PRODUCTION AND CHARACTERIZATION OF CLOVE OIL, EUGENOL AND EUGENYL ACETATE FOR USE AS BIO-ADDITIVES IN A SINGLE CYLINDER DIESEL ENGINE.

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ABSTRACT

Research on the potency of essential oils as diesel fuel bio-additives has been reported. It also has been found that clove oil, eugenol and eugenyl acetate have good potentials of decreasing Break Specific Fuel Consumption (BSFC) with significant improvement of the overall performance of the engine. Clove oil is an essential oil, the content of which is made of eugenol acting as the main component. Eugenol has a bulky structure of two oxygen atoms and can form eugenyl acetate from ester reaction. Eugenyl acetate has a bulkier structure and higher oxygen content than eugenol which leads to optimizing the process of fuel combustion. Clove oil was extracted from cloves using Soxhlet extraction method. The yield was found to be 0.64ml obtained from 10.25g of clove buds. Eugenol compound was isolated from clove essential oil using steam distillation process and Eugenyl acetate was formed by adopting esterification reaction using acetic anhydride aqueous solution. Characterization of the oil samples, diesel fuel and the fuel bio-additives were done using a GC-MS and IR spectrophotometer. The clove oil, eugenol and eugenyl acetate and diesel properties such as acid value (AV), iodine value (IV), saponification value (SV), peroxide value (PV), free fatty acid (FFA) and cetane number (CN) were investigated. The diesel and bio-additive blends (BDC, BDE and BDEA) were also experimentally investigated. The properties determined were relative density, cloud point, pour point, flash point, viscosity and heating value. The experimental results obtained were compared with standard values to know the suitability of using the blends in compression ignition engine. The results revealed that both relative density and viscosity of the blends decreased as percentage of the bio additives increased. All the blends were found to have the same cloud point at 6 ^{0}C with that of diesel, while the heating values of (BDC 0.2%), (BDE 0.2%) and (BDEA 0.2%) blends were 40.55 MJ kg^{-1}, 38.25 MJ kg^{-1} and 35.80 MJ kg^{-1} respectively, which is lower than that of diesel (43.00 MJ kg^{-1}). The values of the physical and chemical properties of the treat rates produced conformed with ASTD standards which implies

that the blends formed are suitable to be used for testing its performance on a diesel engine test rig.

Keywords: Clove oil, Eugenol, Eugenyl acetate, Treat rates.

1.   INTRODUCTION

A number of researches on increasing diesel fuel quality have been conducted. Anbarasu *et al.* (2013) studied the effect of Di-tertiary Butyl Peroxide (DTBP) as Primary Reference Fuels (PRFs) in Homogeneous Charge Compression Ignition (HCCI) engines and the results of the study showed that a DTBP predominant mode of action on Low Octane Number (LON) fuels is thermal while for High Octane Number (HON) fuels it is chemical. Joshi *et al.* (2010) examined the influence of fuel additives such as 2- ethylhexyl Nitrate (EHN), Methyl tert-butyl ether (MTBE), Dimethyl carbonate (DMC), diglyme, monoglyme and ethanol on the exhaust emissions of a diesel engine. The overall results of the study showed that fuel additives have substantial effects on the engine's fuel spray penetration, fuel-air mixing processes, ignition delay, chemical reaction rates, total heat release and have a positive impact on reducing exhaust emissions. However, it is not necessary that these effects are all positive and significant on temperature and every type of emissions (NOx, HC and smoke). Song (2008) analyzed the oxidation behavior of Spark Ignition primary reference fuels with propionaldehyde and DTBP as an additive. Experiment conducted shows an addition of propyl-aldehyde or a negative temperature coefficient (NTC) of DTBP effects during HCCI combustion. The results of research conducted on the quality of fuels and their bio-components were also presented by Chauhan *et al.* (2010) and Canakci (2007). Fuel oxygen content (oxygenates) is one of the parameters for determining the quality of diesel fuel. Song (2008) stated that blending oxygen-containing compounds with diesel fuel leads to an increase in

cetane number and the process of fuel combustion can be completed. The detailed mechanisms of the oxygenated fuels reducing the exhaust emissions of the engine are not properly understood. Babu *et al.* (2012) experiment has shown that the overall oxygen content is not the only important parameter in determining the potential of reduction in exhaust emissions of the oxygenated fuel.

Clove oil is the essential oil containing eugenol as the main component. Eugenol allows splash blending in a solution possibly used for the first time. Analysis showed that eugenol has two oxygen atoms Babu *et al.* (2012). The oxygenated molecular structure also plays a significant role. The bulky structure of eugenol can decrease the strength of Van der Walls bond in diesel fuel and the chain of carbon. Oxygen content and the molecular structure can lead to an increase in the efficiency of the fuel combustion process.

1.0   Statement of the Problem.

Emissions from diesel engines constitute a major source of air pollution which affects human beings and alter the ecosystem. Lack of suitable bio-additive blended with the base fuel (Diesel) in proper ratio (treat rates) lead to the following shortcomings; Incomplete combustion, High Brake Specific Fuel Consumption, Low engine performance, Increasing threat to the environment from exhaust emissions and global warming.

1.1   Significance of the Study.

The significance of the study is to determine the suitability and performance characteristics of the fuels and blends using a four stroke, single cylinder diesel engine test bed.

1.4   Aim and Objectives of the Research.

The aim of this research work is to carry out a potential study on clove essential oil, eugenol and eugenyl acetate for use as bio-additives in single cylinder four stroke diesel engine. This will be realized with the following specific objectives;

i.   to extract clove oil from cloves using Soxhlet extraction method.

ii.   to isolate eugenol compound from the extracted clove essential oil.

iii. to form eugenyl acetate from eugenol by esterification reaction.

iv.   to determine the physical and chemical properties of the fuel.

v.   to form blend samples (treat rates) at different proportions, and

II. MATERIALS AND METHODS

2.1 Materials

2.1.1 Clove oil

Clove bud oil is derived from clove plants which are rich in oxygen molecules, brown, dried, unopened flower buds of Syzygium aromaticum, an evergreen tree in the myrtle family. This tree is a native of Southeast Asian countries like Indonesia (Ismaiel & Pierson, 1990). Three types of essential oil are available from clove species: clove bud oil, clove steam oil and clove leave oil. Each has different chemical composition and flavor. Clove bud oil, the most expensive and the best quality product, contains eugenol (80% - 90%), eugenyl acetate (15% - 17%), and β-caryophyllene (5 -12%). Essential oils are complex mixtures, made up of terpenoid hydrocarbons, oxygenated terpenes and sesquiterpenes. They originate from the plant secondary metabolism and are responsible for their characteristic aroma. Essential oils (also called volatile or ethereal oils, because they evaporate when exposed to heat in contrast to nonessential oils) are odorous and volatile compounds found only in 10% of the plant kingdom and are stored in plants in special brittle secretory structures, such as glands, hairs, ducts, cavities or resin ducts (Ajav *et al*., 2002). The essential oil of cloves has anesthetic and antimicrobial qualities and is sometimes used to eliminate bad breath or to ameliorate the pain of bad tooth. Also, clove bud oil has biological

activities, such as antibacterial, antifungal, insecticidal and antioxidant properties, and are used traditionally as flavoring agent and antimicrobial material in food (Velluti *et al*., 2003).

2.1.2 Eugenol

Eugenol is a phenolic component that can be obtained from a wide range of plant sources including clove oil, nutmeg oil, cinnamon extract and many other plants (Ciccarelli et al., 2008). It owns strong health promoting functions that make it a versatile natural ingredient. Eugenol was firstly extracted from the leaves and buds of *Eugenia caryophyllata* commonly named as clove. Velluti *et al.,* (2003) reported that, eugenol can also be synthesized by allylation of guaiacol with allyl chloride having the similar kind of functional property. Eugenol is present in significant amount in the extracts of numerous medicinal herbs. It has fascinated the attention of several researchers and opened up the gateway of research regarding its utilization as diesel fuel bio additives (Liolios *et al*., 2010).

Table 1: Properties and description of Eugenol.

Properties	Description
Class	Phenylpropanoids
IUPAC name	4-Allyl-2-methoxyphenol
Chemical formula	$C_{10}H_{12}O_2$
Molecular mass	164.2 g mol^{-1}
Solubility in water	Partially soluble
Solubility in organic solvents	Highly soluble
Color	Clear to pale yellow

2.1.3 Eugenyl Acetate

The eugenyl acetate is classified as a flavoring substance belonging to benzenediol chemical group, and is considered safe for use in food by two reputable international committees related to food safety, Joint FAO/WHO Expert Committee on Food Additives (JECFA) and European Food Safety Authority (EFSA) (Ismaeil & Pierson., 1990). The recommended limits vary depending on the type of food, the highest concentrations indicated 25 ppm for meat products and the lowest 2.83 ppm for non-alcoholic beverages. Besides, this compound exhibits several interesting properties such as its good characteristics for use as bio-additives in diesel engines, antioxidant, anticarcinogenic, anti-acaricidal, heart protective agent and inhibitors of tooth decalcification (Carrasco & Espinoza, 2008).

2.1.4 Diesel

Diesel fuels are the fuels used in diesel or compression ignition engines. In diesel engines, the air is compressed to high temperature before the fuel is injected into the cylinder to ignite or detonate. Compared to spark ignition engines, a diesel engine is cost effective because of its operating advantages, greater efficiency, high power output and fuel economy under all loads (Hsu *et al*., 1998). However, it has the disadvantages of noise and emissions of particles and nitrogen oxides (NO_X). Three grades of diesel fuels are in common use: (1) land diesel fuels, used in trucks, buses, trains, or other land transportation vehicles that have high variation of speed and load; (2) marine diesel fuels, used in ships that have variable speed but relatively high and uniform load; and (3) plant diesel fuels, used in electric power generation plants that have low or medium speed with heavy load. Hence, the quality of the diesel fuels depends on the performance requirements of the engine. (Chen *et al*., 2015). Today the majority of the diesel fuels are derived from petroleum, although some may come from other fossil fuel resources such as coal liquefaction fractions and through synthesis, such as Fischer-Tropsch distillates. Sjogren *et al*. (2005) reported that, the

quality of diesel fuels can vary significantly owing to differences in the crude oils from which the fuels are derived and the refinery process streams from which they are blended. For example, there are significant differences in composition between straight run and hydrotreated cracked diesel streams for transportation are the highest and narrowest distillation cuts, while those for power plants are the heaviest and broadest fuel oils (Cookson *et al*., 2008).

2.2 Methods.

2.2.1 Samples collection

The clove seeds were purchased at Muda Lawal main market, Bauchi, Nigeria, which was used as the major raw material for the production of the clove essential oil. Five measures of the cloves were obtained and used for the production of the clove essential oil.

2.2.2 Extraction process of Clove oil using Soxhlet extractor.

50g of the ground clove's buds was weighed and transferred into a filter paper extraction thimble containing the sample which was then place in the Soxhlet extractor fitted at the lower portion with a flask containing 300ml of *n*-hexane solution used as the extraction solvent. The Soxhlet column was then fitted to a reflux condenser and the set up was placed on the heating mantle as temperature increase steadily until *n*-hexane began to boil and the boiling vapor passes through the condenser and was condensed, vapor now falls back on the porous thimble containing the powdered seed sample, *n*-hexane being a solvent dissolved the oil content of the seed sample leading to the formation of homogenous mixture of *n*-hexane and oil which was collected in the receiver of the Soxhlet extractor set- up. The set-up was heated, for about 6 hours. Then the oil extract was concentrated using vacuum evaporator at 40 ^{0}C. The procedure was repeated many times until all the grounded clove material was exhausted.

2.2.3 Extraction Process of Eugenol from Clove oil by Steam Distillation.

150ml of clove oil was added to 125 ml of water and placed in a 250 ml round bottom flask. The contents were heated using a low flame until the mixture boiled. The mixture was then discharged into a Liebig condenser to separate the solvent from the oil extract. The mixture was distilled at a temperature of 68°C until the oil extract was completely free of the solvent. Diethyl ether was then used to purify the oil extract after which it was exposed to the atmosphere for a while to ensure elimination of solvent odor.

2.2.4   Synthesis of Eugenyl Acetate by Solvent-Free Acetylation.

Eugenyl acetate was obtained by acetylation of acetic anhydride with clove essential oil in solvent-free system. The acetylation reaction was carried out in screw-capped flasks at various eugenol to acetic anhydride molar ratios (mol: mol), temperature (°C) and amount of catalyst, according to the conditions defined in the experimental design. After complete dissolution of the substrates, the catalyst was added to the mixture. All experiments were carried out in a thermostatic bath. After the reaction time, the catalysts were filtered and samples were kept at 5°C until the determination of reaction conversion.

2.2.5   Formation of Blends.

Each treat rates samples were formed in 100ml container. 2ml, 4ml, 6ml, 8ml and 10ml of the bio additives (Clove oil, Eugenol and Eugenyl acetate) were added to 98ml, 96ml, 94ml, 92ml and 90ml of diesel fuel respectively. The 100ml blend was poured in a container mounted on a removable drum and fixed to a tumbler mixer, the timer was set to 10 minutes and the blender switched on. The same procedure was repeated for all the samples. The blends were observed after 48 hours and no phase separation was noticed, which implied there is no need to use a binder, a homogenous mixture was formed.

For the purpose of this research work, a total of fifteen blends/samples were prepared as shown. Each sample is labelled appropriately and accordingly as follows; BDC(0.2%), BDC(0.4%), BDC(0.6%), BDC(0.8%), BDC(1.0%), BDE(0.2%), BDE(0.4%), BDE(0.6%), BDE(0.8%), BDE (1.0%), BDEA(0.2%), BDEA(0.4%), BDEA(0.6%), BDEA(0.8%), and BDEA(1.0%) respectively. Where, BDC = Blend of diesel and Clove oil, BDE = Blend of diesel and Eugenol and BDEA = Blend of diesel and Eugenyl Acetate.

Plate I: Blends of diesel and Clove oil.

Plate II: Blends of diesel and Eugenol.

Plate III: Blends of diesel and Eugenyl Acetate.

2.2.6 Determination of Physical properties of the bioadditives.

2.2.6.1 Acid value (AV) of Clove oil.

Acid value (AV) is a number that expresses the quantity of potassium hydroxide required to neutralize the free acids present in 1g of a substance. The acid value is often a good measure of the breakdown of the triacylglycerol into free fatty acids, which has an adverse effect on the quality of many oils (Muhammad and Bamishaiye, 2011). Acid value is the measure of hydrolytic rancidity. In general, it gives an indication about edibility of the lipid. The test was carried out in accordance with ASTM-D1959 (ISO3961) and the acid value was calculated using equation 1 as proposed by (Muhammad and Bamishaiye, 2011).

The acid value was calculated using the formula:

$$AV = \frac{TD \times N \times 56.1}{M} \qquad \ldots (1)$$

where, TD = Titer difference in mL

N = Normality of KOH

M = Molecular weight of KOH in grams. The factor 56.1 is the equivalent mass of KOH

A mass of 300 mg of the oil sample was taken in a conical flash and dissolved in 30 mL of distilled alcohol by gentle warming. It was then titrated against 0.1N KOH using phenolphthalein as indicator until a slight pink color appeared. For this titer value, the acid value was calculated by using equation 1.

2.2.6.2 Saponification value (SV).

The saponification value is the number of mg of potassium hydroxide required to neutralize the free acids and to saponify the esters in 1 g of the substance. The saponification number is a measure of the average molecular weight of the triacylglycerol in a sample. Saponification is the process of breaking down a neutral fat into glycerol and fatty acids by treatment with alkali. The smaller the saponification number the larger the average molecular weight of the triacylglycerol present i.e. saponification value is inversely proportional to the mean molecular weight of fatty acids (or chain length).

Equation 3 was used in computing the saponification value of the produced oil and the test was carried out in accordance with ASTM-D1959 (ISO3961). 2g of sample was accurately weighed and placed in a 250ml flask. 25ml of a mixture of equal volumes of ethanol and potassium hydroxide was added. The mixture was heated in a water bath (coupled to a reflux condenser from the Soxhlet extractor) for 30 minutes while being stirred continuously. 1ml of phenolphthalein was

added as indicator. The resulting mixture was titrated with 0.5N hydrochloric acid. The entire

procedure was repeated without the sample (blank). The saponification value was calculated using

the formula as given in equation 2.

$$\text{Saponification Value (SV)} = \frac{(T.D.) \times N \times 36.5}{2} \qquad \dots (2)$$

Where:

T.D. = Titer difference in mL

N = Normality of KOH

A factor of 36.5 is the equivalent mass of HCl

A mass of 2g of oil was transferred to a round bottom flask and dissolved in 5 mL of

distilled ethyl alcohol. 25 mL of 0.5N alcoholic KOH was added into it and mixed well. The flask

was fitted with a reflux condenser and refluxed for about one hour (till the reaction is complete

and the liquid become clear).

A blank experiment was simultaneously conducted in the same way without taking oil.

Both flasks (one containing the oil sample and another without the oil sample) were cooled. The

inner side of the reflux condenser was inserted into the respective round bottom flask with

minimum quantity of water. 2 drops of phenolphthalein were added and titrated against a standard

solution of 0.5 N hydrochloric acid until the pink color disappeared. The difference between the

test (A) and blank (B) gave the volume of 0.5 N HCl equivalent of KOH used in saponifying (2 g)

of the oil.

2.2.6.3 Ester value (EV)

The ester value is defined as the mass in milligrams (mg) of KOH required to react with glycerin (glycerol or glycerin) after saponifying one gram of fat. It is calculated from the saponification value (SV) and the acid value (AV) as follows (Muhammad and Bamishaiye, 2011):

Ester Value (E.V.) = Saponification Value (S.V.) - Acid Value (A.V.)

% glycerin = E.V. × 0.054664   … (3)

2.2.6.4 Iodine value (IV).

A mass of 0.2 g of clove oil was weighed in a conical flask, 10 ml of chloroform and 25 ml of wijis solution were added to the conical flask and the latter was left in the dark for 30 minutes. 10 ml of 10% potassium iodide solution was added followed by 100 ml of distilled water and the liberated iodine was titrated with 0.1N sodium thiosulphate solution using starch as indicator. The iodine value was determined using equation 5 (Onuwuka, 2005):

$$IV = \frac{(v_2 - v_1) \times M \times 12.69}{w} \qquad \qquad … (4)$$

Where; v_1 = volume of thiosulphate used in titration of sample.

v_2 = volume of thiosulphate used in titration of the blank.

M = molarity of thiosulphate

w = weight of sample.

Alternatively, one of the most commonly used methods for determining the iodine value of lipids is "Hanus method". The lipid to be analyzed is weighed and dissolved in a suitable organic solvent, to which a known excess of iodine chloride is added. Some of the IBr reacts with the double bonds in the unsaturated lipids, while the rest remains (Muhammad and Bamishaiye, 2011).

$$R\text{-}CH=CH\text{-}R + IBr_{excess} \rightarrow R\text{-}CHI\text{-}CHBr\text{-}R + IBr_{remaining} \qquad \dots (5)$$
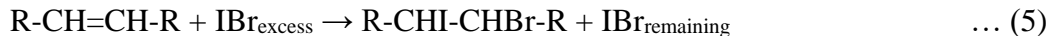
The entire procedure was repeated without the sample (blank). The Iodine value was calculated using the formula below:

$$\text{Iodine Value (I.V)} = \frac{(b-a)\times 0.01269 \times 100}{Weight\ (in\ g)\ of\ Sunstance} \qquad \dots (6)$$

Where, b = Volume of $Na_2S_2O_3$ volume for blank

   a = Volume of $Na_2S_2O_3$ volume for sample

2.2.6.5 Free fatty acid (FFA).

Free Fatty Acid (FFA) is the result of the breaking down of oil. FFA% is usually used to describe the FFA content of oil, while Acid Value (AV) is commonly used to describe the FFA content of essential oil and the FFA was calculated using equation 8 (Muhammad and Bamishaiye. 2011):

$$FFA = AV/2 \qquad \dots (7)$$

2.2.6.6 Peroxide value (PV).

Peroxide Value (PV) of an oil is used as a measurement of the extent to which rancidity reactions have occurred during reaction or storage. The PV is defined as the amount of peroxide per 1kg of oil or fat (Demirbas, 2009). The test for determining PV was carried out in accordance with ASTM-D1960 (ISO3960) and PV was calculated using equation 8

$$\text{Peroxide Value (P.V)} = \frac{S\times N_S \times 1000}{Weight\ (in\ g)\ of\ Substance} \qquad \dots (8)$$

Where;   S = Volume of $Na_2S_2O_3$ in mL (Test blank), and

      N_S = Normality of $Na_2S_2O_3$

2.2.6.7 Cetane number (CN)

The calculated saponification value (SV) and iodine value (IV) were used to calculate the cetane number (CN) which is the ability of fatty acid methyl esters as a fuel to ignite quickly after being injected. Empirical formula was proposed by (Hosamani, et al., 2009) and was used in the work. The higher its value, the better is its ignition quality. This is one of the most important parameters which is considered during the selection of fatty acid methyl esters for use as a biodiesel. Another important criterion for selection of fatty acid methyl esters is its degree of unsaturation, which is measured in terms of iodine value.

$$\text{Cetane Number (CN)} = 46.3 + \frac{5458}{[SV - 0.225 \times IV]} \qquad \dots (9)$$

Where; SV = Saponification value

IV = Iodine value

2.3.   Determination of chemical properties of the bioadditives.

Laboratory tests were carried out using ASTM: D6079-04 standard test procedure to determine the properties of the blends.

2.3.1   Relative density

The relative density, otherwise known as the specific gravity refers to the ratio of the density of a fuel to the density of water at the same temperature (Ajav and Akingbehin., 2002). The density of each of the fuel blends at five different temperatures was measured by means of a capillary stopper relative density bottle of 20 ml capacity.

2.3.2   Cloud point

Cloud point is the temperature at which solidification of heavier components of a fuel resulting in a cloud of crystals within the body of the fuel first appears (Ajav and Akingbehin, 2002). This temperature was determined for each of the fuel blends samples using Armfield

Engineering Teaching and Research Equipment of cloud and pour point apparatus (FM34, June 2010).

2.3.3 Pour point

The temperature at which on further cooling of fuel, results in increased size and number of wax crystals and eventual coalescence of the fuel to form a rigid structure is termed pour point. Cloud and pour points temperatures are of importance in knowing the behavior of fuels in a cold weather. Also, the pour point was determined using Armfield Engineering Teaching and Research Equipment of cloud and pour point apparatus (FM34, June 2010).

2.3.4 Flash point

This is the minimum temperature at which the vapor given off by a fuel when heated will flash when a test flame is held above the surface without the fuel catching fire; It is of importance when determining the fire hazard (temperature at which fuel will give off inflammable vapor).

Flash points of the samples were measured using Armfield Engineering Teaching and Research Equipment (FM60, June 2010).

2.3.5 Viscosity.

The resistance to flow exhibited by fuel blends, as expressed in various unit of viscosity, is a major factor of consequence in establishing their suitability for the mass transfer and metering requirements of engine operation. According to Ajav and Akingbehin (2002), the coefficient of viscosity, η, is expressed as:

$$\eta = \frac{\tau}{S} \qquad \ldots (10)$$

Where: η = Dynamic viscosity, Pa. s

τ = Shear stress, Pa

S = Shear rate, s^{-1}

A U-tube Saybolt viscometer was used for measurement of the dynamic viscosity of the samples at the Department of Chemistry, Abubakar Tafawa Balewa University, Bauchi. The experiments were performed at 20^0C, 25^0C, 30^0C, 35^0C, and 40^oC and the tests were repeated three times and then average values taken. The apparatus was based on the principle of measuring the time of gravity flow (in seconds) of the sample through a specified hole. The dynamic viscosity was calculated from the time by equation 11 (Ajav and Akingbehin, 2002).

$$\eta = 0.07313dt - 5.94458\frac{d}{t} \qquad \dots (11)$$

Where: η = Dynamic viscosity, cP

d = Density of sample, g/ml

t = Flow time, s

2.3.6 Calorific value

The calorific values of the blends were determined with the help of a Gallenkamp ballistic bomb calorimeter. A known amount of fuel was burnt in this bomb calorimeter. The air was replaced by pure oxygen. The maximum deflection of the galvanometer on the control box was recorded after burning the samples. The effective heat capacity of the system was also determined using same procedure, but with pure and dry benzoic acid as the test fuel. The calorific value was calculated as (Ajav and Akingbehin, 2002):

$$Calorific\ Value\ (C.V.) = \frac{(a_2 - a_1)Y}{Z} \qquad \dots (12)$$

Where: C.V. = Calorific value of sample, kJ/kg

a_1 = Galvanometer deflection without sample

a_2 = Galvanometer deflection with sample

Y = Calibration constant

Z = Mass of fuel sample, g

The calibration constant (Y) is given as (Ajav and Akingbehin, 2002).

$$Y = \frac{6.32\, W_1}{a_2 - a_1} \qquad \qquad \dots (13)$$

Where: a_1 = Galvanometer deflection without sample

   a_2 = Galvanometer deflection with benzoic acid.

   W_1 = Mass of benzoic acid.

3. RESULTS AND DISCUSSIONS.

Table 1: Chemical Properties of Clove Oil, Eugenol and Eugenyl Acetate.

Properties	Clove oil	Eugenol	Eugenyl Acetate
Heating value (MJ kg^{-1})	35	35	34
Density (kg m^{-3}) at 25^0C	0.905	1.071	1.065
Acid value (mg KOH g^{-1})	18.51	18.66	18.94
Iodine value (I_2 g 100 g^{-1})	10.79	10.85	10.93
Saponification value (mg KOH g^{-1})	136.88	137.90	137.98
Peroxide value (meq O_2 kg $^{-1}$)	254	253	250
Free Fatty Acid	9.26	9.20	8.95

Table 2: Chemical Properties of Clove Oil, Eugenol and Eugenyl Acetate.

Comparison between experimental and standard values.

Properties	Clove oil Experimental values	*Clove oil Standard values.*	Eugenol Experimental values	*Eugenol Standard values.*	Eugenyl Acetate Experimental values	*Eugenyl Acetate Standard Values.*
Heating value ($MJ\ kg^{-1}$)	35	30 - 40	35	30 - 40	34	30 - 40
Density ($kg\ m^{-3}$) at 25^0C	0.905	0.500 - 1.000	1.000	0.8 - 1.00	1.065	0.500 - 1.000
Acid value (mg $KOH\ g^{-1}$)	18.51	10.00 - 20.00	18.66	16.0 - 20.0	18.94	10.00 - 20.00
Iodine value ($I_2\ g\ 100\ g^{-1}$)	10.79	05.00 - 15.00	10.85	16.0 - 20.0	10.93	5.0 - 15.0
Saponification value ($mg\ KOH\ g^{-1}$)	136.88	100 - 200	137.90	100 - 200	137.98	100 - 200
Peroxide value ($meq\ O_2\ kg^{-1}$)	254	200 - 300	253	200 - 300	250	200 - 300
Free Fatty Acid	9.26	5.00 – 10.00	9.20	5.00 – 10.00	8.95	5.00 – 10.00

Table 3: Physical characteristics of Diesel fuel and diesel fuel + Clove oil

Physical properties determined in accordance with ASTM: D6079-04

Parameters	Diesel Fuel	Diesel fuel + Clove oil
Specific gravity at 25^0C (g/mL)	0.8452	0.83929
API gravity	34.5408	37.1311

Diesel index	53.9527	68.560
Viscosity (cSt)	3.7215	3.6713
Flash point (^{0}C)	73	69

Table 4: Physical characteristics of Diesel fuel and diesel fuel + Eugenol

Physical properties determined in accordance with ASTM: D6079-04

Parameters	Diesel Fuel	Diesel fuel + Eugenol
Specific gravity at 25 ^{0}C (g/mL)	0.8452	0.8473
API gravity	0.8522	0.8536
Diesel index	34.5408	34.2685
Viscosity (cSt)	53.9527	51.3685
Flash point (^{0}C)	3.7215	3.6718

Table 5: Physical characteristics of Diesel fuel and diesel fuel + Eugenyl acetate

Physical properties determined in accordance with ASTM: D6079-04

Parameters	Diesel Fuel	Diesel fuel + Eugenyl acetate
Specific gravity at 25 ^{0}C (g/mL)	0.8452	0.82920
API gravity	0.8522	0.81731
Diesel index	53.9527	66.530
Viscosity (cSt)	3.7215	3.20030
Flash point (^{0}C)	73	66

4. CONCLUSION

From the experimental investigations the following conclusions may be drawn:

1) Clove oil was successfully extracted from cloves using Soxhlet extraction process, the yield of the oil was found to be 0.64ml obtained from 10.25g of clove buds.

2) Eugenol compound was successfully isolated from the extracted clove oil using stem distillation method.

3) Compound of Eugenyl acetate was obtained by acetylation of acetic anhydride with clove oil in solvent free system.

4) The physico-chemical properties of diesel fuel, bio additives and blends were determined as presented.

5) The following treat rates (BDC (0.2%), BDC (0.4%), BDC (0.6%), BDC (0.8%), BDC (0.8%), BDC (1.0%), BDE (0.2%), BDE (0.4%), BDE (0.6%), BDE (0.8%), BDE (1.0%), BDEA (0.2%), BDEA (0.4%), BDEA (0.6%), BDEA (0.8%), and BDEA (1.0%) were successfully formed.

REFERENCES

Ajav, E. A. (2002). Biodegradability Characteristics of Current and newly developed alternative fuels. *SAE Technical Paper*, 199-208.

Anbarasu, A., Saravanan, M., Loganathan, M. (2013). The effect of alcohol addition in a diesel operated DI Engine on Combution, Emission and Performance Characeristics. *International Journal of Green Energy*, 10: 90 - 102.

Babu, P., Rao, K., Rao, B., Srivataba, S., Beohar, H., Gupta, B. (2012). The role of Oxygenated Fuel Additive (DEE) along with Mahuva Methyl Ester to Estimate Performance and Emission Analysis of DI-diesel Engine. *Journal of Biomass and Bio-Energy*, 39: 168-74.

Callahan, T. J., Ryan, T. W., Dodge, L. G., Schwalb, J. A. (1987). Effects of fuel properties on diesel spray characteristics . *SAE Paper* , No 870533.

Canakci, M. (2007). Combustion characteristics of a turbocharged DI Compression ignition engine fueled with petroleum diesel fuels. *Journal of Bioresource Engineering*, 98: 1167-1175.

Carrasco, A., & Espinoza, C. (2008). Eugenol and its synthetic analogues inhibit cell growth of human cancer cells (Part I). *Journal of Chemical Society*, 19: 543-548.

Chen, E.N., Cusatis, P. J., Popeil, E. (2015). 'Validation of the Aromatic Ring Distribution in Diesel Fuel Refinery Streams by Supercritical Fluid Chromatography and Mass Spectrometry'. *Journal of Chromatography*, 637, 181-186.

Ciccarelli, D., Garban, F,. Pagni, A.M. (2008). The flower of Myrtus communis (Myrtaceae): Secretory Structures, Unicellular Papillae, and their Ecological Role. *Flora*, 203: 85-93.

Cookson, D., Smith, B., Loydd, C. (2008). investigation of Chemical Basis of Diesel Fuel Properties. *'Journal of Energy Fuels'*, 854 - 860.

Hosamani, K. M., Hiremath, V. B., Keri, R. S. (2009). Renewable Energy Sources from Michelia Champaca Seed Oil. *Journal Of Biomass and Bio-Energy*, 267-270.

Hsu, C., & Robbins, W. (1994). 'Nitrogen Speciation of Petroleum Polars by Compound Class Seperation and Online LC/MS'. *Journal of High Resolution Chromatography*, 271-276.

Ismaiel, A., & Pierson, M.D. (1990). Inhibition of Growth and Germination of C. botulinum 33A, 40B, and 1623E by Essential Oil of Spices. *Journal of Food Sciences*, 55: 1676-1678.

Liolios, C., Graikou, K., Skaltsa, E., Chinou, I. (2010). Dittany of Crete: A botanical and Ethnopharmacological. *Journal of Ethnopharmacology*, 131:229-241.

Muhmmad, N., & I, B. E. (2011). Detrmination of Saponification, Acid and Ester Values. *Bioresearch Bulletin*, 5: pp51-54.

Joshi, H., Moser, B., Smith, W., Walker, T. (2010). Effects of Blending alcohols with poultry fat methyl esters on cold flow properties. *Journal of Renewable Energy*, 35: 2207-2210.

Onwuka, G. I. (2005). Food analysis and instrument, Theory and Practice. *Journal of Food Science*, pp70-120.

Sjogren, M., Li, H., Rannug, U., Westerholm, R. (2005). A Multi-variate Statistical Analysis of Chemical Composition and Physical Characteristics of Ten Diesel Fuels. *Journal of Fuels*, 983 - 989.

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