Improvement of low-quality diesel through the use of biodiesel

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ABSTRACT

The transportation of petroleum diesel, petrol and jet fuel using the same pipeline lead to the formation of an off-specification product known as the interface. The interface cannot be used on its own as it does not meet the quality specifications. It should be blended with a product of higher quality. Failure to blend the interface results in loss of the product and costs will arise that are associated with its disposal. In this paper, the authors examine the use of jatropha biodiesel to improve the quality of the interface. The tests were performed using the American Society for Testing and Materials (ASTM) methods. Jatropha biodiesel was used since it is being produced locally. Blending ratios of 3%, 5% and 7% interface were used and the biodiesel was found to have average flash point values of 138 °C, 135 °C and 132 °C respectively. These values are greater than 130 °C which is the minimum expected value. The sulphur content and acid number improved indicating that biodiesel can be effectively used to improve the quality of petroleum diesel.

Keywords: biodiesel, off-specifications, interface, blending, petroleum diesel, flash point

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1.0 INTRODUCTION

A multipurpose pipeline is used to transport petroleum-based fuels from one point to another. These products are petrol, diesel and jet fuel. As a result, a mixture of two products called an interface is produced when the products mix. The interface does not meet the specifications hence cannot be used on its own. The interface should be blended with a better quality product to meet the required standards. The blending process is usually delayed since it depends on the availability of higher quality diesel. As a result, the interface increases to millions of liters thus affecting the fuel supply, where less fuel than intended is available to the market, leading to fuel shortages.

According to the National Oil Infrastructure Company of Zimbabwe (NOIC), (2013) diesel with a minimum flash point of 57 °C is accepted in Zimbabwe. Other countries including Zambia, the Democratic Republic of Congo and Tanzania pegged their minimum flash point at values greater than 57 °C. Furthermore, the interface product has flash point values lower than 57 °C and does not meet the specification of diesel. Since some of these countries get their fuel through Zimbabwe, they sometimes wait for a longer period to get the fuel that best suits their specifications. This does not only affect business relations but can also lead to fuel shortages in these countries.

Zimbabwe is currently facing fuel challenges, as a result, the fuel is mostly available at the illegal markets where it is overcharged. There is also a noticeable price increase in petroleum-based fuels. From January 2019 to date, diesel prices have been increasing. The economy is greatly affected as every business is linked to fuel prices. An increase in fuel prices leads to an increase in the transport cost, thus affecting the prices of goods and services. Power grid electricity is affected by load shedding and many companies are losing production time. Some of the companies rely on diesel as an alternative source of fuel, but this is hindered by diesel shortages. Many companies are not operating at their full capacity as they rely on diesel fuel for their dayto-day business. They need fuel for their cars, machinery, and generators. Therefore, fuel shortage leads to a decline in production thereby affecting the economy as a whole.

Biodiesel can be utilized in coming up with blending ratios that can be used in improving the low-quality petroleum diesel. Since biodiesel has good properties such as high flash point and lubrication properties, these could be utilized to come up with a better product (Ajav, Singh and Bhattacharya, 1999). Biodiesel is locally available and effort is being made for its massive production. The production of biodiesel is expected to grow in the next few years due to the increase in the jatropha fields (Matabyu, 2018). This is advantageous as the blending can be done each time an interface is created instead of waiting for higher quality petroleum diesel. This increases the availability of fuel in Zimbabwe and those countries which obtain their fuel from Zimbabwe. The use of biodiesel implies that large quantities of vegetable oil will be needed hence many people will be employed to work in the jatropha fields (Segon et al., 2006). This reduces the rate of unemployment thereby boosting the economy. Also, the pipeline transportation costs will decrease, since they will be fewer petroleum diesel imports. This can reduce diesel prices thereby increasing affordability to customers.

Although in some developed countries the use of biodiesel blends looks common, it seems the popular blending is between biodiesel and good quality petroleum diesel. Developing countries seem to be lagging on the adoption of biofuels particularly biodiesel. This may be because its potential has not been researched and documented. Thus, this research expands the knowledge by assessing if biodiesel can also be used to improve the quality of low-quality petroleum diesel. The study investigates how the blending of petroleum diesel with jatropha biodiesel produced locally in Zimbabwe can improve the low quality petroleum diesel. They are different types of biodiesel manufactured from different countries. These are made from different raw materials and processes, thus the quality of such products is likely to be different. If Zimbabwe is successful in providing a substitute for diesel blending, it will come with many advantages. Considering the vast land in Zimbabwe, creating jatropha fields will not be a challenge, hence creating employment indirectly. According to the knowledge of the authors, it seems no research has been done focusing on the improvements of low-quality petroleum diesel in the Zimbabwe context.

Biodiesel is manufactured to blend petroleum diesel. In Europe, different industrial sectors such as transportation and construction have embraced the use of biodiesel with Germany leading on the production and utilization of biodiesel (Balat and Balat, 2008). Some American companies such as Minnesota have implemented a mandate B5 blend (5% biodiesel and 95% petroleum diesel). An assessment indicates that biodiesel has the potential of replacing 5% or more of petroleum diesel (McCormick et al., 2011).

1.1 Advantages of biodiesel

Biodiesel has several advantages over petroleum fuel. Its properties such as cetane number, oxygen content, viscosity Isioma et al., (2013), and density have a greater influence on the performance of the engines and the gas emissions (McCarthy et al., 2011). Unlike petroleum diesel, biodiesel has an excellent lubricity property and is typically low in sulphur content (Rakopoulos et al. 2010). The presents of sulphur in diesel lead to negative environmental effects such as acid rain formation. Biodiesel can reduce the over-dependence on petroleum, which is more advantageous for those countries that do not have oil reserves. This can help in leveraging on the use of petroleum diesel since biodiesel is produced locally from vegetable oils leading to the reduction in petroleum diesel demand. Apart from that, the use of biodiesel can also help reduce greenhouse gas emissions (Rakopoulos et al., 2008) and health risks (Li et al., 2005) since it is not a fossil fuel. Many air pollutants can be reduced, for example, particulate matter Murugesan et al., (2009), carbon oxides, hydrocarbons, nitrogen oxides and sulphur oxides (Rakopoulos et al., 2008; Isioma et al., 2013; McCarthy et al., 2011). The carbon in petroleum diesel is high as a result it produces more carbon dioxide compared to biodiesel (Ajav et al., 1999). Also, biodiesel is renewable. biodegradable and nontoxic (Murugesan et al., 2009). Considering the advantages of biodiesel, the need for researching biodiesel utilisation is increasing rapidly (McCarthy et al., 2011).

1.2 Significance of the quality tests

Quality tests are important as they determine if products are within specifications before their use. The significance of the quality tests is explained in this section.

1.2.1 Colour and appearance

Colour and appearance are critical as it is readily observed by the customers. They indicate the extent of petroleum product refining. Any deviations indicate a possibility of contamination. Diesel contaminated with water is noticed by a cloudy appearance. The diesel must be clear and bright with a yellow or amber colour. The presence of these materials generally indicates poor fuel handling practices. Water and sediment cause shortened filter life or plugged fuel filters which can lead to fuel starvation in the engine. In addition, water can corrode the engine.

1.2.2 Flash point

Flash point is the lowest temperature that the fuel ignites (Li et al., 2005). It indicates the possibility of diesel forming a flammable mixture with air (Murugesan et al., 2009). Flash point is used to measure the flammability hazard of diesel (Sajjad et al., 2014). It is more important in determining if diesel is not contaminated with a flammable substance such as petrol (Fernando et al., 2007).

1.2.3 Copper strip corrosion

Crude oil contains sulphur compounds, a lot of them are removed during the refining process. The remaining sulphur compounds are corrosive (Sajjad et al., 2014). The corrosive effect depends on the type and amount of the sulphur compounds. The copper corrosion test analyses how corrosive the diesel is (Fernando et al., 2007).

1.2.4 Sulphur content

The sulphur content method measures the amount of sulphur in diesel (Dhingra et al., 2014). The level of sulphur must be carefully monitored because when sulphur is burnt harmful gases such as sulphur dioxide are produced. These gases have detrimental effects on the environment such as causing the formation of acid rain. The knowledge of sulphur content is important to determine the performance and handling properties (Sajjad et al., 2014). The viscosity affects the flow of diesel in the engine (Fernando et al., 2007). Knowledge of viscosity is vital to guide the storage and handling activities (Isioma et al., 2013). Kinematic viscosity predicts the lubricity properties of diesel (Li et al., 2005).

1.2.6 Density

Density is a crucial characterisation of different petroleum products (Li et al., 2005). It is an important test that can be used to check for the contaminations of diesel by other petroleum products. Contaminated diesel has a density outside the expected range.

1.2.7 Acid number

Petroleum products and biodiesel contain acidic compounds that need to be measured. The acid number measures how acidic the diesel is (Fernando et al., 2007). To determine the acid number, base titrations are performed (Sajjad et al., 2014).

1.2.8 Water content

Water content is crucial as water affects the refining and transfer processes. Water affects the performance of the engine and can therefore damage it (Fernando et al., 2007).

2.2.9 Distillation

This method is used to determine the boiling range of petroleum products. The distillation indicates the volatility characteristics of diesel. Distillation is important in assessing the safety, storage and performance characteristics (Fernando et al. 2007; McCormick et al. 2011). It outlines the issues to do with engine warm-up, starting and vapour lock (McCormick et al., 2011). Distillation profile also indicates contamination of diesel with a volatile substance such as petrol.

2. MATERIALS AND METHODS

Quality control tests were performed on the various types of diesel. Samples of biodiesel, petroleum diesel with a low flash point and a diesel interface were used. Firstly, the three samples of jatropha biodiesel were analysed to determine if they meet specifications. Secondly, the three samples of petroleum diesel with a low flash point were analysed. The petroleum diesel was blended with the three biodiesel samples at a blending ratio of 1%, 2% and 3%. The biodiesel was also blended with the interface at 3%, 5% and 7%. The tests performed on the three samples were density, flash point, kinematic viscosity, acid number, copper strip corrosion, water content, sulphur test and distillation.

2.1 Quality control tests

This section describes the tests that were performed on the analyses of the samples.

2.2 Density

Density was performed using a glass hydrometer following the ASTM method D1298. The temperature reading of the sample was recorded using a laboratory thermometer. Readings were corrected to the reference temperature of 20 °C using the petroleum measurement tables.

2.3. Appearance and Colour

The appearance and colour method was done using the visual method. It was conducted by observing the appearance and colour of the sample inside a glass measuring cylinder.

2.4 Water content

The water content test was performed using the distillation method as explained by ASTM method D95. The sample was mixed with a water-immiscible solvent and refluxed. The water-solvent mixture was captured in a calibrated trap, and the volume of water was measured.

2.5 Kinematic viscosity

Kinematic viscosity test was performed using a SETA water bath preheated to 40 °C. ASTM method D445 was used for this test. The time taken for the diesel to flow through the viscometer was recorded. The viscosity was calculated by multiplying the time taken and the calibration constant of the viscometer.

2.6 Copper strip corrosion

A SETA water bath was used to heat the copper strips for 3 hours at 100 °C. The ASTM D130 method was followed during this test. At the end of the experiment, the appearance of the strip was compared with the standards to determine the extent of corrosion.

2.7 ASTM Colour

ASTM D1500 standard method for determining colour ranges of diesel sample was used. The Lovibond petroleum oils comparator, AF650 instrument was used. The colour of the diesel sample was matched with the standards.

2.8 Acid number

The acid number of the sample was determined using the ASTM D974 method. 10g of sample, 100 ml of the titration solvent and few drops of the indicator were mixed and titrated with 0.1 mol/dm³ of potassium hydroxide (KOH). Another titration flask is prepared in the same way but without the sample. This acted as a blank sample. The acid number is determined using equation 1.

$$mg \ of \frac{KOH}{g} = (A - B)M \ \frac{56.1}{W}$$
 [1]

Where A = KOH required for titration of the sample, ml.

B = KOH required for titration of the blank sample, ml.

M = Molarity of the KOH solution.

W = Weight of sample used, g.

2.9 Sulphur content

Sulphur in petroleum products was determined by the lamp method, where the sample was burnt in a closed system as stated by ASTM D4294 method. The sulphur oxides produced during combustion were reacted with hydrogen peroxide and titrated with sodium hydroxide (NaOH) base. The equation for determining the amount of sulphur is given below.

Sulphur content =
$$16.03M \frac{A}{10W}$$
 [2]

Where A is the amount of NaOH solution (in ml) required for titration, M is the molarity of NaOH solution and W is the mass of the sample in grams.

2.10 Distillation

Distillation was conducted using the automatic distillation tester: AD-7 equipment which made use of the ASTM D86 standard test method for distillation of heavy hydrocarbon mixtures. The temperature at 90% volume was noted.

2.11 Flash point

Flash point was determined using the Pensky-Martens closed cup apparatus. ASTM D93 procedure was followed.

3. RESULTS AND DISCUSSION

The quality control tests performed on three samples (samples 1, 2 and 3) of biodiesel gave a flash point range of $140.2 \,^{\circ}\text{C} - 140.4 \,^{\circ}\text{C}$. The acid number ranged from $0.21 - 0.25 \,\text{mg}/100 \text{ml}$. The copper strip corrosion results were all 1A. Table 1 shows the detailed results. The results met the required specification (see appendix 2) as all the values were within the expected ranges.

Test	Sample 1	Sample 2	Sample 3
Flashpoint (°C)	140.4	140.2	140.4
Appearance and Colour	Clear and bright Yellow	Clear and bright Yellow	Clear and bright Yellow
Density at 20 °C (Kg/L)	0.8707	0.8708	0.8706
Water Content (% Volume)	< 0.05	< 0.05	< 0.05
Kinematic viscosity at 40 °C (Centistokes)	4.43	4.42	4.44
Copper strip corrosion 3hrs at 100 °C	1A	1A	1A
ASTM Colour	1	1	1
Acid number (mg/100ml)	0.25	0.24	0.21
Sulphur content (% mass)	0	0	0
Distillation/ 90% recovered (°C)	360	360	359

Table 1: Biodiesel analysis

3.1 Flash point results for biodiesel blending with interface

The flash point results for biodiesel blending with interface are outlined in Figure 1. The average flashpoint values were 138 °C, 135 °C and 131 °C for 3%, 5% and 7% interface respectively. These values are all greater than the minimum required

value of 130 °C. This shows that even on a large amount of interface, the biodiesel met the specifications. Thus, the amount of interface can be reduced through blending with biodiesel.



Figure 1: Flash point at different percentage interface

3.2 Comparison of physical properties for pure biodiesel samples AND interface blends

The comparison of physical properties for pure biodiesel samples are listed in Table 1 and those of interface blends are listed in Tables 2-4. Table 2 shows the results obtained when the biodiesel was blended with 3 % interface. The density ranged from 0.8696 Kg/L – 0.8698 Kg/L.

The kinematic viscosity values ranged from 4.29 – 4.34 centistokes while the water content values were all less than 0.05 % volume. Generally, all the performed tests were within the specifications. This shows that it is possible to blend the biodiesel with 3% of the interface.

Test	Sample 1	Sample 2	Sample 3
Appearance and Colour	Clear and bright Yellow	Clear and bright Yellow	Clear and bright Yellow
Density at 20 °C (Kg/L)	0.8696	0.8698	0.8697
Water Content (% Volume)	< 0.05	< 0.05	< 0.05
Kinematic viscosity at 40 °C (Centistokes)	4.30	4.29	4.34
Copper strip corrosion 3hrs at 100 °C	1A	1A	1A
ASTM Colour	1	1	1
Acid number (mg/100ml)	0.25	0.24	0.21
Sulphur content (% mass)	0.0010	0.0010	0.0010
Distillation, 90% recovered (°C)	349	350	351

Table 2: Blending at 3% interface

Table 3 highlights the results obtained when the biodiesel was blended with 5 % interface. The sulphur content values ranged 0.0012 - 0.0013 % mass while the copper strip corrosion values were all 1B. The performed results are within specifications showing that it is possible to blend the biodiesel with 5 % interface.

Table 4 indicates Tthe results of the blending of biodiesel with 7% interface. The acid number were 0.15, mg/100ml 0.16 mg/100ml and 0.13 mg/100ml for sample 1, 2 and 3 respectively. The copper strip corrosion were all 1B while the ASTM colour values were all 1. The results meet the specifications showing that 7% interface can be used for blending

Table 2: Blending at 5% interface

Test	Sample 1	Sample 2	Sample 3
Appearance and Colour	Clear and bright	Clear and bright	Clear and bright
	Yellow	Yellow	Yellow
Density at 20 °C (Kg/L)	0.8667	0.8670	0.8676
Water Content (% Volume)	< 0.05	< 0.05	< 0.05
Kinematic viscosity at 40°C	4.20	4.22	4.25
(Centistokes)			
Copper strip corrosion 3hrs at 100	1B	1B	1B
°C			
ASTM Colour	1	1	1
Acid number (mg/100ml)	0.23	0.21	0.19
Sulphur content (% mass)	0.0012	0.0013	0.0012
Distillation, 90% recovered (°C)	340	342	342

Table 3: Blending at 7% interface

Test	Sample 1	Sample 2	Sample 3
Appearance and Colour	Clear and bright	Clear and bright	Clear and bright
Density at 20 °C (Kg/L)	0.8638	0.8638	0.8636
Water Content (% Volume)	< 0.05	< 0.05	< 0.05
Kinematic viscosity at 40 °C (Centistokes)	4.05	4.08	4.10
Copper strip corrosion 3hrs at 100 °C	1B	1B	1B
ASTM Colour	1	1	1
Acid number (mg/100ml)	0.15	0.16	0.13
Sulphur content (% mass)	0.0014	0.0014	0.0015
Distillation, 90% recovered (°C)	334	335	334

All in all, the sulphur value increases as the percentage of interface increases showing that the interface contains sulphur compounds. The sulphur content increases as the amount of sulphur compounds increases. Density, kinematic viscosity and acid number decrease as the percentage of interface increases. This is because the interface is lighter, less viscous than biodiesel. Also, biodiesel contains more acid compounds than the interface. From Table 1, it can be observed that 90% of each of the biodiesel

samples analysed were recovered through distillation at around 360 °C. Upon blending the biodiesel with the interface (Tables 2-4), it could be observed that 90% of the samples were recovered at lower temperatures of around 350 °C for the 3% interface, 341 °C for 5% interface, and 333 °C for 7% interface. This is because the interface has a lower boiling point than biodiesel. Also. The tarnish of the copper strip increases with an increase in the percentage of interface and this is due to the increase in sulphur content.

Table 5 illustrates the results obtained from the analysis of the petroleum diesel sample. The flash point values were 58.1 °C, 58.3 °C and 58.6 °C for samples 1, 2 and 3 respectively. The water content values were less than 0.02%

volume for all the samples. The results indicate that although the samples met the specifications (Appendix 2), the flash point was low and close to the threshold value of 57 °C. Therefore, the petroleum diesel was blended with biodiesel

Test	Sample 1	Sample 2	Sample 3
Flashpoint (°C)	58.1	58.3	58.6
Appearance and Colour	Clear and bright	Clear and bright	Clear and bright
	Yellow	Yellow	Yellow
Density at 20 °C (Kg/L)	0.8261	0.8268	0.8269
Water Content (% Volume)	< 0.02	< 0.02	< 0.02
Kinematic viscosity at 40 °C (Centistokes)	3.25	3.25	3.27
Copper strip corrosion 3hrs at 100 °C	1B	1B	1B
ASTM Colour	1	1	1
Acid number (mg/100ml)	0.10	0.11	0.10
Sulphur content (% mass)	0.05	0.051	0.05
Distillation 90% volume (°C)	331	333	334

Table 4: Analysis of petroleum diesel

3.3 Flashpoints after blending of petroleum diesel with biodiesel

Figure 2 illustrates the flash point results obtained when the petroleum diesel was blended with 1%, 2% and 3% biodiesel. The obtained average flash point values were 64.5 °C, 66.2 °C and 74.3 °C for samples 1, 2 and 3. The flash point values increase with an increase in the percentage of biodiesel. This shows that the quality of petroleum diesel can be enhanced by using biodiesel.



Figure 2: Flash point at different biodiesel percentage

3.4 Other quality parameters after blending petroleun diesel with biodiesel

Table 6 shows results for the blending of petroleum diesel with 1% biodiesel. The water content values were less than 0.02% volume for all the samples. The sulphur content values for sample 1 was 0.045% mass and 0.046% mass

for sample 2 and 3. The density range from 0.8270 Kg/L - 0.8280 Kg/L. All the performed tests were within the specifications indicating a possibility of blending petroleum diesel with 1% of biodiesel

.Table 5: Blending of petroleum diesel with 1% biodiesel

	Sample 1	Sample 2	Sample 3
Appearance and Colour	Clear and bright Yellow	Clear and bright Yellow	Clear and bright Yellow
Density at 20 °C (Kg/L)	0.8270	0.8278	0.8280
Water Content (% Volume)	< 0.02	< 0.02	< 0.02
Kinematic viscosity at 40 °C (Centistokes)	3.34	3.37	3.40
Copper strip corrosion 3hrs at 100 °C	1B	1B	1B
ASTM Colour	1	1	1
Acid number (mg/100ml)	0.18	0.14	0.13
Sulphur content (% mass)	0.045	0.046	0.046
Distillation 90% volume (°C)	340	342	341

Table 7 outlines the results for the 2% blend. The density ranged from 0.8300 Kg/L - 0.8304 Kg/L. The copper strip corrosion results were 1B for all the 3 samples and ASTM colour was 1 in all the

samples. The results for all the performed tests were meeting the specifications indicating that a 2% biodiesel blend is possible

Table 6: Blending of petroleum diesel with 2% biodiesel

Test	Sample 1	Sample 2	Sample 3
Appearance and Colour	Clear and bright	Clear and bright	Clear and bright
	Yellow	Yellow	Yellow
Density at 20 °C (Kg/L)	0.8300	0.8302	0.8304
Water Content (% Volume)	< 0.02	< 0.02	< 0.02
Kinematic viscosity at 40 °C	3.55	3.48	3.60
(Centistokes)			
Copper strip corrosion 3hrs at 100	1B	1B	1B
°C			
ASTM Colour	1	1	1
Acid number (mg/100ml)	0.23	0.20	0.19
Sulphur content (% mass)	0.039	0.039	0.041
Distillation 90% volume (°C)	351	352	351

The results for the blending of petroleum diesel with 3% biodiesel is highlighted in Table 8. The kinematic viscosity ranged from 3.99 - 4.29 centistokes, density ranged from 0.8415 Kg/L – 0.8423 Kg/L and the sulphur content range was 0.025% mass – 0.03% mass. All the results met the specifications thus petroleum diesel can be blended with 3% of biodiesel.

Assessing Table 5 - 8 it can be deduced that the density and kinematic viscosity increase with an increase in biodiesel since biodiesel is heavier and denser than petroleum diesel. On the other hand, copper corrosion and sulphur content values decrease as the percentage of biodiesel increases since the biodiesel do not contain any sulphur products. Generally, as the percentage of

biodiesel increases, the quality of the diesel improves

Test	Sample 1	Sample 2	Sample 3
Appearance and Colour	Clear and bright Yellow	Clear and bright Yellow	Clear and bright Yellow
Density at 20 °C (Kg/L)	0.8415	0.8423	0.8420
Water Content (% Volume)	< 0.02	< 0.02	< 0.02
Kinematic viscosity at 40 °C (Centistokes)	4.10	3.99	4.29
Copper strip corrosion 3hrs at 100 °C	1A	1A	1A
ASTM Colour	1	1	1
Acid number (mg/100ml)	0.25	0.25	0.24
Sulphur content (% mass)	0.030	0.025	0.028
Distillation 90% volume (°C)	354	357	359

Table 7: Blending of petroleum diesel with 3% biodiesel

From Table 5, it can be observed that 90% of each of the biodiesel samples analysed were recovered through distillation at around 332 °C. Upon blending the biodiesel with biodiesel (Tables 6-8), it could be observed that 90% of the samples were recovered at higher temperatures of around 341 °C for the 1% biodiesel, 351 °C for 2% biodiesel, and 357 °C for 3% biodiesel. This is because biodiesel has a higher boiling point than petroleum diesel.

4.0 CONCLUSION AND RECOMMENDATIONS

The research outlines the possibility of improving the quality of interface by using biodiesel. Quality k at the possibility of using biodiesel and support its full production. For a compressive analysis, it is necessary to try higher blending ratios such as B10, B20, constituting 10% biodiesel and 20% biodiesel respectively. Further trials can also be done on different types of biodiesel. Furthermore, tests should be done on a running engine to verify these laboratory results. It is also of paramount

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importance to do tests on emissions of gases and other tests like the cetane index for the blended petroleum-biodiesel fuel.

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