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Abstract

Biodiesel blends play vital role in conservation of the ecology. Biodiesels possess enhanced lubrication properties which save energy and enhance the engine life. In this investigation, the lubricity of petrodiesel, Simarouba glauca methyl ester (SGME) blends in petrodiesel, with and without nanoadditivation is assessed by employing four-ball tester as per experimental parameters specified in ASTM D 4172. The FAME mixtures of B10 (10% SGME in petrodiesel), B20, B30 and petrodiesel B0 were characterized. Copper oxide nanoparticles were utilized. Nanoparticles exhibit excellent dispersion in the SGME due to its high oleic acid content. Friction and wear aspects in the form of running-in time and flash temperature parameter (FTP) were investigated. The advantageous variants are 0.75% (B20

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SPECIAL ISSUE MANUSCRIPT

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Abstract Biodiesel blends play vital role in conservation of the ecology. Biodiesels possess enhanced lubrication properties which save energy and enhance the engine life. In this investigation, the lubricity of petrodiesel, Simarouba glauca methyl ester (SGME) blends in petrodiesel, with and without nanoadditivation is assessed by employing four-ball tester as per experimental parameters specified in ASTM D 4172. The FAME mixtures of B10 (10% SGME in petrodiesel), B20, B30 and petrodiesel B0 were characterized. Copper oxide nanoparticles were utilized. Nanoparticles exhibit excellent dispersion in the SGME due to its high oleic acid content. Friction and wear aspects in the form of running-in time and flash temperature parameter (FTP) were investigated. The advantageous variants are 0.75% (B20 and B30) which have shown drop in run-in period manifesting 81% reduction with respect to petrodiesel. Moreover, the favorable variants are 1% (B10), 0.5% (B10 and B20). These have demonstrated noteworthy enhancement in FTP presenting 158% rise over petrodiesel. Presence of abrasion and adhesion type wear was noted.

Keywords Biodiesel · Simarouba glauca · Four-ball tester · Nanoparticles · Run-in time · Flash temperature parameter

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Introduction

Biodiesels manifest outstanding lubricity with respect to the petrodiesel. The FAME mixed with nanoadditives gets supplementary improvement in tribological aspects as compared to neat FAME. Durability of engine parts improves, specifically fuel system parts. These components depend on fuel film only for minimizing friction. The friction amid engine components is lowered because of this better lubricity which further leads to savings in the energy consumption [1, 2]. The tribological attributes of conventional petrodiesel are extremely inferior with respect to the bio-fuels. Hence, finding other alternatives to meet these lubricity requirements is highly essential [2, 3]. A lot of biodiesels reveal improved friction and wear performance compared to traditional petrodiesels. A small number point to inadequate wear attributes due to deterioration and exterior damage which makes the irreversible engine damage. It limits scope of its utilization, and hence stressing the friction and wear characterization of different FAMEs and application of novel nanoadditives for controlling its shortcomings [3]. In addition, several ignored biodiesels ought to be experimented. The use of different nanoparticles to enhance tribological attributes of lubricant oils is done by many researchers. The friction and wear characteristics of nano-La_2O_3 [2] were investigated having 20–1000 nm size. Its 1% additivation showed optimum characteristics manifesting adhesive and abrasive wears for high loads and high speeds, respectively. Thermal conductivity of α-Al_2O_3 (20 nm in size) was investigated [4]. Nanoadditive wt of 3% exhibited increase of 31 and 37%, correspondingly for α-Al_2O_3 and γ-Al_2O_3. The consequent viscosity increments were 38 and 36%, in that order. Oils dispersed with TiO_2 and CeO_2 nanoadditives with appropriate surfactants were made. The minimal wear and

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friction characteristics were exhibited by 1:3 weight ratio of CeO_2 and TiO_2 particles with overall 0.6 wt% [5]. Use of copper oxide nanoadditives also showed improvement in tribological attributes due to its strength and shape stability [6–8]. Tribological investigations on magnesium-doped zinc oxide (ZMO) [9] revealed that the size of nanoadditives strongly controls the paraffin oil lubricant properties proving the best properties for the smallest size. Use of 0.5 wt% hexagonal boron nitride (hBN) in modified Jatropha oil [10] showed improved friction and wear characteristics. Application of lanthanum carbonate (La_2CO_3) and lanthanum oxide (La_2O_3) also showed lot of improvements [11]. The employment of multiwall carbon nanotube dispersed in mineral oil reveals a drop in wear amounting, average 73% in contrast with its neat version as well as a 20% increase in load bearing [12]. Also a very rarely tried silicon dioxide (SiO_2) [8, 13–15] nanoadditive improved the tribology characteristics due to its stability, large surface area and effective dispersion. Furthermore, the use of carbon nanoadditives unstructured carbon, graphite and grapheme showed that 1.0 wt% gives the best friction and wear attributes [16, 17]. In another investigation, application of halloysite nanotubes revealed that oil containing 1.5 wt%. of HNT in base oil of Pongamia gives better friction and wear attributes in contrast with its non-additivated versions [18]. The effective dispersion and fraction amount on mass/volume basis is extremely significant when using the nanoadditives. The fine mixing is ensured through sonication.

The emergence of Simarouba glauca as the prospective material for FAME is noted from another study. Its cultivation was started by NBPGR-India. Its local name is Laxmitaru [19, 20].

Studies were carried out for the use of SG crude oil as a raw material in production of FAME by a miniature scale model [21]. Its physicochemical properties were found and compared with different international protocols. The SGME20 is a suitable biodiesel blend amid all. Also the incineration attributes of the entire blend variants of Simarouba oil are nearly same compared to petrodiesel [22]. As a result, SGME justifies as prospective-cum remarkable option to traditional petrodiesel [8, 14].

The increasing lube-oil costs, its debilitation on earth as well as emphasis to safe guard the environment from its poisonous spillage have directed to prepare and use alternate lube-oils. Biolubricants are replacements to conventional lubricants due to their possession of a number of inborn attributes and are also recyclable. Vegetable oil-based biolubricants in general show added lubricity, additional non-dependence of viscosity on temperature, high flash-point and fewer evaporation losses. Biolubricants are employable in a wide range of lubrication conditions due to their elongated FA strings and the presence of polar-groups in their formation [23].

Consequently, wear and friction characterization of Simarouba glauca FAME is indispensable to ensure the suitability in application. Present work does tribological characterization in terms of running-in time and flash temperature parameter (FTP) of petrodiesel, mixtures of Simarouba FAME in petrodiesel by means of nanoparticle additivation. The four-ball tribometer and copper oxide (CuO) nanoadditives were utilized.

Methodology

Materials

The biodiesel (SGME) was produced from SG crude oil using the transesterification method. Alcohol and esters of alcohol break the bio-oil chemically, producing glycerol. The overall objective of this is reduction of the bio-oil's viscosity leading to improvement in its flow ability. Finally, separation of clean oil is done.

Although ethanol is the favored for this process because of its green and harmless nature, methanol is popularly in use owing to low cost. The reaction balance is shown in Fig. 1 [8, 14].

Methods

Making of Nanoadditivated SGME

The DOE was motivated by full factorial design theme. The nanoadditives having different weight proportions were employed. The nanoadditivation, in either very small or large quantity, might lead to detrimental outcomes as evident from the literature. The selection of percentage fraction depends on diffusion process/duration plus experimental conditions and oil under investigation. Literature suggests that many researchers have used concentrations in the range of 0.2 to 1% with uniform increments. The optimal concentrations are also found within the same range. Hence the similar range of 0.2, 0.25, 0.75 and 1 wt%

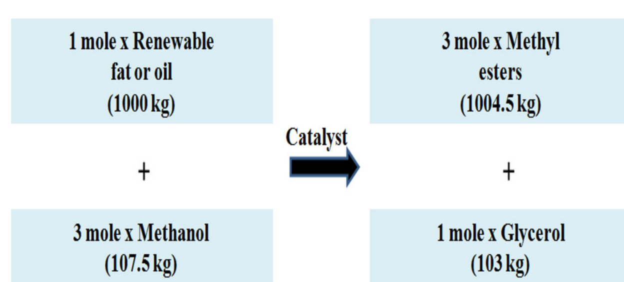

Fig. 1 Reaction Balance [8]

is selected. Dispersion of the CuO nanoparticles in the SGME was done employing a LABMAN LMUC-3 sonicator for the duration of 15 min. It was steady for 7 days [8, 14].

Making of Blends of Additivated and Nonadditivated SGME in Petrodiesel

Mixtures of additivated SGME in petrodiesel were made. The 10%, 20% and 30% variants (B10, B20 and B30) by volume were prepared (Table 1). Thus in all 16 samples were made. The making of nanoadditivated SGME was completed as mentioned earlier. The investigations were done using the variants shown in Tables 1 and 2. Taken as a whole, sixteen variants were experimented on the four-ball tribometer.

Friction and Wear Experiments

The friction and wear experiments were conducted using the four-ball tribometer. Its schematic is shown in Fig. 2 All test components were made dirt-free prior to the conduction of every experiment. The neat petrodiesel with remaining fifteen variants which are shown in Table 2 was tested in the sample-cup of four-ball tribometer. The experiments were conducted as per ASTM D4172 procedure. Chrome alloy steel AISI standard E52100 steel test balls were used with a diameter − 12.7 mm, Grade-25 EP (Extra-Polish) and a hardness-64-66 HRC. Results were systematically analyzed. The test globes were rinsed using acetone following each experiment. Wearing was anticipated in the form of the mean Worn Scar Diameter of the three fixed balls. The COF was documented concurrently throughout every experiment. The following are the experimental parameters for all biodiesel variants: test load: 392 ± 2 N; experiment period: 3600 s.; pace: 1200 ± 60 rpm; temperature: 75 °C ± 2 °C. Worn scars on the fixed 3balls were studied employing SEM for specimens demonstrating maximum and minimum WSD [8, 14].

Run-in Period

The surface geometry gets changed at the beginning of sliding among loaded interfaces [24]. The modifications that take place during starting and stable condition are related to run-in. It is the exclusion of ridges in the contact interfaces by wearing out or plastic warpage in constrained state of motion promoting improved harmonizing and reduced danger of film rupture all through normal operation. It happens at the beginning of movement of parts, moving with respect to each other [25]. The COF along with Ra value behavior of an interface with relative motion consists of the running-in time. It is composed of Stage 1 and Stage 2. In Stage 1, the COF decreases aggressively along with the surface roughness. The plastic distortion is the main cause in changing this interface geometry. Stage 2 consists of minute reduction in COF and surface finish. Reasonable wear happens amid the interface members in this stage because of the exclusion of edge films generated by nanoadditives and O_2 in the oil. The chief reasons impacting the efficiency of run-in are load, velocity and the initial parameters of the material and the oil. Lube-oils and nanoadditives make a notable influence on the alteration in microtopography all through run-in [26]. Significant decrease in the run-in duration and polishing of the interface can be achieved by utilizing lube-oil additives. They change because of breakage by mechanical action, and the surfactants act in response with the new metal interface and plasticize the slender film [27, 28].

Additivation is successful in enhancing the dynamics of wear throughout run-in, and so the metal-to-metal contacts are lessened and the Ra becomes superior mainly by plastic distortion converse to adhesive or an abrasive-type wearing progression. The utilization of nanoadditives reduces running-in period with no harmful results [29]. Dibenzyl disulfide additive was utilized [30] to examine the significance of tribochemical impacts on run-in with the four-ball tribometer. Outcomes showed that tribochemical reactions take place and the surface in contact highly smoothens out. Although lube-oil has a remarkable impact on dropping of the run-in duration, a careful alternative should be chosen to obtain an effective run-in process. The performance of the additivated lubricant depends mainly on intensity of heat at the interface [31]. The running-in durations are established from the concurrent friction variation with time as depicted in Figs. 3, 4, 4 and 6.

Flash Temperature Parameter (FTP)

A unique numeral is defined to express the limiting flash temperature; after that, lube-oil being studied fails for specific condition. Boundary lubrication condition prevails in the four-ball tester. The relation for FTP is as shown below.

Table 1 Blends of petrodiesel with neat biodiesel

Sr. No	Particulars	Amount of variant
1	Neat petrodiesel:(B0)	50 ml
2	Petrodiesel with 10% biodiesel:(B10)	
3	Petrodiesel with 20% biodiesel:(B20)	
4	Petrodiesel with 30% biodiesel:(B30)	

Table 2 Blends of nanoparticles and biodiesel

Sr. No	Sample name	Specimens
1	Neat petrodiesel:(B0)	01
2	Neat petrodiesel + Neat biodiesel: (B10,B20 and B30)	03
3	Neat petrodiesel + Nanoadditivated biodiesel CuO-0.2, 0.5, 0.75 and 1 wt% and B10, B20 and B30 variants	12

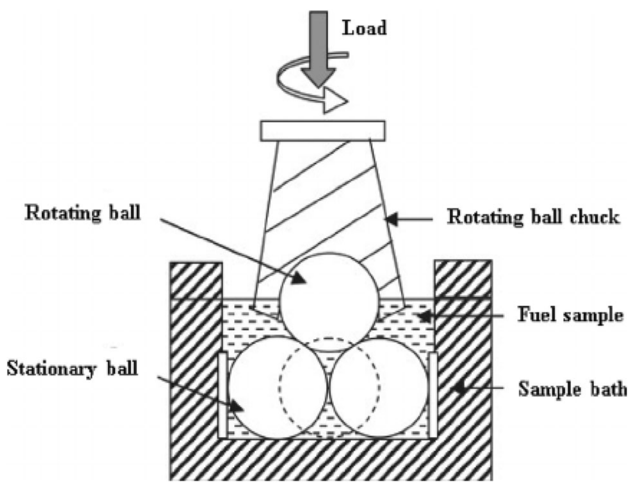

Fig. 2 Kinematic details of four-ball tribometer [3]

Flash Temperature Parameter $=$ Load $/\mathrm{WSD}^{1.4}$ [32]

where W = load in kilograms, WSD = the worn scar diameter in mm at this W.

The higher the FTP, the more acceptable is the lube-oil performance, depicting too little probability of lube-oil film rupture.

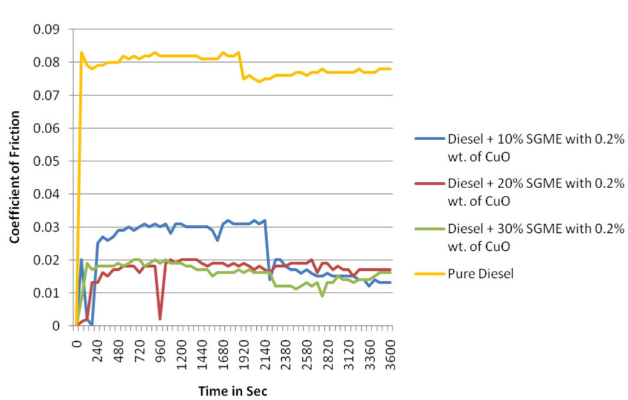

Fig. 3 Influence of 0.2% of CuO nanoadditives and % of biodiesel on friction

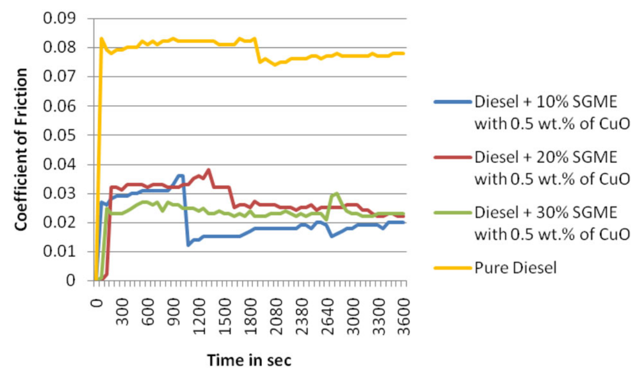

Fig. 4 Influence of 0.5% of CuO nanoadditives and % of biodiesel on friction

Results

Run-in Time

Figures 3, 4, 5 and 6 show the influence of amount of CuO nanoadditives and biodiesel on friction. The behavior of diesel is very poor as compared to additivated biodiesel. Furthermore, a large fluctuation of friction is evident for B10 variant. This is due to low viscosity and inefficient dispersion of nanoadditives. Figure 3 depicts that the optimal friction is prevalent for B30 – 0.2% CuO variant.

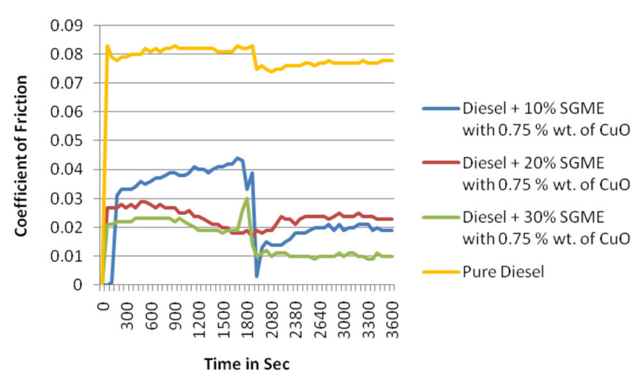

Fig. 5 Influence of 0.75% of CuO nanoadditives and % of biodiesel on friction

The high viscosity and good rolling effect of nanoadditives make this possible. The sudden drop at particular instance is due to initial running-in leading to high-quality surface finish. The same phenomenon manifests in Figs. 4, 5 and 6. This means B30 consistently exhibits efficient behavior. Figure 7 shows change in running-in time as per % of SGME and CuO nanoparticles in blends. B20and B30 blends show the minimum run-in time for 0.75% of nanoadditives. This may be attributed to deposition of additives on the worn surface leading to rapid improvement in the surface finish.

Figure 8 shows behavior of run-in time for CuO nanoparticles as a whole. All % amounts of CuO manifest the decrease in run-in period with SGME fraction going on rising. 0.2%, 0.5% and 1% amount fall almost on the same trend line showing drop in run-in period with the SGME amount going on increasing (Fig. 7). 0.75% amount of CuO shows additional drop in the run-in time proving to be the best option of % amount for B20 and B30 blends. More proportion of nanoadditives does not reveal the drop in running-in period always, but the higher SGME blending indicates superior plus steady performance relating to drop in run-in period. Rise in the proportion of nanoadditives beyond 0.75% is not seen to be beneficial as the run-in time increases for B20 and B30 blends according to Fig. 7. The advantageous blends are 0.75% (B20 and B30) that offer significant lessening in running-in period. The reason behind this is that the small percentages of nanoadditives lack the three body wear. This decreases the initial run-in action leading to relatively large run-in period. The largest proportion of additives increases agglomerations and dispersion problems which results in inefficient running-in. Conversely for 0.75% amount, the above-mentioned factors of three body wear, mending and low agglomerations are favorable, so it shows the beneficial results [33, 34].

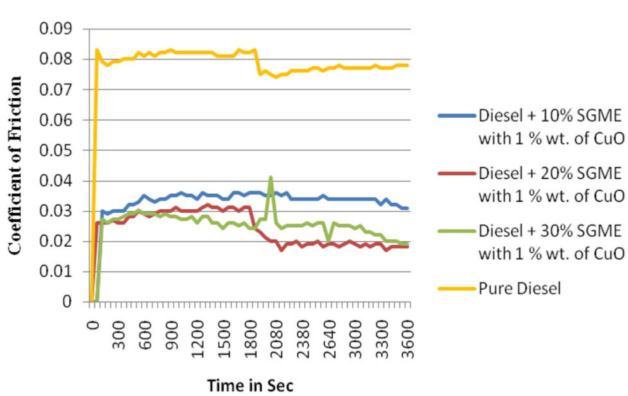

Fig. 6 Influence of 1% of CuO nanoadditives and % of biodiesel on friction

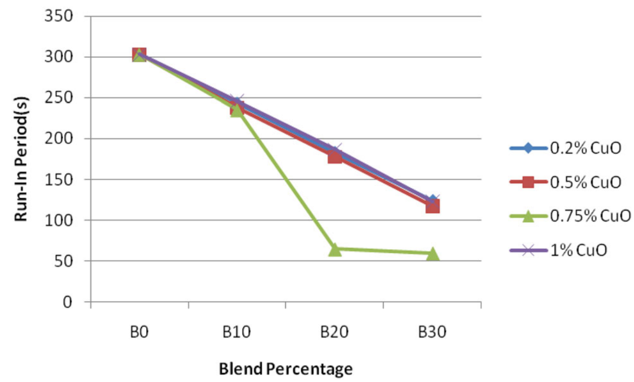

Fig. 7 Change in running-in time as per % of SGME and CuO nanoparticles in blends

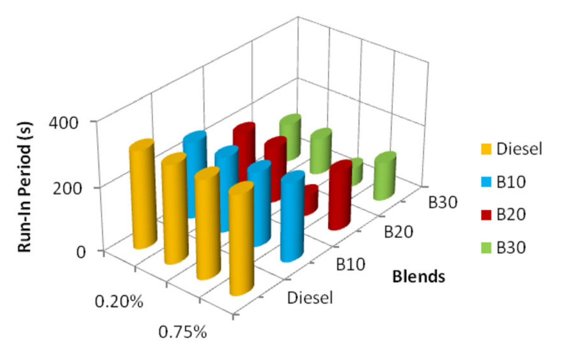

Fig. 8 Change in of running-in time for all percentage variants of CuO nanoadditives

Flash Temperature Parameter (FTP)

Figure 9 shows changes in wear scar diameter for entire blend variants. The B10 blend exhibits the lowest wear behavior for all nanoadditive proportions and hence the good FTP characteristics. Thus the film is more stable for these combinations. Figure 10 depicts the change in FTP as per CuO nanoadditive fractions in the case of 10% SGME blends. From Fig. 10, it is seen that the FTP increases when there is an increase in % of the nanoparticles except for 0.75% amount which may be attributed to shape loss of nanoparticles. It indicated that the increase in the nanoadditive % is advantageous for the CuO and 10% SGME blends. For B20 blends, 0.5% and 1% combination is favorable. Amount of 0.2 and 1% is good in the case of B30 blends giving sustainable lube-oil film (Figs. 11 and 12).

The smallest FTP is established for petrodiesel due to serious wear. The highest assessment of 77.75 for FTP is observed for 1% and 10% SGME variant of CuO among all

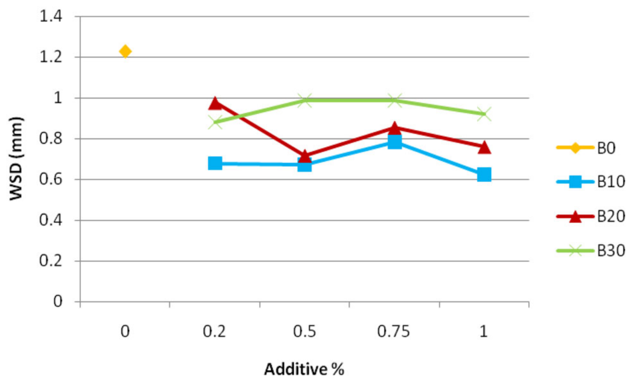

Fig. 9 Impact of % of biodiesel and CuO nanoadditives on wear

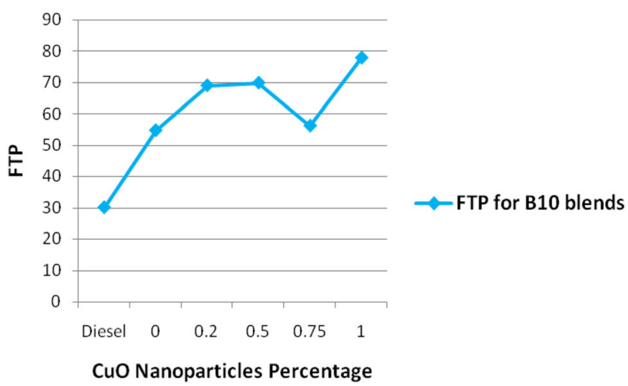

Fig. 10 Change in FTP as per % CuO in B10 blends

of the test samples which is 158% larger than that of diesel. This is credited to the oxidization of SGME in the company of CuO and minimum wear behavior for this blend [33]. Furthermore, the higher blends do not show the benefit of oxidation as they lead to higher wear due to unfavorable effects of agglomerations. Figures 13 and 14 depict

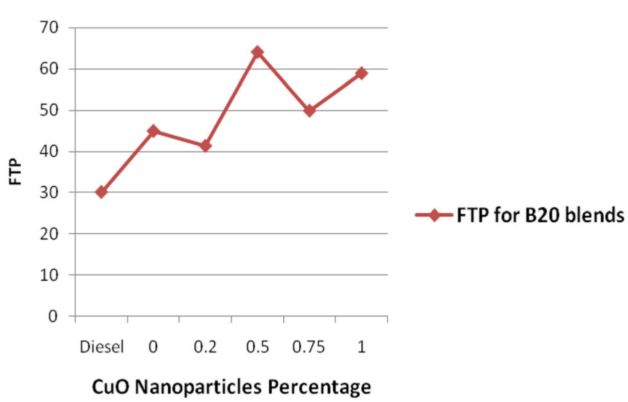

Fig. 11 Change in FTP with % CuO in B20 variants

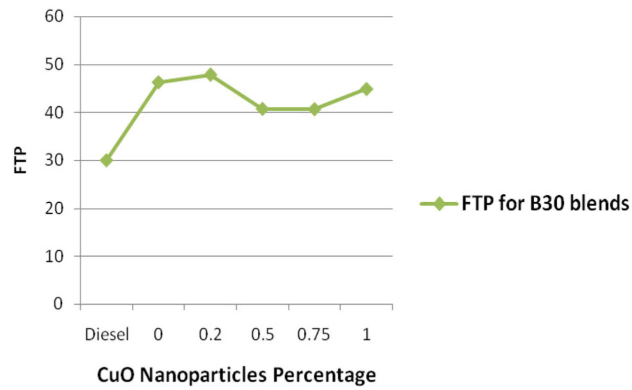

Fig. 12 Change in FTP as per % CuO in B30 variants

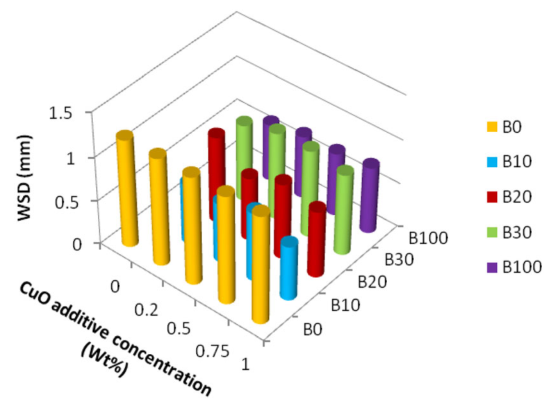

Fig. 13 Wear behavior for all permutations of CuO nanoadditives

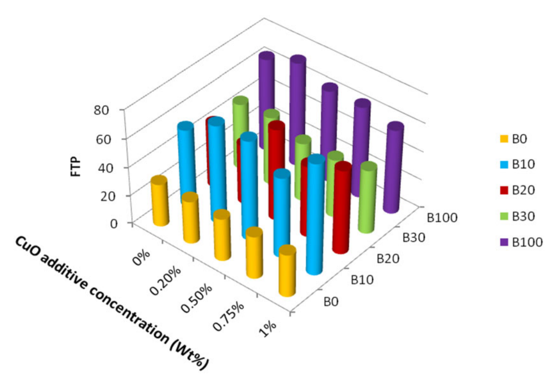

Fig. 14 FTP behavior for all permutations of CuO nanoadditives

behavior of wear and FTP on the whole, for CuO nanoparticles, respectively [33, 34].

The advantageous mixtures are 1% (B10), 0.5% (B10 and B20) giving significant boost in FTP which is due to proper dispersion in the presence of oleic acid [35, 36].

Conclusion

The following conclusions are drawn on the basis of these pioneer experimentations on SGME with reference to literature survey:

- Entire nanoadditive combinations justify to be advantageous, manifesting the drop in running-in period with increasing SGME %.
- Higher fraction of nanoadditives shows the drop in run-in period every time. Also higher SGME amount reveals superior and nearly steady performance in dropping of run-in period.
- CuO nanoadditivated SGME blends consistently reveal small run-in period providing acceptable run-in process with respect to pure diesel.
- Almost entire nanoadditivation variants justify as favorable indicating the boost in FTP with their fraction going on rising.
- Increase in the amount of nanoadditives reveals the higher FTP extra constantly than rise in SGME fraction. That means nanoparticle % has more impact than biodiesel % on FTP.

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Declarations

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

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