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Evaluation of Soya Bio-Diesel as a Gas Turbine Fuel

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Abstract: In the recent past, the crude oil prices have increased immensely as the fossil fuels are depleting, bio-diesel has emerged as an alternative fuel for the petroleum. In this context the use of bio-diesel in the gas turbine seems a solution for power generation problems and their environmental concerns. Vegetable oils, due to their agricultural origin, are able to reduce net carbon dioxide emissions to the atmosphere. However, there are several operational and durability problems which may arise in using straight vegetable oils, which are because of their higher viscosity and low volatility compared to mineral diesel fuel. Bio-fuels, an alternative fuels are having environmental benefit as; they are made from renewable sources. It can be blended in any proportion with mineral Diesel. Many performance and emission tests are being carried out in reciprocating diesel engines that use bio fuel but there are very few tests has been done on gas turbine engines. The gas turbine combustion is steady flame combustion. This feature creates the wide range for the different alternative fuels for clean combustion in the gas turbine, such as natural gas, petroleum distillates, pyrolysis wood gas, biogas of methanisation, *bio-diesel* etc. The present work is an analysis of the Soya bio-diesel production process i.e. trans-esterification, the different parameters affecting on trans-esterification. The different physical and chemical properties of this bio-diesel and diesel has been determined and compared to establish the suitability of the bio-diesel in the gas turbine. An analysis on High Performance Liquid Chromatography (HPLC) has been done to find out the composition of the different fatty acid esters. The effect of these fatty acids on the property of the bio-diesel has also been explained such as viscosity, heat of combustion, cetane No, cold flow properties, lubricity and oxidative stability etc. This will also help us to select best suited bio-diesel for the gas turbine.

Key words: Gas turbine · Bio-fuel · Alternative fuels · Emission · HPLC Chromatograph · Fatty Acids · Trans-esterification

INTRODUCTION

There is a steep rise in the demand of petroleum products in the world and the petroleum reserves are limited in nature. Hence, efforts are under way in many countries, including India, to search for suitable alternative fuels that are environment friendly. Among the different possible sources, fuels derived from triglycerides (vegetable oils/animal fats) also present a promising alternative to substitute diesel fuels. It is biodegradable, non-toxic and possesses low emission properties, also, the uses of this bio-fuel is environmentally beneficial. It has the potential to reduce the level of pollution and the level of global warming.

Chemically, it is referred to as the mono-alkyl-esters of long-chain-fatty acids derived from renewable lipid sources. It is the name for a variety of ester based oxygenated fuel from renewable biological sources. So, it can be considered as a renewable and practically inexhaustible source of energy. Its chemical and physical properties closely resemble those of the petroleum diesel fuel. The advantage of using bio-diesel is its biodegradability and given that all the organic carbon present is photosynthetic in origin, it does not contribute to a rise in the level of carbon dioxide in the atmosphere and consequently to the greenhouse effect [1]. It has reasonable high cetane number and hence possesses less knocking tendency. Personal safety is

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also improved as flash point is about 100°C higher than that of diesel).

It is derived from vegetable oils by modifying their molecular structure through a trans-esterification process. Trans-esterification involves a reaction in a triglyceride and alcohol in presence of a catalyst to produce glycerol and ester.

The use of vegetable oil based fuels is not a recent development, Rudolf Diesel, the inventor of diesel engine, used peanut oil as a fuel for his diesel engine at the world exhibition at Paris in 1900. But, subsequently use of vegetable oils got decreased due to advent of cheap petroleum based fuels. Depending upon climate and soil conditions, different nations are looking into different vegetable oils for diesel fuels. For example, Soya bean oil in the United States, rapeseed and sunflower oils in Europe, palm oil in Southeast Asia (mainly Malaysia and Indonesia) and coconut oil in The Philippines are being considered as substitutes for diesel fuels.

The characteristics of bio-diesel are close to diesel fuels and therefore bio-diesel becomes a strong candidate to replace the diesel fuels. The conversion of triglycerides into methyl or ethyl esters through the trans-esterification process reduces the molecular weight to one-third that of the triglyceride reduces the viscosity by a factor of about eight and increases the volatility marginally. Bio-diesel has viscosity close to diesel fuels. These esters contain 10 to 11% oxygen by weight, which may encourage more combustion than hydrocarbon-based diesel fuels. The cetane number of bio-diesel is around 50. Bio-diesel has lower volumetric heating values (about 12%) than diesel fuels but has a high cetane number and flash point. The high flash point attributes to its lower volatility characteristics.

There is a recent regulation, which has restricted sulfur content in diesel fuel, which in turn has reduced the lubricity in diesel. The bio-diesel addition in diesel blends is an interesting option to enhance the engine performance (higher cetane number) and restoring its lubricity. In addition to this, the use of bio-diesel has a beneficial impact on the environment, since it decreases the emissions of CO, SO2, unburned hydrocarbons, poly aromatic hydrocarbons (PAHs) and particulate matter.

Gas turbine driven co-generation plants can be located close to energy consumption sites, which can produce their own fuel. Since gas turbines are available in large power range, they are well suited for this application. In addition, using bio-diesel for power generation will reduce the consumption of fossil fuels. However, information regarding the use of bio-diesel in gas turbines is limited.

There exists a need to build a knowledge base relating to bio-diesel so that informed decisions by power producers can be made. Before bio-diesel can be used on a commercial basis, the technical feasibility of firing gas turbines with bio-diesel needs to be assessed. The scope of work included here, is to compare the properties of bio-diesel with diesel. For this purpose all the characteristics of soya bio-diesel and diesel have been analyzed on HPLC (High performance liquid chromatography) to find out best suited fatty acid. It will also help to select the source of bio-diesel for gas turbine applications.

Trans-Esterification: Trans-esterification (also called alcoholysis) is the reaction of a vegetable oil with an alcohol to form esters and glycerol. A catalyst is used to improve the reaction rate and yield. Excess alcohol is used to shift the equilibrium toward the product because of reversible nature of reaction [2]. The triglycerides are converted step wise to di-glycerides, mono glyceride and finally glycerol. In trans-esterification method we can use different catalyst. When NaOH or KOH, catalyst mixed with alcohol, the actual catalysts, alkoxide group is formed. For an alkali catalyzed trans-esterification, the alcohol must be substantially anhydrous, because water makes the reaction partially change to saponification, which produces soap [3].

If methanol is used in the above reaction, it is termed methanolysis. Methanol is generally preferred due to its low cost and easy availability. The reaction of triglyceride with methanol is represented by the general equation.

$$\text{Triglyceride} + \text{ROH} \underset{\rightleftarrows}{\text{catalyst}} \text{diglyceride} + \text{R'COOR}$$

$$\text{Diglyceride} + \text{ROH} \underset{\rightleftarrows}{\text{catalyst}} \text{monoglyceride} + \text{R''COOR}$$

$$\text{monoglyceride} + \text{ROH} \underset{\rightleftarrows}{\text{catalyst}} \text{glycerol} + \text{R'''COOR}$$

Here three consecutive and reversible reactions are believed to occur. The first step is the conversion of triglycerides to di-glycerides, followed by the conversion of di-glycerides to mono-glycerides and of mono-glycerides to glycerol, yielding one methyl ester molecule from each glyceride at each step. Hence from one triglyceride, three esters are formed. Here the fatty acid methyl esters (known as bio-diesel) are attractive as alternative diesel fuels.

This process preferably should be used for the FFA (Free fatty acids) level up to 2% [4]. Here the FFA's will remove from the process stream as soap and considered waste. This process reduces the viscosity of triglycerides without affecting the calorific value of the original fuel.

Therefore fuel atomization, combustion and exhaust emissions display better results after trans-esterification. Vegetable oils with high FFA can not be trans-esterified to bio-diesel with base catalysts. The base catalyst will react with the free fatty acid and form the soap which will prevent the separation of bio-diesel (mono esters) and glycerin. By using acid catalysts, bio-diesel could be produced from high FFA oils. The acid catalyzed reaction of the FFA to monoesters was faster than the reaction of triglycerides to monoesters [5]. Acid catalysts appear to effectively convert FFA to esters. So acid esterification followed by base esterification to be the mechanism to produce bio-diesel from high FFA oils [6].

Procedures Followed: In the present work soya oil has been used as a raw material for the production of bio-diesel. The experiment was conducted in the laboratory, the experimental setup comprised of a magnetic stirrer / mechanical stirrer, heating device and a 750 ml glass flask with air tights cap and a water cooled condenser that returned any vaporized methanol to the reacting mixture.

The FFA value of the oil is determined by the titration method. The FFA value of the oil is about half of the acid value of the oil. The acid value of the oil was 0.06 mg KOH/g.

The oil is first heated on the hot plate at about 70-90°C for about 10 minutes, as the water particles present in the oil has to be removed because every molecule of water present in the oil destroys a molecule of catalyst.

In another flask methanol about 200 ml/ kg of vegetable oil is taken, keeping the molar ratio of methanol to oil at about 6:1. The 1% (w/w of oil) KOH is added in this methanol and heated the methanol & KOH mixture at about 40-50°C. Here due to reaction potassium methoxide will form. This potassium methoxide will added in the preheated vegetable oil, the temperature of the oil maintained constant at about 60°C, below the boiling point of the methanol and the stirring rate is maintained at about 600 rpm. This process continued for about 1 hour. The methanol reacts with the fatty acids and transforms it into the bio-diesel and glycerol. After the completion of the process, the composition is taken in to separator and allows the composition to be settled down. This mixture contains triglycerides, di-glycerides, mono-glycerides, glycerol, alcohol and catalyst in varying concentrations. After separation upper bio-diesel was washed with hot distilled water (70-80°C) till the washing remains natural. The moisture was removed from bio-diesel by drying at 90-100°C [7]. The optimized method of producing bio-diesel is shown in Table 1.

Table 1: Optimized parameters for the trans-esterification of Soya Oil

Parameters	
Soya oil	250 gm (density 0.924)
Methanol(molar ratio 6:1 w.r.t.oil)	75 ml (density 0.7918) (232 gm/ 293 ml per kg of oil)
Temperature	55-60°C,
KOH (1%)	2.5 gm
Time Period	60 min
Stirring RPM	600

The most important variables that influence trans-esterification reaction time and conversion are [8]:

- Free fatty acid and moisture;
- Reaction temperature;
- Alcohol to oil ratio;
- Catalyst ;
- Stirring RPM;
- Reactants.

Free Fatty Acid and Moisture: The free fatty acid and moisture content are important parameters for successfully complete the vegetable oil trans-esterification process. For base catalyzed reaction to complete; a free fatty acid (FFA) value should be lower than 2%. The higher the acidity of the oil, smaller is the conversion efficiency. The free fatty acids would be lost as soap due to reaction with the base catalyst. For the oil having higher FFA, two stage esterification processes should be opted. Firstly, acid catalyzed esterification to convert the free fatty acids into fatty acid methyl esters (bio-diesel) and then base trans-esterification will give a higher yield.

Reaction Temperature: Generally, the reaction is conducted close to the boiling point of methanol (60 to 70°C) at atmospheric pressure. The maximum yield of esters occurs at temperatures ranging from 60 to 80°C at a molar ratio (alcohol to oil) of 6:1.

Alcohol to Oil Ratio: Another important variable affecting the yield of ester is the molar ratio of alcohol to vegetable oil. The stoichiometry of the trans-esterification reaction requires 3 mol of alcohol per mole of triglyceride to yield 3 mol of fatty esters and 1 mol of glycerol. To shift the trans-esterification reaction to the right, it is necessary to use a large excess of alcohol. When 100% excess methanol is used, the reaction rate is at its highest. A molar ratio of 6:1 is normally used. However, higher molar ratio of alcohol to vegetable oil interferes in the separation of glycerol.

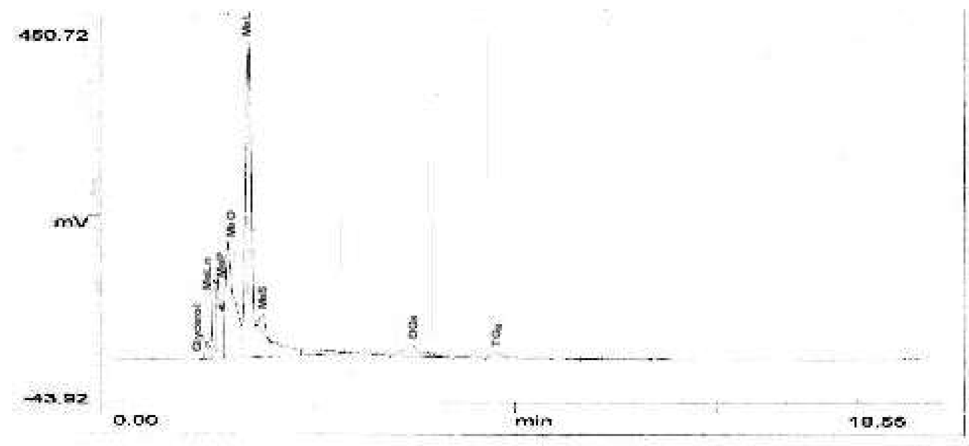

Fig. 1: HPLC Chromatograph of Soya Oil Methyl Ester

Table 2: Fatty acid composition of Soya Oil Methyl Ester

Fatty Acids	Formula	Structure	Wt (%)	Molecular weight
Palmitic Acid	$C_{16}H_{32}O_2$	$C_{16:0}$	13.9	256.4
Stearic Acid	$C_{18}H_{36}O_2$	$C_{18:0}$	2.1	284.4
Oleic Acid	$C_{18}H_{34}O_2$	$C_{18:1}$	23.2	282.3
Linoleic Acid	$C_{18}H_{32}O_2$	$C_{18:2}$	56.2	280.2
Linolenic Acid	$C_{18}H_{30}O_2$	$C_{18:3}$	4.3	278.2

Table 3: Fuel properties of Soya Oil Methyl Ester and diesel fuel

Property	Unit	IS: 15607 Specification for Bio-diesel	Soya oil Methyl Ester	Diesel	Test Methods
Density	.gm/ml	0.87-0.9	0.90	0.8274	IS 1448
Viscosity	cst	3.5 – 5	4.511	1.7283	ASTM D 445
Kinetic viscosity	.mm^2/s	1.9 – 6.0	5	2.089	ASTM D 445/ ISO 3104
Acid value	.mg KOH/g	<0.5	0.2503	0.35	ASTM D 974
Safonication value	.mg KOH/g	….	704	…	ASTM D 974
Calorific value	MJ/kg	------	39	43	Bomb calorimeter
Flash point	°C	>120	178	38	ASTM D 93
Cloud point	°C	--	4	-6	ASTM D 2500
Pour point	°C	---	0	-16	ASTM D 2500
Freezing point	°C	---	0	….	

Catalyst: Alkali metal alkoxides are the most effective trans-esterification catalyst. The alkaline catalyst concentration in the range of 0.5 to 1% by weight yields 94 to 99% conversion of vegetable oil into esters. Both, excess as well as insufficient amount of catalyst may cause soap formation.

Stirring rpm: In the trans-esterification reaction, the reactants initially form a two-phase liquid system. The reaction is diffusion-controlled. As methyl esters are formed, they act as a solvent for the reactants and a single-phase system is formed. After that, mixing becomes insignificant.

Reactants: Impurities present in the oil also affect yields. The free fatty acids in the original oils interfere with the catalyst.

Analysis of Bio-Diesel: The composition of the bio-diesel was analyzed using high performance liquid chromatography (HPLC) with FID detector (flame ionization detector) (model type MERCK Hitachi UV detector L7400). A C-18 column (Merck column) having Mobile phase- Acetonitrile with flow rate 1.2 ml/min. solution preparation was done with cyclo-hexane, used as a carrier solvent. The sample injection was 20 μl. Fig. 1 shows the HPLC chromatogram of Soya oil methyl ester. Comparing this chromatogram with the standard one, peak identification has been done. This method describes the determination of overall contents of fatty acid methyl esters and mono-, di- and tri-glycerides by isocratic liquid chromatography using a density detector with UV detection at 205 nm [5]. The separation was achieved by silica column. So, this is also useful for the study of degree of conversion of the trans-esterification reaction. This can be done by comparing the sum of the areas of the peaks of methyl esters and triglycerides. The fatty acid methyl ester composition is given in Table 2. The sensitivity of UV detection is different for individual triglycerides [5]. The presence of even small amounts of the original unconverted oil compounds in bio-diesel can cause problems in gas turbine and results in increased production of hazardous emissions [9]. Then the weighted average of molecular weight = 275.54 gm/mol, so the molar mass of Soya oil = 826.62 gm/mol. Molar weight of methanol =32 gm/mol.

Comparison of Properties of Biodiesel with Diesel Fuel: Bio-diesel fuel properties depended upon the structure and type of the fatty acid esters present [10]. Palmitic acid and stearic acid present in the oil are saturated acids where as other fatty acids presents are unsaturated acids. Saturated fatty acid esters increase the cloud point, cetane number and stability.

The physical and chemical properties of the bio-diesel were evaluated. The fuel properties of Soya oil methyl ester and Soya oil and diesel were determined and given in Table 3.

RESULT AND DISCUSSION

The trans-esterification reaction of the oil converts it to bio-diesel fuel corresponding in its fatty acid profiles. So, the bio-diesel is a mixture of fatty esters, which are contributing to the properties of the fuel. Both the fatty acid chain length and the type of alcohol used influences on the properties of the bio-diesel fuel. Structural features that influence the properties of bio-diesel are chain length, degree of un-saturation and branching of chain. The main fuel properties which are influenced by the fatty acid profile and are viscosity, lubricity, ignition quality, heat of combustion, cetane number, exhaust emission, cold flow and oxidative stability [11].

Viscosity: Viscosity affects the atomization of the fuel in the combustion chamber. Viscosity increases with chain length and with increasing degree of saturation. Viscosity of ethyl esters is slightly higher than that of methyl esters. Double bond configuration gives lower viscosity. This may be a approach for improving low-temperature properties without affecting other fuel properties.

Heat of Combustion: Heat of combustion is the property of the fuel which indicates the suitability of fatty compounds as diesel fuel. The heats of combustion of fatty esters and tri-glyceroids are in the same range. Heat of combustion increases with chain length.

Cetane No: Cetane No is a prime indicator of fuel quality. The Cetane No of a diesel fuel is related to the ignition delay time, shorter the ignition delay time, the higher the Cetane No and vice versa. Cetane No decreases with decreasing chain length and increasing branching. For conventional diesel fuel, higher Cetane No is correlated with reduced nitrogen oxides (NOx) exhaust emissions. The NOx emission is slightly higher with the bio-diesel, even though the bio-diesel is having higher cetane no as compared to diesel fuel. NOx exhaust emissions increases with increasing unsaturation and decreasing chain length.

Cold Flow Properties: Poor low temperature flow properties, means high cloud points and pour points. The cloud point, which usually occurs at a higher temperature than the pour point, is the temperature at which a liquid fatty material becomes cloudy due to formation of crystals and solidification of saturates. Solids and crystals rapidly grow and clog fuel lines and filters which cause major operational problems. With decreasing temperature, more solids form and it approaches to the pour point, the lowest temperature at which it will still flow. Saturated fatty compounds have significantly higher melting points than unsaturated fatty compounds and in a mixture they crystallize at higher temperature than the unsaturated.

Lubricity: Phenols and polyaromatic compounds are the species imparting lubricity to diesel fuels. Fatty acids possess excellent lubricating properties. There is no significant effect of bio-diesel fatty acid composition on lubricity. Unsaturated acids provide better lubricity than saturated species. Ethyl esters have improved lubricity compare to the methyl esters.

Oxidative Stability: When the condition of bio-diesel changes with time during storage. It is mainly due to the autoxidation. This autoxidation is due to the presence of double bonds in the chains of many fatty compounds. The autoxidation of unsaturated fatty compounds proceeds with different rates depending on the number and position of double bonds.

CONCLUSION

After comparing the properties of Soya bio-diesel with diesel fuel, soya bio-diesel may be considered as a potential substitute for gas turbine fuel.

From the above discussion it shows that the fuel properties of bio-diesel are strongly influenced by the properties of the individual fatty esters in bio-diesel. Both fatty acid and alcohol are having influence on bio-diesel fuel properties such as cetane number, cold flow, oxidative stability, viscosity and lubricity. Generally, cetane number, heat of combustion, melting point and viscosity of fatty compounds increase with increasing chain length and decrease with increasing unsaturation. Therefore to enrich the bio-diesel fuel with desirable properties, certain fatty acids, possibly oleic acid, must be there to exhibits a combination of improved fuel properties.

The development of additives is needed for improving cold flow properties, material compatibility & prevention of oxidation in storage. Further there is a need to reduce the production cost and ensure its availability & quality. For this purpose there is a need to develop less expensive quality test, testing of bio-diesel by HPLC be an option in this regard.

REFERENCES

1. Singh, S.P. and Dipti Singh, 2010. Bio-diesel production through the use of different sources and characterization of oils and their esters as the substitute of diesel: A review. Renewable and Sustainable Energy Reviews, 14: 200-216.
2. Baiju, B., L.M. Das and M.K.G. Babu, 2008. Engine Performance And Emission Studies Using Rubber Seed Bio-diesel And Karanja Bio-diesel As A Fuel In A Compression Ignition Engine. Renewable Energy Asia 2008, IIT Delhi.
3. Vyas, A.P., Jaswant L. Verma and N. Subramaniyam, 2010. A Review on FAME Production Process. Fuel, 89: 2-9.
4. Sharma, Y.C., B. Singh and S.N. Upadhyay, 2008. Advancements in development and characterization of bio-diesel: A review. Fuel, 87: 2355-2373.
5. Meher, L.C., D. Vidya Sagar and S.N. Naik, 2006. Technical aspects of bio-diesel production by trans-esterification a Review. Renewable and Sustainable Energy Reviews, 10: 248-268.
6. Raheman, H. and P.C. Jena, 2008. Bio-diesel production process for vegetable oils with high free fatty acids and their mixtures. Renewable Energy Asia 2008, IIT Delhi.
7. Kalbande, S.R. and Subhash D. Vikhe, 2008. Jatropha and Karanj Bio-fuel: An alternate fuel for diesel engine. Asian Research Publishing Network (ARPN). 3(1): 7-13.
8. Ma, F. and M.A. Hanna, 1979. Bio-diesel production: A review. Bio-source Technology, 70: 1-15.
9. Holcapek, M., P. Jandera, J. Fischer and B. Prokes,1999. Analytical monitoring of the production of bio-diesel by high performance liquid chromatography with various detection methods. Journal of Chromatography A, 858: 13-31.
10. Baiju, B., M.K. Naik and L.M. Das, 2009. A comparative evaluation of compression ignition engine characteristics using methyl and ethyl esters of Karanja oil. Renewable Energy, 34: 1616-1621.
11. Knote, G., 0000. Dependence of bio-diesel fuel properties on the structure of fatty acid alkyl esters. Fuel Processing Technology, 86: 1059–1070.