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# Influence of blend and oxide nanoparticle additive parameters on tribological attributes of Simarouba glauca biodiesel (SGME)

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#### ABSTRACT

Biodiesel blends are vital alternatives for the ecological safety. Biodiesels own friction and wear reduction properties which lead to energy economy and engine durability. In this work tribological attributes of diesel, blends of Simarouba glauca methyl ester (SGME) in diesel, with addition of nanoparticles are investigated using four ball tester. The investigations were conducted on biodiesel blends B10 (10% biodiesel in diesel), B20, B30 and diesel B0. Nanoparticles of silicon dioxide (SiO<sub>2</sub>) were dispersed in base SGME. Nanoparticles have good dispersion in the SGME as it has more percentage of oleic acid. Tribological characteristics in terms of run-in period and flash temperature parameter (FTP) were evaluated using four ball tester for the test conditions as per ASTM D 4172. The favourable combinations are 0.2 % (B30), 1 % (B10 and B20) which gave substantial reduction in run in time showing 44% decrease as compared to diesel. Also the beneficial combinations are 1 % (B10, B20 and B30) which gave significant increase in FTP showing 214% increase over diesel. A combination of abrasive and adhesive wear was evident.

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## 1. Introduction

Bio fuels demonstrate excellent lubricity compared to the diesel fuel. The biodiesel additivated with nanoparticles shows additional enhancement in lubricity with respect to pure biodiesel. Its use improves the life of engine components, particularly fuel injection equipment and high pressure fuel pumps which are lubricated by fuel itself. Lubricity of engine fuel is vital to extend durability of engine parts. It facilitates protection of the surfaces in relative motion from wear. Improved lubricity also lowers the energy consumption by minimizing friction among engine components [1,2]. The lubrication characteristics of traditional diesel fuel are very poor in contrast with the bio fuels. Accordingly, it is very noteworthy to identify different fuels to cope with such growing demands [2,3]. Many biodiesels demonstrate finer tribological behavior than that of the conventional diesels. A few indicate unsatisfactory wear properties because of corrosion and surface spoilage. This leads to non allowable harm to engine. This restricts extent of their usage which underlines tribological investigation of a variety of biodie-

\* Corresponding author. *E-mail address:* ena@amgoi.edu.in (Eknath Nivrutti Aitavade). sels and use of new additives to overcome these limitations [3]. Also some unattended biodiesels need to be investigated in this regard.Numerous researchers have employed a variety of nanoparticles to impart better tribological attributes to lubricant oils. Their use has shown highly beneficial results. The following Table 1 shows the particulars about this. It shows the nanoparticles details and the researchers who have utilized it.

The proper dispersion and percentage quantity on mass/volume base is highly important while employing the nanoparticles. The good dispersion is ascertained by ultrasonication. In the further experimentation [16] biodiesel manufacture from various seeds was reviewed and it showed Alagae,Caster,Cottonseed,Jatropha,Kar anji,Linseed,Mahua,Moringa,Nahor,Neem,Palm,Ricebran,Simar

ouba glauca, Soap nut and waste oils as upcoming seeds for biodiesel making. Simarouba glauca farming was initiated by national bureau of plant genetic resources in Orissa, India. Neglected SGME was deployed in CI engine. Brake thermal (bTH) efficiency of SGME was lower than diesel. It was inferred from the emission analysis that there was a sizeable drop in HC emissions and smoke by 22% and 33% respectively for B50 blend and 40% and 27% drop for B100. But, there was an increase of 8% and 5% NOx emission for B 100 and B50 in that order. Brake thermal (bTH) efficiencies

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Table 1

Use of nanoparticles by researchers.

Sr. No.	Nanoparticles
1.	Lanthanum Carbonate(La <sub>2</sub> CO <sub>3</sub> ) [2]
2.	Different phases of Aluminium Oxide (Al <sub>2</sub> O <sub>3</sub> ) [4]
3.	Cerium Oxide (CeO <sub>2</sub> ) and Titanium dioxide(TiO <sub>2</sub> )[5]
4.	Copper Oxide (CuO) [6,7,20]
5.	Magnesium doped Zink Oxide (ZMO) [8]
6.	Hexagonal Boron Nitride (hBN) [9]
7.	Lanthanum Oxide(La <sub>2</sub> O <sub>3</sub> ), Lanthanum Carbonate(La <sub>2</sub> CO <sub>3</sub> ) [10]
8.	Multiwall Carbon Nano Tubes (MWNT) [11]
9.	Silicon dioxide (SiO <sub>2</sub> ) [12,20]
10.	Carbon nanoparticles-amorphous carbon, graphite and grapheme
	[13,14]
11.	Hallovsite nanotubes [15]

of SGME blends and SGME were slightly lower than that of conventional diesel. Assessment of engine indicated that the performance of SGME diesel blends and SGME were equivalent to that of the standard diesel (Kirloskar TAF1 single cylinder 4 stroke DI engine was used for experimentation [17]. Investigations were done for the utilization of Simarouba glauca seed oil as a feedstock for the making of biodiesel by use of a small size model arranged in India [18]. Fuel characteristics were estimated for Simarouba glauca oil and its biodiesel and compared to ASTM standards, European standards, and different biodiesels. It was observed that engine with 20% SGME blend closely works as diesel. A/F ratio for SGME and its blends is higher than diesel. The mechanical efficiency of diesel is more than the SGME blends to some extent and BO and B2O are observed to be almost closer to each other. Brake Thermal efficiency of SGME at 20% quantity is a bit superior to diesel. The exhaust emission temperature of all the biodiesels are higher than the diesel and it is observed that, at full load the exhaust gas temperature is the maximum, due to stochiometric air fuel ratio prevalent. The B20 has lower average quantity of variation in CO and HC as compared to Diesel. Yet, B20 generates more NOx emission. Still, the B20 is the appropriate biodiesel blend among all as the NOx emission can be lowered with the advanced technologies. It is established that the combustion characteristics of all blends of SGME are almost equivalent as that of diesel [19]. Therefore SGME proves to be potential and noteworthy choice over the conventional diesel fuel [20].

The growing oil prices, the exhaustion of the crude oil amount in the planet, and the insistence to defend the climate from toxic waste caused by lubricating oil and their unrestrained spill out have grown importance in formulating and utilizing substitute lubricants. Bio lubricant oils are substitutes to mineral oils as they own some innate characteristics and are eco-friendly. Vegetable oil-based bio lubricants normally demonstrate additional lubricity, added viscosity index (VI), elevated flash point, and less evaporative wastages. Bio lubricants can be used in boundary as well as hydrodynamic lubrications. This is by virtue of their long fatty acid chains and the existence of polar groups in the constitution of vegetable oil [21].

As a result tribological investigations of SGME are essential for ascertaining its fitness from the tribological aspect. In this work experimental analysis of run-in period and flash temperature parameter (FTP) of diesel, blends of SGME in diesel with addition of nanoparticles as an additive is done using the four ball tester. The Silicon dioxide (SiO<sub>2</sub>) nanoparticles were employed as additives.

## 2. Materials

The Bio diesel used for this work was extracted from Simarouba glauca seeds. It was made by transesterification process. In transes-

terification the chemical breaking of bio oil is done by means of alcohol and esters of alcohol and glycerol is formed. The triglyceride is converted by progressive elimination of an alkyl into a diglyceride, a monoglyceride and finally a glycerol as a byproduct. The purpose of this process is to decrease the viscosity of parent vegetable oil for improving flow characteristics. The gums, waxes and triglycerides are also separated from the vegetable oil.

Although ethanol is the preferred alcohol for transesterification due to its eco friendly nature and lesser perniciousness, methanol is commonly employed due to its economy as compared to other alcohols like ethanol and isopropanol. Hence fatty acid methyl esters (FAME) are leading than the fatty acid alkyl esters. Fig. 1 explains reaction equilibrium. The key physicochemical properties of SGME and blends are shown in Table 2 and Table 3 correspondingly. The Silicon dioxide (SiO<sub>2</sub>) nanoparticles were used. SiO<sub>2</sub> nanoparticles are selected as the same has been least investigated. The criteria for its fitness are its non-toxicity, tastelessness, eco friendliness, chemical stability, high temperature resistance, large surface area, small particle size, effective dispersibility, suspension, vibration, liquefaction and high-quality thixotropy. Furthermore the SiO<sub>2</sub> nanoparticles do not settle easily because of small specific gravity. Also these are cheap and easily obtainable. Many present nanoparticles are unable to maintain its own characteristics at high loads and hence exhibit low-grade lubricating and anti-wear performance at these heavy loads. Therefore developments in the additives so as to boost the application range of the lubricant are needed [20,22].

## 3. Methods

## 3.1. Preparation of nanoparticles based Oil

The Silicon dioxide (SiO<sub>2</sub>) nanoparticles were independently dispersed in the base oil (SGME) with amount of 0.2, 0.25, 0.75 and 1% wt. using an ultrasonicator (Model-LMUC-3, Make- LAB-MAN) for 15 minutes. Each SGME and nanoparticles mixture was steady for at least 7 days [20].

## 3.2. Preparation of blends of SGME and Modified SGME in Diesel

Blends of SGME and modified SGME in diesel were prepared with 10%, 20% and 30% concentration (B10, B20 and B30) by volume. Similarly for modified SGME with SiO<sub>2</sub> nanoparticles overall sixteen samples were prepared. The Table 4 shows details of the pure SGME samples. The preparation of nanoparticles based oil samples on the basis of percentage weight concentration criteria in the oil is done. The constituents were base SGME with additive weight concentration as 0.2%, 0.5%, 0.75% and 1% on weight basis. The experimentation was carried out on the samples shown in Tables 4 and 5. Overall sixteen samples were tested on four ball tester.



Fig. 1. Transesterification reaction equilibrium [20].

#### Table 2

The key physicochemical properties of SGME [20].

Sr. No.	Property	Value
1.	Flash point[ASTM D93]	138 °C
2.	HCV [ASTM D6751]	37.5 MJ/Kg
3.	Kinematic Viscosity [D445]	5.38 mm²/s at 40 °C
4.	Density [ASTM D1448]	0.876 gm/cc

#### Table 3

The key physicochemical properties of SGME blends.

Blend	HCV MJ/Kg	Viscosity mm <sup>2</sup> /s	Density gm/cc
Diesel	45.6	4.9	0.822
B10	39.8	5.1	0.827
B20	38.9	5.23	0.830
B30	38.5	5.33	0.838
B100	37.5	5.38	0.876

#### Table 4

Blends of diesel and pure SGME.

Sr. No.	Blend details	Quantity of each sample
1. 2. 3. 4.	Pure Diesel(B0) Diesel with 10% SGME (B10) Diesel with 20% SGME (B20) Diesel with 30% SGME (B30)	50 ml

Table 5

Sample details with percentage weight concentration of nanoparticles, diesel and SGME.

Sr. No.	Blend details	No. of samples
1. 2. 3.	Pure diesel (B0) Pure diesel + Pure SGME (B10,B20 and B30) Pure diesel + Modified SGME with nanoparticles of SiO <sub>2</sub> (0.2, 0.5, 0.75 and 1 % Weight) and B10, B20 and B30 variants.	01 03 12

### 3.3. Tribological tests

The tribological tests were done on a four ball tester. Fig. 2 shows the kinematic details of the test set up. All the test apparatus were cleaned out before each test. The pure diesel and other fifteen samples as listed in Table 5 were taken for test in the cup of Four Ball Tester. The tests were carried out according to ASTM D4172 (Standard Test Method for Wear Preventive Characteristics of Lubricating Fluid-Four Ball Method). Chrome alloy steel AISI



Fig. 2. Four ball tester kinematic details [3].

standard E52100 steel test balls were utilized having diameter of 12.7 mm, Grade 25 EP (Extra Polish) and a hardness of 64-66 HRC. Test outcomes were compared with each other. The steel balls were cleaned with acetone after every test. Wear rates were measured in terms of the average WSD of the three lower specimens. The friction coefficient was recorded in real-time for the period of each test. The test conditions for each sample were as per ASTM D4172 which are shown as below:

- 1. Test Load : 392±2N
- 2. Test Duration : 3600 sec.
- 3. Speed :1200 +/- 60 rpm
- 4. Temperature :75°C+/- 2°C

Scar surfaces on the balls were studied using SEM for chosen balls representing highest and lowest WSD [20].

## 4. Run-in period

When there is relative motion between surfaces under load for the first time, the surface topography gets modified [23]. The changes which occur between start-up and steady state are associated with running-in (also called breaking-in or wearing-in). Summer-smith [24] states running-in as: "The elimination of crests in the mating surfaces by wear or plastic deformation in restricted situation of running imparting better matching and decreased threat of film breakdown throughout usual working".

The friction and surface finish behavior of a sliding / rolling contact has the running-in period, i.e. Phase I and Phase II. In Phase I, the coefficient of friction sharply lowers as well as the Ra, value. The plastic deformation is the major reason in varying the surface topography. In Phase II, there is small drop off in the coefficient of friction and Ra. Moderate wear takes place in this phase due to the elimination of boundary layers created by additives and oxygen in the lubricant between mating elements. The major factors affecting the efficacy of running-in are load, velocity and the first characteristics of the materials and the lubricant. Lubricants and additives have a noteworthy effect on the modification in microgeometry throughout running-in [25]. Considerable reduction of the running-in time and smoothening of the surface can be obtained by using additives in the oil. The additive changes due to shatter by mechanical action, and the surface active substances react with the fresh metal surface and plasticizes the thin layer [26.27].

Lubricant additives are effective in improving the mechanism of wear during running in and that's why boundary lubrication conditions are minimized and the surface finish is improved principally by plastic deformation in contrast with adhesive or an abrasive wear process. The use of additives lowers the running-in time devoid of any detrimental effects [28]. Murakami et al. [29] used a Dibenzyl Disulphide (DBDS) additive to investigate the importance of tribochemical effects on running-in in 4-ball tester. Results indicated that oxide films and Sulphur compounds are produced and the rubbing surface becomes very smooth. Even though lubricant has a noteworthy effect on reduction of the running-in time, a cautious option must be taken for attaining an optimal for the running-in process. The behavior of the lubricant and in specifically the additives relies chiefly on temperature at the contact [30].The run in periods were estimated from the real time COF graphs as shown in the Figs. 3 to 6.

### 5. Flash temperature parameter (FTP)

A distinct number is utilized to convey the critical flash temperature beyond which a lubricant under investigation will have



Fig. 3. Effect of 0.2% of SiO\_2 nanoparticles in modified SGME and % of SGME in diesel blends on COF.



Fig. 4. Effect of 0.5% of  ${\rm SiO}_2$  nanoparticles in modified SGME . and % of SGME in diesel blend on COF.



Fig. 5. Effect of 0.75% of  $SiO_2$  nanoparticles in modified SGME and % of SGME in diesel blends on COF.

breakdown for particular situation. Four ball tester works in boundary lubrication condition. The formula for the flash temperature parameter is as follows for four ball tester.

FTP =  $\frac{W}{d^{1.4}}$  [31]

In which *W* is the load in kilograms, and *d* is the wear scar diameter (WSD) in millimeters at this load [31]. The highest FTP value indicates satisfactory lubricant behavior, showing meager chances of lubricant film rupture.



Fig. 6. Effect of 1% of  $SiO_2$  nanoparticles in modified SGME . and % of SGME in diesel blends on COF.

### 6. Results and discussion

#### 6.1. Run-In period

It is noted from Figs. 3 to 6 that B0 shows more unsteady state coefficient of friction with longer time period amongst all. This shows that the biodiesel decreases the run in period to large extent. The FAMEs show such better scuffing characteristics. The reason is that the absorbed ester molecules act as coating agents on surface of materials. The run-in time diminishes gradually with the rise in biodiesel percentage till 20% and after that it happens to be sharper. That means the role of biodiesel percentage between 20 to 30% is more. But for B10 biodiesel 0.5% SiO<sub>2</sub> is not advisable as it exhibits maximum run in period of 415 sec. Also for B30 blend 1% SiO<sub>2</sub> is not advisable which shows increase in run in time of 293 sec. with increase in blend percentage. The lowest run in period of 173,179,175 sec. is demonstrated by B10, B20 and B30 blends for 1% and 0.2% SiO<sub>2</sub> concentration respectively. Figs. 7 and 8 show overall behaviour of run in time for SiO<sub>2</sub> nanoparticles.

#### 6.2. Flash temperature parameter

Fig. 9 shows variation of WSD for all the combinations. Fig.10 shows the Variation of FTP with  $SiO_2$  nanoparticles percentage for B10 blends. As seen in Fig. 10 the FTP goes on increasing with the increase in the percentage. This means increasing the nanoparticle percentage is beneficial for the  $SiO_2$  and B10 blends.  $SiO_2$  proves to be superior as compared to diesel showing the highest FTP for 1% amount. Thus addition of nanoparticles proves to be



Fig. 7. Variation of Run-In Period with blend and SiO<sub>2</sub> nanoparticles percentage.

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Fig. 8. Overall summary of variation of Run-In Period for all combinations of  $SiO_2$  nanoparticles.



Fig. 9. Effect of % of SGME and SiO<sub>2</sub> nanoparticles in blends on WSD.



Fig. 10. Variation of FTP with SiO<sub>2</sub> nanoparticles percentage in B10 blends.

beneficial with respect to stability of the lubricant film. Nanoparticles have good dispersion in the SGME as it has more percentage of oleic acid [32,33]. A combination of abrasive and adhesive wear was evident [20]. The lowest FTP is found for diesel due to heavy wear. B20 blends and 1% combination as seen in Fig. 11 also shows the similar behavior. In this case also SiO<sub>2</sub> shows favorable behavior with respect to the highest FTP value but it is slightly inferior as compared to B10 and 1% variant. Likewise 1% SiO<sub>2</sub> is good for B30 blends also (Fig. 12). The maximum value 94.53 for FTP is seen in 1% (B10) combination of SiO<sub>2</sub> amid each of the tested samples. This may be attributed to the oxidation of SGME with SiO<sub>2</sub> [34]. Figs. 13



Fig. 11. Variation of FTP with SiO<sub>2</sub> nanoparticles percentage in B20 blends.



Fig. 12. Variation of FTP with SiO<sub>2</sub> nanoparticles percentage in B30 blends.



Fig. 13. Overall summary of variation of WSD for all combinations of  ${\rm SiO}_2$  nanoparticles.

and 14 show overall summary of variation of WSD and FTP for all combinations of  $SiO_2$  nanoparticles respectively.

## 7. Conclusions

Based on these pioneering investigations as per the literature survey, following conclusions can be drawn.

1% and 0.2% amounts of SiO<sub>2</sub> nanoparticles prove to be beneficial, exhibiting the decrease in run in time as the biodiesel percentage goes on increasing. Only for B30 biodiesel blend 1% SiO<sub>2</sub>



Fig. 14. Overall summary of variation of FTP for all combinations of  ${\rm SiO}_2$  nanoparticles.

shows increase in the run in time which is undesirable, as it may cause loss of power in friction and chances of damage to the surfaces in contact.

- Increase in the percentage of nanoparticles does not show the decrease in run in time consistently, but the increase in biodiesel percentage shows good and almost consistent behavior with respect to decrease in run in time.
- The beneficial combinations are 0.2 % (B30), 1 % (B10 and B20) which give appreciable reduction in run in time. Biodiesel blends with addition of nanoparicles show low run in time giving satisfactory run in process as compared to pure diesel.
- All the nanoparticle percentage combinations prove to be beneficial exhibiting the increase in FTP as their percentage goes on increasing.1% combination shows the highest increase in the FTP. Increase in the percentage of nanoparticles shows the increase in FTP more consistently than increase in biodiesel percentage. Increase in blend percentage does not show such behavior with respect to rise in FTP.
- The beneficial combinations are 1 % (B10, B20 and B30) which give appreciable increase in FTP. Biodiesel blends with addition of nanoparicles consistently show high FTP giving acceptable behavior as compared to pure diesel.

## **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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