

Review Paper

The Effect of the Addition of Biodiesel in the Fossil Diesel to Its Characterizing Parameters

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Abstract: Nowadays it is clear that all the scientific efforts are directed of finding the alternative resources for the fuels, in all national and international levels of different countries, as well as in our country. Due to its importance, there have been a lot of literature survey and are established some experimental set-up to try profiting biodiesel using different feedstocks usually form the wastes. As it can be understandable, there are a lot of processes to reach the required quality of the biodiesel in order to be ready to use for operation in internal combustion engines. One of the reasons for this resistance is a certain lack of knowledge about the effect of biofuels on engine emissions. This paper presents environmental and economic benefits from the use of biodiesel, and the impact on the improvement of qualitative indicators of the amount of biodiesel added to fossil diesel. The purpose is to maintain constant engine performance, due to changes beginning with the influence of the quantity of fuel to power motor, fuel consumption and thermal efficiency. Which is the most important and what should be emphasized more in this scenario, it is fact that the comparisons between environment biodiesel emissions and fossil diesel. There are closely related come presence in the burning gases the following material such as nitric oxides and particulate matter, the latter not only in mass and composition, but also in size distributions.

Keywords: biodiesel, diesel, emissions, environment, characterization

Introduction

Energy sources are classified as renewable and non-renewable. Energy obtained by hydro, solar, wind, biomass and wastes are renewable energy sources, while fossil fuels are non-renewable energy sources as was mentioned in (Roy, 2004).

The issues of energy availability and its security have caused serious concerns around the world and prompted researchers to look for better alternatives to reduce the dependency on petroleum products. Fossil fuels have a negative effect on environment, by emitting CO_2 , CO_3 , NO_3 and smoke emissions when used as fuel in combustion devices. NO_x and CO₂ cause greenhouse effect and SO_x cause acid rains as was mentioned in (Kalam *et al.*, 2003). Biofuels produced from lignocellulosic materials and vegetable oils provide a feasible solution to the twin crises of fossil fuel depletion and environmental degradation. Biodiesel is considered as a promising alternative fuel for diesel engines. It is an oxygenated fuel made from vegetable oils and animal fats by the conversion of the triglycerides to esters (primarily methyl esters) via various esterification processes as was mentioned in (Ramadhas et al., 2005). The fuel characteristics of biodiesel are similar to that of fossil diesel fuel and it permits the biodiesel to use as an alternative fuel for diesel engines without any major modification. Its additional advantages include outstanding lubricity, excellent biodegradability, superior combustion efficiency and low toxicity, among other fuels as was mentioned in (Balat et al., 2010). Many studies show that unburned hydrocarbons (HC), carbon monoxide (CO) and sulfur levels are significantly less in the exhaust gas, while using biodiesel as fuel. However, a noticeable increase in the oxides of the nitrogen (NOx) levels is reported with biodiesel as was mentioned in (Sahoo et al., 2009), (Demirbas et al., 2011), (Lapuerta et.al., 2008), (Narayana et al., 2008). Although biodiesel is considered as a potential alternative fuel, it has some demerits like poor cold flow properties and lower oxidation stability than petroleum fuels as was mentioned in (Knothe, 2005; Dunn 2005). Saturated compounds are responsible for the unfavourable cold flow properties observed in biodiesel, and the unsaturated esters are mainly responsible for the reduced oxidation stability as was mentioned in

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(Dunn, 2005). Treatment with oxidation inhibitors containing hindered phenols is the most common approach to increase the oxidative stability of biodiesel.

A growing concern over the environmental effects of diesel and diminishing natural resources has led to the development of biodiesel. Biodiesel has promising potential as eventually replacing most of the diesel used in automobiles. Currently, a significant amount of air pollution is contributed by pollutants from car exhaust and fuel emissions. This then leads to the question of how does exhaust and emissions from biodiesel differ from diesel. Would using biodiesel improve fuel emissions or will this new fuel have no substantial effect on the environment? Petroleum diesel has many combustion products such as: carbon dioxide, carbon monoxide, nitrogen oxides, Sulphur dioxide, polycyclic aromatic hydrocarbons, and particles of soot, dust, smoke, and aerosols (particulate matter). Carbon dioxide contributes to global warming by acting as a "greenhouse gas" and keeps heat from escaping into the atmosphere. Nitrogen oxides lead to formation of ozone along with hydrocarbons and accounts for the ground level smog present in major cities. Hydrocarbons are also suspected of being carcinogenic and particulate matter can lead to complications in health and the respiratory system as was mentioned in (Demirbas, 2005). Long term diesel emission is harming the environment, so if biodiesel does produce a significantly lower amount of air pollution then the incentive for everyday use is even stronger.

The definition of biodiesel is the mono alkyl esters of the fatty acids derived from vegetable oils. Alcohol and a catalyst are mixed with vegetable oil producing glycerin and methyl esters, the biodiesel component, through transesterification as was mentioned in (Lue et al., 2001). This process is necessary in order to lower the viscosity of the oil and increase fuel efficiency. It is also important to remember that there are multiple types of biodiesel based on the type of oil used. Palm seed, soybean, and peanut oil are all commonly used for biodiesel as was mentioned in (Chen et al., 2007). Different types of oil may lead to slightly different emission results. Based on current research the most popular and most successful way of collecting and analyzing car exhaust and emissions is by using a dilution tunnel for the initial collection (Chen *et al.*, 2007). A dilution tunnel is a large tube or tunnel that provides space where the gases from car exhaust can mix and become diluted enough for later analysis. In order to determine the differences between petroleum and biodiesel emission, car exhaust will be collected and analyzed with a dilution tunnel. Car exhaust is a logical source for fuel emissions because the exhaust is a mixture of gases, vapors, and solids providing a source for multiple emission products as was mentioned in (Aulich *et al.*, 2005).

Biodiesel as a Fuel and as a Blending Component

As a Fuel

Biodiesel (B100) is defined as "a fuel comprised of monoalkyl esters of long-chain fatty acids derived from vegetable oils or animal fats." In addition, it must meet all of the parameters as defined within the ASTM specification D6751, "Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels" as was mentioned in (Harris 2005). Biodiesel is a fuel designed as a blendstock for use in blending with petroleum diesel fuel. It is not intended for use with gasoline. Biodiesel has been proven to reduce the emissions of hydrocarbons, carbon monoxide and particulates when used alone or with blends that include petroleum diesel. Biodiesel has excellent lubricity properties and is typically low in sulphur content, thus meeting the needs of the EPA and new generation fuels.

As a Fuel Additive

Nearly every Original Equipment Manufacturer (OEM) approves the use of up to 5% biodiesel (B5) when blended with diesel fuel that meets its appropriate specifications as found within ASTM D975. These specifications are not dependent upon the oil or fat used to produce the biodiesel, or the specific process employed. However, it is critical to understand that the results, and some performance criteria, may vary based upon the feedstock used. The conformance of the product to the ASTM specifications is a requirement for any and all tax incentives and credits. Due to the handling of hazardous materials and large quantities of flammable chemicals during the reaction, the production of biodiesel should only be undertaken by trained professionals. Federal, state and local laws may exist that require special permits for the production and handling of fatty acid methyl esters and the components used to manufacture such as standard put in the Table 1.

_	Test Method	Limits	Units				
Water and Sediment	ASTM D2709	0.05 max	% volume				
Kinematic Viscosity 40 ⁰ C	ASTM D445	1.9 - 6.0	mm2/s				
Sulfated Ash	ASTM D874	0.02 max	% mass				
Sulfur							
S 15 Grande	ASTM D5453	0.0015 max	% mass				
S 500 Grade	ASTM D5453	0.05 max	% mass				
Copper Strip Corrosion	ASTM D130	No 3 max					
Alcohol Content (One of the following must be met)							
Methanol Content	EN 14110	0.20 max	% volume				
Flash Point, Closed Cup	D93	130 min	^{0}C				
Cetane Number	ASTM D613	47 min					
Cloud Point	ASTM D2500	Raport to Customer	^{0}C				
Carbon Residue	ASTM D4530	0.05 max	% mass				
Acid Number	ASTM D664	0.50 max	mg KOH/g				
Free Glycerin	ASTM D6584	0.02	% mass				
Total Glycerin	ASTM D6584	0.24	% mass				
Phosphorus	ASTM D4951	10 max	ppm				
Vacuum Distillation End Point	ASTM D1160	360 °C max	⁰ C				
Oxidative Stability	EN 14112	3 min	hours				
Cold Soak Filtration	Annex to D6751	360 max	seconds				
Calcium & Magnesium (combined)	EN 14538	5 max	ppm				
Sodium & Potassium (combined)	EN 14538	5 max	ppm				

Table 1. Standard Specification for Biodiesel Fuel Blend Stock (B100) For Middle Distillate Fuels

Each of the parameters listed within the specifications is designed, and limits set accordingly, to ensure that the product is fit for purpose. Each result must conform to the specifications to help ensure that biodiesel may be used as a fuel without causing harm. If any parameters are found to not meet these specifications, that fuel is technically not biodiesel and is in jeopardy of losing any applicable tax credits. The following have been some characteristics already studied and considered for the characterization of the impact to the resulting biodiesel property:

Relationship of Properties to Performance

Cloud Point: While the Cloud Point must be reported, there are no minimum or maximum requirements. It is vital to understand the importance of this value in relation to the performance and handling of B100 at low ambient temperatures. The Cloud Point is the most conservative temperature at which components begin to precipitate from the fuel that may cause operability issues. Cloud Point results will vary significantly depending upon the feedstock from which the methyl ester was created.

Monoglycerides are partially converted fats and oils found within biodiesel. While not reported separately in the U.S., they are accounted for as part of the total glycerin. The monoglycerides formed as the result of different feedstocks have inherently different properties. They all have somewhat higher melting and Cloud Points, as opposed to the methyl esters. This may lead to the appearance of precipitates just above the reported Cloud Point. It has been shown that the presence of even small amounts of saturated monoglycerides will significantly raise the Cloud Point of biodiesel, while unsaturated monoglycerides will not. These saturated monoglycerides are one of the more common culprits in filter plugging. This material will appear as a thick, waxy coating. The monoglycerides formed from tallow or palm, or those that are saturated by nature, have significantly higher melting points that will require more diligence and more energy to dissolve back into solution. The monoglycerides derived from soy and canola are much less saturated, leading to considerably less impact on filterability.

Corrosion and Deposits: Acid Number the Acid Number is a relative indicator of the acidic impurities, degradation and/or oxidation of the fuel. Free fatty acids arise in part through the hydrolysis of the feedstock fats and oils. Improper processing or oxidation may also lead to higher values. These oxidative products are associated with fuel system deposits and corrosion. Unfortunately, organic acids vary widely in corrosion properties, and the results cannot be used to predict failures.

Free and Total Glycerin the Free Glycerin value records the level of by-product glycerin that remains in B100. The Total Glycerin result measures the amounts of unconverted and partially converted fats and oils. Excessive levels of these components may lead to storage tank and fuel system filter plugging, along with engine fouling.

Oxidative Stability The oxidative stability of the fuel is related in part to the Acid Number results. As the biodiesel degrades, or oxidizes, organic acids or polymers are created as a by-product which may lead to corrosion or filter plugging. The Oxidation Stability result is an accelerated test used to predict the fuel's stability for longer-term storage, possibly up to six months.

Combustion: Cetane Number for diesel fuel is a rough equivalent to Octane Rating for gasoline. The value provides a measure of the ignition characteristics of the fuel in compression ignition engines. The lowest value for typical biodiesel is the same as a "premium petroleum diesel" at 47.

Flash Point the Flash Point is used in shipping and safety regulations to define flammable and combustible materials. This result is used to determine the classification for the Department of Transportation (DOT) regulations. It is important to note that a typical result of 130° C for biodiesel is almost twice that of petroleum diesel (approximately 70° C) and therefore much safer to handle and transport. The Flash Point is also used to ensure the residual methanol left in the fuel after biodiesel processing will not negatively affect combustion and other fuel system components.

Visual Appearance While there is no correlation between the colour of biodiesel and its performance as a fuel, it is critical that the sample be free of undissolved water, sediment and suspended matter. At room temperature, the sample should be clear and transparent. Any cloudiness or haze may be an indication of impurities or excess water that may be present.

Material and Methods

Entry on the part of this paper is devoted with more attention to Biodiesel. In other papers of the nowadays specialized literature, there are more information for the way of its production, how to make it suitable for handling and other settings. These parameters will be compared with those of biodiesel, and from the resultant acts will see which of these parameters used to change with the addition of diesel to biodiesel in different quantities. In total 300ml product was analysed where we add biodiesel to diesel were mixed in different ratios, samples differed by addition of 15 ml biodiesel more than previous sample as can be seen in the table 1. Each parameter was defined by different analytical and instrumental methods.

Results and Discussion

The following table 1 are provided qualitative characteristics of mixtures in various ratios according to a preliminary plan of mixing. Biodiesel produced were mixed with fossil diesel traditional, where in this case we have used only one-party diesel. Interesting part of this study was to determine Sulphur content because for the results achieved, we see clearly important influence of biodiesel to reduce the amount of sulphur in fuel and different property characterization was determined as shown in the Table 2. In the Figure 1 it is shown the graphical presentations of the standard distillation curve for B5 type mixture.

Nr	BD + Diesel	Temp	d_t^4	d4 ²⁰	$\mathbf{n}_{\mathrm{D}}^{\mathrm{t}}$	n_D^{20}	Pf	Р
	(300ml)	(°C)	(gr/cm ³)	(gr/cm ³)			(°C)	(°C)
1	15+285	25	0.82	0.832	1.461	1.459	58	75
2	30+270	25	0.82	0.832	1.462	1.460	73	95
3	45+255	25	0.822	0.832	1.462	1.460	76	89
4	60+240	25	0.824	0.832	1.462	1.460	64	71
5	75+225	25	0.824	0.832	1.462	1.460	64	70

Table 2. Qualitative characteristics of compounds in various reports

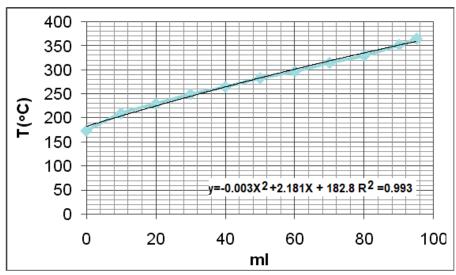


Figure 1. Distillation curve for B5

In the Figure 2 it is shown the graphical presentation of the experimental standard distillation curve for B25 type mixture.

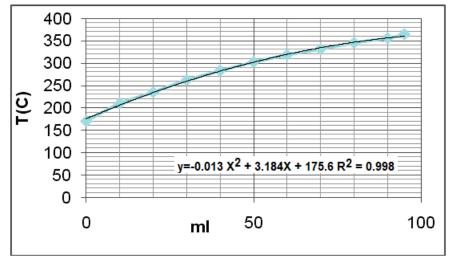


Figure 2. Distillation curve for B25

For both type of mixing we have statistically treated all data from the standard experimental distillation curve, realized in our laboratory, and we have calculated the best fit regression coefficients which was shown in both graphs. In the Table 3we have shown the experimental evaluation of the Sulphur content depending on the ratio of the mixture

Table 3: Sulphur content depending on the ratio of the mixture

Nr.	Туре	Sulphur content (mg/l) apparatus Multi EA 3100 Standard ISO 20846:2011	Sulphur content (ppm) Apparatus XRF Standard ASTM D 7220
1	B5	7.77	8.7
2	B10	7.35	8.3
3	B15	7.76	8.12
4	B20	7.05	7.4
5	B25	7.12	6.8

Conclusions

This paper presents the effects of biodiesel produced by us, as additive in petroleum diesel. The properties of diesel, biodiesel and their mixtures, were compared.

The development of biodiesel is a positive sign of the growing concern for the environment and the impact we are leaving on it. Searching the effects of biodiesel emission is a forward step because it begins to look at what other consequences the daily use of this new fuel might bring. There are some recommendations from the international research done on biodiesel and has suggested that the use of biodiesel in main city traffic has few negative impacts on the environment.

Some by-products with the exception of nitrogen oxide are less than those from petroleum diesel. Producing this fuel is also more friendly to the environment in some points, and certainly, more responsible than diesel. The main reason why biodiesel has yet to become widely available is due to the fact that producing the fuel is still much more expensive than the cheaper petroleum.

Hopefully research will continue to be done, to reach more effectiveness of biodiesel produced with different fed stock, as well as other alternative fuels and in the near scientists intend in the future to find best way of profiting biodiesel from organic wastes.

References

Aulich T, DeWitt M, Corporan E, Larson, V, Monroig O, Reich R, Seames W, (2005) Impacts of Biodiesel on Pollutant Emissions of a JP-8-Fueled Turbine Engine. *Air & Waste Manage. Assoc.*, 55, 940-949.

Balat M, Balat, H, (2010) Progress in biodiesel processing. Applied Energy 87: 1815-1835.

- Chen K, Lee W, Lin Y, Wu, TA. (2007) New Alternative Fuel for Reduction of Polycyclic Aromatic Hydrocarbon and Particulate Matter Emissions from Diesel Engines; *Air & Waste Manage. Assoc.*, **57**, 465-471.
- Demirbas A, Demirbas MF, (2011) Importance of algae oil as a source of biodiesel. Energy Conversion and Management 52:163-170.
- Demirbas A, (2005) Biodiesel Impacts on Compression Ignition Engine (CIE): Analysis of Air Pollution Issues Relating to Exhaust Emissions; *Energy Sources*, **27**, 549-558.
- Dunn R.O., 2005. Effect of antioxidants on the oxidative stability of methyl soyate (biodiesel). *Fuel Processing Technology* **86**, 1071-1085.
- Harris D, (2005) Exploring Chemical Analysis Freeman and Company, New York.
- Kalam M.A., Husnawan M, Masjuki H.H., 2003. Exhaust emission and combustion evaluation of coconut oil powered indirect injection diesel engine. *Renewable Energy* **28**(15), 2405-2415.
- Knothe G., 2005. Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters. *Fuel Processing Technology* 86:1059-1070.
- Lapuerta M. O. Armas. 2008. Effect of biodiesel fuels on diesel engine emissions. *Progress in Energy* and Combustion Science **34**, 198-223.
- Lue Y, Yeh Y, Wu C, (2001) The Emission Characteristics of a Small D.I. Diesel Engine Using Biodiesel Blended Fuels; J. Environ. Sci. Health, A36(5),845-859
- Narayana L, Gattamaneni R, Subramani S, (2008) Combustion and emission characteristics of diesel engine fuelled with rice bran oil methyl ester and its diesel blends. *Thermal Science* **12**, 139-150.
- Ramadhas AS, Muraleedharan C, Jayaraj S, (2005) Performance and emission evaluation of a diesel engine fueled with methyl esters of rubber seed oil. *Renewable Energy* **30**, 1789-1800.
- Roy GD, (2004) Non-Renewable Energy Sources, Khanna Publications. New Delhi.
- Sahoo PK, Das LM., Babu MK., Arora P, Singh VP, Kumar NR, Varyani TS, (2009) Comparative evaluation of performance and emission characteristics of jatropha, karanja and polanga based biodiesel as fuel in a tractor engine. *Fuel* **88**, 1698-1707.