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# IMPACT OF USING BIODIESEL AS A LUBRICITY ADDITIVE IN PETROLEUM DIESEL FUEL

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***Abstract***
*The production of ultra low sulfur diesel fuels is related to worsen of some specific for them properties - eg. lubricity, the oxidation stability, the electrical physical properties. Tests conducted with low sulfur No. 2 diesel fuel on High Frequency Reciprocating Rig (HFRR) showed that it causes unacceptable wear due to poor lubricity. Reduced lubricity could be corrected by addition of a high lubricity additive, like as biodiesel.*
*Biodiesel, which is synthesized from bio-oil, is a realistic alternative of diesel fuel because it provides a fuel from renewable resources and has lower emissions than petroleum diesel. It is biodegradable and contributes a minimal amount of net greenhouse gases or sulfur to the atmosphere. More specifically, biodiesel cuts down on the amount of carbon dioxide, hydrocarbons, and particulate matter released into the environment. Biodiesel can be blended in any proportion with petroleum-based diesel fuel and the impact of the changes is usually proportional to the fraction of biodiesel being used. The objective of this study was the investigation of the effect of biodiesel blend level on some important physical properties connected with sulfur content, wear, low temperature operability, self ignition and density. Tribological results showed that the tested ester (Rape Methyl Ester) was suitable for increasing the diesel gas oil lubricity to a satisfactory level.*

***KEY WORDS:*** *Diesel fuel, ester, RME, biodiesel, blending, cold flow properties, lubricity, analyses.*

## 1. INTRODUCTION

Worldwide legislation on diesel fuel quality has become more stringent over the last decade and can be expected to be more so in the future. The tightening of diesel specifications are being considered by the European Commission, which requires a maximum of 50 ppmw sulfur as well as yet-to be specified minimum cetane number and maximum polyaromatics levels. Refining technologies are available for meeting 15 ppmw sulfur for road transport diesel, but technologies required to produce ultra low sulfur diesel (ULSD) are not necessarily the same as those for producing diesel with high cetane number and low polyaromatics [1]. In a typical refinery, diesel fuel is produced from more blending components derived from crude distillation and conversion units. Currently, only hydrocracker kerosene and gasoil come close to meeting the new proposed 15 ppmw cap in sulfur. All other streams would require further hydrotreating or hydrogen-based processing to meet the future specs for highway diesel.

There are other desulphurization technologies in various stages of development, which are not currently commercially ready. Examples are: *Sulphur adsorption* eg. S-Zorb process developed by Phillips Petroleum [1]; *Biodesulphurisation* – eg. a process being developed by Energy Biosystems [2] and

*Chemical oxidation and extraction* - eg a process being developed by Petrostar [3].
The production of ultra low sulfur diesel fuels, also is related to worsen of some specific for them properties - eg. lubricity, the oxidation stability, the electrical physical properties.
Reduced lubricity could be corrected by addition of a high lubricity additive, like biodiesel. Biodiesel has been in the news in recent years as a possible alternative to conventional, petroleum derived diesel. More specifically, biodiesel refers to a family of products made from vegetable oils or animal fats and alcohol, such as methanol or ethanol, called alkyl esters of fatty acids [4]. For these to be considered as viable transportation fuels, they must meet stringent quality standards. One popular process for producing biodiesel, modeled in this report is "transesterification" [ 5-6].
Our working definition of biodiesel is a diesel fuel substitute made by transesterifying rapeseed oil with methanol. In industry parlance, it is called rape methyl ester (RME).
The objective of this study was the investigation of the effect of blending biodiesel with No. 2 diesel fuel on the main physical properties of the blends: density, low temperature flow properties, lubricity, cetane index, distillation curve correlated with sulfur content.
Although the impact of fatty acid esters on the lubricity of automative diesel was been closely examined, their impact of RME on the tribological properties has not been examined in detail.

## 2. EXPERIMENTAL AND INVESTIGATION METHODS

To assess the impact of the synthesized biodiesel on the properties of diesel gasoil, a low sulfur No. 2 diesel fuel obtained by a representative Romanian refinery was used for all experiments as a base fuel.

Rapeseed methyl ester (100% biodiesel) was made successfully under following conditions for transesterification: 1) room temperature; 2) 1.0% potassium hydroxide catalyst 3) 100% excess of the stoichiometric amount of 200 proff alcohol; 4. extremely vigorous agitation with a little splashing until the reaction mixture becomes homogeneous. The transesterification reaction procedure as well as the method for analysing the composition of reaction mixtures has been previously described [6].

Experimental blends of 0 (B0), 5 (B5), 10 (B10), 20 (B20), 30 (B30), and 50 (B50), percent biodiesel were prepared by the authors. These blends were prepared with care in condition is used when preparing small blends (volume) of a given liquid.
*Table 1* lists the diesel fuel and RME properties, along with the Romanian standard methods of testing. Methyl ester of rape seed oil has some properties that compare reasonable well with those of representative No. 2 diesel fuel.
As regards the investigated properties for diesel gas oil-biodiesel blends, they are focused on some important tribological fuel properties, as well as some properties including density, cloud point, distillation properties, and calculated cetane index. The CFPP, flash point, density and sulfur content for diesel gas oil -biodiesel blends are carried out in certificated laboratories. All tribological measurements were carried out using the HFRR apparatus, according to the CEC F-06-96 method. The lubricating efficiency of the fuels was estimated by measuring the average wear scar diameter (WSD) of the spherical specimen by using a photomicroscope. The wear scars quoted are corrected to give WS 1.4 values.
*Lubricity* represents an important property of diesel fuel performance; a single tankful of fuel with extremely low lubricity can cause a fuel pump to fail catastrophically. There are three ways to evaluate the lubricity of a fuel: 1) a vehicle test; 2) a fuel injection equipment bench test, and 3) a laboratory lubricity test [7-9]. Two laboratory lubricity tests have been recently been standardized by ASTM: the Scuffing Load Ball-On Cylinder Lubricity Evaluator method (SLBOCLE) - ASTM D 6078 - and the High-Frequency Reciprocating Rig method (HFRR) – ASTM D 6079. These tests are relatively quick, inexpensive, and easy to perform. At present work, the lubricity test is carry out according to HFRR method (apparatus with high frequency reciprocating motion).
The reported repeatability of the HFRR is +/- 0.8 and the reproducibility is +/- 0.136.
*Low temperature operability* depends on the size and shape of wax crystals in fraction.

**Table 1. Selected fuel properties for diesel and biodiesel fuel**

| Fuel property | Diesel | Biodiesel | Romanian Standard Method |
|---|---|---|---|
| Kinematic viscosity, @40°C, cSt | 2,2 | 3.2 | SR ISO 3104 |
| Density, kg/mc@ 15,56 °C | 0.8420 | 0.8833 | SR EN ISO 3675 |
| Water content, ppm by wt | trace | 616 | EN ISO12937I |
| Sulfur, ppmw | 140 | 7 | SR ISO 14596 |
| Distillation curve, ASTM 86<br>...0%<br>10%<br>20%<br>30%<br>40%<br>50%<br>60%<br>70%<br>80%<br>90%<br>95% | <br><br>50% v/v at 250 °C<br>90 % v/v at 332 °C<br>95 % v/v at 360 °C | <br>300ºC<br>342ºC<br>345 ºC<br>350 ºC<br>356 ºC<br>360 ºC<br>363 ºC<br>365 ºC<br>369 ºC<br>374 ºC<br>388 ºC | SR ISO 3405 |
| Flash point (PM closed cup), °C | 56 | 126 | SR EN 22719 |
| CFPP, °C | - 25 Class F | -2 | SR EN 116 |
| Cetane number | 51 | - | SR ISO 5165 |
| Cetane index | 47,83 | 61 | SR ISO 4264 |
| Oxidation stability, g/m$^3$ | 18 | - | SR EN ISO 2205 |
| Copper plate corrosion ( 3h at 50°C), class | 1 | 2C | SE ISO 2160 |
| Lubricity, (wsd 1.4) at 60°C) | 600 | | SR ISO 12156/1 |
| Refractive Index | 1.4629 | 1.4533 | SR ISO 1218 |

It has been focused on dynamic tests that simulate flow through a filter in the fuel filter in the fuel system, rather than on static physical property tests, like as cloud point. One dynamic test that has been accepted in Europe is the Cold Filter Plugging Point (CFPP). In this test, the sample is cooled by immersion in a constant temperature bath. Thus the cooling rate is non-linear, but fairly rapid- about 40ºC/hour. The CFPP is the temperature of the sample when 20 ml of the fuel first fails to pass through a 45-micron wire mesh under 2kPa vacuum in less than 60 seconds.

Therefore, the objectives of this work were to study the behaviour of No. 2 diesel fuel-RME blends at low temperatures by the measurements of CFPP.

## 3. RESULTS AND DISCUSSIONS

In this study are determined and discussed physical properties of the biodiesel that provide its advantages or disadvantages over petroleum-based diesel fuel. The physical properties of formulated blends, such as specific gravity, distillation characteristics, cetane index, viscosity, are closely interrelated. Isolating the impact of any one particular property in followed study is difficult.

<u>Sulfur content.</u> The data associated with the sulfur content of biodiesel blends are represented in Fig. 1. The data varied in a linear fashion as the concentration of biodiesel increased in relation to the petroleum diesel fuel. Biodiesel (B100) generally contains less than 15 ppm sulphur (in our case 7 ppmw) and the test for low sulphur fuel is ASTM D 5453.

These data confirmed the earlier investigations which reveal that the reduction of the diesel fuels sulfur content is related with the deterioration of their lubricity [16].

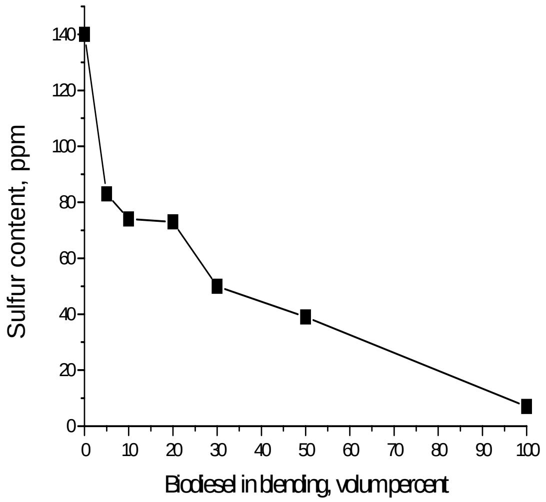


**Fig. 1:** *Effect of biodiesel level on sulfur content of diesel fuel-biodiesel blends*

Density. The density of biodiesel blends is important because a constant volume of fuel is injected into a fixed amount of air within the diesel engine. The data concerning density at 15 °C of the biodiesel blends are presented in Fig. 2. The data varied in a linear fashion as the concentration of biodiesel increased in relation to the petroleum diesel fuel. Except the density of B 50 (0.8549) all densities of the blends are in compliance with the Diesel fuel specification EN 590 requirements.

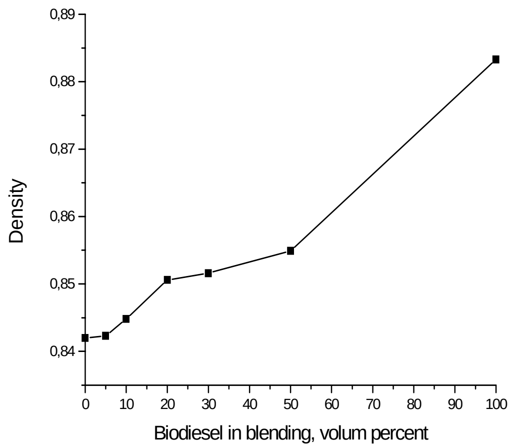


**Fig. 2:** *Effect of biodiesel ratio on density of diesel fuel-biodiesel blends*

Distillation curve and T-95% (Fig. 3). The distillation range for each fuel blend was used to determine the calculated cetane index. The data associated with the distillation points of the analysed blends showed a curvilinear fashion as the concentration of biodiesel increased in relation to the petroleum diesel fuel. However, chemical analyses procedures or curvilinear regression analysis procedures must be used to determine the distillation curve of a biodiesel/diesel fuel blend. The reduction in T-95 has a potential major effect on the biodiesel/diesel pool by increasing the requirement for additional lighter blendstock in the pool or adding conversion capacity.

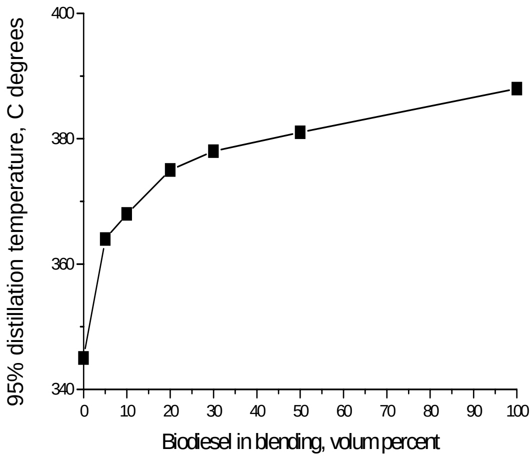


**Fig. 3:** *Effect of biodiesel level on T 95% of diesel fuel-biodiesel blends*

Calculated cetane index (CCI). CCI is based on specific gravity and the 10, 50 and 90% distillation temperatures of the fuels and gives numbers that correlate with the cetane engine test methods. Since the calculations invoke bulk fuel properties, cetane index, are not affected by the presence of cetane number improvers (diesel ignition improvers). These additives increases the cetane number of the fuel, but do not change its cetane index. The relationship used to calculate the cetane index of the studied blends has following four variable equation (SAE J313 1989 and ASTM 4737).

$$CCI = 45{,}2 + (0{,}0892)(T_{10N}) + [0{,}131 + (0{,}901)(B)](T_{50N}) + [0{,}0532 - (0{,}42)(B)[T_{90N}] + [0{,}00049][(T_{10N})^2 * (T_{90N})^2] + (107)(B) + (60)(B)^2,$$

where:

*CCI* is Calculated Cetane Index by four variable equation;

$T_{10N} = T_{10} * 215$ (°C);

$T_{10}$ = 10% distillation temperature, °C, determined by ASTM D86 and corrected to standard barometric pressure;
$T_{MN}$ = $T_{50} * 260$ (°C);
$T_{50}$ = 50% distillation temperature, °C, determined by ASTM D86 and corrected to standard barometric pressure;
$T_{90N}$ = $T_{90} * 310$ (°C);
*T90* = 90% distillation temperature, °C, determined by ASTM D86 and correction to standard barometric pressure;

*B* = $[e^{(3,5)(DN)}] - 1$;
*DN* = D – 0,85, and
*D* = specific gravity at 15°C determined by ASTM D1298.

Cetane index values had a linear variation with the increasing of the biodiesel concentration versus petroleum diesel fuel (Fig. 4). Additional analyses showed that a simple mathematical interpolation is not an adequate method to determine the cetane index of other biodiesel blend.

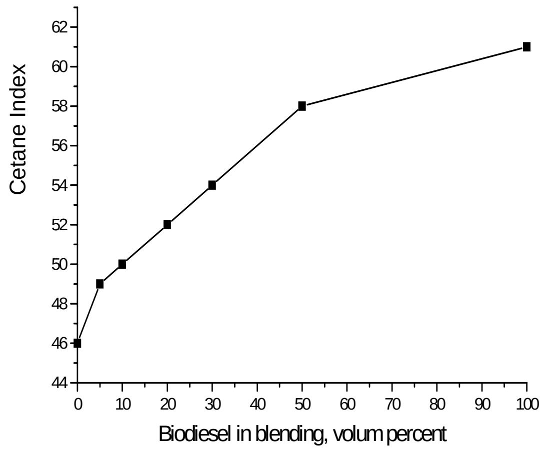


**Fig. 4:** *Effect of biodiesel level on cetane index of diesel fuel-biodiesel blends*

Cold filter plugging point. Two test methods exist for examining the low-temperature properties of diesel fuel, the Low-Temperature Flow Test (LTFT) used in North America – ASTM D 4539) and the Cold Filter Plugging Point (CFPP), used in Europe. CFPP results showed nearly linear dependence with the respect to cloud point (CP). Under most conditions CFPP was nearly equivalent to low–temperature flow test (LTFT) as a predictor of operability limits.

Values for cold filter plugging point parameter for all experimental blends are lower than the limiting value, according to the Romanian standard specification (no more -15ºC). Blending No. 2 diesel fuel with RME acts to depress cloud point and cold filter plugging point by a few degrees (Fig. 5).

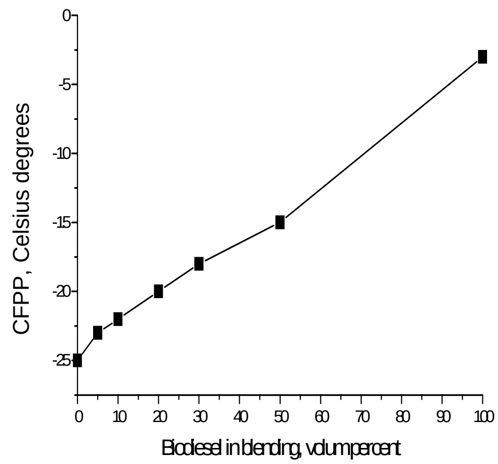


**Fig. 5:** *Effect of biodiesel level on CFPP of diesel fuel-biodiesel blends*

Lubricity. Biodiesel has excelent lubricity properties and its adding to low sulfur No. 2 Diesel fuel might provide a ultra low sulphur fuel, with excellent properties

The lubricity of petroleum diesel fuel was at one tome believed to be directly related to the viscosity of the diesel fuel. Although viscosity and fuel temperature tend to be correlated with a high lubricity diesel fuel, it has established that other compounds are responsible for the natural lubricity of diesel fuel. It has also determined that the removal of the sulfur has no lowered the lubricity of the fuel like as the removal of oxygen and nitrogen during desulphurization.
Figure 5 shows that a five percent replacement of No. 2 diesel fuel with biodiesel will provide adequate lubrication for the injection system of a diesel engine. The increase in lubricity for the number one diesel fuel, when additized to the level of 5 percent, fell short of the ASTM HFRR lubricity standard. Based on these data, at least five percent biodiesel will need to be added to increase the lubricity of the new ultra low sulfur No. 2 diesel fuel under 460 microns.

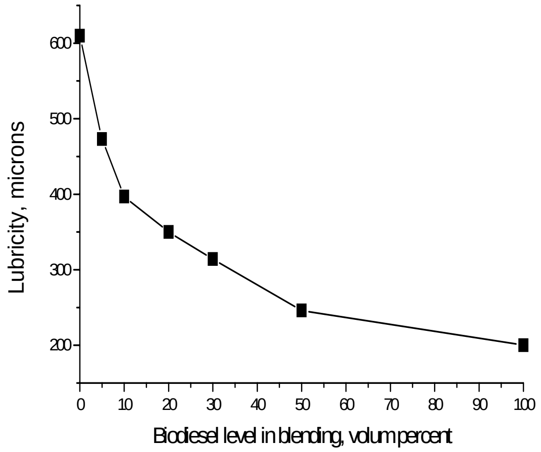


**Fig. 6:** *Effect of biodiesel level on lubricity of diesel fuel-biodiesel blends*

## 4. CONCLUSIONS

The data available via engine and diesel fuels suggested that the lubricity below 50 ppm and later 15 ppm low sulfur petroleum diesel fuel will be lower than the existing 350 ppm low sulfur diesel fuel. Petroleum distributors are planning to use a lubricity additive top revent premature failure of the diesel fuel injection system when the new diesel fuel is mandated into use by the EPA on June, 2006. Several lubricity tests procedures have been developed by the engine manufactures together with the petroleum industry in an effort to ensure that the diesel fuel injection system does not fail prematurely. The HFRR test procedure appears to be gaining in popularity as the EN has adopted this test procedure as a standard EN 590.

Production of diesel fuels with low sulphur content as to meet the requirements of EN 590 for improve lubricity and cetane number it is necessary to add biodiesel in conventional low sulfur No. 2 Diesel fuel.

In this work, various blends of biodiesel and low sulfur diesel fuel were systematically characterized, so that correlations between the fuel properties could be observed. As was noted in the literature, the physical-chemical properties of biodiesel/ No. 2 Diesel fuel blends do not always change in a linear fashion.

Blending biodiesel into petroleum diesel at even low levels can increase the lubricity of diesel fuel. As little as 5% biodiesel RPE can significantly increase fuel lubricity. The exact blending level required to achieve adequate lubricity will depend on the properties of the conventional diesel. Preliminary experiences suggests that at 5% biodiesel imparts adequate lubricity.

From the analyses performed, it was determined that the RME is a potential for being an additive or a subsitute for diesel fuel, and appear to give a better lubrication performance.

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