The lubricity of ethanol-gasoline fuel blends

La lubricidad de las mezclas etanol-gasolina

John Agudelo[1], Álvaro Delgado[1], Pedro Benjumea[2]*

[1] Facultad de Ingeniería. Universidad de Antioquia. Calle 67 N.° 53-108. Medellín, Colombia

[2] Alternative fuels group. Institute of energy. Faculty of Mines. Universidad Nacional de Colombia sede Medellín, Colombia

Abstract

In this work the lubricity of several ethanol (hydrated or anhydrous) / gasoline fuel blends was measured by using a conventional HFRR tester. Tests were carried out at 25ºC with no water vapour pressure control, according to the ASTM D6079 standard. According to the results the range of variation of the mean wear scar diameter was small among tested fuels in the range E-20 to E-85, indicating that the addition of ethanol, anhydrous or hydrated, did not impact significantly blend lubricity. The addition of hydrated ethanol (96% v/v) slightly improved blend lubricity in comparison with the addition of anhydrous ethanol. The higher mean wear scar diameters, lower fluid film traces and higher friction coefficients obtained for all tested fuels, in comparison with the typical values for diesel fuels, indicate the necessity of using lubricity additives when gasoline or ethanol / gasoline blends are used in new engine technologies requiring higher pressures in the fuel injection system.

----- *Keywords:* Lubricity, wear scar, gasoline, ethanol

Resumen

En este trabajo se midió la lubricidad de varias mezclas etanol (hidratado o anhidro) / gasolina usando un equipo HFRR convencional. Las pruebas se efectuaron a 25 ºC sin control de la presión de vapor del agua, de acuerdo con la norma ASTM D6079. De acuerdo con los resultados obtenidos el rango de variación del diámetro medio de la huella de desgaste fue pequeño entre los combustibles probados, indicando que la adición de etanol, anhidro o hidratado, no impacta significativamente la lubricidad de la mezcla. La adición de etanol hidratado (96% v/v) mejoró ligeramente la lubricidad de la mezcla en comparación con la adición de etanol anhidro. Los mayores

* Autor de correspondencia: teléfono: + 57 + 4 + 219 85 49, fax: + 57 + 4 + 219 85 49, correo electrónico: jragude@udea.edu.co (J. Agudelo)

diámetros medios de la huella de desgaste, menores películas de fluido y mayores coeficientes de fricción obtenidos para todos los combustibles probados, en comparación con los valores típicos de los combustibles diesel, indican la necesidad de usar aditivos de lubricidad cuando se usen mezclas etanol/gasolina en nuevas tecnologías de motor que requieran mayores presiones en el sistema de inyección de combustible.

----- *Palabras clave:* Lubricidad, huella de desgaste, gasolina, etanol

Introduction

Fuel pump and some components of the injection system of internal combustion engines are lubricated by the fuel itself. Problems associated with inadequate fuel lubricity were firstly identified in the aeronautical industry in the 1960s and subsequently in light-duty diesel engines when low-sulfur fuel was introduced [1]. Several studies have reported that the key agents for a good lubrication are the highly polar fuel compounds (especially those containing oxygen and nitrogen) which act forming a protective layer on the metal surface [2]. However, many of these surface-active polar compounds are eliminated during fuel processing causing loss of lubricity [3, 4], and so it has to be restored by using anti-wear additives.

Since diesel fuel pumps operate at much higher pressures than their gasoline counterparts, the lubricity requirements for diesel fuels are generally more stringent than for gasoline. In fact, lubricity has not been a quality issue for multipoint port injected spark ignition engine fuels. Consequently, little research work has been done in this area and there is no a specific standard test for gasoline lubricity, as it is for diesel fuels [5-10]. Nevertheless, there have been anecdotal reports of fuel pump failures, some of them related to poor gasoline lubricity [11]. The development of direct injection gasoline engines requiring high pressure injection pumps and the introduction of several constraints to fuel composition, including reductions of sulfur content for enhancing catalyst life and performance, are becoming important reasons for considering lubricity as a key property for gasoline fuels.

The little reported technical work on gasoline lubricity have been focused on determining the effect of fuel composition, detergent additives, commercial anti-wear diesel additives, and oxygenate content on this property.

According to a work sponsored by the Ford Motor Company, the lubricity of a reformulated gasoline containing oxygenates (Methyl Tertiary Butyl Ether –MTBE-) and a high aromatic content was not unusual or markedly different from commercially available non-oxygenated gasoline fuels [12]. However, Eleftherakis et al. [11] reported that both aromatics and MTBE enhanced gasoline lubricity. Wei et al. [5] modified a conventional high frequency reciprocating rig (HFRR) by deepening the fuel holder and covering the lubricant test chamber with a close-fitting lid in order to measure the wear performance of gasoline and diesel fuels. They found that commercial gasoline containing detergent additives had a wide range of variation in lubricity (from poorer to slightly better than Class 1 Sweden low sulfur diesel fuel -680 μm-). They concluded that detergent additives did not significantly affect fuel lubricity and that commercial lubricity additives for diesel fuels were also effective for gasoline. Spikes, et al. [6] investigated the lubricity of a range of refinery streams used in gasoline blending and found that high olefin contents led to lower wear than highly paraffinic and aromatic streams. They recommended the blending of different streams in order to obtain acceptable fuel lubricity levels. Wei, et al. [7] using their modified HFRR tester, tested five gasoline fuels with a sulfur content, nitrogen content and kinematic viscosity ranging from 27 to 140 ppmw, 0 to 20 ppmw and 0.37 to 0.64 mm_2/s (at 37.8 ºC), respectively. Tests were

carried out at water vapor pressures ranging from 1.0 to 1.5 kPa and a fuel temperature of 25ºC. All tested gasoline fuels had a wear scar diameter in the range of 700-850 μm. The gasoline with the lowest wear contained the highest olefin content (19%), highest viscosity (0.53 mm^2/s at 37.8ºC) and an aromatic content of 35% v/v. A content of 11% of MTBE as oxygenated additive in gasoline led to the highest wear (850 μm), while it was found that detergent additives reduced wear. Refinery streams with higher sulfur and dienes or diolefins contents exhibited the best anti-wear results. The most important factor affecting wear in the absence of dienes was viscosity, wear felt linearly with fuel kinematic viscosity. Fusco et al. [8] used a conventional HFRR diesel fuel lubricity tester to measure the lubricity of different ethanol / gasoline fuel blends according to ASTM D6079 standard at 25ºC. They found that the mean wear scar diameter increases (worse lubricity) with ethanol content ranging from around 200 μm to E20 (20% v/v of ethanol added to gasoline) to almost 780 μm for neat ethanol. They also found that lubricity decreased strongly with water content. According to the literature review carried out, among work published there are conflicting results indicating that more research has to be done in order to clarify the effect of fuel composition and additivation on gasoline lubricity.

In several countries, including Colombia, there are plans for increasing the ethanol content in commercial gasoline fuels going from low concentrations at the level of additive (until 10%) to high ones until 85%. In the last case, ethanol actually becomes the base fuel and gasoline the additive. The aim of this work is to further examine the effect of ethanol content on gasoline lubricity. In that sense the lubricity of representative ethanol / gasoline fuel blends using hydrated and anhydrous ethanol was evaluated according to ASTM D6079 standard at 25ºC using a conventional HFRR tester.

Experimental

A commercial gasoline complying with the European norm EN 228 [13], with an octane number of 95 and a sulfur content of 10 ppmw was tested. Anhydrous ethanol (99.7%) produced by fermentation of wheat, barley and corn, fulfilling the European norm EN 15376:2007 [14] was provided by Abengoa Bioenergy. Hydrated ethanol with a water content of 4% w/w was supplied by Panreac Chemical products.

The base gasoline fuel was blended with ethanol (hydrated and anhydrous) in proportions of 5%, 10%, 20%, 50% and 85%, which are commonly called E-5, E-10, E-20, E-50 and E-85 indicating the volumetric content of ethanol in the blend. The selection of those blends is justified because these ethanol proportions have often been used in transportation fleets and sold in filling stations in several countries. In fact, Colombia has approved standards for E-10 (anhydrous) blend, and the government is planning to introduce flex fuels based on blends up to 85% v/v of ethanol from renewable resources. The E-50 blend is not commonly used as the others, but its selection is justified because this proportion allows explaining the results tendency.

Equipment and procedure

The lubricity tests were carried out in a High Frequency Reciprocating Rig (HFRR) of PCS Instruments. The ASTM D6079 standard was selected because it considers a temperature of 25°C which is more adequate when there may be concerns about fuel losses derived from its volatility or degradation. In this method a sample of the fluid under test is placed in a reservoir which is maintained at a specified test temperature. A fixed steel ball is held in a vertically mounted chuck and forced against a horizontally mounted stationary steel plate with an applied load. The test ball is oscillated at a fixed frequency and stroke length while the interface with the plate is fully immersed in the fluid reservoir. The ambient conditions during the test are used to correct the size of the wears scar generated on the test ball to a standard set of ambient conditions. The corrected wear scar diameter is a measure of the fluid lubricity [1].

11

Prior to each test, all the components of the HFRR having contacted the tested fuels were subjected to a cleaning procedure composed of three 10-minute immersions in an ultrasonic bath with toluene (the first and the second) and with acetone (the third). All tests were performed twice and when differences in the wear scar were higher than 20 mm an additional test was carried out. During the tests, which lasted 75 minutes, the samples were shaken at a frequency of 50 Hz. They remained open to the atmosphere, which favored the ethanol losses by evaporation from the samples, so experiments were carried out taking care that the fuel did not evaporate at all during the entire test. Afterwards, the size of the wear scar was measured in an electronic microscope Leica DM IRM equipped with a 100 magnification lent. The mean diameter of the scar observed in the HFRR ball (MWSD) was obtained from the maximum and minimum measurements as prescribed in the standard. The resulting scar size was not corrected by atmospheric water vapor pressure as it was not contemplated in the standard.

The fluid film trace is obtained by a contact resistance circuit which applies a 15mV potential across the specimen contact and a balance resistor in series, forming a potential divider circuit. The series resistance is set by the electronic unit and is set to 10 Ohms by default. The potential drop across the contact is thus a measure of the contact resistance, as compared to the balance resistor. A low or zero film reading 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 specimens.

Results and discussion

Properties of the neat fuels

Table 1 compares several properties of the three main fuels tested. Figure 1 shows the effect of ethanol content on the blend vapor pressure. As can be seen in 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 the neat fuels is very similar. According to figure 1, the vapor pressure of the blends with lower ethanol content (5% and 10%) is higher than of the neat fuels. This behavior has been explained as a result of the formation of azeotropes between ethanol and hydrocarbons boiling in the range 30°C to about 120°C [15].

Table 1 Fuel properties

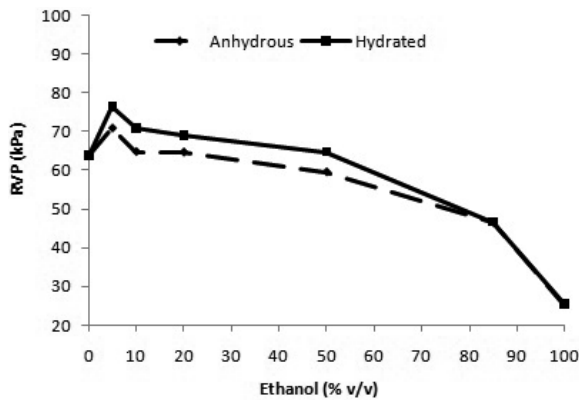| Properties	Gasoline	Anhydrous ethanol	Hydrated ethanol
Density at 15ºC (kg/m³)	750	792	800
Normal boiling point (°C)	39.7-212.2	78.0	78.3
Viscosity at 40ºC (mm²/s)	0.8	1.13	1.2
Reid vapor pressure at 37.8 °C (kPa)	63.8	25.3	25.4
Gross heating value (MJ/kg)	46.28	28.05	26.93
Mean wear scar diameter, MWSD (µm)	639	632	605
Sulfur (ppmw)	10	0	0
Water (ppmw)	208	1970	41,000

Figure 1 The effect of ethanol content on blend RVP

Figures 2, 3 and 4 show photos captured with the optical microscopy of the wear scar of neat gasoline, anhydrous and hydrated ethanol, respectively. The mean wear scar diameters reported in table 1 were obtained as the half adder of greater perpendicular distances taken on the microscope images. These results indicate that the lubricity of a polar molecule such as ethanol is slightly better than that of gasoline (mixture of hydrocarbons) and that some water in ethanol may enhance its anti-wear characteristics.

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

Typical MWSD values for commercial diesel fuels are between 200 and 460 µm as reported by Lapuerta et al. [16]. The better lubricity of diesel fuels in comparison with gasoline and ethanol may be explained by its higher viscosity

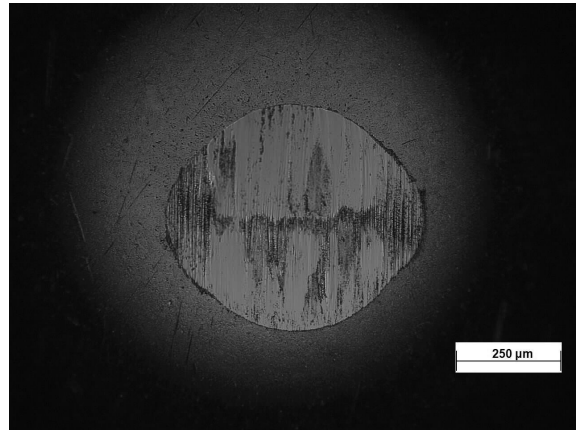and its additive package including anti-wear components.

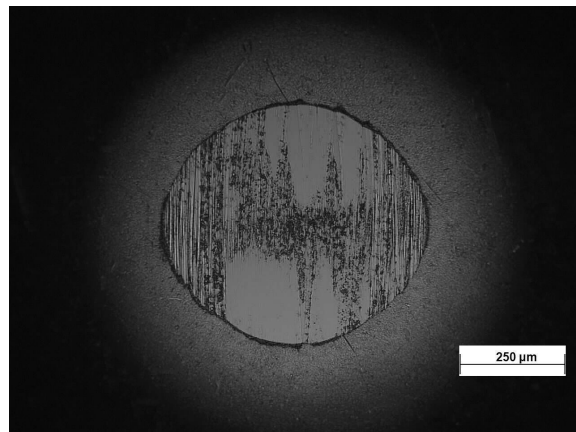**Figure 3** Microscopic view of the anhydrous ethanol wear scar (x100)

Figure 4 Microscopic view of the hydrated ethanol wear scar (x100)

The effect of ethanol content on blend lubricity

Table 2 shows the HFRR results (MWSD, film and friction coefficient) for the tested ethanol/gasoline blends.

Figure 5 shows the variation of the blend MWSD with ethanol content. For blends greater than E-10 the variation of the MWSD followed a similar trend regardless ethanol nature: anhydrous or hydrated. In the range from 20% to 85% the

13

MWSD exhibited slightly variations, being always greater for the anhydrous ethanol blends. The worst performance was shown by the E-5

anhydrous ethanol blend while the best lubricity characteristics corresponded to the E-10 hydrated ethanol blend.

Table 2 HFRR results for ethanol/gasoline blends

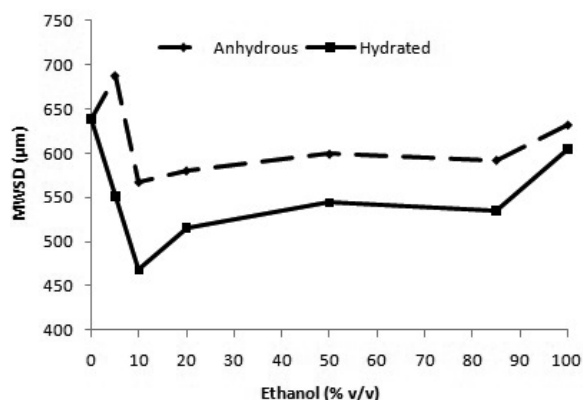| Fuel	Anhydrous			Hydrated		
	MWSD (µm)	Film	Friction	MWSD (µm)	Film	Friction
E-5	688	22.4	0.362	551	36.4	0.320
E-10	567	38.8	0.291	468	48	0.237
E-20	580	32.4	0.287	515	39	0.243
E-50	599	5.1	0.291	544	7	0.256
E-85	592	3.4	0.274	535	6	0.269
Ethanol	632	3.0	0.3	605	4	0.338

Figure 5 The effect of ethanol content on blend MWSD

The high MWSD of the E-5 anhydrous ethanol blend can be related to the high fuel vapor pressure azeotrope formed at this ethanol concentration. High volatilities could promote excessive fuel loses during the test affecting negatively fuel lubricity.

The complex molecular interactions resulting from having water in the blends appear to slightly favor their lubricities. In addition to the strong hydrogen bonds contained in water molecules, the polarity of the OH groups contained in ethanol molecules can form hydrogen bridges causing

relatively strong attractive forces between molecules in liquid phases.

In spite of using similar experimental conditions, several results obtained in this study differ from those published by Fusco et al [8]. The cited authors reported a more pronounced variation of the MWSD with ethanol content in the range E-20 to E-85. In particular, they reported a MWSD for E-20 around 200 µm, which is too low for a low viscosity fuel without anti-wear additives. In this study the measured values for the E-20 anhydrous and hydrated ethanol blends were 580 µm and 515 µm, respectively. Additionally, Fusco et al reported a strong decrease in fuel lubricity with water content while in this study it was determined a slightly decrease in the MWSD with water content.

Figure 6 shows the variation of the fluid film trace of the tested fuels with ethanol content. It may be a chemical film formed by additives, or a partial hydrodynamic film if the specimen speed and viscosity are high enough [16]. A low or close to zero film reading means that the potential drop across the contact, and hence the contact resistance is very low, i.e., there is significant metal-to-metal contact taking place between the

test specimens. This is usually associated with a high friction force and wear.

As can be seen in figure 6, low ethanol proportions improved the film trace, but for blends greater than E-50 the film was deeply affected. Additionally, there was not an appreciable effect of water content on the film trace. While typical film traces for diesel fuels greater than 90 have been reported [16], in this work a film of 22 was measured for gasoline. A high film reading means that the metal surfaces are being separated.
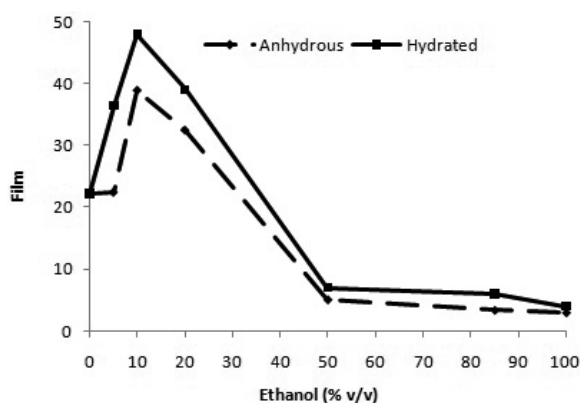

Figure 6 The effect of ethanol content on blend fluid film trace

Figure 7 shows the variation of the friction coefficient with ethanol content for all tested fuels. A high friction coefficient is normally an indicative of a poor lubrication with significant metal-to-metal contact and wear taking place. While typical values of the friction coefficient for diesel fuels around 0.15 have been reported [16], in this work a friction coefficient of 0.34 was measured for gasoline. This may be explained by the higher diesel fuel viscosity and its additive package. In general terms, it can be said that ethanol slightly improved the friction coefficient, which corresponded to a slightly increase in lubricity. Additionally, water did not appear to appreciably affect the fuel friction coefficient.

Conclusions

In this work the lubricity of representative ethanol (hydrated and anhydrous) / gasoline fuel blends
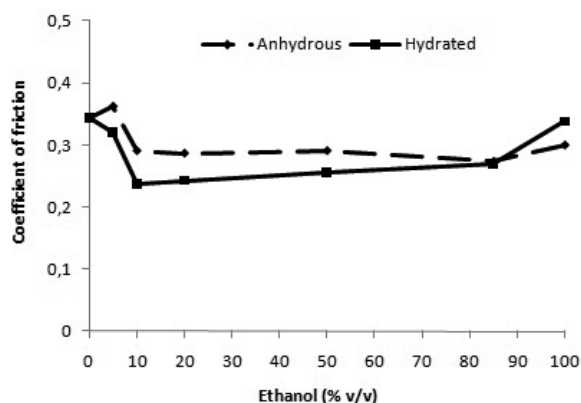
was measured by using a conventional HFRR tester.

Figure 7 The effect of ethanol content on blend friction coefficient

In general, the range of variation of the mean wear scar diameter was small among fuel tested in the range E-20 to E-85, which means that the addition of ethanol, anhydrous or hydrated, does not impact significantly blend lubricity.

The lubricity of the anhydrous ethanol / gasoline blends appeared to undergo a significant decrease at low ethanol contents. The high MWSD of the E-5 anhydrous ethanol blend may be related to the high vapor pressure azeotrope formed at this ethanol concentration.

Results indicated that the addition of hydrated ethanol (96% v/v) slightly improved blend lubricity in comparison with the addition of anhydrous ethanol.

The higher MWSD, lower film traces and higher friction coefficients obtained for all tested fuels in comparison with the typical values for diesel fuels indicate the necessity of using lubricity additive when gasoline or ethanol / gasoline blends are used in new engine technologies requiring higher pressures in the fuel injection system.

Acknowledgements

References

1. D. Margaroni. "Industrial Lubrication and Tribology". *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. Understanding 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. European norm UNE EN-590: 2004. Standard specification for Automotive fuels. Diesel. Requirements and test methods. 2004.

10. ASTM D 975: 2004 Standard specification 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 specification for Automotive fuels –unleaded petrol – Requirements and test methods. 2008.

14. European norm EN 15376:2007. Standar specification 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.