THE INFLUENCE OF NATURAL AND SYNTHETIC ANTIOXIDANT ON OXIDATION STABILITY AND EMISSION OF SAPOTA OIL METHYL ESTER AS FUEL IN CI ENGINE

by

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In this present study oxidation stability of sapota oil methyl ester with synthetic and natural antioxidant additives using Rancimat test is investigate. The performance and emission characteristics of the B20 blend of sapota oil methyl ester with different antioxidant additive are evaluated in a Diesel engine. The natural antioxidants namely citric acid, rosemary extract and leaf extract and synthetic antioxidants namely pyrogallol, propyl gallate and butylated hydroxylanisole are selected. Addition of all the antioxidant additive found to have improved the oxidation stability of the biodiesel to the required level. Pyrogallol is found to be the best among the synthetic antioxidant, while leaf extract is the best among the natural antioxidant. From the emission test it is found that B20 has better emission characters compared to diesel except NO_x. Further the addition of leaf extract slightly reduces the NO_x emission of B20 and appreciably suppresses smoke emission.

Key words: *antioxidant additive, natural antioxidant, sapota biodiesel, Diesel engine, emission, performance*

Introduction

The ever increasing population and urbanization have resulted in overutilization of conventional fossil fuel [1]. The greenhouse gas emission from the fossil fuels are constantly degrading the planet and causing global warming and other pollutant emission related problems. As such, the situation demands for an alternate source of energy that can be used to overcome the forecasted future energy crisis [2]. In the past two decades alternative fuels received much more attention due to the depletion of world's fossil fuel reserves, ever increasing fuel price and increased environmental concerns [3, 4]. Biodiesel derived from fatty acids of vegetable oils and animal oils is an attractive source of fuel for internal combustion engines [5, 6].

While using biodiesel as fuel in Diesel engine, slighter power loss is inevitable due to the lower calorific value and higher viscosity of the biodiesels [7, 8]. Higher viscosity of the biodiesel results in poorer atomization and causes starting difficulties in low temperature [9]. Biodiesel offers better emission characteristics except NO_x comparing to diesel fuel due to the

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presence of oxygen as an integrated part of the fuel, it also offers positive results such as lower wear and friction characteristics in the tribological aspects [10-15].

In spite of many beneficial properties of biodiesel, poorer oxidation stability due to the presence of unsaturated components affects the biodiesel during the storage and distribution. Oxidation of biodiesel leads to formation of oil degradation compounds such as free acids, ketones, alcohols, and peroxides [16]. Oxidation of biodiesel will produce gums and sediments which results in injector fouling, clogging of fuel filter, deposition in combustion chamber, and failure of fuel system. The oxidation of the biodiesel can be reduced by eliminating the materials which initiates the oxidation or by adding antioxidants to suppress the initiation and propagation of free radicals [17].

Synthetic antioxidants such as butylated hydroxyanisole, butylated hydroxytoluene, propyl gallate (PG), pyrogallol (PY), and tertiary butylhydroquinone has increased the oxidation stability of the biodiesel which has been studied and reported by many researchers [18, 19].

Natural antioxidants such as tocopherol, ascorbic acid, carotenoid, and flavonoid are biodegradable and non-toxic and can beused as antioxidants for biodiesel [20]. In this context, the antioxidant activity, performance and emission characteristics of leaf extract (LE), rosemary extract (RE) and citric acid (CA) as additive with sapota biodiesel is to be studied.

The present study is to evaluate the oxidation stability of biodiesel from non-edible sapota oil. Sapota (*Achraszapota*) commonly known as chiku is mainly cultivated in India for its fruit value, while in south-east Mexico, Guatemala and other countries it is commercially grown for the production of chickle which is a gum like substance obtained from latex and is mainly used for preparation of chewing gum. Fatty acid profile of sapota oil shows 64.15% oleic acid which is a mono unsaturated fatty acid. Sapota oil methyl ester (SOME) contains about 83.93% of total unsaturated fatty acid, which would results in poor oxidation stability of the fuel.

The present study is to investigate the oxidation stability of SOME with antioxidant additives using Rancimat test. In addition, performance and emission characteristics of the B20 blend of SOME with antioxidant additive is evaluated by using a Diesel engine test set-up. Two categories of antioxidants such as natural and synthetic antioxidants are selected. Natural antioxidants are CA, LE, RE, the synthetic antioxidants are PY, PG, and butylated hydroxylanisole (BHA).

Material and method

Biodiesel extraction

Sapota oil is extracted by a mechanical expeller form the dried sapota seeds. Extracted oil is filtered to remove the finely suspended particles in the oil. Acid value of oil is measured by knowing the quantity of potossium hydroxide (KOH) required to neutralize the oil sample and it was found to be less than 2.5 hence, base catalysts is used as catalyst for esterification. The KOH is used as catalyst and methanol (CH_3OH) was chosen as alcohol for esterification processes. The physical properties of the biodiesel is found by carrying out Standard ASTM testing methods and it is shown in tab. 1. Fatty acid composition of the sapota oil is given in tab. 2.

Additive preparation

The LE is prepared by mixing 100 ml of polar solvent (ethanol) with 500 grams of micro wave dried and grinded green leaf. Then it is stirred well for three hours after which an emerald green slightly opalescent liquid on top of dark green powder appears. This solution is allowed to settle for one hour and then the debris is removed from the dark green solution by filtering using filter paper. The resulting solution contains carotenoid (α-carotene and β-carotene), chlorophyll (chlorophyll a and chlorophyll b), proteins and fatty acids dissolved in ethanol.

The CA acid is dissolved in 99.5% ethanol before adding to biodiesel since it is insoluble in esters. The RE, PY, PG, and BHA was purchased and mixed in required ratio.

Table 1. Physical properties of SOME and diesel

Property (units)	ASTM D6751 limits	EN14214 limits	SOME	Diesel
Density at 15 °C [kgm^{-3}]	–	860-900	880	860
Viscosity at 40 °C [mm^2s^{-1}]	1.9-6.0	3.5-5.0	4.32	2.97
Acid value [mg KOH g^{-1}]	0.5 max	0.5 max	0.2	–
Heating value [$MJkg^{-1}$]	–	–	37.4	42.0
Cetane number	47 min	51 min	55	46

Table 2. Fatty acid profile of sapota oil

Fatty acid	Chemical structure	Percentage in SOME
Palmitic acid	C 16:0	13.27
Stearic acid	C 18:0	2.80
Oleic acid	C18:1	64.15
Linoleic acid	C18:2	17.92
Linilenic acid	C 18:3	1.86
Total saturated	–	16.07
Total unsaturated	–	83.93

Test procedure

The oxidation stability of the SOME with different antioxidants in four different proportions is identified using Rancimat Instrument. Performance and emission test is conducted in a Kirloskar SV1 engine, by using diesel, 20% of biodiesel with 80% diesel (B20), B20 with the best proportion of best natural and synthetic antioxidant additive. The line diagram of test engine shown in fig 1. Specification of the test engine and the various measuring equipment's are given in tabs. 3 and 4, respectively.

The engine is allowed to run on diesel fuel under idling condition without load for 15 minutes to warm up. The tests are carried at a constant speed of 1500 rpm. When switching over the test fuel, engine is allowed to run for 20 minutes under idling condition with the new test fuel to make sure that it has been filled in the entire fuel system and fuel line. During the experiments, the engine is allowed to run for 20 minutes to attain steady-state at each loading condition. Each experiment is conducted thrice at each load and the average data was considered for calculation to avoid human errors and to minimize the uncertainties in measurement.

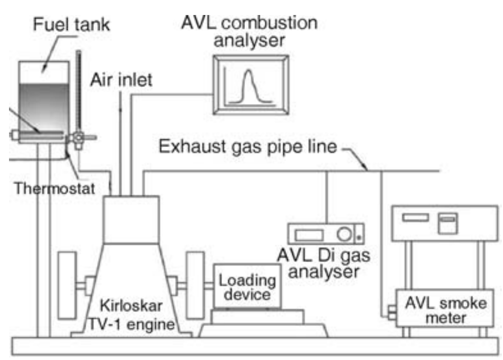

Figure 1. Schematic diagram of test set-up

Results and discussions

Oxidation stability of SOME

Oxidation stability of SOME is determined by Rancimat equipment. The oxidation stability of the SOME did not meet the requirement of EN14214 for 6 hours, this is due to the presence of more volume of unsaturated fatty acids in the SOME. The presence of natural antioxidant in vegetable oil, tocopherol is also a factor influencing the oxidation stability of the biodiesel. Improvement of the oxidation stability up to the required mark, antioxidant additives are mixed with the SOME. Six different antioxidant additives are considered in this study. Three synthetic antioxidants PY, PG, and BHA are selected based on the quality, suitability, and cost

Table 3. Specification of test engine

Make and model	Kirloskar SV1
Type	Single cylinder, 4 stroke, DI, water cooled, Diesel engine
Power, [hp]	5.7
Bore, [mm]	87.5
Stroke length, [mm]	110
Compression ratio	18:1
Injection pressure	220 bar
Load type	Eddy current dynamometer

also from the previous studies. Three natural antioxidants are LE, RE, and CA are selected. The LE is a new attempt to use as an antioxidant additive in biodiesel.

The antioxidants chosen in this study are doped in four different proportions such as 500, 1000, 1500 and 2000 ppm. The effect of antioxidant additives and its proportion on oxidation stability of SOME is shown fig. 2. From the figure it is clear that the antioxidant stability of the biodiesel increases with the increase in additive concentration in the fuel. The antioxidant activity is in the order of PY > PG > LE > BHA > RE > CA. The antioxidant activity of synthetic antioxidant depends on the number of hydroxyl (–OH) group present in the antioxidants. The PY and PG contains three –OH in their aromatic ring while the BHA contains only one –OH in their structure. The hydroxyl group is very active and hydrogen is abstracted from it and donated to oxidize the free radicals. The resulting antioxidant is a very stable radical which will further reacts with the free radical of the fatty acid to suppress the oxidation. Among the natural antioxidants CA possess very low antioxidant ability and LE possess the higher antioxidant capability. The addition of LE increases the oxidation stability of the biodiesel; it is due to the presence of carotenoid in the LE, which is a good anti-oxidant in suppressing the auto oxidation of fatty acids.

Table 4. Details of instruments used

Instruments	Make and model	Range	Accuracy	Uncertainty [%]
Gas analyzer	AVL, digas-444	CO 0-20% CO_2 0-20% HC 0-10,000 ppm NO_x 0-5000 ppm	±0.01% ±0.01% ±20 ppm ±10 ppm	±3% ±3% ±2 ±2
Smoke meter	AVL-437	0-100 HSU	±0.1 HSU	±1
Load cel	–	0-50 kgf	±0.1 kgf	±1
Pressure pickup	PCB piezotronics, S111A22	0-500 psi	±0.01 psi	±1
Crank angle encoder	–	–	±1°	±1
Temperature sensor	K-type	0-900 °C	±1 °C	±1
Speed sensor	–	0-10,000 rpm	±10 rpm	±1

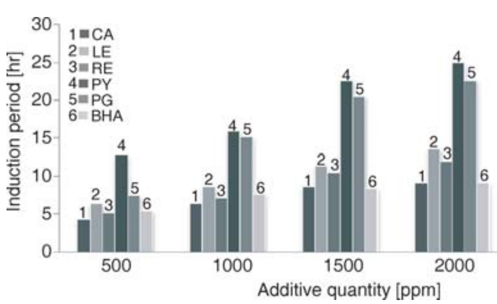

Figure 2. Variation of oxidation stability with additive proportion

Carbon monoxide emission

The CO emission highly depends on the combustion efficiency of the engine and fuel chemistry. The CO emission indicates the efficiency of fuel to get burned inside the engine cylinder.

The incomplete combustion of the fuel due to deficiency of oxygen for combustion, cold engine, and poor quality of the fuel are the reason for CO emission. Variation of CO emission for mineral diesel, B20, B20 with 2000 ppm of LE (B20 + LE) and B20 with 2000 ppm of PY (B20 + PY) is shown in fig. 3. Figure shows that the CO emission of B20 fuel is considerably reduced in all load condition. This is due to the presence of oxygen in the SOME and higher cetane number of the fuel, which reduces the ignition delay and allows the products of combustion to be inside the high pressure and temperature region which would in turn converts the intermittent products of combustion CO into CO_2. Additives have a slighter effect on CO emission. Addition of LE results slighter increase in CO emission due to the poor combustion property of the carotenoid present in the LE. The PY does not have any considerable effect on CO emission of B20.

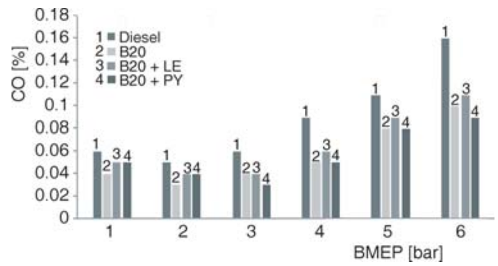

Figure 3. Variation of CO with BMEP

Hydrocarbon emission

Variation of HC emission of various fuels is shown in fig. 4. Diesel engine fuel composes of HC. The HC which does not take part in the combustion process will be coming through the tail pipe as a HC emission. The HC emission of SOME is lower than the diesel due to the presence of oxygen and better combustion properties of the B20. Additives do not have any significant impact on the HC emission characteristics of the engine.

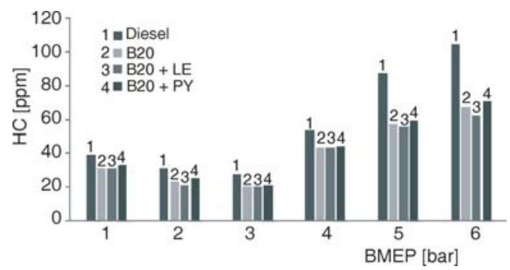

Figure 4. Variation of HC with BMEP

Smoke

Variation of smoke with BMEP is shown in fig. 5. The B20 blend of SOME has the slightly lower smoke emission comparing to the diesel. Addition of LE with B20 further reduces the smoke emission because of the smoke suppressing characteristics of the LE. Addition of LE results in 5% reduction in smoke of B20 at full load. Smoke emission of the fuel is in the order of diesel > B20PY > B20 > B20LE.

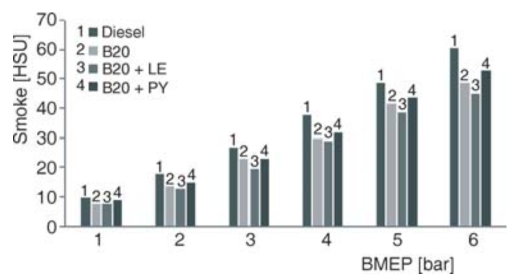

Figure 5. Variation of smoke with BMEP

Oxides of nitrogen emission

High flame temperature, higher peak pressure inside the combustion chamber, nitrogen content of parent fuel and residence time of the fuel inside the combustion chamber are the major reason for NO_x emission of a Diesel engine. The variation of NO_x with BMEP is shown in fig. 6. The SOME contains oxygen as an integrated part of the fuel results in the better combustion which

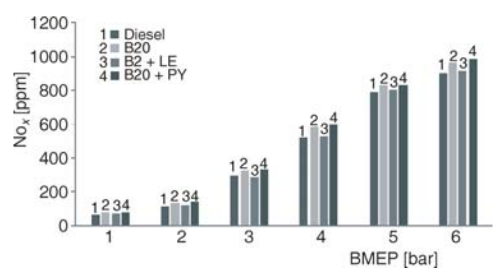

Figure 6. Variation of NO_x with BMEP

will increases the NO_x emission of SOME. Higher bulk modulus of the SOME slightly advances the fuel injection timing, increases the residence timing of the fuel inside the combustion chamber increases the NO_x emission. Use of LE has a considerable effect on the NO_x emission of the B20, there is about 5% reduction in NO_x emission while using LE comparing to B20 at full load.

Conclusions

The following conclusions are drawn from the experimental study.

- B20 blend of SOME can be used as a fuel in a Diesel engine without any modification; the oxidation stability of the fuel is lower than the required level due to the presence of higher unsaturated fatty acids.
- Addition of synthetic antioxidant and natural antioxidant has increased the oxidation stability of the fuel to the required level.
- PY is found to be the best antioxidant among the synthetic antioxidant, while LE is best among the natural antioxidant.
- From the emission test it is found that B20 has better emission characteristics comparing to diesel except NO_x, the addition of LE slightly reduces the NO_x emission of B20 SOME and appreciably suppresses smoke emission level.

Acronyms

B20 – 20% biodiesel with 80% diesel
BMEP – brake mean effective pressure
BHA – butylated hydroxyl anisole
CA – citric acid
DI – direct injection
HSU – Hartridge smoke unit
LE – leaf extract
PY – pyrogallol
PG – propyl gallate
ppm – parts per million
RE – rosemary extract
SOME – sapota oil methyl ester

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