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POTENTIAL OF WASTE COOKING OILS AS BIODIESEL FEED STOCK

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اكتسب الديزل الحيوي أهمية كوقود بديل لمحركات الديزل. حيث يتميز تصنيع الديزل الحيوي من الزيت النباتي بالسهولة والنفع البيئي. كما أنه يمكن تصنيع الديزل الحيوي بكميات كبيرة من زيوت الطهي المستعملة. وتهدف هذه الورقة إلى تحليل إمكانية استخدام زيوت الطعام المستخدمة ومدى ملائمتها لإنتاج الديزل الحيوي وكذلك مقارنة خصائص الوقود الحيوي المنتج من الزيوت المستعملة والغير مستعملة. وقد تم مقارنة الوقود الحيوي المنتج من زيت النخيل المستعمل والغير مستعمل ومقارنة هذا الوقود الحيوي مع الديزل المحلى المتوفر من حيث كفاءة المحرك والغازات المنبعثة نتيجة الاحتراق. ودلت النتائج على أن الكفاءة الحرارية للوقود المصنع من الزيوت المستعملة تكون مقاربة لتلك الناتجة من الوقود الحيوي المصنع من الزيوت غير المستعملة. إلا أنه في حلات التحميل العالي للمحرك فإن كفاءة الديزل الحيوي المصنع من الزيوت المستعملة تقل بمقدار 2%. وتقل نسبة غازات الهيدروكوبون الناتجة من الديزل الحيوي المصنع من الزيوت المستخدمة بمقدار 35% عن تلك الغازات الناتجة من الديزل المحلي.

Over the last few years biodiesel has gained importance as an alternative fuel for diesel engines. Manufacturing biodiesel from plant oil is relatively easy and possesses many environment benefits. Besides, what makes biodiesel all the more attractive is that it can be derived from waste cooking oil produced in large quantities in public eateries. The purpose of this paper is to analyze the potential of waste cooking oil (WCO) for their suitability as feed stock for biodiesel preparation and to compare the fuel properties of the derived esters of WCO (WCO-biodiesel) with those esters of fresh oil and baseline diesel fuel. The palm oil based WCO-biodiesel and esters of fresh palm oil are transformed into respective biodiesel, by transesterification process. Tests are conducted to compare these biodiesels with the baseline local diesel fuel in terms of engine performance and exhaust emissions. The results indicate that the thermal performance of esters of WCO closely resemble the performance of esters of fresh oil. At higher load operation of esters of WCO fueled engine suffers nearly 2 % brake thermal efficiency loss. Interestingly hydrocarbon emissions of WCO-biodiesel fuel were observed to be approximately 35% lower than baseline diesel operation.

Keywords: Waste cooking oil; Polar compounds; Engine performance; Emissions.

1. INTRODUCTION

Biodiesel is the name given to clean burning alternative fuel produced from domestic renewable resources. The main commodity sources for biodiesel in India is non-edible oils obtained from plant species such as Jatropha Curcas (Ratanjyot), Pongamia Pinnata (Karanj), Calophyllum inophyllum (Nagchampa), Hevca brasiliensis (Rubber) etc. According to ASTM standards Biodiesel is technically defined as ,"the mono alkyl esters of long chain fatty acids derived from renewable liquid feedstock, such as vegetable fats and animal oils ,for use in compression ignition (CI) engines"[1].

United State produces biodiesel from edible oil (mainly soya oil), the pure biodiesel costs around $ 1.4 to $2.4 per gallon depending upon purchase volume and the delivery costs and competes with low sulfur diesel oil. However, it is costlier to normal diesel which is $1.2 to $1.5 per gallon[2,3]. In India the production of biodiesel from edible oils is currently much more expensive than petroleum diesel fuels due to the relatively high costs of vegetable oils. The cost of biodiesel can be reduced if non-edible oils, and used frying oils are considered instead of edible oils. Non-edible oils such as Mellia azadirachta (Neem), Bussia Latifolia (Mahua), Pongamai Pinnata (Karanja), Orbignaya maritiana (Babassu), Ratanjyot (Jatropha), etc. are easily extracted in many parts of the world including India, and are relatively cheap

Table 1. Production of oil seeds (million tons) in 2002-2003 in India

Oil Type	World	India
Soya bean	123.2	4.3
Cottonseed	34.3	4.6
Groundnut	19.3	4.6
Sunflower	25.2	1.32
Rapeseed	34.7	4.30
Sesame	2.5	0.62
Palm Kernels	4.8	NA
Copra	4.9	0.65
Linseed	2.6	0.20
Castor	1.3	0.51
Niger	0.8	0.08
Rice bran	NA	NA
Total	**253.6**	**21.18**

compared to edible oil. While India is short of petroleum reserve, it has large arable land as well as good climatic conditions (tropical) with adequate rainfall in large regions to account for relatively large biomass production each year. Since edible oil demand being higher than its domestic production, there is no possibility of diverting this for production of biodiesel. Fortunately there is a large region of degraded forest land unutilized public land, field boundaries and fallow lands of farmers where non-edible oil-seeds can be grown.

The production of oilseeds in the year 2002-2003 is depicted in the Table 1[4], From the table it is evident that , India the second largest country in terms of population, but contributes only 8.35% to the total world's oil seed production. Thus, the use of vegetable oils as thermal energy sources would require more efforts to increase the production of oil seeds and to identify more and newer plants that yield high oil content seeds.

The use of waste material as a source of alternative fuel is a practice of increasing popularity among the researchers worldwide. One such high value waste product is waste cooking oil (WCO) or abused fryer oil. According to INE (Spanish National Institute of statistics) about 74,000,000 lt. of waste olive oil collected every year and discarded inappropriately[5]. With the mushrooming of fast food centers and restaurants in India, it is expected that considerable amounts of used-frying oils will be discarded into the drains. These can be used for making biodiesel, thus helping to reduce the cost of water treatment in the sewerage system and assisting in the recycling of resources.

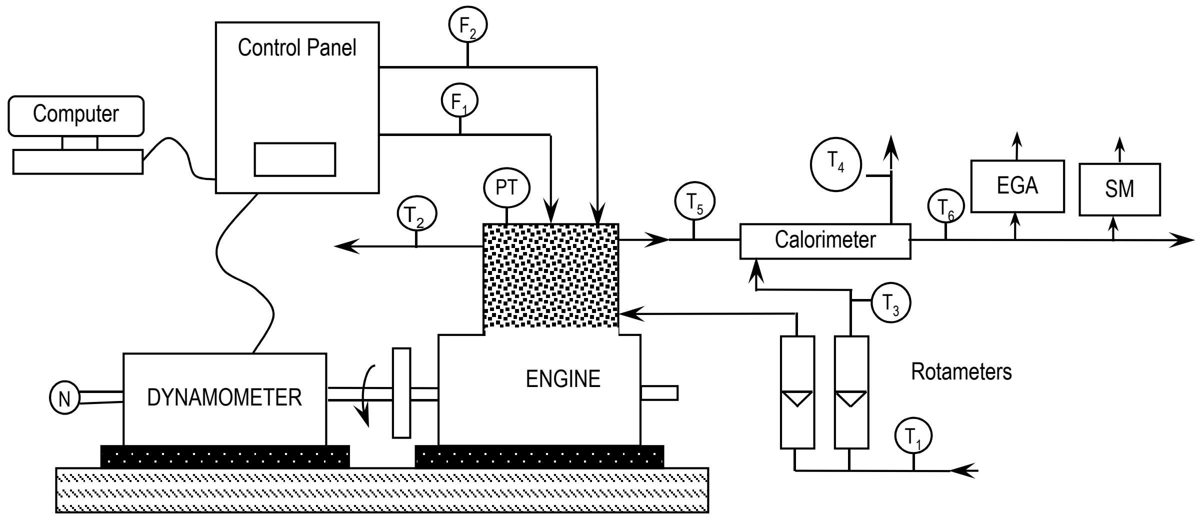
Generally cooking oil used for frying are sunflower oil, palm oil, coconut oil etc. as they are easily available, and especially so of the coconut oil which is abundantly available in south India. It is well known fact that, when oils such as these are heated for an extended time (abuse), they undergo oxidation (degradation) and give rise to oxides. Many of these such as hydroperoxides, epoxides and polymeric substances have shown adverse health/biological effects such as growth retardation, increase in liver and kidney size as well as cellular damage to different organs when fed to laboratory animals [6,7].

An alternative to prevent inappropriate disposal of WCO is by recycling it. The main use of recycled WCO is in the production of animal feeds and in a much smaller proportion in the manufacture of soaps and biodegradable lubricants. Some health risks can be traced from the use of recycled cooking oils in animal feeding, such as undesirable levels of contaminants, particularly PAHs (Polycyclic aromatic hydro-carbons), PCBs (Polychlorinated biphenyls), dioxins and dioxin related substances [7]. By consumptions of animal origin foodstuffs like milk, meats, poultry and other products, these undesirable contaminants enter the human body and cause serious long term health hazards. As these contaminants are liposoluble, they accumulate in organic lipids and finally in the body, and thereby their concentration increases gradually over the years. In other words, the body is exposed not only to a single acute action, but also to a chronic action of bioaccumulation of these hazardous compounds over the years[7]. Hence utilizing the recycled WCO in any way is not advisable from health standpoint. Besides the ill health effects of these WCO (abused oils), their disposable could also have a large environmental implication, because of high COD (Chemical oxygen demand)[7].

The primary objective of this paper is to examine the potential of waste cooking oil (WCO) for their suitability as feed stock for biodiesel preparation and to compare the fuel properties of the methyl esters of WCO (WCO-biodiesel) with those of esters of fresh oil and base line diesel fuel and also to investigate the emissions and performance of a diesel engine running on above biodiesels.

2. TEST MATERIALS AND METHODS

Three kinds of test material were used in the present study, first test material is a petroleum diesel obtained from local petrol bunk. Second test material is a Biodiesel derived from fresh un-used palm oil through transesterification reaction. Third test material is the Waste cooking oil Biodiesel. The WCO samples used in this study were of palm oil, since its most commonly used oil in the restaurants and hostel kitchens. The fatty acid composition of palm oil is dominated by palmitic, oleic, and steraric fatty acids and in addition to it much less proportions of myristie, lauric, linolenic, and capric acids[8]. The waste cooking oil, (WCO) was collected from different hostel kitchens and cafeterias and was tested at authors Institute facility. The WCO samples collected were allowed to stand for about 2-3 days so that impurities would settle down. Then WCO was filtered to remove food residues and solid precipitate in the oil. Filtration was followed by the measurement of total polar material (TPM) using a standard cooking oil tester.



T_1, T_3	Inlet Water Temperature	F_2	Air Intake DP unit
T_2	Outlet Engine Jacket Water Temperature	PT	Pressure Transducer
T_4	Outlet Calorimeter Water Temperature	N	RPM Decoder
T_5	Exhaust Gas Temperature before Calorimeter	EGA	Exhaust Gas Analyser
T_6	Exhaust Gas Temperature after Calorimeter	SM	Smoke meter
F_1	Fuel Flow DP (Differential Pressure) unit		

Figure 1. Experimental setup

Table 2. Test Fuel Properties

Characteristics	Fresh Oil Biodiesel	Esters of WCO [WCO-Biodiesel]	Diesel
Density at 40^0 C (Kg/m^3)	870.6	876.08	807.3
Specific Gravity at 15.5°C/15.5°C	0.887	0.893	0.825
Distillation temperatures			
10% Recovery temperature	324	340	165
50% Recovery temperature	336	345	265
90% Recovery temperature	312	320	346
Flash Point ^{0}C	159	160	53
Fire Point ^{0}C	165	164	58
Kinematic Viscosity at 40^0C (mm^2/s)	2.701	3.658	1.81
Calorific value (kJ\kg)	40120.78	39767.23	42347.94
A.P.I. Gravity	27.83	26.87	39.51
Cetane Index	50.025	50.54	56.21
Aniline Point (C)	NA	NA	77.5

Note: Tests were conducted at laboratory standards. “NA” stands for not available.

Before transesterification process, it was ensured that the oil contained very little amounts of water in it because every molecule of water would destroy a molecule of catalyst. The filtered WCO was subjected to drying by heating it to 100^0 C for at least fifteen minutes with continuous stirring. The samples of WCO were decanted and then transesterified using methanol in presence precisely calculated amount of catalyst namely sodium hydroxide to get fatty acid methyl ester, which is called as “WCO Biodiesel”.

Fuel properties such as density, specific gravity, flash point, fire point, viscosity, calorific value and cetane index determined by standard procedure and results are shown in Table 2 for comparison. The property values listed in the Table 2 were evaluated twice and the values depicted in the above table are that of the average.

3. EXPERIMENTAL SETUP

The engine performance test was conducted on a single cylinder, four-stroke, naturally aspirated, open chamber (direct injection) water-cooled, 5.2 kW output computerized diesel engine test-rig. The engine was directly coupled to an Eddy current dynamometer that permitted engine motoring either fully or partially. The schematic diagram of the experimental setup is depicted in Figure 1 and the engine characteristics are cited in Table 3.

The fuel is supplied to the test engine by an external tank of 5 liter capacity, which could easily be drained with the help of three way stop valve for change of fuel. A glass burette of 100cc was also attached in parallel to this tank and was used for fuel flow rate measurement. For every fuel change the fuel line was purged out of the residual fuel. The engine was made to run under full load for at least 30 minutes to stabilize on new fuel conditions. Test-rig was provided with necessary equipment and instruments for recording the dynamic combustion pressure and crank-angle measurements. Provision was also made for interfacing airflow, fuel flow, temperatures and

Table 3. Test Engine characteristics

Engine	Four-Stroke, single cylinder, constant speed, water cooled diesel engine
BHP	7BHP @ 1500 rpm
Bore x Stroke	87.5 x 110 mm
Stroke Volume	661.5 cc
Compression Ratio	17.5:1
Connecting rod length	234mm
Dynamometer	Eddy current
Length of the load cell from axis of crank shaft	175mm
Load measurement	Strain gauge load cell
Water flow measurement	Rotameter
Fuel and air measurement	Differential pressure unit
Speed measurement	Rotary encoder
Interfacing with Computer	ADC card
Emissions measurement	5 gas analyzer, MRU make.

load measurement with computer. The setup facilitates, the study of engine performance for brake power, indicated power, frictional power, BMEP, IMEP, brake thermal efficiency, indicated thermal efficiency, mechanical efficiency, volumetric efficiency, specific fuel consumption, A/F ratio and heat balance. Windows based engine performance analysis software package was used for online performance evaluation. During the test, the engine exhaust was measured for the emissions like NO_x, CO, CO_2, O_2. A calibrated German make MRU delta 5-Gas analyzer was used for the emission measurement. It consists of flexible probe with stainless steel nose. Once the calibration protocol for 150 second is completed, the probe is then introduced to the sample stream for emission measurement. MRU delta 5 gas analyzer incorporates a microprocessor technology, which provides instantaneous emission readings with a good accuracy.

4. RESULTS AND DISCUSSION

4.1 Biodiesel production process from waste cooking oils

The used cooking oil (WCO) has properties different from the properties of refined / crude fresh cooking oils. During frying process; presence of heat and water accelerates the hydrolysis of triglycerides and increases content of free fatty acids in oil. Oxidation stability of the oil is disturbed because of the contact of hot oil with food, and peroxide value of oil increases. Viscosity of oil increases considerably, because of the formation of dimeric and polymeric acids and glycerides[9,10]. Correspondingly, molecular mass and iodine value decreases and saponification value and density increases. The free fatty acid and moisture content are important process parameter for the biodiesel production i.e. transesterification process. They are the vital key for determining the viability of the vegetable oil transesterification process. Thus the process of biodiesel production from

Table 4. Titration values

Sample	Titration readings (Average of 2 trails)	Additional NaOH required per liter of oil
Fresh oil	<0.2 ml	0.2 gm.
WCO	2.9 ml	2.9 gm

WCO differs from that of fresh oil. The problem with processing WCO is that they usually contain large amounts of free fatty acids that cannot be converted to biodiesel using an alkaline catalyst due to formation of salts (soap) and hence smaller is the conversion efficiency. The soaps prevent separation of biodiesel from glycerin fraction and is in agreement with literatures [10,11].

The moisture content in WCO should be removed before starting up the transesterification and excess free fatty acids should be neutralized. In the present study the free fatty acids were naturalized by using additional catalyst (NaOH) and moisture was dried out by heating the feed stock to 100^0C for a period of 15 minutes with continuous steering. However, to neutralize the free fatty acids accumulated in the WCO, extreme care has to be taken. This is because, during the neutralizing the free fatty acids, as both excess as well as insufficient amount of catalyst may cause soap formation[11]. Hence to determine the correct amount of catalyst required, a titration must be performed on the oil being transesterified. One simple method is presented below, using a chemical indicator called phenolphthalein. In the titration, 0.1% of NaOH in distilled water is titrated against the titration sample which is essentially a solution of 10ml of Isopropyl alcohol and 1 ml of oil sample with 2-3 drops of indicator. The end point of the titration is marked when the titration sample turns pink (magenta), and stays pink for 10 seconds. The number of milliters of 0.1% NaOH solution needed is equal to the number of extra grams of pure sodium hydroxide catalyst needed to produce the proper reaction to make biodiesel from WCO. Table 4 depicts the titration values and additional amount of catalyst required for the test fuels under study.

Engine performance test:

Engine performance test was carried out at various loads starting from no load condition to the rated full load using diesel, Fresh oil Biodiesel and WCO-Biodiesel. The test was conducted at a constant speed equal to the engine rated speed. Steady state readings were taken during each trial test, and an average of the two was recorded.

Figure 2 shows the variation of brake thermal efficiency with total equivalence ratio for three different test material viz, petroleum diesel, Fresh oil Biodiesel and WCO Biodiesel. It is observed that the thermal performance of the WCO-biodiesel is marginally less by 1-1.85% compared to base line diesel operation. However, the thermal performance of WCO-biodiesel almost resembles to fresh palm oil

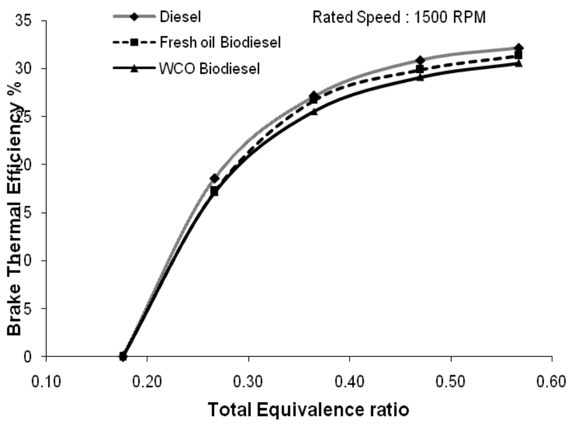


Figure 2. Brake thermal efficiency versus total equivalence ratio

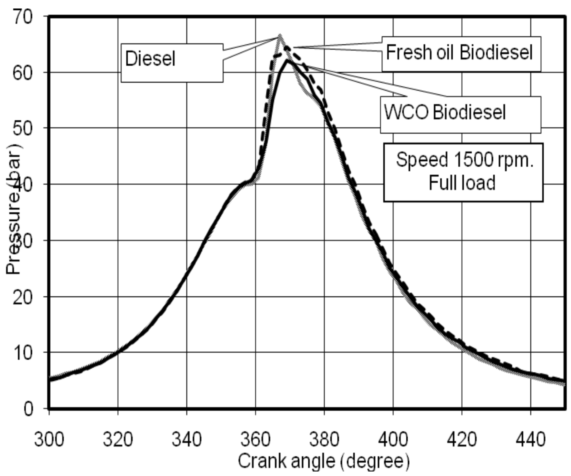


Figure 3. Pressure versus crank angle diagram for the three test fuels

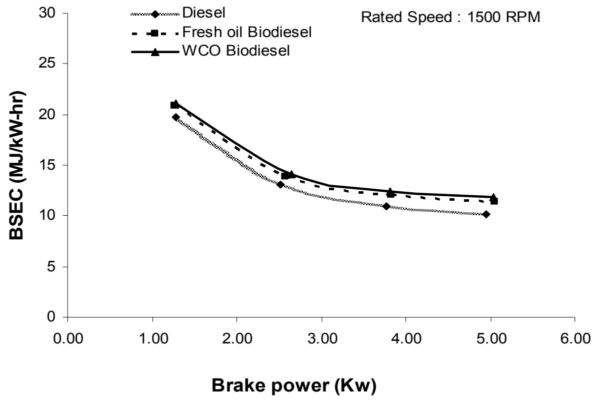


Figure 4. BSEC versus brake power developed for the three test fuels

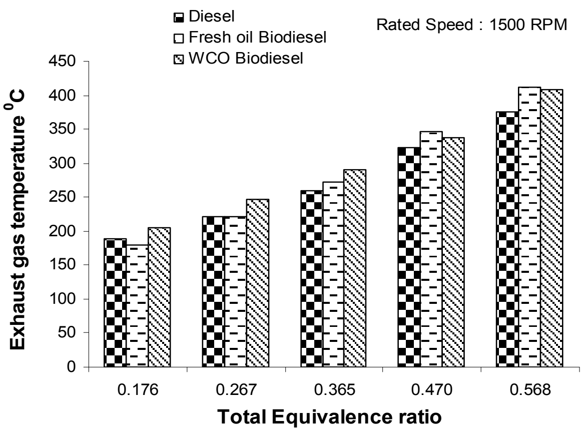


Figure 5. Exhaust gas temperature versus total equivalence ratio

biodiesel. The poor performance of the WCO biodiesel may be attributed to its higher viscosity and lower cetane index.

Viscosity of WCO-biodiesel is almost double that of diesel as depicted in Table 3. Because of its higher viscosity spray characteristics are greatly affected as high viscous nature of fuel minimizes the fineness of atomization. On the other hand, the cetane index of the WCO-biodiesel is lower than the diesel by 5 units. Hence both factors combine to increase the physical delay period, which results in poor engine performance. The increase in delay period results in poor combustion and causes low peak pressure as depicted in Figure 3.

It is also observed that, peak pressure developed is away from TDC, thereby decreasing the length of expansion. The maximum peak pressure was observed to be at 5^{o}ATDC crank angle for petroleum diesel, where as for both Fresh-oil-biodiesel and WCO-biodiesel the maximum peak pressure was observed at 9^{0}ATDC degree crank angle. Since, the performance of the WCO-biodiesel is marginally poor than the base line diesel, the engine requires higher input energy per kilowatt output as depicted in Figure 4.

In WCO-biodiesel operation the combustion is delayed due to higher physical delay period. As the combustion is delayed, injected WCO-biodiesel fuel particles may not get enough time to burn completely, hence some fuel mixtures tends to burn during the later part of expansion, consequently afterburning occurs. The exhaust gas temperature is a convenient scale to study the extent of afterburning. And it was observed that the exhaust gas temperature was reasonably higher for WCO-biodiesel compared to baseline diesel as depicted in Fig.5. Hence certain extent of afterburning can be expected during the WCO biodiesel operation.

However, the NO_x emission of WCO-biodiesel was negligibly higher than that of baseline diesel fuel as depicted in Figure 6. NOx emission is primarily a function of pressure, temperature and total oxygen concentration inside the combustion chamber. Though the combustion temperature and pressure is low for biodiesel operation, the NOx emission is almost the same as that of diesel operation. This may be because of one of the interesting characteristics of the biodiesel, i.e. its oxygen content in its structure. Invariably all fatty acid mythel esters (biodiesel) have some level of Oxygen bound to its chemical structures[12]. Hence, oxygen concentration in WCO-biodiesel fuel might have influenced the NO_x formation.

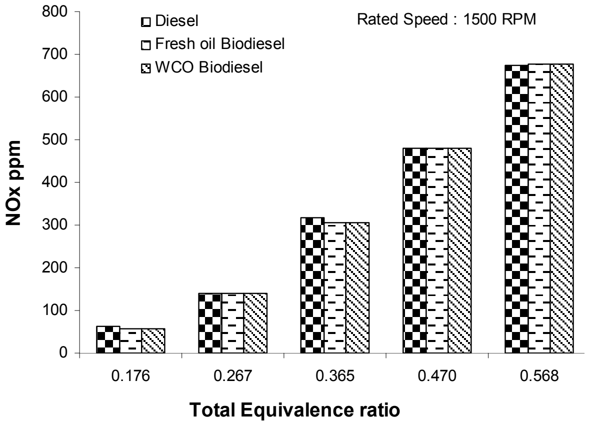


Figure 6. NOx emission versus total equivalence ratio

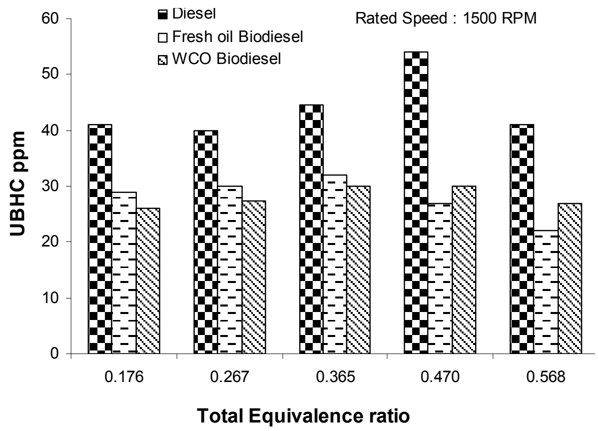


Figure7. UBHC emission versus total equivalence ratio

Figure 7 shows the variation of UBHC emissions with total equivalence ratio. For a CI engine the unburnt emission are far more less than that of SI engine. Interestingly UBHC emissions were approximately 35% lower for Fresh oil biodiesel and WCO-biodiesel operation compared to baseline petroleum diesel fuel operation. This reduction may be attributed to the complete combustion of the fuel droplets. The combustion process is untimely during WCO-biodiesel operation; but the complete oxidation of the fuel mixture takes place at the afterburning stage of the combustion, hence the oxidation of fuel mixture is far more complete than that of baseline diesel combustion. Furthermore, combustion is catalyzed due to the fact that WCO-biodiesel has additional oxygen molecule in its chemical structure, which may influence the oxidation of individual fuel molecule.

However, other emissions of WCO-biodiesel such as CO, CO_2, and O_2 were almost same as that of baseline diesel operation. On the other hand the waste cooking oil has very low level of sulphur content compared to petroleum diesel. Hence the sulphate emissions are vertically eliminated.

5. CONCLUSION

The findings of this work clearly indicate that, biodiesel derived from waste cooking oil [WCO] is perhaps the greenest liquid fuel available because of the primary ingredient being a post-consumer waste product. Public should be made aware of the ill effects that WCO (overused or abused) oil has on health and utilizing the recycled WCO for human consumption in any way is not advisable from health standpoint. A chemical route to convert this WCO into WCO-biodiesel is recommended in this paper. WCO-biodiesel when used in CI engine has shown an impressive performance and emission characteristics. They are:

- Performance of the pure WCO-biodiesel was only marginally poorer at part loads compared to the base line diesel performance.
- At higher loads engine suffers from nearly 1 to 1.5 % brake thermal efficiency loss.
- Thermal performances of WCO biodiesel closely bear a resemblance to the performance of fresh oil biodiesel.
- From emission standpoint the NOx, CO and CO_2 emissions were approximately same as that of base line diesel emissions.
- Interestingly hydrocarbon emissions of WCO-biodiesel fuel were lower than base line diesel operation.

Nomenclature

WCO	Waste Cooking oil
PAH	Polycyclic aromatic hydrocarbons
PCB	Polychlorinated biphenyls
BSEC	Brake Specific energy consumption

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