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Physico-Chemical Analysis and Combustion Characteristics of Bio-Diesel

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Abstract: The present study concentrates on identification of the combustion characteristics of Bio-Diesel. The Bio-diesel has been identified as one of the substitute to petroleum diesel because of its close resemblance. In the present investigation, we identify certain combustion characteristics of bio-diesel made from transesterification of Karanj oil using methyl alcohol. The physicochemical parameter of it are measured and compared with diesel oil. The droplet combustion of bio-diesel, diesel and one to one mixture ratio bio-diesel and diesel were carried out in an experimental setup specifically designed and fabricated for droplet combustion study. The combustion studies were carried out in three conditions: stagnant air, air flow and oxygen flow. We analyze the physicochemical properties of these fuels in the light of their composition and volatility. The combustion behavior of these fuels in different environment has been highlighted.

Keywords: Karanj-oil, Biodiesel, Droplet, Transesterification, Hydrocarbons

I. Introduction

In recent years, efforts are being made throughout the World to reduce the consumption of liquid petroleum fuels wherever is possible. Two general approaches are in use. First is to switch over the energy consumption devices on alternative energy source which are either abundant or are reproducible. The second is to enhance the efficiency of combustion devices. This can be achieved by understanding the physicochemical process involved during the combustion. Such knowledge is also beneficial in view of propulsion, mitigation of combustion generated pollution and control of fire hazard in handling combustibles.

In literature, some works have been reported in the area of combustion of liquid fuels. The aim was to maximize the efficiency and minimize the environmental impact of the devices which burn these fuels on the one hand and judge their suitability for the devices which are emerging with the advancement of technology on the other hand. In all liquid fuel based engines, whether it is a diesel engine, or a liquid propellant rocket engine or an industrial furnace, the reactants are fed into the combustion chamber in the form of finely divided droplet arrays. The combustion of such droplet arrays inside the combustion chamber depends on various parameters. Some of them, such as physicochemical, thermodynamic and combustion properties are inherited by reactants and others are associated with combustion devices. These are droplet size, droplet velocity, droplet size distribution, pressure, temperature and gaseous composition inside the combustion devices. The involvement of all these parameters are so closely interrelated in actual engine that it is extremely cumbersome if not impossible to pin point their effective role in the process of combustion. Hence, combustion and vaporization of an isolated droplet in a quiescent atmosphere was chosen as one of the tool for understanding the basic phenomena by most of the researcher in this area due to its simplicity and cost effectiveness. Early analysis on the evaporation and combustion of liquid fuel droplet was carried out by Godave and Spalding[1] in 1953 and proposed d^2 -law under the assumption spherically symmetrical fuel drop and flame front, quasisteady state, constant properties, Lewis number one and infinitely fast chemical reactions in the gas phase. The d^2 -law yields good estimates of the gasification rate as well as for the flame standoff ratio which were constant over time. Gregory and Calcote[2] studies the details of droplet vapor reactions and found that the combustion reactions occur in the vapour phase. The drop, on leaving the spray nozzle of a turbojet, was subjected to an atmosphere of a greatly increased temperature. It was concluded that condensation of vapour may occur on the surface of the droplet resulting in liquid-liquid reaction and the heat transfer between the liquid and vapor becomes of slight importance. Hall and Diederichsen[3] carried out the droplet combustion of liquid fuels at 710°C and at different pressures varying upto 20 atmospheres for suspended droplets as well as falling droplets under natural convection condition. It was concluded that the distance between the droplet surface and flame is roughly proportional to $-1/2$ power of the pressure in the range of pressure investigated and mass rate of burning of droplet diameter with power index of 0.96. Natarajan [4] carried out the droplet combustion of freely falling n-pentane fuel droplet at pressures upto 615 lb in⁻² absolute in a specially designed high pressure droplet combustion setup and effect of pressure on mass consumption rates, flame geometry and drag coefficients were estimated and compared with available data. In experimentation, Natarajan and Ghosh [5] study the velocity histories of vaporizing fuel droplets injected downward in the stagnant gas. Considering three possible cases of drag coefficient and assuming a general “ D^n -relation” for the depletion of the vaporizing drop. It was concluded

that the velocity histories depend on the index 'n' which can be related to the nature of the rate controlling phenomena during the combustion process. Lasheras [6,7] with an aim of improving combustion efficiency, studied the disruptive burning characteristics of isolated fuel droplets of binary n-paraffin mixture and fuel droplets containing alcohol or water. It was concluded that fragmentation of liquid droplets during combustion of multicomponent fuel included a secondary atomization of primary fuel resulting in more uniform fuel/air mixing and hence efficiency. Saitoh [8] measured the ignition time of fuel drops of varying diameter. They observed the ignition time decreases as the droplet diameter decreases at the region near the ignition limits and the ignition occurs more rapidly as the droplet increases when the initial droplet temperature is high.

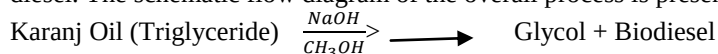
However, an exhaustive study of bio-diesel in terms of physiochemical as well as combustion characteristics is required before its substitution to diesel. Very little information is available in the literature regarding the method of production of biodiesel from different sources and about their physical as well as chemical properties. It has been sought as an effective alternative fuel to conventional diesel. Although vegetable oils may be used directly as fuel in diesel engines without refining but it possess several problems mainly related to viscosity and therefore very difficult to burn in IC engines. Demirbas [9] had developed a method to produce bio-diesel by the method of transesterification. BD fuel is a renewable substitute fuel for petroleum diesel or petrodiesel (PD) fuel made from vegetable or animal fats. It was emphasized that BD fuel can be used in any mixture with PD fuel as it has very similar characteristics except lower exhaust emissions. Biodiesel is renewable, biodegradable, non-toxic, and essentially free of sulfur and aromatics. Madras et al have developed a method of synthesis of bio-diesel from transesterification of sunflower oil by supercritical alcohol at temperature (200-400°C) at 200 bars. It was observed that nearly complete conversions were possible by this process. Measurement of the temperature dependent viscosity of biodiesel fuels was investigated by Kerschbaum et al [11] with special reference to design micro heat exchanger. Testing was done in the temperature range of 258-303° K. it was found that an exponential equation based on the usual Arrhenius form describes all measurements, however below 273K the viscosity sharply rises within 2K and then further increases. The section II of this paper presents the experimental details. The section III briefs steps to be followed for synthesis of Biodiesel from Karaj oil. The physical and chemical properties are found out in section IV. The droplet combustion study of Biodiesel is conducted in section V of this paper. The results and discussions are made in section VI. Finally, his concluding remarks are presented in section VII.

II. Experimental Details

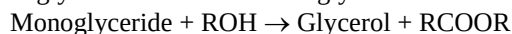
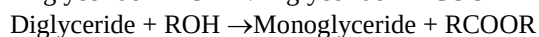
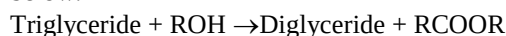
This section aims to identify certain combustion characteristics of bio-diesel made from transesterification of Karanj oil using methyl alcohol. The physicochemical parameter of it were measured and compared with diesel oil and one to one ratio mixture of bio-diesel and diesel. The droplet combustion of bio-diesel, diesel and one to one ratio mixture of bio-diesel and diesel were carried out in an experimental setup specifically designed and fabricated for droplet combustion study. The combustion studies were carried out in stagnant air, in air flow and oxygen flow. Attempts have made to analyze the physicochemical properties of these fuels in the light of their composition and volatility. The combustion behavior of these fuels in different environment has been highlighted.

III. Synthesis of Biodiesel

In this section, we present the process of transesterification of Karanj oil using methyl alcohol for preparing bio diesel. The schematic flow diagram of the overall process is presented in Fig.1.



Actually three consecutive and reversible reaction occur in the transesterification process, which are given below.



IV. Determination of Properties

In this section, four important properties of Biodiesel are determined.

A. Viscosity measurement – Standard ASTM D2270 method using Redwood viscometer was applied for viscosity measurement of bio-diesel, diesel and one to one ratio mixture of biodiesel-diesel mixture. The kinematic viscosity was calculated by the equation. $V = AT - B/T$, where A – Instrument constant (0.00264), B – Instrument constant (1.90) and T – Time is in second.

B. Specific Gravity measurement– West Phal Specific Gravity Apparatus and the procedure given with apparatus was applied to estimate the specific gravity of the oils.

C. Carbon Residue and Ash content estimation– Carbon residue was determined using Conradson Apparatus and ash content was determined by the standard ASTM D482-80 method. The results are expressed as percentage of the original weight of the oil.

D. Flash point and Fire point – The close flash and fire point were determined by the Pensky Martens Apparatus whereas the open flash and fire point of the oil sample were determined by Cleveland Apparatus. The significance of these points is that they predict the possible fire hazards during transportation, storage and handling.

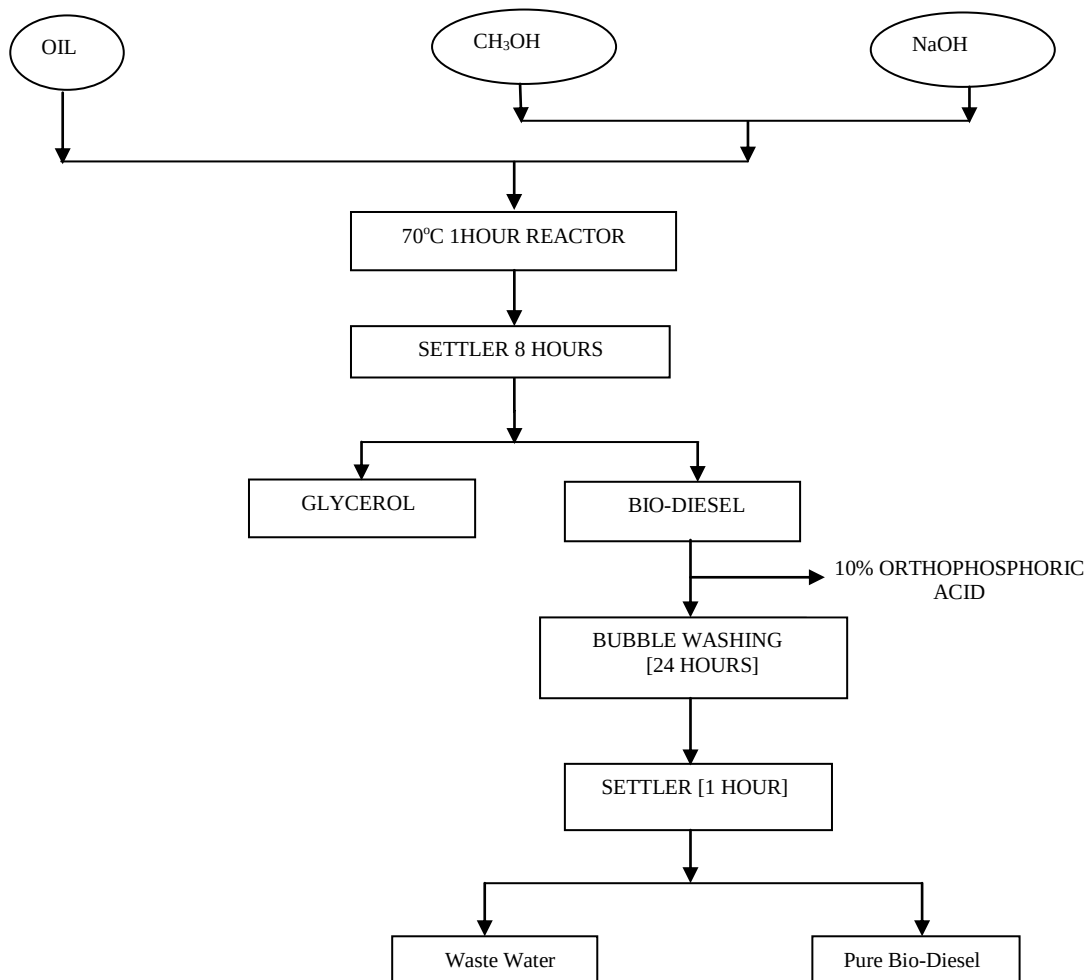


Fig.1: Flow Diagram for Synthesis of Bio-diesel from Karanj Oil

V. Droplet Combustion Studies of Biodiesel

In this section, we present a model for combustion studies of Biodiesel. It essentially consists of a heating chamber, droplet injection system, recording system and provision to create different environment inside the combustion chamber at various pressure level. The heating chamber was a rectangular box of inside dimension 240*120*320 and was made from 12.7mm (1/2 inch) thick stainless steel plate. All precautions were taken to ensure the box leakage proof and to withstand the high chamber pressure. Two electrical heating elements of output 1000 watts were fixed vertically at the center of each bigger size plates facing each other for the purpose of heating the chamber. The position of heating elements is adjusted in such a way that the distance between the two elements remains about 30mm. Two glass windows of sizes 30*220mm and 50*240mm was made centrally vertical to visualize the droplet combustion and for the recording purpose. Arrangement for fixing the droplet injection system, thermocouple, exhaust gas outlet were provided in the top plate. The temperature control inside the chamber ($\pm 10^{\circ}\text{C}$) was carried out by regulating voltage supply manually with the help of two diammerstat connected in the power line of the heating elements. The temperature measurement inside the chamber was done using K-type (Chromel-Alumel) thermocouple. The thermocouple was placed at the center in between the heating rods. Two digital multimeters were connected to measures the thermocouple output in millivolts as well as in $^{\circ}\text{C}$. High pressure oxygen, air and nitrogen gas were used to create different environment inside the combustion chamber. The droplet injection system consists of an aluminum cylinder of 32mm inner diameter and 60mm height fitted with an air tight piston. In the base of the cylinder, provision was made to fix the capillary tubes of different dimensions. Fuels were sucked in the cylinder through capillary by the upward movement of piston. The drops were formed at the tip of the capillary tube by slightly pressing the piston. Photographic technique was used to study the project the droplet combustion in the present work. A digital

camera of model number FX280EU supplied by Sony Cyber shot was used to capture images during combustion. The highest speed was selected in the present investigation.

Table 1 Physical and chemical properties of diesel, bio-diesel and 1:1 ratio mixture of diesel and bio-diesel

	Diesel	Bio-diesel	1:1 ratio mixture of diesel & Bio-diesel
Density (kg/m ³)	783	867	825
Viscosity (poise)	0.0628	0.0976	0.08695
Specific gravity	0.752	0.816	0.756
Ash content (%)	0.0974	0.02267	NA
Carbon residue (%)	0.108	0.5445	NA
Open flash point (°C)	44	170	76
Open fire point (°C)	46	172	79
Close flash point (°C)	42	165	74
Close fire point (°C)	45	170	77
Aniline point (°C)	132	128	146

VI. Results and Discussion

This section presents the important findings and discusses those. The Table 1 presents the numerical value of various physiochemical parameters of biodiesel, diesel and one to one ratio mixture of bio-diesel and diesel. It was observed that except ash content, all other parameters have higher value for bio-diesel in comparison to commercial diesel. Further, addition of diesel in bio-diesel drastically reduces the flash point and fire point of bio-diesel. In case of bio-diesel, the open flash point is 170°C which is approximately four times higher than the diesel (44°C) and for bio-diesel and diesel mixture it is 76°C which is less than double of diesel. Similar results have been obtained for fire points of these fuels. Low flash and low fire point for diesel as compared to biodiesel as per expectation. Diesel is a mixture of hydrocarbons and possesses a high rate of volatilization as compared to bio-diesel which is a mixture of methyl ester of aliphatic acids. Moreover, the tendency of oxidation of hydrocarbons is much more than the other organic substance. Further, the combustion depends on chemical composition, volatility and ignition characteristics of the fuels. Liquid fuels when heated in air/oxygen form a combustible gaseous mixture in the immediate vicinity of the fuel surface. The concentration of this mixture depends on the bulk temperature of the liquid fuel consumed, its evaporation rate as that temperature, surrounding pressure and concentration of the oxidizer in the surrounding gases. This combustibles mixture gets activated leading to initiation of combustion reactions when exposed to high energy source. When the concentration of the combustible mixture is marginal it gets consumed instantly results a flash of light. The next flash will be seen when appropriate quantity of combustible mixture is formed. However, if the evaporation rate of the fuel is increased which is possible by increasing the bulk liquid temperature, concentration of combustible mixture becomes sufficient to sustain the flame till heat and mass transfer from and to the controls the burning of the fuel. Low flash and low fire point for diesel is compared to biodiesel as per expectation. Diesel is a mixture of hydrocarbons and possesses a high rate of volatilization as compared to bio-diesel which is a mixture of methyl ester of aliphatic acids. Moreover, the tendency of oxidation of hydrocarbons is much more than other organic substance. Further, the combustion depends on chemical composition, volatility and ignition characteristics of the fuels. Liquid fuels when heated in air/oxygen form a combustible gaseous mixture in the immediate vicinity of the fuel surface. The concentration of this mixture depends on the bulk temperature of liquid fuel consumed, its evaporation rate at that temperature, surrounding pressure and concentration of the oxidizer in the surrounding gases. This combustibles mixture gets activated leading to initiation of combustion reactions when exposed to high energy source. When the concentration of the combustible mixture is marginal it gets consumed instantly results a flash of light. The next flash will be seen when appropriate quantity of combustible mixture is formed. However, if the evaporation rate of the fuel is increased which is possible increasing the bulk liquid temperature, concentration of combustible mixture becomes sufficient to sustain the flame till heat and mass transfer from and to the flame controls the burning of the fuel.

The Table 1 also presents the percent of carbon residue and percent of ash content of bio-diesel and diesel. It has been found that the carbon residue value of bio-diesel is 0.5445% whereas it is 0.108% for diesel. These results show that the carbon residue of bio-diesel is approximately five times higher than that of diesel. A possible explanation of such difference in values can be examined viewing the process of thermal cracking of these oils on heating. Diesel being a mixture hydrocarbons (C₁₅H₃₂ to C₁₈H₃₈) plus minor traces of inorganic substances evaporates/decomposes mostly in lower molecular weight saturated/unsaturated hydrocarbons on heating. Also during the process of thermal cracking, interactions of these compounds may take place. Such reactions may lead to formation of carbon. In case of bio-diesel also, similar pattern is followed on heating. However, it is being an ester of fatty acids; the probability of number of compounds formed during heating is increased.

Therefore, it is quite possible that more carbon atoms gets detached from hydrogen, or oxygen or both and remains as carbon residue.

Here, we make an interesting observation that the ash content of bio-diesel is much lower than diesel. The data shows that the ash content of bio-diesel is 0.02267% whereas for diesel, it is 0.0974%, approximately four times more as compared to bio-diesel. Ash content is defined as the percentage weight of nonvolatile combustion products obtained during the complete combustion of oil in the presence of air. These results show that the combustion of bio-diesel is less polluting than the diesel.

In the later part of experimentation, attempts were made to study the droplet combustion of these fuels. Drops were made at the tip of the capillary tube of size 1mm and 2.3mm internal diameter in the preheated combustion chamber and photographed with the help of digital camera. The speed of the camera was fixed at 16 frames per second. At this speed, the time interval between two successive frames will be 62.5 milli second. The speed and the distance between the combustion chamber and camera were kept same in all experiments. The combustion was carried out in stagnant air, in air flow and in oxygen flow. Attempts were made to maintain the precombustion conditions similar in all the experiments. It was observed that none of the fuel burned at preset temperature of the chamber (350°C) even after a long exposure to this temperature. The minimum ignition temperature as observed in the present investigation varies from fuel to fuel. It is $365 \pm 5^{\circ}\text{C}$ for diesel, $385 \pm 5^{\circ}\text{C}$ for bio-diesel and $375 \pm 5^{\circ}\text{C}$ for mixture. It also noticed that droplet burning occurs with the emission of black smoke as evidence from carbon deposition on the surface of capillary tube for all the fuels considered in the present work. Inspection of droplet flame reveals that it is a bright white surrounded by yellowish flame. The flame shape is not spherical. It is stretched in vertical direction. Although, it is not clear from the photograph that whether a single drop is burning or bunch of drops are burning together or drop size has changed during burning because of collapsing of smaller drops, nevertheless, the photograph clearly shows that flame disappears after 5th frame that is in 0.25 sec approximately. Similar observations were made when 2.3 mm size capillary was used to produce the drop. In case of bio-diesel droplet flame, the flame except size was similar to diesel flame. The flame disappearance time was more (0.46 sec) for bio-diesel flame. For mixed fuel flame, the flame elongation is maximum but the flame disappearance time is 0.32 sec, less than bio-diesel. In the second set of experiment, the air was flown into the chamber from the bottom and was allowed to escape from the top of the chamber. It shows the burning of bio-diesel fuel under this condition. It was found that the minimum chamber temperature, at which the ignition takes place, is higher in flowing air condition. However, the smoke formation and carbon deposition is less than stagnant air condition. The central part of the flame was bright white and was covered by a yellowish flame envelope. In case of 1 mm capillary, the flame was found attached to the capillary, the flame width is more; flame stretching is less than the flame stretched from capillary and starts falling down. The burning continues till it reaches the bottom of the chamber. In the third set of experiment, attempts were made to combust the fuel drops in oxygen environment. Oxygen was flown in the chamber for sufficient time before the experimentation to ensure maximum replacement of air by oxygen. It shows the burning of biodiesel fuel under this condition. It was observed that the flame is brilliant white in the inner portion and it is surrounded by bluish flame. The yellow flame as observed in previous cases does not exist in the combustion in oxygen medium. In these experiments, neither smoke was visible during burning nor carbon deposition on capillary tube noticed. The flame was broader in size even for 1mm diameter tube but it remains attached to capillary tube, however it separates out from capillary tube of size 2.3mm. During the burning process, continuous bursting sound was heard and it was seen that bigger the size flame fragments into smaller size flame. This phenomenon was not observed in previous cases.

VII. Conclusions

The following conclusions emerge from this study.

1. Transesterification method for synthesis of bio-diesel results the yield around 84% and bio-diesel has high value of density, viscosity and specific gravity.
2. The flash point and fire point (open and close) are much higher approximately four times for bio-diesel as compared to diesel. Addition of diesel in bio-diesel brings down these points drastically.
3. The carbon residue value for bio-diesel is much higher as compared to diesel; however the % of ash content of bio-diesel is much lower than the % of ash content of diesel. These results indicate that the presence of inorganic matters in bio-diesel is low as compared to diesel. Hence the combustion of bio-diesel is more pollution free.
4. During the droplet combustion experiments, it was observed that each fuel has a specific temperature range in which it combust. Below and above this range, the combustion is lower for diesel fuel in stagnant air condition.
5. In complete combustion as evidenced from huge smoke formation, carbon deposition and flame was formed when these fuel droplets were burned in stagnant air and in flowing air condition. However, in oxygen environment, it is observed that there is no smoke, no carbon deposition and the look of the flame was brilliant white covered by bluish flame envelop.

6. Intermittent bursting sounds during combustion were heard during combustion of fuels in oxygen medium. However, such fragmentation went unnoticed while the drops were burning in air.
7. During the analysis of results, it was felt that the more investigation on bio-diesel is required before making it a competent substitute of diesel.
8. The flame remains attached to the capillary when its diameter was 1mm. its shape was not spherical but looks like a hanging stick. The stretching of flame is more in flow condition as compared to stagnant condition. Increasing the diameter of the capillary tube, the width of the flame increases and the flame has a tendency to detach itself from the capillary tube.

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