EMISSION ANALYSIS ON THE INFLUENCE OF FERROFLUID ON RICE BRAN BIODIESEL

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ABSTRACT

Increase in NO_x emission is one of the important drawbacks for using biodiesel as an alternative for petroleum diesel. Several studies had been carried out to reduce the NO_x emissions level in biodiesel. The present work is the result of an attempt wherein ferrofluid is added to rice bran oil methyl ester in the way of analyzing its effects on emission characteristics. Magnetite concentrate is exothermic and is known for its characteristics of releasing copious heat at higher temperatures. Nanofluid using magnetite was synthesized by reacting Iron II ($FeCl_2$) and Iron III ($FeCl_3$) in an aqueous ammonia solution to form Magnetite Fe_3O_4 (Ferro fluid). Release of heat by magnetite during the combustion process would counterbalance the conventional limitations related with biodiesel such as increased delay period, inferior combustion rate and higher NOx emissions etc. Experiments were conducted with Rice Bran Oil Methyl Ester (RBOME) and Rice Bran Oil Methyl Ester with addition of ferrofluid (RBOMEF) and are compared with petroleum diesel. RBOMEF was prepared comprising 97.7% biodiesel, 2% magnetite based ferrofluid and 0.3 % surfactant by volume was used in a Compression Ignition engine. The experimental analysis found a decrease in HC, CO and NOx emissions of 10.8%, 9.1% and 8.49% respectively.

Key words: Ferrofluid, Nanofluid, Rice bran oil, Emissions.

1. INTRODUCTION

Biodiesel is a promising alternative fuel over diesel as it emits lesser quantity of carbon monoxide, hydrocarbon and particulate matter. Conversely, Biodiesel fuelled engine also emits significant measure of nitric oxide (NO_x) emission when compared with petroleum diesel [1 &2]. The possible reason for increase in NO_x emission is due to drop of engine power when fuelled with biodiesel [3]. There are many techniques followed to reduce NO_x emissions when fuelled with biodiesel. The concept of using water based nanofluids to reduce NO_x emission in compression ignition engines is an active area of research. Addition of water based nanoparticles in liquid fuels acts as a catalyst to promote the combustion and result in complete burning of fuels. [4]. Studies have shown that by adding water based nanofluid to biodiesel results in reduction in heat flux, thermal loading and metal temperature of combustion chamber components. Water based nanofluids alters the chemical composition of fuel which has encouraging impact on emission characteristics [5]. Nanosized energetic metals have enviable combustion characteristics such as high heat of combustion and fast energy release rates. Further, nanosized particles can be dispersed into high-temperature zones for direct oxidation reaction, rapid energy release, and enhanced propulsive performance with increased density impulse [6]. Many studies have been conducted to explore the impact of adding nanoparticles to fluid properties. Results revealed an enhancement in thermal conductivity, mass diffusivity and radiative heat transfer of fuel with addition of nanofluid [7].

Nanoparticles with a high surface area to volume ratio increase the contact among fuel and oxidizer and reduce various emissions [8]. Nanoparticles affect the time scale of chemical reactions and result in reduced delay period and emissions [9]. Moreover, it has been experimentally found that by adding nanoparticles to the fuel increases the ignition probability of the mixture consequently reducing emissions [10].This present work employs rice bran oil methyl ester as biodiesel. The most important reason for choosing Rice bran oil as a fuel is based on the selection of low-cost feed stock with high value added by- products. In addition, the chemical properties of rice bran are closer to that of petroleum diesel. The properties of transesterifed rice bran methyl ester fall well within the acceptable limit of ASTM standards. Rice bran is obtained as a by-product during polishing of rice from its kernel. Rice bran is dried to remove the water present in it. It is then fed to oil extractor which extracts oil by crushing. The oil obtained is classified as defatted and crude rice bran oil. Defatted rice bran oil with 16-20% of protein content is used for edible purpose. Crude rice bran oil with 23-24% free fatty acid is used as the main source of biodiesel production process. Crude rice bran oil is converted into its rice bran methyl ester by conventional transesterification process. Many studies have proved that the rice bran methyl ester when blended with diesel or used directly in engine has resulted in reduction in CO, HC and smoke emissions. Gagendeep singh [11] used rice bran oil and ethanol blend in a single cylinder direct injection diesel engine. He found reduction in CO, HC and smoke

emissions citing excess amount of oxygen present in rice bran oil as the cause. Narshima and Rajesh[12] studied the emission characteristics of rice bran oil in single cylinder diesel engine. He too found reduction CO and HC with increase in NO_x emissions indicating the availability of excess oxygen present in the fuel as the reason. Senthil kumar and Manimaran [13] used rice bran oil as a biodiesel in diesel engine and found significant reduction in CO, HC, NO_x and Smoke emissions owing to higher oxygen content and improved combustion. In recent times, adding nanoparticles to liquid fuel is subjected to a lot of investigation. Arul Mozhi Selvan [6] studied the impact of cerium oxide nano particles of size 32 nm with a dosing level of 25 ppm using diesterol in diesel engine. They found a significant reduction in NO_x emissions. Shafii[9] investigated the effect of water based ferrofluid with a size of 10 nm and a concentration of 0%, 0.4%, and 0.8% by volume in diesel fuel to views its effects on performance and emissions characteristics. It was found that the magnetic particles improves the combustion characteristics and reduce NO_x emissions. Kao [14] analyzed the effect of aqueous aluminum nanofluid in single cylinder diesel engine fuelled with diesel. By adding 40-60 nm of aluminum nanofluid to diesel, 4.1% of smoke emissions and 6.2% of NO_x emissions were found. This was attributed to increase in chaotic movements and reducing in settling velocity of the particles which aids combustions. However, the impact on addition of ferrofluid to rice bran oil methyl ester has never been experimented.

The present experimental study is aimed to examine the effect of ferrofluid on the various properties of rice bran methyl ester and also its influence on emissions characteristics. Experiments were conducted with RBOME and RBOMEF and are compared with petroleum diesel. RBOMEF was prepared comprising 98.7% biodiesel (Rice bran oil methyl ester), 1% magnetite based ferrofluid and 0.3% surfactant by volume was used in a CI engine. The experimental analysis revealed a decrease in HC, CO and NO_x emissions of 10.8%, 9.1% and 8.49% respectively.

2. EXPERIMENTAL MATERIAL & METHODS

2.1 Materials and Reagents
2.1.1 RICE BRAN OIL

Rice bran oil is extracted from the hard outer brown layer of rice after chaff (rice husk). Rice bran is the by-product of rice milling that contains 15-23% lipids which cannot be used for edible purposes and hence it is could be used as potential alternative fuel. Usage of low-priced, non-edible feedstock could possibly reduce the cost involved in production process. The alcohol used in this work is methanol with 99.5% purity. Potassium Hydroxide (98.5% purity) is used as catalyst for transesterification process.

2.1.2 FERROFLUID

The ferrofluid used in this study is water-based. The synthesis involved the reaction between Iron II ($FeCl_2$) and Iron III ($FeCl_3$) ions in presence of aqueous ammonia solution to form magnetite (Fe_3O_4) adapting the following Eq. 1.

$$FeCl_2 + 2FeCl_3 + 8NH_3 + 4H_2O \rightarrow Fe_3O_4 + 8NH_4Cl. \qquad Eq.(1)$$
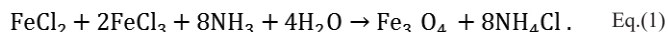
The cited procedure claims that those nano particle diameters are on the order of 10nm [11]. In addition, aqueous tri methyl ammonium hydroxide $((CH_3)_3NOH)$ solution which was used as a surfactant can surround the magnetite particles with hydroxide anions and tetra methyl ammonium cations to create electrostatic inter particle repulsion in an aqueous environment [15]. The most significant reason for using ferrofluid is that the magnetic nano particles can be collected from exhaust using magnetic billets. Furthermore, it can be easily diluted to biodiesel and as a result it can collect the benefits of water- biodiesel emulsions.

2.2 *Apparatus & procedure*
2.2.1 PREPARATION OF BASE FUEL (RBOME):

Ester was prepared by batch transesterification process in a 1000 ml glass vessel reactor equipped with a magnetic stirrer, resistance heater & 'K' type thermocouple. Suitable arrangements were provided to control reaction temperature and stirring speed. Molar ratio of 5.9:1(methanol to Rice bran oil) and catalysts of 0.51% by weight of rice bran oil was used in transesterification procedure. 700g sample of Rice bran oil in the reactor was heated till 60^0C. Measured mixture of solution containing catalysts mixed in methanol was added and mixed at a constant stirring speed of 300 rpm for 60 minutes. This ensured uniform reactivity of solution by accelerating the reaction rate. The mixture was subsequently allowed to cool in the vessel yielding two distinct layers of ester and glycerol. Ester was then separated, washed with water and dried for further investigation. The ester thus obtained following conventional procedure is referred as RBOME. Table 1. Show fatty acids compositions of rice bran oil using Gas-liquid chromatography technique.

Table 1. Fatty acids compositions of Rice bran oil.

Fatty acids	Percentage	Method
C14:0 Myristic acid	0.8%	
C16:0 Palmitic acid	21.6%	Gas-Liquid Chromatography
C18:0 Stearic acid	2.8%	
C18:1 Oleic acid	37.5%	
C18:2 Linoleic acid	35.4%	
C18:3 α-Linolenic acid	1.9%	

2.2.2 PREPARATION OF MODIFIED BASE FUEL (RBOMEF):

Copper strip corrosion test plays a very significant role in selection of dosage level limit of metal based additive to biodiesel. Fe_3O_4 (Ferrofluid) has a property to corrode the engine parts if the limit exceeds 1% by volume as listed in ASTM limit of class 1b. The measure of ferrofluid and surfactant (aqueous tetra methyl ammonium hydroxide solution) in the base fuel (RBOME) is 1% and 0.3% respectively by volume basis. The required quantity of the RBOME, ferrofluid and surfactant is measured and mixed by ultrasonic agitator with constant agitation for better mixing and homogeneous suspension. Modified base fuel was kept in a glass vessel for examination at room temperature to observe the phase change characteristics. In stability test, due to the presence of surfactant ferrofluid showed long term stability and homogeneity with Rice bran oil methyl ester; hence the modified fuel can be used reliably for engine tests. Although the modified base fuel proved encouraging results on stability and homogeneity it was used straight away after preparation to study the accurate consequence of ferrofluid on emissions characteristics of Rice bran oil methyl ester. The fuel thus obtained following above procedure is referred as RBOMEF. Details for ferrofluid are listed in Table 2.

Table 2. Details for ferrofluid.

Chemical name	Fe_3O_4
Average size of particle	10 nm
Appearance	Black
State	Liquid

2.3 Comparisons on Fuel properties of RBOME and RBOMEF:
The effect of adding ferrofluid on fuel properties such as kinematic viscosity, flash point, water content, calorific value, cetane index and density is investigated. The comparison of fuel properties between RBOME, RBOMEF
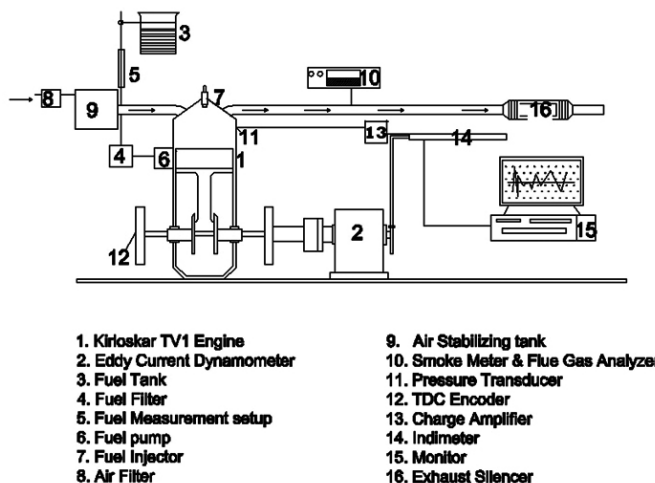
and Diesel is presented in Table 3. There is a significant change in all the properties with addition of ferrofluid. Kinematic viscosity is increased by 3.56% with addition of ferrofluid. This is due to increase in resistance between fluid layers which increases viscosity. Flash point is increased by 3°. Higher flash point is desirable for safer handling of fuel. RBOMEF is comparatively safe when compared to base fuel. Water content is increased by 0.02% with addition of ferrofluid. Since ferrofluid has considerable measure of water present in it, there is a marginal increase in water content. Other property such as cetane index, calorific value and density of RBOMEF is improved by 5.45%, 2.60% and 2.97% respectively. This is due to positive effects of ferrofluid as cited by Shafii [9].

Table 3. Properties of Diesel, RBOME and RBOMEF.

Properties	RBOME	RBOMEF	Diesel	ASTM standards
Kinematic Viscosity [cst]	6.32	6.55	4.30	ASTM D445
Flash point [^oC]	138	144	50	ASTM D93
Water content [%]	0.13	0.15	0.00	ASTM D2709
Density [gm/cc]	0.882	0.910	0.820	ASTM D4052
Calorific Value [kJ/kg]	38123	39143	42957	ASTM D240
Cetane Index	52	55	46	ASTM D976

2.4 *Engine test set-up & procedure*
Experimental analysis is carried out by means of four stroke, two cylinder, air cooled diesel engine. Table.4 shows the specification of engine. An eddy current dynamometer is coupled with engine to vary the load on engine. Eddy current dynamometers use a varying magnetic field in a coil to generate eddy currents. Magnetic field induced creates a torque which opposes the engine shaft's direction of rotation which is referred as load. The load to the engine is varied by altering the load on dynamometer by switching on or off the load resistances. Bank of electrical resistances is used to supply to load to dynamometer and is measured by means of load cell attached with arm. Load power (Load power= is calculated from measurement of voltage V and current intensity I applied. Figure 1 shows the layout of engine setup. Engine exhaust was linked to AVL444 di gas analyzer for monitoring the engine emissions. Details of gas analyzer and smoke meter are shown in Table 5. Experiment is initially conducted with diesel following RBOME and RBOMEF at different loads viz 0% to 100% insteps of 25%. In order to fix the base line all the parameters necessary for evaluating the emissions were measured. Constant engine speed of 1500 rpm was maintained at all loads and test fuels.

1. Kirloskar TV1 Engine
2. Eddy Current Dynamometer
3. Fuel Tank
4. Fuel Filter
5. Fuel Measurement setup
6. Fuel pump
7. Fuel Injector
8. Air Filter
9. Air Stabilizing tank
10. Smoke Meter & Flue Gas Analyzer
11. Pressure Transducer
12. TDC Encoder
13. Charge Amplifier
14. Indimeter
15. Monitor
16. Exhaust Silencer

Fig. 1. Layout of engine and instrumentation set up.

Table 4. Engine specifications.

Make	Kirloskar
Stroke	4
Cylinder	Two
Rated Power	4.4 kW
Rated speed	1500 rpm
Bore dia(D)	87.5 mm
Stroke(L)	110mm
Compression ratio	17.5:1
Cooling	Air cooled
Loading device	Eddy current dynamometer

Table 5. Gas analyzer and Smoke meter details

Parameters	Model	Range	Accuracy	Uncertainty
CO	AVL 444 di gas analyzer	0-10 % Volume	0.01	±3%
HC		0-20000	± 10 ppm	±2%
NOx		0-5000 ppm	± 10 ppm	±2.5%
Smoke	AVL 437 Smoke meter	0-100 % opacity	± 1% full of scale reading	±4%

2.5 Error Analysis

Equation 2 indicates the error analysis for HC emissions. Method proposed by J.P. Holman which is extensively accepted is followed to calculate error analysis for all emissions. According to his root-mean square method the uncertainty of the variable can be found by the following equation.

$$\sigma_{HC} = \left[\frac{\sum_{i=1}^{n}\left((HC)_i - \overline{(HC)}\right)^2}{n-1}\right]^{\frac{1}{2}} \qquad \text{Eq.(2)}$$

The uncertainty in Δ (HC) in hydrocarbons is calculated by Eq.(3)

$$\frac{\sigma_{HC}}{\sqrt{n}} \qquad \text{Eq.(3)}$$

Where n   =   number of HC measurements,

$\overline{HC}$ =   mean value of HC measurements,

σ_{HC} =   unbiased standard deviation for HC measurements.

By following the above equation, the error analysis of other emissions such as CO, NO_x and Smoke were analysed.

## 3   RESULTS AND DISCUSSION

To examine the consequence on adding ferrofluid the emissions such as Carbon monoxide (CO), unburned hydrocarbon (UHC), Oxides of Nitrogen (NO_x) and Smoke opacity is measured and examined. The measurements were analyzed with respect to emissions and the corresponding outcomes are detailed as follows.

3.1 Carbon monoxide (CO)

Loss of chemical energy is an outcome of CO emissions. Variation in CO emissions with load is shown in "Fig. 2". It is evident from the figure that CO emissions from RBOME and RBOMEF are lower than diesel. CO emissions from RBOME and RBOMEF were 10.1% and 12.2% lower when compared to diesel. Since the oxygen content in both the fuels are higher than diesel oxidation reaction is enhanced and thereby result in lesser CO emissions. CO emission is found to increases with increase in load for all fuels. With rise in load quantity of fuel injected is more causing lesser oxidation of CO and result in higher CO emissions. The average CO emissions from RBOMEF at all loads is 6.34% lesser than RBOME. This is due to effect of ferrofluid which undergoes catalytic oxidation reaction by providing surplus oxygen. Similar results were reported by Arul Mozhi Selvan [6] by adding nanoparticles to liquid

fuel. In addition nanofluid enhances the physical properties of fuel and result in lesser CO emissions. Further, ferrofluid undergoes catalytic oxidation reaction and improves the mixing rate of fuel with air. This result is in agreement with work done by Sadhik Basha and Lenin [5&7].
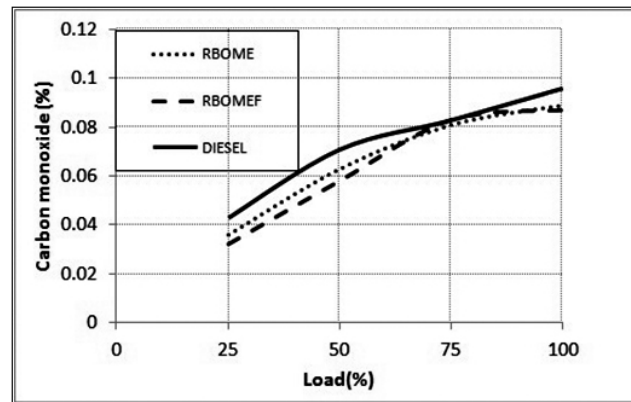
Fig. 2. Change in CO emission with loads.
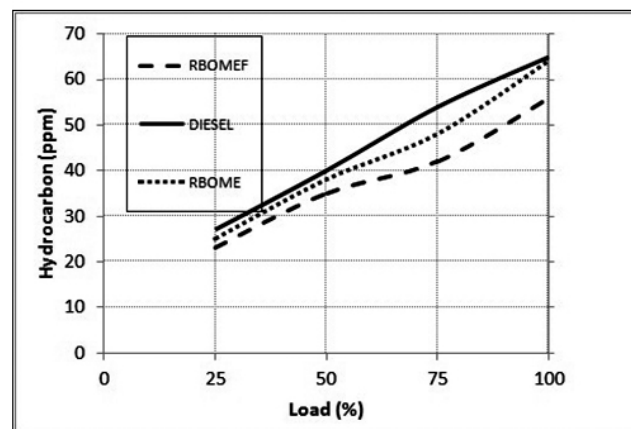
Fig. 3. Change in HC emissions with loads.

3.2 Unburned hydrocarbon (UHC)

Variation in HC emissions with load is shown in "Fig.3". The average HC emission from diesel at all loads is found to be 43.5 ppm while that from RBOME and RBOMEF were 42.7 ppm and 36.0 ppm respectively. HC emissions from RBOME and RBOMEF were 10.6% and 17.58% lower than that of diesel. This is due to higher oxygen content in both methyl ester promoting better combustion and resulting in lesser HC emission. The average HC emissions from RBOMEF at all loads is 9.1% lesser than RBOME. Nanofluid as an oxidation catalysts oxidise HC and lowers the carbon combustion activation temperature. Furthermore, nanoparticles significantly increase the ignition probability of the mixture and reduce HC emissions. Similar reduction in HC was cited on experimental work by Kannan and Patel [8 & 16].

3.3 Oxides of Nitrogen (NO$_x$)

Figure 4 shows variation in NO$_x$ emissions with load. NO$_x$ emissions from RBOME and RBOMEF were 13.5% and 16.74% higher than that of diesel. Formation of NO$_x$ depends on oxygen concentration in the fuel. Since both RBOME and RBOMEF has higher oxygen content comparing diesel, Increase in NO$_x$ is obvious. NO$_x$ emission for RBOME is 8.49% higher than RBOMEF. Ferrofluid exhibits a high catalytic activity leading to enhancement in combustion and reduction in the NO$_x$ emissions. Additionally, water in the nanofluid enhances the thermal conductivity and latent heat evaporation. This leads to reducing in NO$_x$ emissions. This result is in agreement with similar trial done by Patel [16].
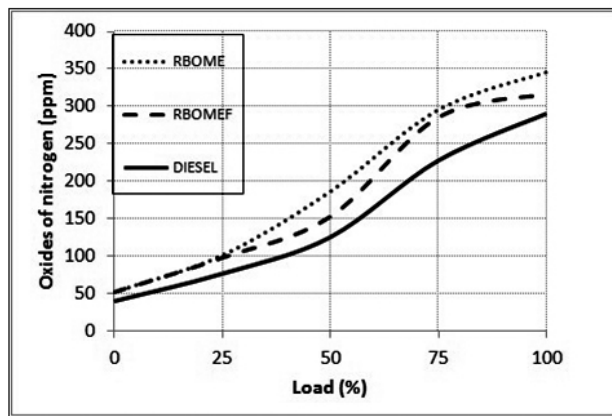

Fig. 4. Change in NOx emission with loads

3.4 Smoke opacity

Figure 5 shows exhaust smoke emission of RBOME, RBOMEF and Diesel for various loads. Smoke emission for RBOME and RBOMEF is less than diesel. This is due to higher oxygen availability in methyl esters prompting combustion rate. Smoke emission from RBOMEF is 3.85% lesser than RBOME. Addition of nanofluid to RBOME has resulted in better evaporation and improved ignition characteristics. The other reason is due to presence of surplus oxygen which acts as oxidation catalysts. This is in agreement with similar work done by Shafii and Patel [9 & 16].
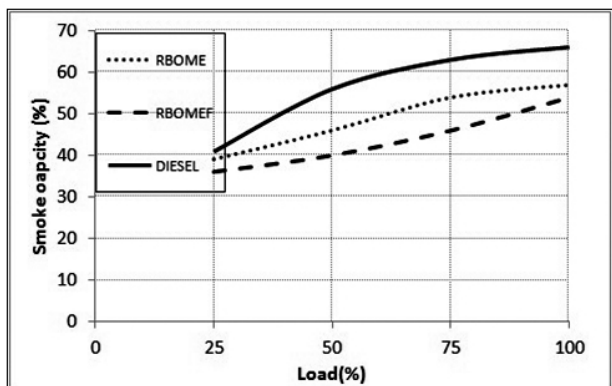

Fig. 5. Change in smoke emission with loads

4 CONCLUSIONS

Emission analysis on the influence of magnetite nanofluid on rice bran oil methyl ester is carried out in two cylinder CI engine. Addition of magnetite in nano form, to the biodiesel along with surfactant controls the eco-friendliness of biodiesel. The following are the main conclusions drawn from this work,

(1)   CO emission reduces significantly by 6.34% by adding ferrofluid to methyl ester.

(2)   HC emission reduces by 6.34% with addition of ferrofluid.

(3)   NO$_x$ drops by 8.49% by adding ferrofluid.

(4)   Smoke reduces by 3.85% by adding ferrofluid to rice bran methyl ester.

Hence addition of nanofluid to rice bran methyl ester results in superior combustion and thereby reducing emissions persisting in conventional biodiesel.

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Nomenclature

CI	Combustion ignition
RBOME	Rice bran oil methyl ester
RBOMEF	Rice bran oil methyl ester with addition of Ferrofluid
CO	Carbon monoxide
UHC	Unburned Hydrocarbon
NO_x	Nitrogen oxide