Experimental investigations for rheological characteristics of TiO$_2$ nanoparticles doped diesel, biodiesel fuel blends for use in compression ignition engine

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Abstract. The present experimental study aims to investigate the variations in rheological characteristics of TiO$_2$ nanoparticles doped biodiesel diesel fuel blends at different temperatures and nanoparticle mass fractions. Fuel blends of Acacia Concinna biodiesel (AC BD) in the volume fraction of 40% are mixed with in the remaining 60% volume fraction of mineral diesel. Fuel blends are modified by doping TiO$_2$ nanoparticles in the weight fraction of 0.1, 0.2, 0.3 and 0.4 g/liter in biodiesel diesel fuel blends. These modified fuel blends (MNF) are prepared by means of mechanical stirring and ultra-sonication process, which are tested on Rheometer in a temperature range of 293K–363K under different shear rates. The experimental results showed that at concentration of 0.4 g/liter the viscosity of modified fuel blend (MNF0.4) was 7.16% more than the viscosity of mineral diesel. This increase in viscosity of MNF fuel blends are undesirable due to the fact that high injection pressure is required for proper atomization and combustion of fuel, which otherwise overshadows the gain in total heat release rate due to high heat of combustion of TiO2 nanoparticles. Furthermore, rheological characteristics of nanoparticle mixed modified fuel blends are found to be non-Newtonian and shear thinning. The findings of present study ascertain us that modified fuel blend up to 0.2 g/liter of TiO2 nanoparticle concentration (MNF0.2) in AC can be used as alternative fuel without much modifications in the operating and design parameters of existing diesel engine.

Keywords MNF fuel blends, TiO2 nanoparticles, Acacia Concinna biodiesel, Shear rates, Rheological characteristics

1. Introduction
Limited fossil fuel reserves with high usage rates and associated environmental issues forces the scientific community to search new class of fuels which are renewable, sustainable, economical, environment friendly having rheological properties close to that of conventional fuels [1-3]. Biodiesel produced from non-edible oils put themselves as an alternative to fossil derived fuels. As a result, researchers are attempting to use biodiesels in different volume fractions with mineral diesel as blended fuel for compression ignition engines [4, 5]. Biodiesels comprises various lipid sources derived from vegetables and animal fats which require both esterification and Trans-esterification reactions for its production [6, 7]. However due to high oxygen content and biodegradability the combustion of biodiesel blended diesel fuel produced less pollutant emissions than base diesel fuel [8, 9]. Several studies revealed that increase in biodiesel fraction in the blended fuel decreases the performance characteristics of diesel engine [10]. The high viscosity and lower heat of combustion of biodiesel fuel deteriorates the
combustion behavior of blended fuel and produce less engine power with high specific fuel consumption [11-13]. To overcome these issues researchers are focusing on various fuel modification techniques such as mixing of alcohols (ethanol, isopropanol, iso butanol and n-decane etc) and biodiesel in suitable quantity with mineral diesel. [14, 15]. However, these additives reduce the blend viscosity, but the heat of combustion still remains at lower values compared to diesel fuel alone. Another effective fuel modification technique is the doping of energetic nanoparticles in a very small fraction with blended fuel and is widely accepted by the researchers worldwide [16-18]. This method is very efficient in achieving the desirable fuel properties such as high thermal conductivity, high heat transfer rates, high heat of combustion and better ignition characteristics, but at the same time increases the viscosity of blended fuel drastically [19, 20]. Hence there is a tradeoff between heat of combustion and viscosity values of modified nanofluid fuel of biodiesel diesel blends comprising nanoparticles in different concentration. Experimental studies on nanoparticle mixed biodiesel diesel fuelled diesel engine showed better overall engine performance with significant reduction in pollutant emissions due to their high catalytic activity during combustion [21-23]. On the other hand, some studies on nanofluid fuels have reported a notable increase in viscosity compared to usual fuels used in engines [24]. Furthermore, it has been reported that, variation in nanoparticle fraction and temperature of fuel blend, registered an influential change in nanofluid fuel viscosity. As a fact that, fuel injection system of compression ignition engines are designed for an injection pressure of 160-220 bar when operated at mineral diesel alone. The blending of diesel with biodiesel and nanoparticles increases the modified fuel blend viscosity, hence higher injection pressures are desirable which otherwise would result in coarse fuel droplets with more penetration length, poor atomization and spray patterns and erratic combustion inside the engine cylinder [25]. The increase in viscosity of nanofluid fuel has a negative effect on engine performance. Therefore, the rheological properties of any modified fuel under mechanical stress condition, pressure and temperature along with its behavior as Newtonian and Non-Newtonian fluid plays a vital role in engine performance, combustion and emission characteristics. The research outcomes of few important studies on nano fluids are summarized and presented in Table-1.

**Table-1 Research outcome of previous studies on rheological behavior of Nano fluids**

| Researcher/Autho r | Nanomaterial | Temperature range (°C) | Nanoparticle size (nm) | Mixing fraction | Fluid behavior |
|--------------------|--------------|------------------------|------------------------|-----------------|---------------|
| Ding et al. [26]   | TiO2/EG      | 20-60                  | 70-100                 | 0.5-0.8 wt%     | Non Newtonian shear thinning |
| Kole et al. [27]   | Al2O3/EG-Water | 10-50                 | 25                     | 0.1-1.5         | Shear thinning   |
| Mehrali et al. [28]| GNP/distilled water | 20-60                | 0.025-0.1               | Shear thinning   |
| Abad et al. [29]   | CuO,Al2O3,TiO2/oil | 15.6                | 40,15,20               | 1-2             | Shear thinning   |
| Anoop et al. [30]  | SiO2/mineral oil | 25-140               | 20                     | -               | Non Newtonian   |
| Kumar et al. [31]  | Cu-Zn/vegetable oil | 30                  | 25                     | Non Newtonian   |

It is evident from the available literature that most of the research studies on various nanofluid deals with the heat transfer behavior including thermal conduction, phase change heat transfer and convective heat transfer [32-36]. Few experimental studies however, are also available on the rheological behavior of nanofluids but so far very scare studies have been performed on rheological properties of nanofluid fuels for use in compression ignition engine [37-39]. In the present work viscosity of modified fuel blends have been investigated under the influence of varying temperature, TiO2 nanoparticle
concentration and shear rates. The obtained results can be of much use for the designing of engineering systems as well as for the proper selection of operating parameters for an injection system of conventional diesel engine fuelled with modified nanofluid fuel blends of biodiesel diesel and TiO2 nanoparticle concentration.

2. Experimentation methodology

The present experimental work was carried out, by preparing modified fuel blends comprising (60% diesel + 40% Acacia Concinna biodiesel) mixed with weight fraction of 0.1, 0.2, 0.3 and 0.4 g/liter of commercial grade TiO2 nanoparticles of size < 100 nm using two step method. These nanoparticles were procured from M/s Sigma Aldrich. The prepared sample mixed with 1.0 vol% of isopropanol, which was then transferred to ultrasonicator for proper dispersion and stable suspension of nanoparticles in biodiesel diesel fuel blend. The rheological behavior of prepared modified nanofluid fuel (MNF) blends at different of TiO2 nanoparticles concentration was measured using an Anton Par Rheometer (Graz, Austria), which has recorded the viscosity for different temperatures and shear rates. Physicochemical properties of TiO2 nanoparticles, Acacia Concinna biodiesel (AC BD) and MNF fuel blends are shown in Table-2,3.

| Properties            | Values                   |
|-----------------------|--------------------------|
| Density               | 4.23g/cm³                |
| Molar mass            | 79.9378 g/mol            |
| Purity                | 98%                      |
| Size                  | 25nm                     |
| Melting point         | 1,843°C                  |
| Color                 | White                    |
| Morphology            | Hexagonal crystal         |

The viscosity of biodiesel diesel blend (AC BDD) and modified fuel blends MNF0.1, MNF0.2, MNF0.3 and MNF0.4 were investigated under the shear rate of 0-100 s⁻¹ and within the temperatures range of 293K-363K.

| Sl.No | Properties            | Diesel | AC BD | MNF0 | MNF0.1 | MNF0.2 | MNF0.3 | MNF0.4 |
|-------|-----------------------|--------|-------|-------|--------|--------|--------|--------|
| 1.    | Density (kg/m³)       | 82.5   | 892.4 | 859.6 | 838.4  | 834    | 842.2  | 851.7  |
| 2.    | Viscosity (cst) at 40°C | 3.03   | 5.76  | 4.05  | 3.27   | 3.07   | 3.164  | 3.342  |
| 3.    | Flash point (°C)      | 52-96  | 138   | 87.5  | 82.71  | 80.5   | 82.3   | 84.7   |
| 4.    | Calorific value(MJ/kg)| 42.5   | 37.95 | 38.4  | 37.38  | 36.13  | 34.6   | 33.2   |
| 5.    | Cloud point (°C)      | 4.0    | 10.8  | 7.9   | 7.02   | 6.81   | 6.94   | 7.24   |
| 6.    | Pour point (°C)       | -6     | 6.5   | -2.2  | -2.8   | -3.0   | -2.8   | -2.59  |
| 7.    | Cetane number         | 51     | 54.98 | -     | -      | -      | -      | -      |
3. Accuracy in measurement
In order to validate the measurement accuracy, initial experiments were conducted on AC BDD fuel blend at temperatures of 293K – 363K. The obtained results on viscosity data were plotted against the experimental results of Aworanti et al. [40] for comparison which are shown in Figure 1. It was evident from the figure that experimental data of present work falls within a very close agreement with Aworanti viscosity data.

According to Figure 1, there observed a slight variation in both the plotted results, this variation might be due to the fact that in the present study AC biodiesel have been considered where as Aworanti considered soybean biodiesel. Furthermore, both these studies were carried out at different shear rates. Due to very less influence of shear rates at high temperatures, both studies have very close viscosity values. The viscosity values of different blends have been measured repeatedly at every selected temperatures and shear rates. The average viscosity data (few data) are shown in Table 4.

4. Results and Discussion
4.1. Properties of AC biodiesel/MNF fuel blends
The physicochemical properties of AC biodiesel and modified (MNF) fuel blends (density, viscosity, cloud point, pour point, flash point, calorific value and cetane number etc) was evaluated and compared with the properties of mineral diesel as mentioned in Table- 2. It could be seen that properties of AC biodiesel and MNF fuel blends in comparison to diesel fuel have a significant variation, whose values may change further w.r.t. operating variables of the engine. The presence of high molecular weight fatty esters in AC BDD tends to increase density (892 kg/m³), viscosity (5.76mm²/sec), cloud point (10.8°C)
pour point (-2.2 °C) and flash point (138°C) which was significantly higher than mineral diesel. The low calorific value of AC BD (10.5% less than diesel) signifies more fuel consumption of AC BD than diesel for same power output. The density of all MNF fuel blend after mixing with TiO2 nanoparticles were observed to be 0.25- 4.06% higher than diesel. Though, oxygenated AC BD have high cetane compared to diesel, still the increased fraction of BD in diesel showed a negative effect on fuel viscosity. Further, the mixing of TiO2 nanoparticles (0.2-0.4g/liter) as combustion catalyst in AC BDD fuel blend, have registered a drop (5.91- 13.24%) in heating value of all MNF fuel blend compared to AC BDD (MNF0) fuel blend and mineral diesel respectively. Similarly the results pertaining to the density of prepared MNF fuel blend have shown 0.25- 4.06% increase in density compared to mineral diesel. This increase in density may lead to higher pressure drop in the fuel line which in turn would reduce the mass fuel discharge rate through volumetric fuel injection pump. This decrease in fuel discharge tends to compensate low heating value of MNF fuel blends compared to mineral diesel. However, at dense concentration of TiO2 nanoparticles in AC BDD fuel blend, the precipitation and fast agglomeration of nanoparticles tends to exhibit poor blend stability which may lead to inferior combustion and engine performance compared to AC BDD fuel blend and diesel.

4.2. The effect of temperature on viscosity of modified fuel blends

Viscosity, a resistance to flow due to internal fluid friction, is one of the dominant parameter which defines its suitability as commercial grade fuel for use in automobiles. In general, the viscosity values of AC BD, AC BDD fuel blend and various MNF fuel blends are higher in comparison to mineral diesel. These high viscosity values are very undesirable for use in diesel engines, which otherwise adversely affect the fuel injection/atomization, performance, emission and combustion characteristics of a diesel engine. The higher viscosity makes the fuel more prone to form engine deposits.

The viscosity variations of modified fuel blends as a function of temperature is shown in Figure-2. From the plotted results it can be seen that for each of the blends with different weight fraction of TiO2 nanoparticles, the decrease in viscosity values follows a non-linear trend with temperature. Also at a particular temperature, the decrease in viscosities of MNF fuel blends at different TiO2 nanoparticle concentration in AC BDD fuel blend is not constant. The viscosities of the entire fuel blends at low temperature are moderately high (7.5- 6.4 at 293K) which further decreases with increase in temperature. Nevertheless, engine manufacturers never accept fuel blends with high viscosities which do not fall within the specified viscosity limits of diesel fuel.

![Figure-2](https://example.com/image.png)

**Figure-2** Effect of temperature on viscosity of modified fuel blends

According to the Figure-3, there observed a high percentage reduction in the relative viscosity of modified fuel blends with increase in temperature. Relative viscosities of blends are evaluated
considering viscosity of diesel (2.45 cst) as base line. However, the viscosity of blends with low concentration of nanoparticles falls within reasonable limit of viscosity values that can be used for diesel engines worldwide (4.1cst at 293K to 2.32 cst at 363K). Furthermore, at all operating temperature, blends of low nanoparticle concentration (MNF0.2) have shown the least enhancement in relative viscosity among all tested fuel blends. This trend of variation in viscosity might be due to intermolecular interaction (Vander Wall forces) between AC BDD fuel oil and nanoparticles as well as stable and homogeneous suspension of nanoparticles in above fuel blend. However, with further increase in nanoparticle concentration (>0.2 g/liter) in AC BDD fuel blend, the irreversible agglomeration tends to increase the viscosity values of MNF0.3 and MNF0.4 fuel blends. These findings ascertain us that modified fuel blend (MNF0.2) can be used further for actual engine testing without much modifications in the operating and design parameters of existing diesel engine.

Figure 3 shows the variation of shear stress w.r.t shear rate of fuel blends with different fraction of TiO2 nanoparticles. The enhancement in viscosity and the behavior of modified fuel blends are judged by the slope of curve. Modified fuel blend MNF0.1and MNF0.2 have shown near linear relation between shear stress and shear rate, whereas base fuel blend of AC BDD (MNF0) and blends of high nanoparticle concentration (MNF0.3and MNF0.4) fuel blends have an increasing slope of curvature, thereby exhibiting higher blend viscosities. Therefore, their behavior was found to be similar to that of non-Newtonian fluid with steady shear deformation.

4.3. Effect of shear rate on viscosity

The variation in viscosity of AC BDD (MNF0) and TiO2 nanoparticle mixed modified (MNF) fuel blends as a function of shear rate is shown in Figure-5. As can be seen, that applied shear tension creates deformation in all the fuel blends which tends to decreases the blend viscosity. Base fuel blend AC BDD (MNF0) and MNF fuel blend at low nanoparticle fraction (MNF0.1 and MNF0.2) showed less deformation/shear thinning with applied shear as compared to high nanoparticle concentration (MNF0.3 and MNF0.4) fuel blends. This reduction in viscosity was attributed to the fact that when shear rates are low, the spindle which rotates the fluid, changes the fluid molecule structure temporarily. The alignment of fluid molecules in the direction of increasing shear offers less resistance causing a reduction in viscosity. Further at high shear rates, maximum amount of possible shear ordering has been attained, thus more shear rates are required to break the agglomerated TiO2 nanoparticles down to smaller sized particles. Therefore, high nanoparticle concentration (MNF 0.3 and MNF0.4) fuel blends have registered...
slightly higher viscosity values at all shear rates than low nanoparticle concentration (MNF 0.1 and MNF0.2) fuel blends.

![Figure-4 Shear stress vs. shear rate of modified fuel blends at 313K temperature.](image1)

![Figure-5 Viscosity vs. shear rate of modified (MNF)fuel blends at 313K temperature.](image2)

5. Rheological investigations
Rheological investigations have been carried out, whenever any fluid is modified to achieve certain specific properties (thermal conductivity, viscosity, surface tension etc) according to their application in different engineering systems. In order to characterize the modified fuel blends (Newtonian or non-Newtonian) Ostwald de Waele model has been used in the present study. The relationship for which is as follows:

\[ \tau_{OW} = m\gamma^n \]  \hspace{1cm} (1)

In this equation, \( n \) represents power law index, \( m \) is the consistency index (0.5), \( \tau_{OW} \) shows shear stress. The value of power law index (\( n \)) defines the rheological characteristics, which can be evaluated by taking the log of equation-1 and is expressed as:

\[ \ln(\tau) = \ln(m) + n\ln(\gamma) \]  \hspace{1cm} (2)

The values of power law indices for modified fuel have been calculated by logarithmic method in the temperature range of 293K – 363K, and the results are shown in Table-5.
| Temperature (K) | MNF0 | MNF0.1 | MNF0.2 | MNF0.3 | MNF0.4 |
|----------------|------|--------|--------|--------|--------|
| 293            | 0.9786 | 0.9854 | 0.9996 | 0.9857 | 0.9772 |
| 303            | 0.9769 | 0.9853 | 0.9985 | 0.9836 | 0.9753 |
| 313            | 0.9752 | 0.9842 | 0.9972 | 0.9714 | 0.9744 |
| 323            | 0.9728 | 0.9829 | 0.9964 | 0.9682 | 0.9706 |
| 333            | 0.9701 | 0.9808 | 0.9945 | 0.9678 | 0.9695 |
| 343            | 0.9692 | 0.9792 | 0.9936 | 0.9662 | 0.9868 |
| 353            | 0.9684 | 0.9776 | 0.9928 | 0.9649 | 0.9673 |
| 363            | 0.9547 | 0.9756 | 0.9917 | 0.9564 | 0.9511 |

As can be seen from Table-5 that for MNF0.2 fuel blend the power law indices (n) value lies very close to 1.0, hence at all temperatures it can be treated as close to Newtonian fluid whereas AC BDD (MNF0) fuel blend and high nanoparticle concentration mixed modified (MNF 0.3 and MNF0.4) fuel blends have power law indices (n) well below 1.0 hence treated as non-Newtonian and shear thinning. Further it was observed that, increase in nanoparticles fraction in fuel blends led to more non-Newtonian behavior and cause instability in modified nanofluid fuel structure.

6. Summary and Conclusion

In the present experimental work, rheological behavior of nanoparticle laden biodiesel diesel fuel blends was evaluated. Modified nanofluid fuel (MNF) blends of AC BDD (40 vol% biodiesel and 60 vol% diesel) mixed with TiO2 nanoparticle in a concentration of 0.1, 0.2, 0.3 and 0.4 g/liter of blend have been tested for various physico-chemical properties. The effect of temperature and shear rates on viscosity values of above MNF fuel blends were studied. It can be concluded from the results that MNF0.2 blend have shown minimum increase in relative viscosity of 7.1% at 293K temperature compared to diesel. By experimental findings, it was revealed that shear rates of MNF0.2 fuel blend has a near linear relationship with shear rates, hence treated as very close to Newtonian fluid and the change in viscosity with the application of shear was less noticed compared to other nanoparticle mixed fuel blends. The values of power law indices (n) for AC BDD (MNF0) fuel blend and high nanoparticle concentration mixed modified (MNF 0.3 and MNF0.4) fuel blends lie below 1, which indicates there non-Newtonian behavior. The viscosities of B20D80 0.1TiO2 blend fall within the specified range of international standard for petroleum diesel. This means that B20D80 0.1TiO2 A. Concinnia biodiesel and diesel fuel blends can be used efficiently in diesel engines with minor change in engine operating parameters.

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