

Research Article

Evaluation of Physio-Chemical Properties of Binary Blends of Mineral Diesel and Biodiesel

Pakistan.

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Abstract

Diminishing fossil fuel reserves have stimulated research into biofuel as potential renewable and sustainable replacements for fossil diesel. The present research aims to characterize and investigate the behavior of mineral diesel and biodiesel blends. The biodiesel oil was prepared from sunflower oil collected from the local market. Binary blends of mineral diesel and biodiesel in various proportions were prepared, e.g. 5%, 10%, 15%, 20%, 25%, and named as B5, B10, B15, B20, B25. Their various physicochemical properties were measured using standard ASTM/API methods, including specific gravity, API gravity, cloud point, pour point, aniline point, flash point, fire point, diesel index, viscosity, and distillation behavior. API gravity, aniline point, and diesel index decrease as the amount of biodiesel blended increases in the blend, while pour point, cloud point, flash point, fire point, and specific gravity increase with an increase in the amount of biodiesel blended in the commercial diesel oils.

Keywords: Biodiesel, Minrals, Mineral Diesel, Biofuels, Biodiesel, Physic-Chemical Characteristics

1. Introduction

The scientific community has been investigating new types of renewable energy sources, primarily in response to the greenhouse effect caused by the increasing use of fossil fuels. Alternatives such as biodiesel and ethanol have emerged as potential solutions to meet the rising energy demand while mitigating environmental impacts [1]. Among these alternatives, biodiesel has gained significant recognition as the most widely accepted substitute for diesel engines due to its technical, environmental, and strategic advantages. In comparison to fossil diesel, biodiesel exhibits enhanced lubricity, lower toxicity, a higher flash point, and biodegradability [2, 3].

Furthermore, biodiesel, being oxygenated, undergoes more complete combustion, resulting in reduced emissions of harmful substances and pollutants. It significantly decreases emissions of CO2, particulate matter, CO, Sox, volatile organic compounds, and unburned hydrocarbons. Moreover, biodiesel's improved biodegradability, reduced toxicity, and enhanced lubricity contribute to its environmental appeal when compared to conventional diesel fuel [4]. However, biodiesel has been associated with potential increases in nitrogen oxides (Knox) emissions. Additionally, biodiesel derived from vegetable oils or animal fats generally exhibits higher density, viscosity, cloud point, and certain number, while possessing lower volatility and heating value compared to diesel [5, 6]. Given that biodiesel and diesel are fully miscible, blending them in any proportion is feasible and recommended to enhance biodiesel's qualities [7, 8]. Nonetheless, differences in the chemical properties between biodiesel and diesel can impact their physicochemical characteristics, consequently affecting engine performance and pollutant emissions [9, 10].

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Biodiesel can be blended with diesel fuels and utilized in diesel engines with minimal or no modifications [11]. However, the fuel properties of biodiesel-diesel fuel blends undergo alterations based on the biodiesel content, as biodiesel possesses distinct fuel characteristics compared to conventional diesel fuels [12]. Prior to employing biodiesel-diesel fuel blends in a diesel engine, several crucial properties necessitate characterization [13]. These properties encompass kinematic viscosity, density, pour point, flash point, and distillation characteristics of the blends [14].

Kinematic viscosity stands as a paramount fuel property [15]. The application of biodiesel in diesel engines faces limitations due to certain physical properties, particularly viscosity [16]. Viscosity exerts influence on atomization quality, fuel droplet size, and penetration, thereby impacting combustion quality. Insufficient viscosity can lead to fuel system leakage, whereas excessive viscosity hampers fuel atomization, causing incomplete combustion, increased engine deposits, elevated energy requirements for fuel pumping, and wear on fuel pump elements and injectors. Moreover, higher viscosity poses challenges in cold weather conditions, as viscosity rises with decreasing temperature [17, 18].

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Density serves as a fuel property directly influencing engine performance characteristics. Numerous performance factors, such as certain number and heating value, are closely tied to density. This property affects fuel atomization efficiency. Additionally, diesel fuel injection systems meter fuel by volume, meaning that changes in fuel density impact engine power output due to variations in injected fuel mass [19].

Pour points define the lowest temperature at which fuel can still flow before gelling occurs. They serve to assess the cold flow operability of fuel, particularly crucial in cold climate conditions. Biodiesel exhibits a higher pour point compared to diesel fuels due to its elevated saturated fatty acid content. Blending biodiesel with diesel fuel presents an alternative approach to mitigate the cold temperature challenges associated with biodiesel [20].

Distillation involves determining the range of boiling points for fuels and serves to characterize the fuel based on the boiling temperatures of its components. Distillation characteristics provide valuable insights into engine performance and safety. The distillation range of diesel fuel impacts properties such as viscosity, flash point, and density. The flash point, defined as the lowest temperature at which the vapor above a sample ignites upon the application of an ignition source, holds significant importance. One notable advantage of biodiesel is its higher flash point compared to diesel fuel. While the flash point does not directly affect combustion, it enhances the safety of biodiesel in terms of storage, fuel handling, and transportation considerations [21, 22].

The current research aims to investigate the physicochemical properties of biodiesel-diesel blends with varying proportions. The objective is to examine the influence of biodiesel content on blend properties and establish a correlation between the blend proportion and its characteristics.

2. Experimental

2.1Chemical and reagents

All chemicals used were of analytical grade. Premium diesel oil sample was collected from Shell filling station in Peshawar city. The vegetable oil (sunflower oil) used for production of biodiesel was collected from the local market.

2.2 Biodiesel Preparation

Biodiesel was produced by alkaline catalyzed Tran's esterification of crude sunflower oil methyl esters. In a typical procedure 250 ml of sunflower oil was taken in 500 ml round bottom flask, and 50 ml of methanol was added to it 0.0875 ml of 1 % NaOH solution was added to it, and placed on hot plate. The mixture was stirred for about 20 min to 30 min at 60 oC. The mixture was transferred to separating funnel and allowed to stand. The bottom layer (glycerol, methanol and most of the catalyst) was drained out. The upper layer (methyl esters, some methanol and traces of the catalyst) was cleaned thoroughly by washing 5 times with water. The solution was then heated to 80 C for 30 min until cleared. The biodiesel layer was stored in glass bottle for further processing. The yield of biodiesel was 80 % [23, 24].

The optimum conditions for the methanolysis of sunflower oil were found to be methanol/sunflower oil molar ratio 6:1; reaction temperature, 60 °C, and NaOH catalyst concentration, 1.00% (w/w).

2.3 Blending of biodiesel and commercial diesel oil

The biodiesel produced in the laboratory was mixed with petro diesel in definite proportions, and stirred together to prepare blends of various compositions. Blends of five different compositions were prepared, mentioned as following:

| Amount of Petrodiesel (ml) | Amount of biodiesel (ml) | Sample code |
|----------------------------|--------------------------|-------------|
| 95 | 05 | В5 |
| 90 | 10 | B10 |
| 85 | 15 | B15 |
| 80 | 20 | B20 |
| 75 | 25 | B25 |

Table 2.1. Composition of biodiesel-petro diesel blends

2.4 Physic-chemical characterization of blends

The blends prepared by mixing biodiesel and commercial diesel oil were characterized by determining their different physical chemical properties. These included density, API gravity, aniline point, cloud point, diesel Index, flash point, fire point, pour point, specific gravity, kinematic viscosity and distillation behavior. All the parameters were determined by using standard ASTM/API procedures.

2.4.1 Determination of Specific Gravity and Ape Gravity

ASTM Standard test method was used to measure the density of the biodiesel, diesel fuel and their blends. Density and specific gravity was determined with the help of gravity bottle or pycnometer. A 25ml pycnometer was taken and filled with the sample, its mass was measured with digital balance. From the mass and volume of the sample, density was calculated. The density of water was also measured using the same procedure. The specific gravity of the samples was calculated from the densities of the water and the sample. The API gravity was calculated using the following equation [25]. API gravity = 141.5/Specific gravity -131.5

2.4.2 Determination of Pour point and Cloud point

The pour point and cloud point of the sample were measured using a pour point apparatus. Approximately 25 ml of the sample was taken in a sample tube, and a thermometer was

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securely inserted into the tube using a cork, ensuring that the thermometer bulb was submerged in the sample without touching the tube walls. The sample tube was then placed into an ice bath. The fluidity of the sample was periodically checked by tilting the tube slightly. The temperature at which the sample exhibited cloudiness or haze was recorded as the cloud point. To determine the pour point, the tube was removed from the ice bath, and the observed temperature at which the oil sample stopped flowing was recorded as T1. Subsequently, the sample tube was placed outside the ice bath in a beaker, and the temperature at which the oil sample began to flow again was noted as T2. The pour point was calculated as the average of T1 and T2 [26].

2.4.1 Determination of Kinematic viscosity

Kinematic viscosity of samples was measured through Ostwald viscometer. The standard procedure was applied as reported in literature. All the sample and blends of biodiesel viscosity was noted and compared the reported data as in literature [27].

2.4.2 Determination of Aniline point

Aniline point of the blends was determined through Aniline point apparatus applied standard procedure as reported in literature. The aniline point of the samples was compared with the literature [28].

3. Results and Discussion

In the present study, binary blends of biodiesel and petro diesel were prepared in various proportions. Biodiesel was synthesized from sunflower oil in the laboratory, while petro diesel was obtained from a local filling station. The biodiesel-petro diesel blends underwent characterization through the determination of various physicochemical properties

the determination of various physicochemical properties, including density, specific gravity, API gravity, kinematic viscosity, pour point, cloud point, flash point, fire point, diesel index, and distillation behavior, among others. A detailed discussion of the results for each characteristic is provided below.

3.1 Specific gravity and API gravity

Results of density, specific gravity and API gravity are given in table 3.1. It is clear from the data that the diesel oil shows the specific gravity of about 0.869, and the pure biodiesel show specific gravity of 0.989. Among the various blends i.e. B5 to B20, the specific gravity linearly increases from 0.863 to 0.986, as the proportion of biodiesel increases. The standard values of specific gravity for the biodiesel and petro diesel are 0.88 and 0.85 respectively. However, the data show that the biodiesel has very value of specific gravity and therefore the blends also show high values of specific gravities [29].

The API gravity is a more convenient value for the assessment of specific gravity of the fuels developed by American Petroleum Institute [25]. The standard or recommended value of API gravity for the diesel oil suitable for compression engine is around 40. However the data show that the API gravities of biodiesel and petro diesel blends in different proportions i.e. B5, B10, B15, B20 and B25 as well as original biodiesel is fairly less than the diesel range [30].

| Sample | Density g/cm ³ | Specific Gravity | API gravity |
|----------------|---------------------------|------------------|-------------|
| Mineral diesel | 0.869 | 0.869 | 33.2 |
| B5 | 0.863 | 0.863 | 32.4 |
| B10 | 0.945 | 0.945 | 18.09 |
| B15 | 1.041 | 1.041 | 4.33 |
| B20 | 1.044 | 1.044 | 3.93 |
| B20 | 1.051 | 1.051 | 3.01 |
| Biodiesel | 1.17 | 1.17 | - |

Table 3.1. Density, specific gravity, and API gravity of biodiesel-petrodiesel blends

3.2 Cloud point and pour point

The pour point and cloud point represent the highest temperatures utilized to assess the cold flow characteristics of fuel oil. These points establish the minimum temperature thresholds at which the fuel can be conveniently handled [31]. The pour point indicates the presence of long-chain paraffin's or wax content in the petroleum fraction, which tends to crystallize at low temperatures, posing challenges for oil transportation and storage. The pour point is a significant property that determines the suitability of oil usage in colder regions where temperatures drop below freezing point. Under such conditions, the oil becomes non-flow able, leading to pipe blockages. To mitigate this issue, various chemical additives known as pour point depressants are incorporated to minimize oil freezing at low temperatures. The recommended pour point range for diesel fuels typically falls between -35 to -15 °C. [32].

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| Table 3.2: Pour point and | Cloud point of biodiesel- | petro diesel blends |
|---------------------------|---------------------------|---------------------|
|---------------------------|---------------------------|---------------------|

| Sample | Cloud point °C | Pour point °C |
|-------------------|----------------|---------------|
| Commercial diesel | 14 | -11.5 |
| В5 | 15 | -10 |
| B10 | 15.5 | -9.5 |
| B15 | 16 | -7.5 |
| B20 | 15.6 | -4 |
| B25 | 20 | -2.5 |
| Biodiesel | 4 | Below -2.5 |

Table 3.2, summarize the values of cloud and pour points for pure petro-diesel, biodiesel and their blends in various proportions. The data shows that for biodiesel and petro-diesel the values of pour point were < -2.5 and -11.5 oC, whereas the values of cloud point were 4 and 14 oC. Whereas in case of biodiesel and petro diesel blends the values of cloud point gradually increases from 15 to 20 oC, and the values of pour point decreases from -10 to -4 oC as the amount of biodiesel increases. Since the biodiesel is rich in high molecular weight fatty esters, which tends to solidify at low temperature and leads to increase the pour point [32]. Therefore, as the amount of biodiesel increases in petro-diesel blends, the pour point values linearly increase. It is clear from the data that the pour point values of the blends occur in the recommended range [33].

3.4 Determination of kinematics viscosity:

The kinematics viscosity was determined at 40°C using Ostwald viscometer. In a typical procedure, the viscometer was filled with the samples by one end and sucked up to the designed mark on the upper part of small bulb. Stop watched was turn on simultaneously as the sample was allowed to flow. By the time when liquid surface reached to the lower mark, stopwatch was stopped and the time flow was recorded. The viscosity of water also determined similarly using the flow rate and viscosity of each sample was calculated [34].

3.4.1 Determination of Aniline point and diesel index

Aniline point was determined using aniline point apparatus. Equal volume of aniline and oil (25 ml) were taken in the sample tube and the thermometer was fixed into it with the help of a cork. The sample tube was placed in oil bath and started heated gently. The temperature was noted as T1 when the samples were miscible initially. Heating is stop and tube is allowed to cool. The temperature, where the two phases are separate out was recorded as T2. The aniline point was calculated as the average of both temperatures [35, 36].

The diesel index of sample was calculated from value of aniline point and API gravity using the following relation [37].

D.I = Aniline point × API gravity/100

4. Conclusion

The current study yields the following conclusions: The specific gravity, API gravity, cloud point, flash point, aniline point, and diesel index range from 0.869 to 1.17, 33.2 to 3.01, 14 °C to 4 °C, 78 °C to 92 °C, 92 °C to 105 °C, 69 °C to 25 °C, and 20.7 to 1.4, respectively. The boiling point of blends increases with higher biodiesel content due to the presence of larger molecular esters in biodiesel. API gravity, aniline point, and diesel index decrease as the proportion of biodiesel in the blend increases. On the other hand, pour point, cloud point, flash point, fire point, and specific gravity increase with higher biodiesel content in commercial diesel oils. Biodiesel derived from sunflower oil proves to be a favorable choice with significant potential, meeting requirements and ensuring future fuel supply.

4.1. Conflicts of interest

The authors have no conflicts of interest to declare. All co-authors have seen and agree with the contents of the manuscript and there is no financial interest to report. We certify that the submission is original work and is not under review at any other publication.

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