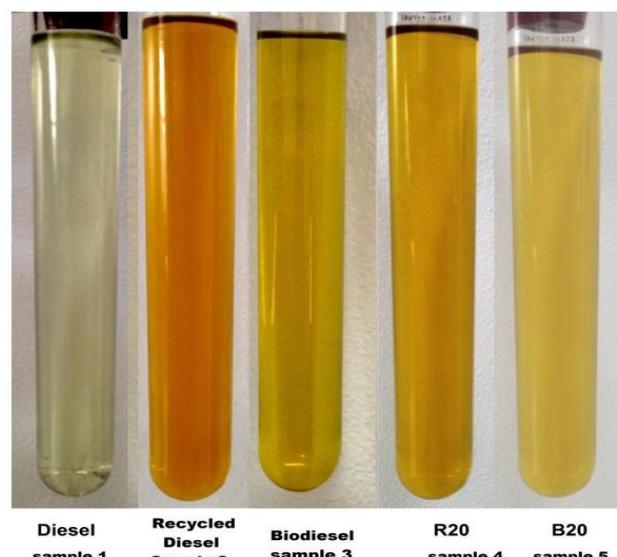


Figure 3- Example of different tested diesel samples

III. GENERAL CHARACTERISTICS OF DIESEL

All diesel fuels are characterized by some of the properties, it's include: color, density, kinematic viscosity, sulphur content, flash point, pour point, total acid number, water content, ash content, carbon residue and cetane number etc.

Density and specific gravity (ASTM D1298)

Density is the ratio of mass of a substance to the volume of the substance. The density of pure water at 4 degree centigrade is considered as the baseline for specific gravity. Specific gravity is the ratio of density of substance to the density of pure water determined at the same temperature. It is measured using hydrometer (Leimco, Range 0.8000 to 0.9000, serial no: 809303). The density was observed at 60°F and the value recorded.

Color (ASTM D1500)

Color is an important quality characteristic for petroleum products, and can also be used to detect product contaminations. Diesel fuel color varies with the crude source, refinery methods and the use of dyes. Previously, diesel fuel was sold without any dyes added to it, known as clear diesel, was available at regular gas stations. Nowadays red, blue, green coloring dyes are added to diesel at very low level to differentiate the purpose of uses. In UAE pale green dye added to diesel available in all the gas stations. To determine ASTM color, the diesel sample is compared against standard color discs in the Petroleum Colorimeter (Koehler, Light source: Tungsten halogen lamp)

Viscosity (ASTM D445)

Viscosity is the resistance offered to the flow of fluid. It is ordinarily expressed in terms of the time required for a standard quantity of the fluid at a certain temperature to flow through a standard orifice. The higher the value, the more viscous the fluid. Since viscosity varies inversely with

temperature, its value is meaningless unless accompanied by the temperature at which it is determined. The kinematic viscosity is the ratio of the dynamic viscosity to the density of the fluid and it is measured using viscometer (Viscodenplus, Martechnic, hamburg, serial no: 2011/0643)

Sulphur Content (ASTM D4294)

Sulphur content is the first diesel fuel property to be widely controlled by legislation, aimed at limiting exhaust

emissions. Sulphur is present in all crude oils and as well as all refined products. When diesel fuel is burned the sulphur combines with oxygen (SO_x) to create emissions that contribute to decreased air quality and have negative environmental and health effects. The main environmental concerns related to sulphur emissions are acid rain and the formation of particulate matter. Sulphur is emitted from vehicles in the form of sulphate particles (SO_4). Along with nitrogen oxides (NO_x), these particles contribute to particulate matter (PM) formation.

All over the world, to avoid the environmental impacts due to sulphur compounds nowadays using Low Sulphur Diesel (500 ppm), Ultra Low Sulphur Diesel (15 ppm) in on-road diesel fuel engines.

The amount of sulfur in diesel is measured using X-ray fluorescence analyzer (Oxford, Bench top Lab X3500) and recorded.

Flash point (ASTM D93)

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. The flash point has no effect on engine performance or on its ignition qualities. It is controlled to meet safety requirements for fuel handling and storage.

Flash point measured by using Pensky-Martens Closed Cup Tester (TANAKA Flash point tester, APM-8, serial no: 33626). At least 75 milliliters are required for this test. The sample is stirred and heated at a slow, constant rate in a closed cup. The cup is opened at intervals, and an ignition source is moved over the top of the cup. The flash point is the lowest temperature at which the ignition source causes the vapors above the liquid to ignite.

Total acid number (ASTM D 664)

The Total Acid Number (TAN) indicates the amount of acid content present in the Diesel. To prepare the sample a mixture of toluene, isopropyl alcohol and water is dissolved into a diesel sample. Then it's titrated against potassium hydroxide solution using an auto titrator. The TAN is the amount of potassium hydroxide required to neutralize the acid present in one gram of the Diesel. The Auto titrator (KEM, Japan, and AT-710B) performs this analysis using a motor driven dispenser, stirred reaction vessel and electrodes which sense the completion of reaction by measuring the potential difference between two electrodes.

Water Content (ASTM D 6304)

Diesel fuel will always contain a certain percentage of

water because of the crude oil source. The presence of moisture in diesel fuel seriously affects the rate of performance of a fuel on ignition.

By using the coulometric and volumetric Karl Fischer titration instruments, we can measure water content in fuels. The basic principle of the water determination according to Karl Fischer, is a reaction of iodine with water in an alcoholic solution with presence of sulfuric acid and a base. With the volumetric method the iodine can be accurately added through a piston burette or coulometric directly produced in the reaction vessel.

The difference between the volumetry and coulometry mainly exists in the manner of dosing the iodine for the titration. The water content of the all the diesel samples measured by KF volumetric Titrator (Kem, Japan, MKV-710B).

Ash content (ASTM D 482)

Ash content in diesel fuel can damage fuel injection system and cause combustion chamber deposits. The methodology to measure ash content in the sample is placed in a crucible, ignited, and allowed to burn. The carbonaceous residue is heated further in a muffle furnace (LSC, casline, temperature range up to 1200°C) to convert the entire carbon to carbon dioxide and all the mineral salts to oxides (ash). The ash is then cooled and weighed.

Carbon Residue (10% MCRT) (ASTM D 4530)

The amount of carbon residue remaining after a diesel sample has been subjected to thermal decomposition. It is mainly considered to be a by-product of fuel after the combustion. High amounts of residue can be damaging to the environment and poisonous to living things also. For example when diesel is burned and used by a motor vehicle engine, it produces exhaust that contains carbon monoxide.

The test method that is used to calculate the amount of carbon residue is known as Ramsbottom Carbon Residue (RCR). This test is used to determine how much residue a fuel is likely to leave. It also helps calculate the fuel's tendency to combust or burn. Residue can also be calculated as the Micro Carbon Residue (MCR) or the Conradson Carbon Residue (CCR).

Micro Carbon Residue Tester (stanhope-seta) used to measure the Carbon residue for all the diesel samples. The samples should be distilled to remove 90 % (V/V) of the flask charge. The 10 % bottom remaining is then tested for carbon residue by this test method. The test is conducted by placing a weighed quantity of diesel into a glass container and heated to 500°C under an inert (nitrogen) atmosphere in a controlled manner for a specific time. The carbonaceous-type residue remaining is reported as a percent of the original sample as micro carbon residue.

Pour point (ASTM D 97)

The pour point is the lowest temperature at which a petroleum product will begin to flow. The diesel oil contains waxes and paraffin's, it forms solidify haziness at lower temperatures and its start to arrest the flow of diesel fuel.

Koehler, K46100 Pour Point Apparatus is used to measure pour point. The diesel sample is cooled inside a cooling bath to allow the formation of paraffin wax crystals. At about 9 °C above the expected pour point, and for every subsequent 3 °C, the test jar is removed and tilted to check for surface

movement. When the specimen does not flow when tilted, the jar is held horizontally for 5 sec. If it does not flow, 3 °C is added to the corresponding temperature and the result is the pour point temperature of the corresponding sample.

Cetane number (ASTM D 613)

Cetane number indicates the combustion speed and measure the ignition delay of a diesel fuel. It is measured in a single cylinder test engine (CFR Engine – Cooperative fuel research engine) with a variable compression ratio. The reference fuels used are mixtures of cetane, which has a very short ignition delay (CN: 100), and alphamethyl naphthalene (CN: 0), which has a long ignition delay.

The percentage of cetane in the reference fuel is defined as the cetane number of the corresponding fuel. The cetane number scale covers the range from zero to hundred, but typical diesel testing is in the range of 30 to 65 cetane number (for biodiesel the range is 46-52 CN).

All the five diesel samples, the above parameters tested as per ASTM standard and the results are tabulated in table no 1.

Table 1. Summary of results for all the diesel samples

| Samples | Unit | Method | Diesel | Recycled diesel | Biodiesel | R 20 | B 20 |
|----------------------------|----------|----------------|--------|-----------------|-----------|--------|--------|
| Color | - | ASTM D 1500 | 0.5 | L 2.5 | 2 | 2 | 1.5 |
| Density @15°C | Kg/L | ASTM D 1298 | 0.8142 | 0.8352 | 0.8675 | 0.8234 | 0.8347 |
| Kinematic Viscosity 40°C | cSt | ASTM D 445 | 3 | 3.7 | 4.5 | 3 | 3.09 |
| Sulphur content | ppm | ASTM D 4294/03 | 500 | 3150 | 15 | 2880 | 91 |
| Flash point | °C | ASTM D 93 | 76.5 | 61 | 166.1 | 72.5 | 80.5 |
| Total Acid Number | mg KOH/g | ASTM D 664 | 0.1 | 0.47 | 0.71 | 0.22 | 0.29 |
| Water Content | ppm | ASTM D 95 | 201 | 280 | 477 | 209 | 231 |
| Ash Content | % mass | ASTM D 482 | 0.01 | 0.034 | 0.02 | 0.017 | 0.014 |
| Carbon Residue, (10% MCRT) | % mass | ASTM D 4530 | 0.2 | 0.12 | 0.1 | 0.19 | 0.27 |
| Cetane Number | - | ASTM D 975 | 47 | 44 | 52 | 47 | 50 |

IV. RESULTS AND DISCUSSION

The density affects the fuel's spray penetration as it is injected into the combustion chamber and it's also a factor in measuring the heat value of the fuel. High-density fuels also have a higher viscosity thus, influence injection characteristics. Thus, density is a good indicator of the amount of heat available in a given amount of fuel. The density of biodiesel is higher (0.8765) than the all the diesel samples. The higher density, the tighter particles are packed in the substance. Therefore, large mass of fuel is injected to ignition chamber and hence produced more power and emissions.

But the disadvantage is increase in fuel density leads to increase in particulate matter emission because the diesel engine power is directly controlled by the fuel supply, not by

control of the air/fuel mixture as in conventional gasoline engines. The density also is affected by oxidation of fuel. The density has direct relation with fuels molecular weight, thus oxidation of fuels can increase the mass of fuel by producing by products and sediment, and therefore it results in increase of density. The higher density can cause more fuel consumption due to advance of injection.

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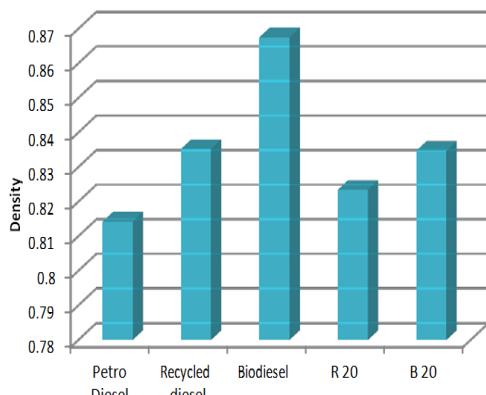


Figure 4 - Results of density of all the diesel fuel samples

Viscosity is generally an important property which impacts the performance of fuel injection systems and it has a strong influence on fuel atomization. The viscosity of diesel fuel is normally specified at 40°C. When compared to all other samples, biodiesel having high viscosity (4.8 cSt) resulting its forms larger fuel droplets and increases spray penetration during injection. More over high viscosity is necessary for lubrication and protection of the injection equipment from wear. But the disadvantage is it may cause too much pump resistance, filter damage and adversely affect fuel spray patterns due to high viscous.

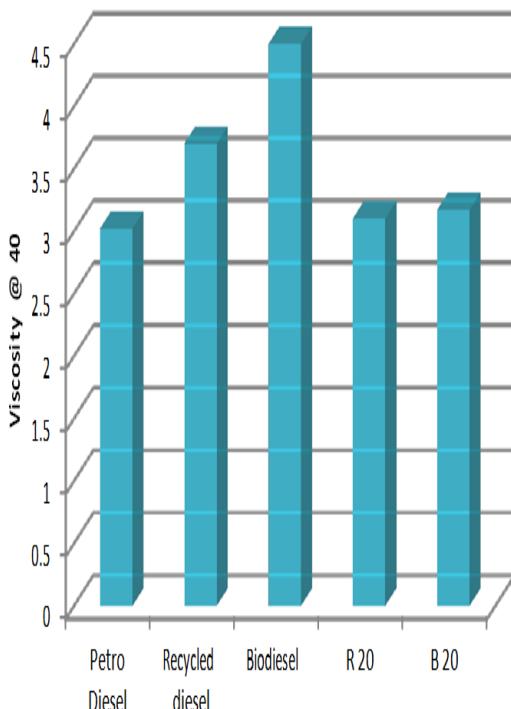


Figure 5 - Results of viscosity of all the diesel fuel samples

The slightly high viscous nature of recycled diesel is due to its origin used lube oil. R20, B20 samples viscosities almost same with petro diesel. If the viscosity of diesel is lower than the limit, leads to injector or pump leakage, loss of fuel system calibration, and it's also influences the fuel delivery rate and

the atomization of the fuel.

When compared the sulphur content of all diesel samples, the biodiesel having least value, which is less than 15ppm. It's clearly reveals that, the diesel engine's harmful emissions to the atmosphere enormously controlled by the usage of bio diesel and biodiesel blends

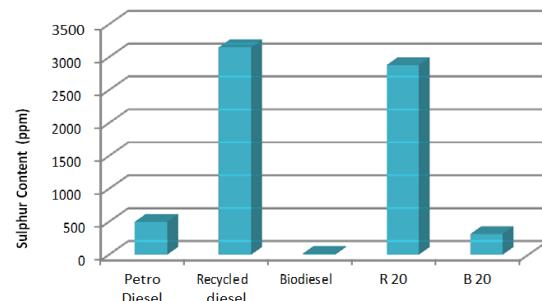


Figure 6 - Results of sulphur content of all the diesel fuel samples

The sulphur content of recycled diesel is very high 3150 ppm, because it is derived from used engine oil and it may contains many different additives which are contribute to improving its sulphur content.

The Flash Point is used in shipping and safety regulations to define flammable and combustible materials. It is important to note the flash point result 166.1 °C for biodiesel is more than twice that of petroleum diesel (approximately 76 °C) and therefore much safer to handle and transport. The blended fuel R20, B20 flash points are almost equal to the petro diesel flash point. Among all the samples the flash point of Recycled diesel is lowest 61°C because of the presence of light ends of oil. A low value of flash point indicates the presence of low volatile contaminants to diesel.

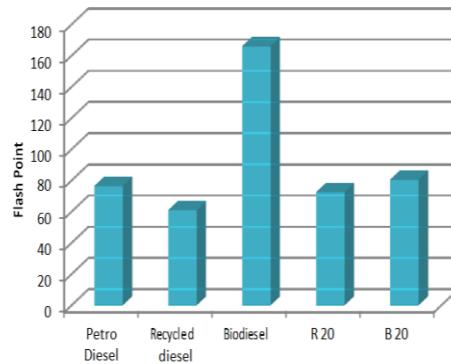


Figure 7 - Results of flash point of all the diesel fuel samples

The TAN value of biodiesel is the highest (0.71 mg of KOH), the recycled diesel stands next (0.49 mg of KOH) and the lowest value is for petrol diesel. The main reason for this trend can be due to unsaturation level of the biodiesel. Hence the biofuels containing unsaturated fatty acid with double bonded long chain hydrocarbons have more susceptibility to oxidation and it has an inverse relation with acid value.

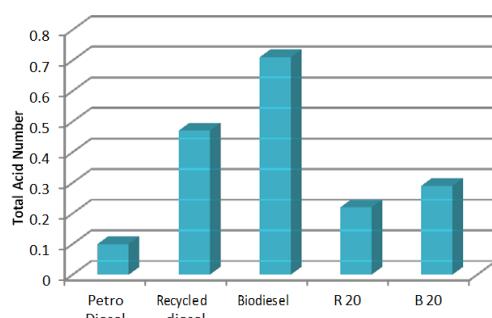


Figure 8 - Results of TAN of all the diesel fuel samples

Temperature can also affect the TAN value. If fuel is exposed to high temperature oxidation occurs due to higher rate of reaction of fuel molecules with oxygen in the air, resulting in increase of TAN value. Increase of TAN value can be considered as a result of oxidation of the fuel which may lead to gum and sludge formation besides corrosion. Lower the acid numbers decrease the oxidation characteristic of diesel and greater the stability.

Water content is an important property, because it indicates the purity of diesels. The moisture accumulated in diesel can corrode metallic parts of engine and fuel system.

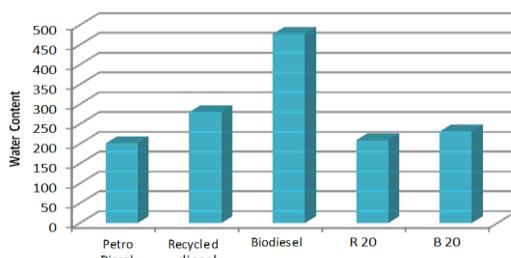


Figure 9 - Results of water content of all the diesel fuel samples

Biodiesel fuels are much more hygroscopic than diesel oil fuels which absorbs more moisture. Among the all samples, biodiesel has the highest value (477 ppm) and the

recycled diesel stands after it with (280 ppm). By decreasing the content of biodiesel and recycled diesel in blends, the level of water content decrease. The presence of excessive water contamination will affect the viscosity of the diesel and this may give rise to emulsion formation and can also lead to ignition problems.

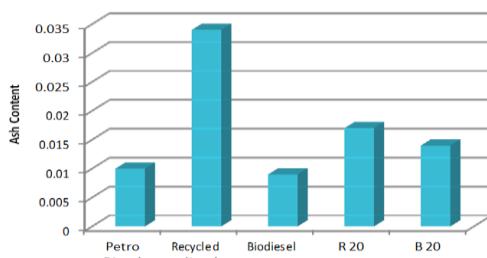


Figure 10 - Results of ash content of all the diesel fuel samples

The ash forming materials like abrasive metallic solids may be present in diesel fuel and its can affect injector, fuel pump. The higher ash content of recycled diesel is due to the presence of higher contaminants. Biodiesel having least ash content as well as least carbon residue value, these indicates

among all the diesels, biodiesel only produce lowest particulate emission and pollutants during the combustion process.

The cetane value of diesel fuel is an indicator of how readily and completely the fuel will burn in the combustion chamber. Among all the samples, biodiesel having higher cetane number 52, indicates it will ignite faster than other diesel and more completely it will burn. These attributes are important because as the fuel burns faster and more completely, the engine experiences greater performance and produces fewer harmful emissions.

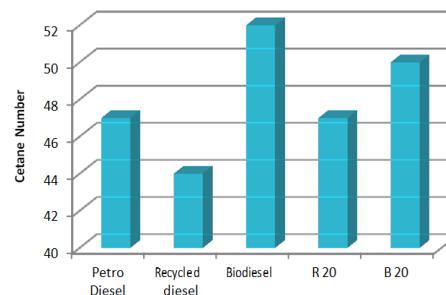


Figure 11 - Results of cetane number of all the diesel fuel samples

The B20 and petro diesel having the cetane values 50 and 47 respectively. A high-cetane diesel fuel provides more complete combustion, improved cold starts, less engine noise and knocking, lower exhaust emissions like nitrogen oxide, hydro carbon, carbon monoxide, and particulate matter. Because of the contaminants in recycled diesel, the cetane value is 44, its affect the smoother running and prohibits the better performance of the engine.

From the results presented, it is clear that we can effectively use the renewable fuels like biodiesel, recycled diesel, and its blends with our traditional petroleum diesel. In terms of environmental assessment and renewability, biodiesel have the potential to replacing the petroleum diesel in the future or being used in blends with petroleum diesel to improve performance of engine and reduce toxic exhaust emissions. The proper usage of diesel from used engine oil, also workable in some extent and it will also reduce environmental impacts and pollution. This paper gives a brief review on the production process of the most waste oils available in now days in order to use them in diesel engine. From the results obtained we can summarize the produced diesel from used cooking oil and used lube oil, are technically suitable, economically viable and less responsible to pollute environment.

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