Lubricity of gasoline and alcohol-gasoline fuel blends

The fuel pump and some components of the injection system of internal combustion engines are lubricated with the fuel itself. Problems related to insufficient fuel lubricity were first identified in the aviation industry in the 1960s, and then in light diesel engines, when low-sulfur hydrotreated diesel fuel of emission standard 5 was introduced [1]. Some studies have reported that the key agents for good lubrication are highly polar compounds (especially those containing oxygen and nitrogen), which act to form a protective layer on the metal surface [2]. However, many of these polar surfactants are eliminated during oil refining and fuel production, thus causing a loss of lubricity [3, 4], and therefore it has to be recovered with antiwear additives.

Since diesel fuel pumps operate at much higher pressures (up to 220 MPa in high-pressure diesel fuel pumps versus 10-20 MPa in gasoline pumps) than gasoline engines, the requirements for lubricity of diesel fuel are generally more stringent than requirements for gasoline. In fact, the lubricity of gasoline was not an issue for a spark ignition, carburetor, or injection engine. There is currently no standard gasoline lubricity test like diesel lubricity test [5-10]. However, there have been reports of fuel pump failures, which were sometimes attributed to poor lubricity of gasoline [11].

With the development of gasoline engines and advent of direct injection engines, fuel (gasoline) is injected at the pressure of up to 200 atmospheres, and in this case a problem similar to that for diesel fuel appears: high-pressure diesel fuel pumps started to fail due to the low lubricity of gasoline. Gasoline itself is a solvent used to degrease metal surfaces, and in this case, on top of that, the sulfur content decreases during hydrotreating and production of hydrocarbon fuels. Now it’s time for gasoline. The lubricity of gasoline is becoming a key property and quality characteristic of commercial gasoline for direct gasoline injection engines. Few technical studies on gasoline lubricity have focused on determining how gasoline lubricity is impacted by the formulation of fuel composition, detergents, commercial antiwear additives for diesel engines, and the presence of oxygenates. According to studies sponsored by Ford Motor Company, the lubricity of modified gasoline containing oxygenates (MTBE) and high aromatic content differed little from commercially available non-oxygenated gasoline fuels [12]. However, Eleftherakis et al. [11] reported that both aromatic hydrocarbons and MTBE enhance the lubricity of gasoline. Wei [5] modified the conventional High Frequency Reciprocating Rig (HFRR) by deepening the fuel holder and covering the lubricant testing chamber with a tight-fitting lid. They found out that

commercial gasoline containing detergents had a wide range of variation in lubricity from lower lubricity to lubricity slightly better than Swedish Class 1 Low Sulfur Diesel (680 μm). They concluded that detergents did not significantly affect the lubricity of gasoline, and that commercial diesel lubricity improvers were also effective for gasoline. Spikes et al. [6] studied the lubricity of some refinery streams used in gasoline blending and found that high olefin content resulted in less wear compared to high paraffinic and aromatic streams. They recommended blending different streams to obtain an acceptable level of fuel lubricity. Wei et al. [7] used a modified HFRR tester to test five gasoline fuels containing sulfur, nitrogen and with kinematic viscosity ranging from 27 to 140 ppmw, 0 to 20 ppmw, and 0.37 to 0.64 mm^2/s (at 37.8 °C), respectively. Tests were carried out at water vapor pressures ranging from 1.0 to 1.5 kPa and a fuel temperature of 25°C. All tested gasoline fuels had a wear scar diameter in the range of 700-850 μm. The lowest wear gasoline had the highest olefin content (19%), the highest viscosity (0.53 mm^2/s at 37.8°C) and an aromatics content of 35% v/v. The 11% MTBE as oxygenated additive in gasoline resulted in the highest wear (850 μm), and detergents were found to reduce wear. Refinery streams containing more sulfur and dienes or diolefin showed the best antiwear performance. The most important factor affecting wear in the absence of dienes was viscosity, while wear felt linearly with kinematic viscosity of the fuel. A conventional HFRR Diesel Lubricity Tester was used to measure the lubricity of various ethanol and gasoline blends in accordance with ASTM D6079 standard at 25 °C. They found that the mean wear scar diameter increased (degraded lubricity) if ethanol content ranges from about 200 μm for E20 (20% v/v of ethanol added to gasoline) to almost 780 μm for neat ethanol. They also found that lubricity decreases dramatically as water content grows. According to the literature review, the published papers showed discrepant results, thus necessitating additional research to clarify the effect of the composition of fuel and additives on gasoline lubricity. Some countries are planning to increase the ethanol content in commercial gasoline fuels, going from low concentrations at the additive level (up to 10%) to high concentrations up to 85%. In the latter case, ethanol actually becomes the base fuel and gasoline becomes an additive. The goal of this work is to further study the effect of ethanol content on gasoline lubricity. In this context, the lubricity of representative ethanol / gasoline fuel blends using hydrated and anhydrous ethanol was evaluated in accordance with ASTM D6079 at 25 °C using a conventional HFRR tester.

Commercial gasoline with an octane rating of 95 and a maximum sulfur content of 10 ppmw, compliant with European standard EN 228 [13], was tested. Anhydrous

ethanol (99.7%) obtained by fermentation of wheat, barley and corn complies with European standard EN 15376:2007 [14]. Hydrated ethanol with a water content of 4.1% w/w was supplied by Panreac Chemical Products. The base gasoline fuel was blended with (hydrated and anhydrous) ethanol in proportions of 5%, 10%, 20%, 50% and 85%, commonly referred to as E-5, E-10, E-20, E-50 and E-85, which means volumetric ethanol content in the blend. These blends were chosen because these ethanol proportions were often used in vehicles and sold at gas stations in some countries. E-50 blend is not usually used like others, but its choice is justified as this proportion explains the trend of results.

Equipment and procedure

Lubricity tests were carried out on the High Frequency Reciprocating Rig (HFRR).

Instruments. ASTM D6079 standard was chosen because it takes into account a temperature of 25 °C, which is more appropriate when concerns about fuel loss caused by volatility or degradation may arise. In this method, a sample of the liquid to be tested is placed in a tank which is kept at the specified test temperature. A fixed steel ball is held in a vertical chuck and pressed against a horizontal stationary steel plate with an applied load. The test ball vibrates at a fixed frequency and travel length while the plate interface is completely immersed in the fluid-filled tank. The ambient conditions during the test are used to adjust the size of the wear scar formed on the test ball to a standard set of ambient conditions. The adjusted wear scar diameter is a measure of fluid lubricity [1].

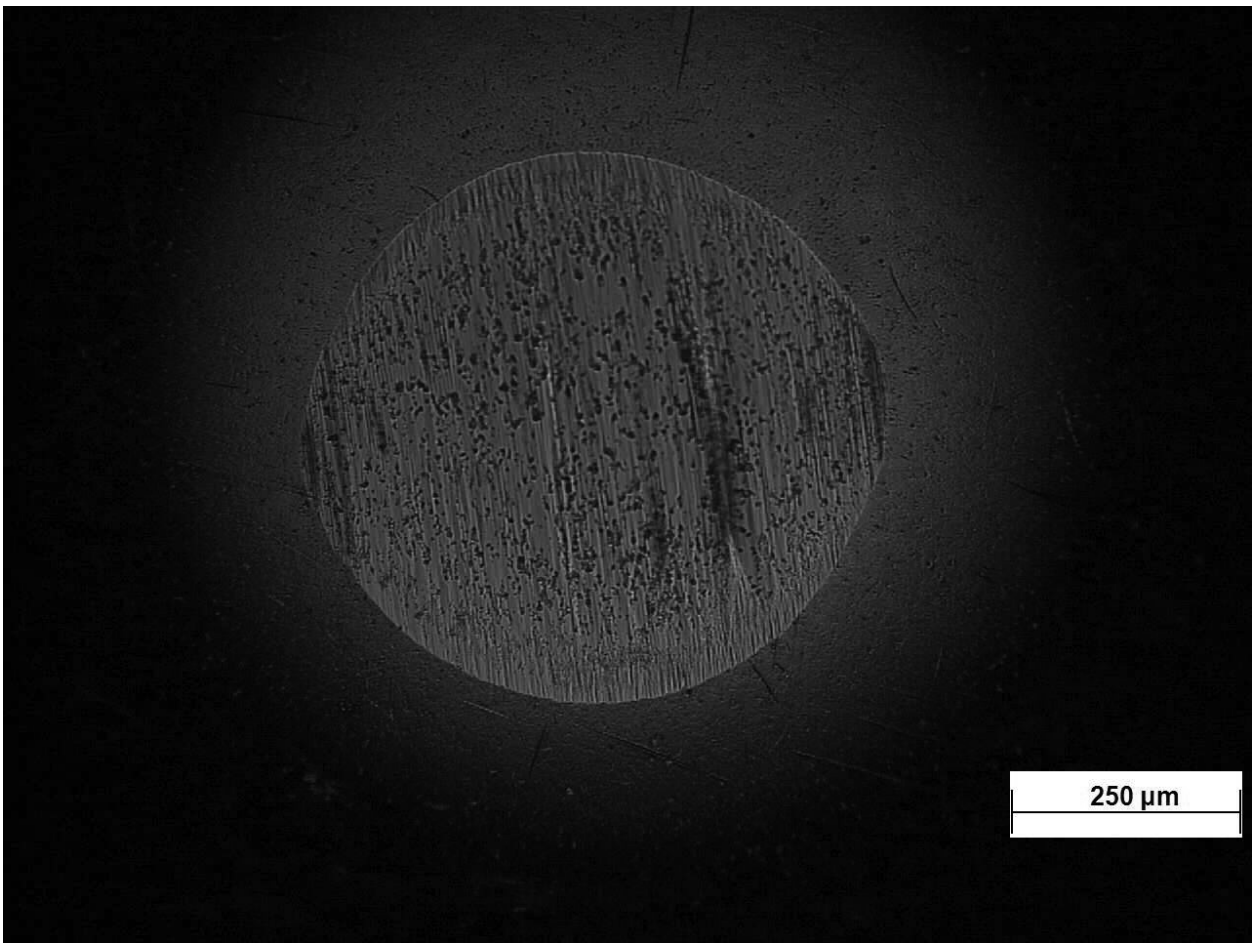

Figure 2 Microscopic view of the gasoline wear scar (x100)

Prior to each test, all HFRR components that came in contact with the test fuel were subjected to cleaning 3 times, each for 10 minutes, by immersing them in an ultrasonic bath with toluene (first and second time) and acetone (third time). All tests were run twice, and when the differences in wear scar exceeded 20 mm, an additional test was performed. During the test which lasted 75 minutes, the samples were shaken at a frequency of 50 Hz. They remained open to the atmosphere, which contributed to the loss of ethanol by evaporation from the samples, so the experiments were carried out with care to ensure that the fuel did not evaporate at all during the entire test. Then the size of the wear scar was measured in Leica DM IRM electronic microscope with 100x magnification power. The mean diameter of the wear scar observed in the HFRR ball (wear scar diameter) was obtained from maximum and minimum measurements prescribed by the standard. The resulting wear scar size was not adjusted for atmospheric water vapor pressure, as it was not stipulated in the standard. The size of the liquid film was determined using a contact resistance circuit that sequentially applies a potential of 15 MV through the sample contact and a balancing resistor, thus forming a potential divider circuit. The series resistance is set by the electronic unit

by default to 10 ohms. Thus, the potential drop across the contact is a measure of contact resistance versus balancing resistor. A low or zero film value means that the potential drop across the contact and hence the contact resistance is low, i.e. there is significant metal-to-metal contact between the test samples.

Results and discussion

Properties of neat fuels

Table 1 compares some properties of three main fuels tested. Figure 1 shows the effect of ethanol content on saturated vapor pressure of the blend. As can be seen from Table 1, some ethanol properties such as density, normal boiling point, vapor pressure and gross heating value differ significantly from those of gasoline. However, the viscosity of neat fuels is very similar. According to research results shown in Figure 1, the vapor pressure of lower ethanol content blends (5% and 10%) is higher than that of neat fuels. This behavior was attributed to the formation of azeotropes between ethanol and hydrocarbons boiling within the range from 30 °C to about 120 °C [15].

Table 1. Fuel properties

Item	Parameter	Gasoline	Anhydrous ethanol (99.8%)	Hydrated ethanol (95.9%)
1.	Density at 15 ºC (kg/m^3)	750	792	800
2.	Normal boiling point (°C)	39.7-212.2	78.0	78.3
3.	Viscosity at 40 ºC (mm^2/s)	0.8	1.13	1.2
4.	Reid vapor pressure at 37.8 °C (kPa)	63.8	25.3	25.4
5.	Gross heating value (MJ/kg)	46.28	28.05	26.93
6.	Mean wear scar diameter (μm)	639	632	605
7.	Sulfur content (ppm)	10	0	0
8.	Water content (ppm)	208	1 970	41 000

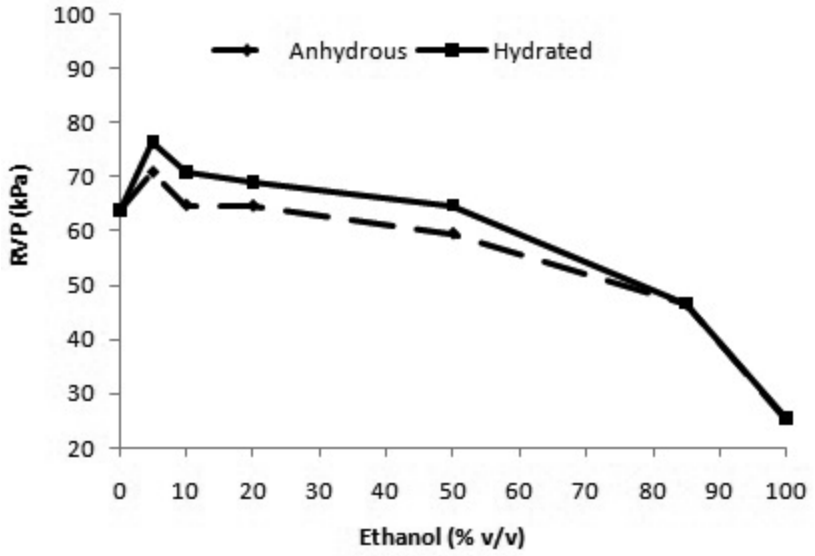

Figure 1 The effect of ethanol content on blend RVP

Mean wear scar diameters shown in Table 1 were obtained as the average of maximum and minimum scar diameters measured on microscope images. These results show that the lubricity of a polar molecule such as ethanol is slightly better than that of gasoline (a mixture of hydrocarbons) and that some water in ethanol can improve its antiwear performance. Wear scar values for commercial diesel fuels typically range from 200 to 460 μm. The superior lubricity of diesel fuel compared to gasoline and ethanol may be attributed to its higher viscosity and an additive package including antiwear components.

Effect of ethanol content on the blend lubricity

Table 2 shows HFRR results (wear scar, film and friction coefficient) for tested ethanol and gasoline blends.

Item	Fuel blend	Anhydrous ethanol (99.8%)			Hydrated ethanol (95.9%)		
		Wear scar	Film	Friction coeff.	Wear scar	Film	Friction coeff.
1.	E-5	688	22.4	0.362	551	36.4	0.320
2.	E-10	567	38.8	0.291	468	48	0.237
3.	E-20	580	32.4	0.287	515	39	0.243
4.	E-50	599	5.1	0.291	544	7	0.256
5.	E-85	592	3.4	0.274	535	6	0.269
6.	Ethanol	632	3.0	0.3	605	4	0.338

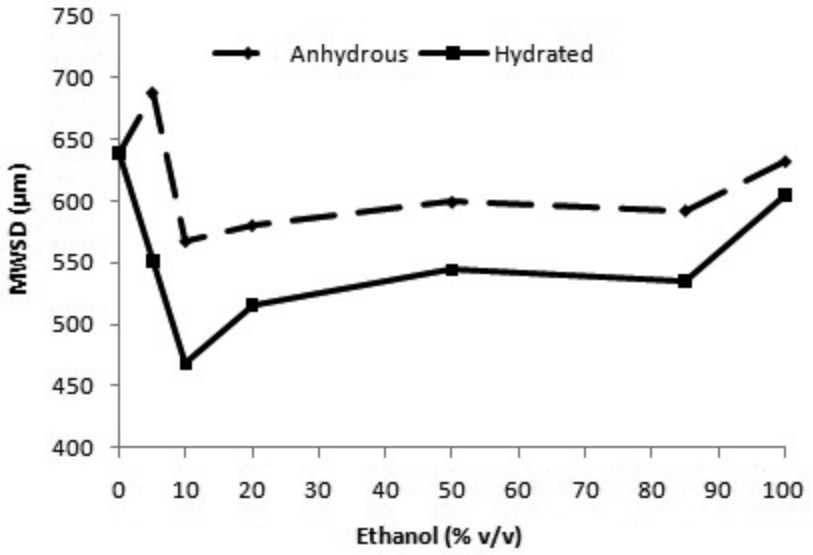

Figure 5 The effect of ethanol content on blend MWSD

Figure 5 shows wear scars for variations of ethanol-containing blends. For blends above E-10, wear scar variations followed a similar trend regardless of whether the ethanol was anhydrous or hydrated. In the range from 20% to 85%, wear scar diameters exhibited slight variations, which were always greater for anhydrous ethanol blends. The worst performance was shown by anhydrous ethanol blend E-5 while the best lubricity was shown by hydrated ethanol blend E-10.

The high wear scar index of anhydrous ethanol E-5 may be attributed to a high fuel vapor pressure of the azeotrope formed at this ethanol concentration. High volatility might lead to excessive fuel loss during testing, which will adversely affect lubricity of the fuel. Complex molecular interactions resulting from the presence of water in blends seem to slightly contribute to their lubricity. In addition to strong hydrogen bonds contained in water molecules, the polarity of OH groups contained in ethanol molecules can form hydrogen bridges causing relatively strong attractive forces between molecules in the liquid phase. Despite similar experimental conditions, some results obtained in this study differ from those published by Fusco et al. [8]. The cited authors reported a more pronounced variation in the ethanol-containing wear scar within the E-20 to E-85 range. Specifically, they reported a wear scar of about 200 µm for E-20, which is too low for a low viscosity fuel without antiwear additives. The values for anhydrous and hydrated ethanol blends E-20 measured in this study were 580 µm and 515 µm, respectively. In addition, Fusco et al. reported a sharp decrease in the lubricity of water-containing fuels, while this study reports a slight decrease in water-containing wear scar.

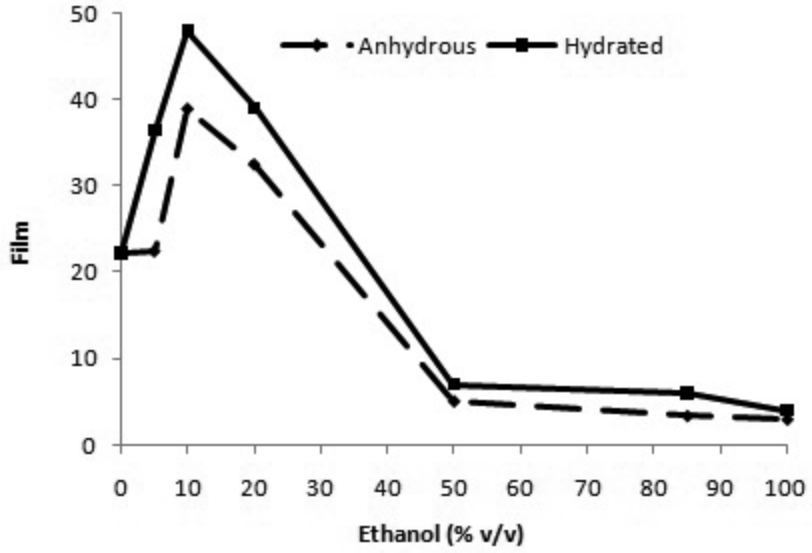

Figure 6 The effect of ethanol content on blend fluid film trace

Figure 6 shows variation in the size of the liquid film of tested ethanol-containing fuels. This can be a chemical film formed by additives, or a partial hydrodynamic film, if the velocity and viscosity of the sample are high enough [16]. If the film index is low or close to zero, it means that the potential drop across the contact and hence the contact resistance is very small, i.e. there is significant metal-to-metal contact between the test samples. This is usually due to high frictional forces and wear. As seen in Figure 6, low ethanol proportions improved film tracing, but for blends above E-50 the film was severely damaged. In addition, no noticeable effect of water content on the film trace was observed. While typical film traces for diesel fuels over 90 were reported [16], film 22 was measured for gasoline in this paper. A high film index means that metal surfaces are separating.

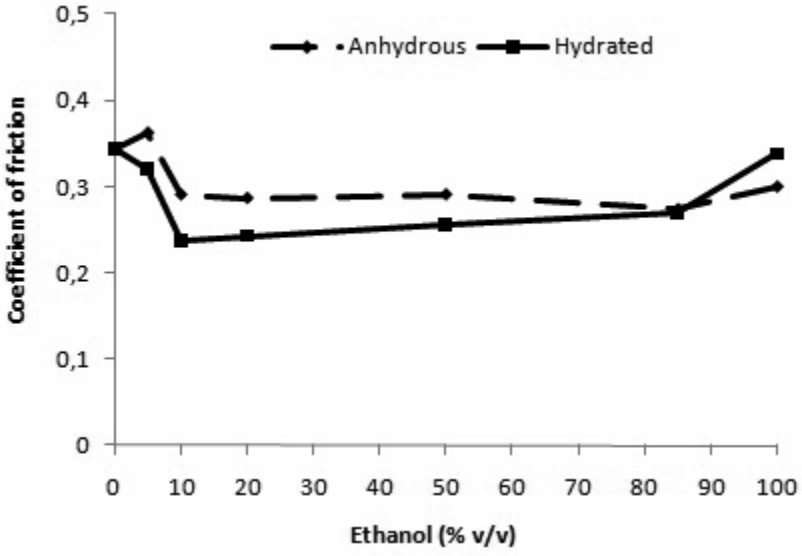

Figure 7 The effect of ethanol content on blend friction coefficient

Figure 7 shows variation in the friction coefficient for all tested ethanol-containing fuels. A high friction coefficient generally means poor lubrication with significant metal-to-metal contact and wear. While typical friction coefficient values for diesel fuels were reported to be about 0.15 [16], the friction coefficient for gasoline measured in this paper was 0.34. This may be attributed to a higher viscosity of diesel fuel and its additive package. In general terms, one could say that ethanol slightly improved the friction coefficient, which showed a slight increase in lubricity. In addition, water did not appear to have a noticeable effect on the fuel friction coefficient.

Conclusions

In this paper, the lubricity of (hydrated and anhydrous) ethanol / gasoline fuel blends was measured using a conventional HFRR tester. Overall, the range of variation in the mean wear scar diameter was small among fuels tested in the E-20 to E-85 range, which means that the addition of (hydrated or anhydrous) ethanol does not significantly affect the lubricity of the fuel blend. The lubricity of anhydrous ethanol and gasoline blends appears to be significantly reduced when ethanol content is low. The high value of the wear scar of anhydrous ethanol blend E-5 may be due to formation of an azeotrope with a high saturated vapor pressure at such ethanol concentration. The results showed that the addition of hydrated ethanol (96%) slightly improved the lubricity of the blend as compared to the addition of anhydrous ethanol. As for gasolines produced under the traditional technology without the addition of ethyl alcohol, their antiwear properties are at a critical level and average 700-900 μm according to ASTM D6079 method using the HFFR instrument (at 25 °C). A higher wear scar, lower film traces and higher friction coefficients obtained for all tested fuels compared to typical values for diesel fuels highlight the need to use a lubricity improver when using gasoline or ethanol/gasoline blends in new engines requiring higher pressure in the fuel injection system.

References

1. D. Margaroni. “Industrial Lubrication and Tribo logy”. *Fuel lubricity*. Vol. 50. 1998. pp. 108-118.
2. S. Safran. *Statistical thermodynamics of surfaces, interfaces, and membranes*. Westview press. New

York. 2003. pp.208-225.
3. M. Nikanjam, P. T. Henderson. *Lubricity of Low Sulfur Diesel Fuels*. SAE technical Paper. Warrendale. U.S. N. Giles (editor). 1994. pp. 743-760.
4. R. H. Barbour, D. J. Rickeard, N. G. Elliott. U nderstanding diesel lubricity, SAE paper 2000-01-1918. 2000. pp. 134-141.
5 D. P. Wei, S. Korcek, H. A. Spikes. *Comparison of the lubricity of gasoline and diesel*. SAE paper 962010. 1996. pp. 62-69.
6. H. A. Spikes, D. Wei, S. G. Korcek. "The lubricating properties of gasoline fuel". *Proceedings of Fuel Symposium.* Munich. 3-5 september 1996. pp.12-19.
7. D. P. Wei, H. A. Spikes, S. Korcek, "The lubricity of gasoline". *Tribology transactions*. Vol. 42. 1999. pp. 813-823.
8. F. Fusco. D. Katsuki, A. Sinatora. "Wear and corrosion evaluation of electric fuel pumps with ethanol/gasoline blends". *SAE paper 2005-01-2196*. 2005. pp. 356-364.
9. Europ ean norm UNE EN-590: 2004. Standard specifi cation for Automotive fuels. Diesel. Requirements and test methods. 2004.
10. ASTM D 975: 2004 Standard specifi cation for diesel fuel oils. 2004
11. J. G. Eleftherakis, M .J. Harrigan, X. Tao. "Development of a benchtop fuel lubricity assesment method". *SAE paper 941915*. 1994. pp. 1732-1741.
12. California Air Resource Board publication. CaRFG. "(California Reformulated Gasoline) performance and compatibility test program". *Californa Air Resources Boa*rd. 1996. pp. 23-27.
13. European norm EN 228: 2008. Standard specifi cation for Automotive fuels –unleaded petrol – Requirements and test methods. 2008.
14. European norm EN 15376:2007. Standar specifi cation for Automotive fuels – Ethanol as a blending component for petrol - Requirements and test methods. 2007.
15. Z. Muzíková, M. Pospíšil, G. Šebor. "Volatility and phase stability of petrol blends with ethanol". *Fuel*. Vol. 88. 2009. pp. 1351-1356.
16. M. Lapuerta, M. Contreras, J. R. Agudelo. "The lubricity of etanol-biodiesel-diesel fuel blends". *Energy and Fuels*. 2010. 24. 1374-1379.