

Physico-Chemical Characteristics of Ethanol–Diesel Blend Fuel

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Abstract: In this research we are discussing the physicochemical characteristics of sweet diesel after desulphurization alone and also these characteristics are tested with the adding of high purity HPLC ethanol (99.9%). Those fuel properties of ethanol blended with diesel were experimentally determined to find their stability and to increase their properties and efficiency in the diesel engines. First we made 4 blends of diesel with ethanol and the fifth sample was pure diesel. The samples were 0% ethanol and 100 % diesel, the second sample was 5% ethanol and 95 % diesel, the third sample was 10 % ethanol and 90% diesel, the fourth sample was 15 % ethanol and 85 % diesel and the fifth and last sample was 20 % ethanol and 80 % diesel. The physicochemical characteristics of the diesel ethanol blends were determined by the following experiments (cetane number, ASTM distillation, flash point, pour point, kinematic viscosity, ASTM density and calorific value).the aim of this research is to obtain an optimum blend of diesel ethanol fuel to help in improving the diesel engines and to lower the emission in the engine and the exhaust gases produced in the engines. This blend we obtained in this research was done to meet the EURO 5 standards and regulations, also to help to make an economic improvement in the industry of diesel in Egypt and in the world. The diesel ethanol blend was to be an effective fuel as we will see in the different tests and ASTM methods. Many tests and experiments done during this research project and the obtained results were similar to the EURO 5 standard emissions regulation.

Index Terms: Emission, Diesel Blends, Crude Oil, Blendstock.

I. INTRODUCTION

Nowadays we rely mainly on crude oil and its products, crude oil is a great source of energy .crude oil is found deep in the ground, crude oil is a mixture of hydrocarbons formed of organic matter which consist of carbons and hydrogen with small amounts of sulphur, oxygen, nitrogen, metals, crude oil is measured by API it measures the crude density if the API is high then we have a fine crude oil and products and if the API is low so the crude is value in the market is bad and has low value and contains high asphaltting products which gives bad market value to the crude we have crude oil goes under various refinery process which convert it into many products. [1-15] Crude oil separates into lighter components that have many uses in our worlds nowadays. first the crude is preheated and desalted and then enters a crude distillation where the

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lighter products comes first like the light naphtha comes first then heavy naphtha, kerosene, jet fuel, diesel fuel, gasoil, liquefied petroleum gas (LPG), Gasoline ,residual fuel oil and Asphaltenes and resins. Asphalt is the heaviest product of the crude oil which has high boiling point; Asphaltenes are used in the manufacturing of coke which is also used to get energy and power from it.[16-24]The main composition of crude oil is carbon and hydrogen (hydrocarbons) besides other elements with low proportions crude oil is subdivided into two categories which are elements and groups. [25-34]

The main aim of this research is to produce environmental diesel with a limited pollutants. In Egypt the used diesel fuel contain a high amount of contaminants which pollute environment after its ignition. The main pollutants emitted after combustion of diesel fuel in heavy trucks are greenhouse gases (CO₂, CO), NO_x(NO, NO₂) and SO_x (SO₂, SO₃). [35-44] These gases contribute too many disease which affect the human's health badly. Environmental diesel is the key to solve this crisis. Environmental diesel can be obtained through blending it with oxygenated compounds. The main role of these compounds is to diminish the greenhouse gases which have a bad impact on the society. One of the most oxygenated compounds is ethanol which shows a good impact on reducing emission yielded from combustion of diesel fuel. Environmental diesel will aid to reduce greenhouse gases, saving energy and keep our environment clean. [45-53]

The addition oxygenated compounds to diesel oil is mainly to increase it cetane number.A high demand for such as addition is to reduce the great use of crude oil which will sooner or later come to an end. In other words using the oxygenated compounds as additives to diesel oil will extend the life span of this crude oil (from which diesel oil is being extracted) biofuels that are biologically extracted from natural sources are the main additive used to achieve such as objectives.

These compounds are used today as diesel substitutes for many reasons some of which are reducing, complete dependency on petroleum products. Using biofuels even in the form of blends helps us to reduce the high daily consumption of petroleum products. One more important goal that makes biofuels usage is that they reduce the pollutant impact on the environments example given: the green house gas emission (mainly sulphur and carbon dioxide). There emission created the global warming problem causing great disturbance in the



weather stability. The wide use of biofuels in the near future means reducing these harmful emissions. One more objective to this usage is that it will support the agricultural community which is characterized by a clean environment and these improve the economy.

In this research project we are using sweet diesel after desulphurization blended with HPLC ethanol that has purity of 99.9 volume %. Diesel ethanol blend is made to improve the physical and chemical characteristics and properties of the diesel fuel we burned in the diesel engine. The diesel ethanol blend tries to meet with the EURO standards to lower the exhaust gases, emissions and sulphur content, also to increase the physicochemical characteristics of the blend. And to prove that the use of oxygenated compounds like ethanol is very important to be used in blending. As it may save a great amount of fossil fuels that we all know that the fossil fuels are limited and will finally be finished, also the fossil fuel cause a great part of pollution for the environment as the pollution rate is always increasing with the increase of years and technology.

Now we will check these properties of the blend by making many tests and ASTM methods on the blended fuel like (density and API, viscosity, calorific value, flash point, pour point, ASTM distillation and cetane number). Through these tests we will know the properties of the diesel ethanol blends are favorable or not, if they will reduce the emission and exhaust gases on the engine and reduce the pollution on the economic environment. And also would improve the diesel blended with oxygenated compounds (ethanol) industry and enlarge the industry scale of improving these types of fuel. And try to obtain the optimum blend of diesel and ethanol to try to meet with the EURO 5 standard regulations. The sweet diesel we used in this research has its physicochemical properties that we will compare them with the properties of the blended diesel with ethanol. [6, 12-18] API (American Petroleum Institute), the value of API largely determines the commercial price whether it's the API of the actual crude oil or the products. The viscosity and relative weight of diesel fuel also varies with API and it can exist in either liquid or solid state. The properties may vary in terms of proportion of hydrocarbon elements, sulfur content etc. as it is extracted from different geographical locations all over the world.

Diesel fuel is mainly classified into many categories. Those categories are based on the API values.

As 100% diesel fuel is defined as having API gravity between 35 API and 50 , By knowing which category a certain diesel fuel falls under, we can predict most of the properties of the diesel fuel. This makes it easy to assess the crude as well as place a commercial value to the crude.

As stated above, the API is also linked to the specific gravity and gives us a hint on the diesel fuel viscosity. The relation below illustrates the relation between API and specific gravity (S.G).

$$API = \frac{141.5}{S.G} - 131.5$$

Using this relation, we understand that if there's a high API value; the S.G value is low and vice versa. Having a low specific gravity is preferred since it estimates lighter components in the diesel fuel, which is much valuable in today's market than the heavier components. (6)

This experiment is discussing one of the main physical properties of diesel, which is API. The API is an indication to the quality of diesel oil and affects its price significantly. The API of diesel is measured through standard tests performed by ASTM. As the API increase it indicates that yield of light cuts is high and in turn its value will be high too. While as API decrease it indicates that yield of heavy cuts (undesired cuts) is higher than light cuts which in turns lower the price of diesel oil sharply as the heavy cuts do not have a high market value and useless. Nowadays the technology of refineries become more advanced and be able to perform a deep refining to extract light cuts from heavy cuts like thermal cracking , fluidized catalytic cracking and coking. In these experiments API is measured for 5 samples classified as the following (A, B, C, D, and E). The difference between samples is in the amount of ethanol blended with diesel. Adding ethanol to diesel shows a good performance in increasing API of mixture as ethanol is lighter than diesel itself.

Accurate determination of the gravity of diesel is necessary for the conversion of measured volumes to volumes at the standard temperature of 60°F (15.56°C). This procedure is most suitable for determining the API gravity of low viscosity transparent liquids. This test method can also be used for viscous liquids by allowing sufficient time for the hydrometer to reach temperature equilibrium, and for opaque liquids by employing a suitable meniscus correction. Additionally for both transparent and opaque fluids the readings shall be corrected for the thermal glass expansion effect before correcting to the reference temperature.

When used in connection with bulk oil measurements, volume correction errors are minimized by observing the hydrometer reading at a temperature as close to reference temperature as feasible. Gravity is a factor governing the quality of diesel. However, the gravity of a petroleum product is an uncertain indication of its quality. Correlated with other properties, gravity can be used to give approximate hydrocarbon composition and heat of combustion.

Gravity is an important quality indicator for automotive, aviation and marine fuels, where it affects storage, handling and combustion.

II. EXPERIMENTAL WORK

Five different pycnometers were used each containing a fixed volume of different diesel/ethanol blend. Knowing the volume, it helped calculating the sample's density and API. A digital Mass Balance



was used to weigh the pycnometers when empty and another time when contained a sample from the blend. By knowing the mass difference (before and after), it could be used to help calculate the density of the sample of blend. The pycnometers containing samples from the five different blends were placed in a water bath similar to the one shown here. The colder temperature caused the sample to shrink; the pycnometers were then topped off again in order to reach their correct volume.

Figure 1. Experimental Setup

Diesel quality is expressed by cetane number or by the cetane index. the cetane number (CN) is expressed in the terms of volume percent of cetane ($C_{16}H_{34}$) which has ignition



(CN =100) in a mixture with alpha - methyl - naphthalene ($C_{11}H_{10}$) which has low ignition quality (CN = 0). Diesel fuel includes No.1 diesel (super diesel) which has cetane number of 45-55 and it is used in high speed engines, trucks, and buses. And also there is NO.2 diesel that has cetane number of 40. The cetane number is an important fuel property for diesel engines as it has a great influence on engine start, stability, emissions, and peak cylinder pressure and combustion noise. The higher the cetane number the better the good cold start ability for the motor or engine and lower the noise and gives better efficiency and longs the engines life. The cetane number of the blended fuel depends on the amount and type of additive used in the blend.



Figure 2. Cetane Meter

The objective of this test is to know and identify the diesel characteristics and its quality and its operating parameters and how this parameters change with the change of the blend (additive) percentage. This method is used also to as an investigation for the auto ignition quality and knowing how the emission is reduced and how the efficiency of the engine is

increased. The higher the cetane number the better the good cold start ability for the motor or engine and lower the noise and gives better efficiency and longs the engines life. The cetane number of the blended fuel depends on the amount and type of additive used in the blend. This test explains the determination of cetane number which is an important variable in rating the quality of diesel fuel. The test uses standard single cylinder, four-stroke cycle, variable compression ratio, indirect injected diesel engine. The cetane number ranges from 0 to 100, but common testing ranges from 30 to 65. The objective of this test (equation) is to know the cetane number in another way or to compare the actual cetane number with the cetane index. The equations of the cetane index are tested by the ASTM and published to be used within the testing. The cetane index is also done if there is no testing engine to be used to know the cetane number. The cetane index does not differ from the cetane number it ranges of positive or negative 2 numbers from the cetane number as it measures the cetane range of minimum 30 to maximum 65 or exceeds it depending on the blend or additive used in the test with the diesel. The pour point is defined as the lowest temperature at which the sample will flow. It indicates how easy or difficult it is to pump the diesel fuel, especially in cold weather. It also indicates the aromaticity or the paraffinity of diesel. A lower pour point means that the paraffin content is low. Pour points for the whole diesel boiling above 232 C (450F) are determined by standard tests like ASTM D97. The pour point is one of three crucial points that must be indicated for any sample. The first point to measure is the cloud point. The cloud point is the lowest temperature at which oil becomes cloudy and the first particles of wax crystals are observed as the oil is cooled gradually under standard conditions. Those standard conditions are set for the three points. After the cloud point, the pour point is reached. The pour point is as stated before is the lowest temperature at which the sample flows. Knowing this point is crucial and its importance is discussed in greater detail below. After the pour point the freezing point is reached. From its name, this point is the point where the flow no longer flows and is has frozen. Those three points obviously depend on the type of sample we have. For example, a sample that is naturally heavy would have a harder time to flow thus it would have a high pour point. On the other hand, a sample that is naturally light would need greater cooling to reach its pour point, which would therefore have lower point.

The significance of this test is important for any petroleum product. Knowing the pour point of a sample helps indicate how easy or difficult the sample flows under certain conditions. This property is especially important in countries where the climate is usually cold. For example, if the weather is cold, a sample could face difficulty in flowing, which could result in blockage in pipelines. In addition, the amount energy needed for

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pumping those samples is taken into consideration depending on the pour point of the sample.

The sample is first heated using a warm water bath to heat the sample 45°C. This is a standard temperature where all the samples reach before the process of gradual cooling begins. This heating also helps arrange the atoms and allows the sample to become homogeneous in order to obtain a fair test. The cooling is done using cold ethanol and the sample is observed at every 3°C. The reason ethanol is used as the cooling solvent is because it has a lower freezing point than water. Sometimes the cooling is needed to reach values lower than 0°C which cannot be done with water because it would freeze and won't be able to cool the samples effectively. At every 3°C the sample is taken out and its flow is observed by tilting the cylinder. If the sample is unable to flow for five consecutive seconds then the pour point is reached. If however the sample does flow then further cooling is done for another 3°C and flow is observed again. The pour point is labeled as the temperature that is just above the point where flow does not occur. In other words, the point that we want to reach is not the point where the flow does not flow but the point just before that.

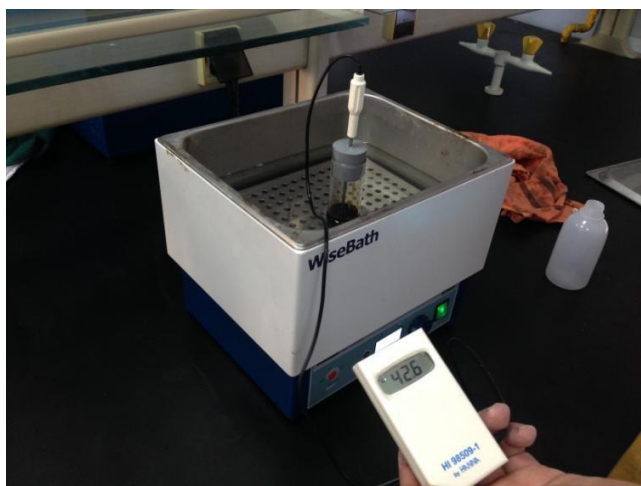


Figure 3. Pour Point Experiment Setup

The figure above shows the jacket where the cylinder containing the sample is placed where it is subjected to cooling using ethanol. The thermometer placed at the top is used to indicate every 3°C difference in sample where the sample is taken out and tilted to observe whether the sample flows or not. This was conducted to five samples: (0%, 5%, 10%, 15%, 20%). The results of all five samples are discussed below. The second figure shows the sample placed in a water bath. Here the sample is subjected to heating to reach the standard temperature of 45°C.

In addition this temperature was reached to obtain a good mixture of the sample where molecules are organized and becomes totally homogenous.

The flash point of a fuel is the temperature to which the fuel must be heated to produce a vapor/air mixture above the liquid fuel that is ignitable when exposed to an open flame

under specified test conditions. There are several ASTM methods for measuring flash points, using either closed cup or open cup testers. Open cup methods will generally produce results that are higher than those measured with closed testers, and should not be used with volatile substances. The flash points of lubricating oils can be determined by ASTM method D 92/IP 36 - Standard Test Method for Flash and Fire Points by Cleveland Open Cup (ASTM D 92). For determining the flash points of other oils, methods D 93/IP 34 - Standard Test Methods for Flash Point by Pensky-Martens Closed Tester and D 56 - Standard Test Method for Flash Point by Tag Closed Tester are the most commonly used. The main target of this experiment is to determine flash point for diesel sample and diesel/ethanol blends. The flash point temperature is one measure of the tendency of the test specimen to form a flammable mixture with air under controlled laboratory conditions. It is only one of a number of properties which must 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 classifications. The specimen is placed in the cup of the tester and, with the lid closed, heated at a slow constant rate. An ignition source is directed into the cup at regular intervals. The flash point is taken as the lowest temperature at which application of the ignition source causes the vapor above the specimen to ignite.

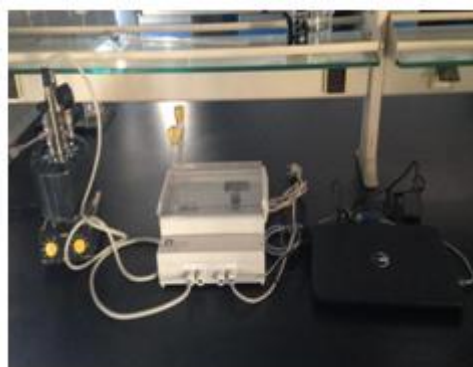


Figure 4. Open Cup Flash Point Test

This apparatus is mainly consists of an open cup which is responsible for holding sample, controlled heater to heat sample gradually and produce sufficient vapours. Also it has a source of ignition which ignites vapours once it appears in the presence of air. Viscosity is a parameter that measures resistance to flow ability of liquid or gas. It is defined as the force exerted between two sliding layers of liquid or gas moving at different velocities. Viscosity (or coefficient of viscosity) is the proportional constant between this force (shear) and the velocity gradient (rate of deformation due to shear or rate of shear). One of the major physical characteristics that should be identified for diesel and its products is viscosity. Many petroleum products, and some non-petroleum materials, are used as lubricants and the correct operation of the equipment depends upon the appropriate viscosity of the liquid being used. In



addition, the viscosity of many petroleum fuels is important for the estimation of optimum storage, handling, and operational conditions. Thus, the accurate determination of viscosity is essential to many product specifications

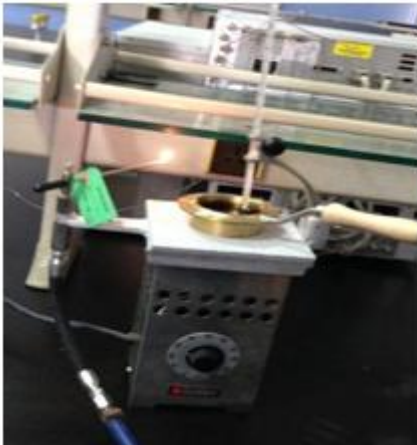


Figure 5. Viscosity Meters

The figure above shows how the apparatus for the viscosity measurement is set up. The sample being tested is placed in the equipment shown on the left-hand side. There, the sample is subjected to heat and pressure. Those two parameters and their effect of the dynamic viscosity are studied here. Electrical signals recorded as the experiment runs over 300 times are then sent to a computer where they are tabulated.

Run, temperature, pressure, dynamic and kinematic viscosities are listed in order to compare different runs that operate at different conditions.

III. RESULTS AND DISCUSSION

The first step in this experiment is to bring the five samples of diesel ethanol blends and place each sample in the cup of 70 ml of each sample then place the thermometer and adjust the heater. Then try to notice the change of temperature with the sample until a flash happens then this is the flash point.

Table 1 Flash Point of samples

Sample	Flash point, °C
E0	76
E5	27
E10	26
E15	25
E20	25

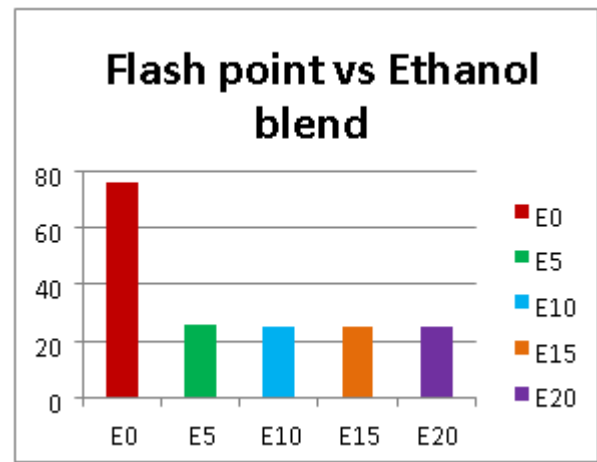


Figure 6. Flash Point Vs. Ethanol Blend

This experiment is a very important experiment (flash point), as it indicates the final point of the fuel we have that we could heat at without an ignition happens. The flash point method is a type of safety method to be used in every refinery plant. The flash point of the pure diesel without any additive is found to be very high unlike the ethanol blends. There was a definite decrease in the flash point of the blends and this was because the ethanol has a very low flash point and this made the blend likely preferable to the diesel motor as it increases the startup of the engine. The pour point method is an ASTM method (D97). This experiment determines the final point at which the fluid could flow in any tube or in very low climate engine. The first step in this experiment is to bring the empty pour point testing tubes and then place the samples in them. Then place the tubes or cylinders in the ethanol path at constant temperature. Place the corks in each tube with the digital thermometer and start cooling the device and then notice each sample after 3 Celsius degrees for 5 seconds. If there is no flow for 5 seconds then this is the freeze point of the sample and the pour point is the point before the freeze point.

Table 2 Pour Point of samples

Sample	Pour point, C°
E0	-3
E5	-6
E10	-12
E15	-18
E20	-21

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Table 3 ASTM Distillation Results

volume	E0	E5	E10	E15	E20
0	175	78	78.1	77.5	77.9
5	218	80	79.6	78.5	79.6
10	231	206	82	79	79.9
15	242	224	228.6	79.8	79.9
20	252.5	239.9	239.1	215.4	80.1
25	257.6	245.4	250	230.2	212.6
30	265	253.8	256.5	241	229.4
35	266.7	260.3	260.2	251.3	242.1
40	273.7	265	269.2	257.6	252.5
45	279.3	270.3	274.9	266.9	260.6
50	286	275.9	280.9	273.5	266.7
55	288.2	280.8	284.7	275	273.7
60	294.2	284.7	290.8	282.4	279.3
65	302	290.8	297	289.3	287
70	308	301.3	302.8	295.5	294.2
75	309.1	309.1	310.2	304.4	301.9
80	317.2	317.2	319.5	313.7	312.3
85	325.2	325.2	328.1	323.5	321.2
90	339	336.6	337.8	333.3	332.9
95	346	346.5	346.5	346.6	346.2
96	352	351.8	351.7	351.8	352.2
97	357.2	357.2	357.2	356.5	355.6
98	360	359.3	359.4	358.7	358.9

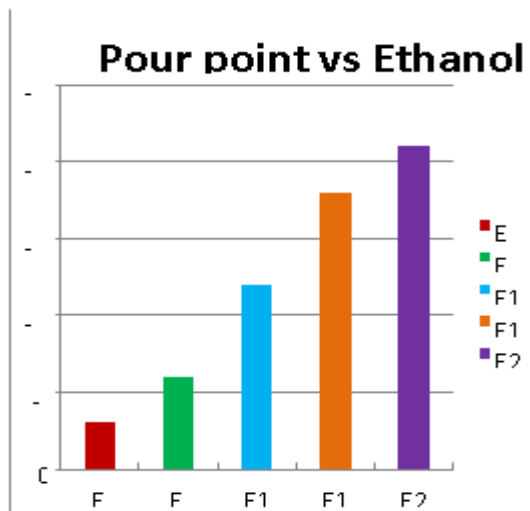


Figure 7. Pour Point Vs. Ethanol Blend

This test or method has a major importance, as it finds the last point that the fluid could flow in transportations and in the engine in cold climate countries. Here we found that the pour point decreases with the increase of the ethanol percentages in the diesel. Making it very useful in transporting it in very long distances may be under the sea with very low temperature.

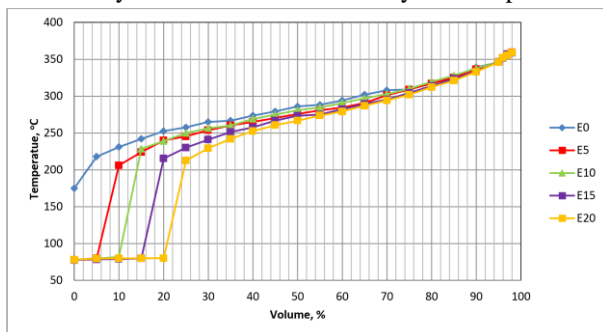


Figure 8. ASTM Distillation Fractions

This experiment is very important as it studies one of the major physicochemical characteristics for diesel ethanol blending. Distillation of diesel gives us all the fractions and all the boiling points ranges. Many standard tests can be performed to obtain distillation curve relate temperature with volume percent of sample like ASTM, TBP, EFV, GC. The distillation curve for diesel is vital as we compare distillation curve (IBP, T50%, FBP) to the standard tests (ASTM, TBP, EFV, GC). We also noticed that as we increase the percentage of the ethanol in diesel the boiling point range increase. This is for the ethanol has very low boiling range than that of diesel boiling range. This test indicates that the viscosity of the blend decrease as the volume percentage of the ethanol increase, this is for the ethanol has a very low viscosity compared to that of the diesel. Also we noticed that the viscosity of the diesel ethanol blend decreases as the temperature of the fuel in the device increases. In calorific value test we use an oxygen bomb to determine the heat content or the calorific value of the sample we have as like ASTM D4809. Increasing the heat content of the sample means that it gives high energy and efficiency and earlier ignition in the motor.



Figure 9. Oxygen Bomb Vessel for Determining Heat Content



Figure 10. Ash Content

Mass of ash content = 0.019 g of a 2 gm sample.
The calorific value of the optimum blend of 10 % ethanol = 43192.5 kJ/kg

IV. CONCLUSION

The physicochemical characteristics for the diesel ethanol blends were determined. Also, an optimum blend of ethanol diesel blend which was 10% ethanol by volume to meet the EURO 5 regulations and standards for reducing emissions. This enabled production of a high environmental diesel fuel. So, it is feasible to maximize the production rate of commercial diesel and enlarge the economic industry and use of sweet commercial diesel blended with HPLC ethanol (99.9 purity).

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