Gasoline lubricating ability as an indicator for pump, injection and engine wear failures

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ABSTRACT

The objective of this paper is the evaluation of the tribological properties of automotive gasoline fuels and their possible effect on pump and injection fuel systems. The lubricating ability of gasolines, because of their very low viscosity, depends mostly on their boundary film-forming properties. The differentiation of the properties' effect on lubricity reinforce the idea of the complicated wear mechanism that take place under the specific conditions of the experiments and the important role of the compositional characteristics of the fuel. Potassium concentration seems to play a significant role even in very low concentrations protecting satisfactorily from wear.

1. INTRODUCTION

In the late 1980s and early 1990s, environmental concern about the toxic and harmful emissions from diesel and gasoline engines led to large reductions in the amounts of sulphur and the development of reformulated gasoline fuels.

The topic of gasoline lubricity has recently become more urgent with the possible introduction of direct-injection gasoline engines, which will necessitate high-pressure gasoline injection pumps, a development that is most likely to place considerably more emphasis on the lubricating ability of gasoline, accelerating wear especially in rotary distributor fuel pumps. According to pump manufacturers this loss of lubricity may be the difference between fuels from a controlled laboratory environment and a cost-conscious production environment [1].

The modern processes of hydrotreating gasoline fuel to remove sulphur may take off some of the fuel lubricating capability (from the year 2005, Euro 4 emissions specifications have defined the limit of 50 ppm S for the countries of E.U.). The lubricity of aviation kerosene and diesel fuel appears to arise from very small quantities of polar, quite high boiling point components. It is realized that the overcoming increase in the severity of refinement of gasoline fuels makes very difficult to analyze these components and chemically identify them, as they vary greatly depending upon the origin of the fuel.

Fuel quality in recent years became increasingly important, not only for its role in the actual performance of the vehicles, but also for its impact on the emissions. However, the fuel pump at the service stations is the point at which the actual specifications of the fuels should be ascertained. This paper presents results of a survey in gasoline samples obtained from service stations in Athens, where the public buys its fuel.

In Greece, three main types of gasoline are sold in the service stations: new super or LRP gasoline with a Research Octane Number of 96 (96 RON) for the non-catalytic cars and unleaded gasoline with a Research Octane Number of 95 (95 RON) and super unleaded gasoline with a Research Octane Number of 98 (98 RON) for newer cars equipped with a catalyst. Some service stations also sell super unleaded with a Research Octane Number of 99 or 100 (99+ RON) but the market share of this product is very small. Unleaded gasoline is the cheapest gasoline and it is marked with quinizarin, while new super and super unleaded gasoline have similar prices (and they are quinizarin free). This price differential is the main motive to mix the cheaper with the more expensive fuel. Most gasoline adulteration cases involve the illegal mixing of the cheaper unleaded into the LRP or super unleaded gasoline. Less common is the mixing of much cheaper heating fuel into the gasoline. In such cases, the sulphur content can be used as a physical marker, which characterizes the fuel quality [2].

Gasoline lubricity is a complex phenomenon, involving many complicated and intercorrecting factors, such as the presence of water, oxygenates, diolefins, diaromatics, the effect of viscosity and the synergistic effect of different wear mechanisms. The lubricity mechanism of gasoline is quite different from that of diesel fuels that leads to severe adhesive wear. With low-sulphur fuels, adhesive wear is seen instead of corrosive and mild oxidative wear, and deposits build up on top land [3].

The emissions from motor vehicles contribute about 90% of airborne lead in urban areas. So, it was committed to phase out leaded petrol to reduce ambient lead concentrations as much as possible. On the other hand, valve seat recession (VSR) occurs when there is insufficient lubrication between the exhaust valve and seat. The mechanism of valve seat wear is a mixture of two major mechanisms. Iron oxide from the combustion chamber surfaces adheres to the valve face and becomes embedded. These hard particles then embed into the valve seat and cause abrasive wear or valve recession leading to early engine failure. For this reason, there are a number of anti-wear additives on the market that protect car's valve seats. Additives with active ingredients of either potassium, sodium, phosphorous or manganese have been shown to give protection to exhaust valve-seats. Although no additive is as effective as lead, it has been shown that correct dosing will provide adequate protection to exhaust valve-seats under normal driving conditions [4]. The new specifications in the Greek market determined as appropriate additive the potassium at the concentration level of 10-20ppm (mg/kg). Because there is a small possibility that mixing of some anti-wear additives on the market could result in engine damage, the potassium additive was mixed from the refinery production [5].

2. EXPERIMENTAL PROCEDURE

The two principal problems in testing gasoline are evaporation of gasoline fuel due to its very high volatility, and the extreme sensitivity of gasoline lubricity to tiny amounts of contaminant. Researchers have recently reached to the solution to modify the conventional HFRR test method for studying diesel fuels, principally by deepening the fuel holder so that a larger sample of fuel could be accommodated and by covering the lubricant test chamber with a close-fitting lid. The test rig was also completely enclosed in a plastic box from PTFE. This enabled the humidity of the test to be controlled, a factor that has been shown to influence wear of fuels, and also helped contain gasoline vapors [6,7].
The test conditions used for the gasoline tests were chosen to be identical to those specified for diesel fuel tests according to ISO 12515-1. A fuel temperature of 25^0C was employed in all gasoline tests.
The following gasoline properties were determined since they are directly related to the exhaust emissions: Octane Number, Benzene, Toluene, Xylene, Olefins, Saturates, MTBE and Total Aromatics were established using the mid-IR method, while Sulfur and Nitrogen content was measured using the ANTEK 9000NS elemental analyser [8,9,10]. Gasoline vapour pressure measurements were conducted with a Setavap Vapour Pressure tester 22420-3. The Setavap Vapour Pressure results were converted to DVPE in strict conformance with the requirements of ASTM D 5191 method, using the appropriate conversion equation. Potassium content was measured using the Atomic Absorption Spectrometry (AAS) according to IP 456. Viscosity was determined at 15^0C using the Anton Paar viscometer. Distillation data including the value of residue were obtained according to the procedure of ASTM D86. Also, was used the ASTM D 4530 method for the calculation of residue and the examination of adulteration with heavier distillates or solvents. It should be mentioned that sulphur content is a physical marker concerning the matter of gasoline adulteration with heavier distillates of petroleum. Water content and conductivity (at 20^0C) were also measured according to the standards ASTM D 1744 and D 3114, respectively [11,12].

One hundred and six (106) samples of gasolines were collected from service stations located all over Athens and its suburbs. They consist of 36 samples of new super gasoline, 37 samples of unleaded gasoline and 33 samples of super unleaded. After all the samples of gasoline were collected and examined to fulfil the specifications, 13 samples were found to be adultered (3 unleaded, 8 new super and 4 super unleaded).
Emphasis was given to the experimental procedure because of the amount of samples and properties measured, in order to ensure that no contamination or lighter substances loss would influence the final result after the processing of the measured values. The values of the properties were statistically analyzed and compared as a completely randomized factorial experiment to assess whether and how the different type of gasoline fuel and the measured properties affect the lubricity [13]. The lubricating properties of gasoline fuels were expressed from the value of mean wear scar diameter (MWSD1.4) of the spherical specimen, detected using a photomicroscope to an accuracy ± 1μm and was corrected at the absolute water pressure 1.4 kPa at the temperature of 25^0C.

3. RESULTS AND DISCUSSION

3.1 GASOLINE LUBRICITY EVALUATION

Examination of the gasoline lubricity has shown that the majority of the samples were above the acceptance limit of diesel lubricity, the 460-μm limit (Figure 1). We cannot include the repeatability limit calculated according to equation 1 for diesel fuels because such an assumption is not scientific tested and experiments must be carried out for the determination of the repeatability and reproducibility limit of gasoline fuels. This means that research studies must determine the effect of temperature and humidity on gasoline lubricity for wears greater than 600 μm. Regarding the effect of the test apparatus' modification, mentioned above, this limit must be restricted to lower values. This enhances even more the experimental observation of greater lubricity values for gasoline than that of a common diesel fuel.

$$\mathrm{r} = 139 - \left(0.1688 \times \mathrm{WS}\ 1.4\right) \quad , \quad 360 \leq \mathrm{WS}\ 1.4 \leq 600 \quad (1)$$

On the contrary, most of the samples of new super gasoline were near the limit of 460-μm indicating that the presence of the potassium additive had a main effect on the lubricating properties of fuels. Adulterated new super gasolines with unleaded gasoline have poorer lubricating properties, as shown in Figure 2. The effect of sulphur content in gasoline lubricity is depicted in Figure 3. It is obvious that unleaded and super unleaded gasolines have much higher lubricity values than LRP gasolines. Especially, below the level of 50 ppm are observed extremely high lubricity values.

There was no linear or other type correlation between the concentration of potassium and the lubricity, but it seems that with a concentration of 4 ppm K may be a significant reduction of MWSD1.4 value near the limit of 460 μm. The factors most likely to cause the observed differences in lubricity are the bulk fuel composition, the use of additives and the use of oxygenates.

Figure 1. Lubricity values for the three gasoline types.

Figure 2. LRP gasoline lubricity values and adulterated samples.

Figure 3. Effect of the sulphur concentration on lubricity.

3.2 FUEL COMPARISON

The adulterated fuel samples were isolated and two statistical computations were carried out each time, one with these samples and the other without.

The spread of the values can be depicted using boxplots. In Figure 4 is shown the median, quartiles, and extreme values of lubricity for each type of gasoline fuel. In each box plot is displayed the 50% percentage of samples' population in the square area, the 75% percentage of them within the upper and lower limit and the extreme values which are cases with values more than 3 box lengths from the upper or lower edge of the box. It is shown that LRP gasolines have a much better representative sample population indicating good lubricating properties compared with the other two types of gasoline. One unleaded gasoline has shown extreme good lubricity value, 279μm, but it is mainly caused by the use of special anti-wear or other additives. For the samples, which were not identified as adulterated, a descriptive analysis has been made. The results are shown in Table 1.

Because all the properties were not normally distributed for correlation analysis with Pearson correlation coefficient, were chosen the correlation coefficients of Spearman and Kendall's tau-b to be computed. The effect of the properties on the gasoline lubricity is different for each type of gasoline fuel. The chemical structure and the related individual physical properties seemed to interconnect in their effect on lubricity in different degree for each type of fuel.

More specifically, the statistically significant coefficients showed that unleaded gasolines seem to have lower values of wear as sulphur and nitrogen content, saturates and viscosity increased. On the contrary, unleaded gasolines seem to have greater values as toluene, oxygen, MTBE and vapor pressure increased.

LRP gasolines seem to have lower values of wear as sulphur and nitrogen content, conductivity (no-adultered samples), saturates and viscosity increased. On the contrary, LRP gasolines seem to have greater values as the benzene, aromatics and xylene increased.

Finally, super unleaded gasolines seem to have lower values of wear as sulphur content, nitrogen content and olefins increased. On the contrary, super unleaded gasolines seem to have greater values as toluene, xylene, water, benzene, aromatics and oxygen increased.

The results above were extracted after bivariate correlation analysis to measure how variables are correlated and the values of the correlation coefficients are shown in Table 2.

Table 1. Data of descriptive analysis for gasoline lubricity.

Table 2. Data of correlation analysis between lubricity and physicochemical properties.

3.3 COST ESTIMATION AND GASOLINE LUBRICITY IN GREECE

The prices were all estimated under escalation of the currency because the samples were gathered periodically from February of 2001 to September of 2003.

If we calculate the ratio of MWSD1.4 versus the price for all the gasoline samples, then the samples of LRP gasoline can easily be characterised, in comparison to the rest samples, as cost beneficial fuels regarding the fewer resulting wears on the car pump and injection system per currency unit. This can easily be indicated in the Figure 5. The three distinct baselines are representative of each fuel and portray the ratio of limit 460 μm versus the mean price (in €) of each fuel category. The generality of LRP samples are near to their baseline.

Figure 5. Effect of lubricating properties on saved cost from pump and injection wear.

3.4 VISCOSITY AND DENSITY EFFECT

Due to no specification limit of viscosity in gasoline, was decided to test all the samples at the temperature of 15^0C. During the statistical process, was espied a linear correlation between the viscosity and density (R^2= 0,76). In Figure 6 is shown that correlation linearity for the total of gasolines and each fuel severally.

This is an obvious interconnecting factor as concerns the effect of density or/and viscosity on gasoline lubricity and each gasoline type separately. Both these properties are greatly influenced from the composition of the fuel, nitrogen, sulphur and MTBE content.

That enhances the opinion that the compositional characteristics of the fuel do influence the gasoline lubricity in considerable degree.

Figure 6. Graphs indicating linear correlation between viscosity and density at 15^0 C.

3.5 POTASSIUM CONTENT

With confidence we can say that the potassium additive for valve recession plays an important role in the boundary-forming characteristics of LRP gasolines. As long as a “minimum” is maintained, the lubricity of the fuel seems to be more acceptable than that of unleaded and super unleaded samples. It is not easily to determine this limit but as shown in Figure 7, we can expect good results even when the potassium concentrate is less than 4 ppm.

Also, conductivity of LRP gasolines was much greater than that of unleaded and super unleaded gasolines. The main effect on that is due to the organic salt of potassium, but there is not good linear correlation between conductivity and potassium content (R^2= 0,51). In Figure 8 could see the difference between the conductivity for each type of fuel.

Due to its incompatibility to modern catalytic converters, we could not use potassium additives - alkyl, aryl or alcoxy potassium compounds or other - as additives for gasoline lubricity.

Figure 7. Potassium content and gasoline lubricity.

Figure 8. Conductivity values at 20^0C for each type of gasoline fuel. Effect of the potassium concentration.

4. CONCLUSIONS

From this study it was concluded that:

1. To a large extent, gasoline lubrication has to rely on its bulk components to provide good film forming lubricating ability, except the inherent ability of tiny polar amounts or other impurities to provide film-forming characteristics during an applicant load. Conductivity values of LRP gasolines indicate the influence of such polar compounds as potassium additives and their ability to be activated to form chemical bonds in the metal surface.
2. Fifteen gasoline samples were found to be adulterated based on the quinizarin tracing and the sulphur concentration. Also, some of these samples were found to mixed up with aromatic solvents. But, most of the key properties of the gasoline fuels were found to comply with the current EU and Greek legislation.
3. The findings of this research, verified the poorer lubricating properties of gasoline fuels compared with that of diesel fuels. Different type of gasoline fuel is affected in different degree from the compositional characteristics of the fuel and its physico-chemical properties.
4. Potassium concentration seems to play a significant role even in very low concentrations protecting satisfactorily from wear under boundary conditions. This anti-wear performance promotes this type of gasoline as cost-beneficial in the market.
5. Current initiatives to ban MTBE in a relatively short period of time and alternatives to substitute it, may offer a better perspective in gasoline lubricity. The amount of water that could be absorbed during handling must be take into account.
6. It is known that certain alkali compounds may accelerate the oxidation of certain organic compounds, which are found in the gasoline fuels. So, research study on the oxidation stability of gasoline fuels and its effect on gasoline lubricity must take place in this direction.
7. It must be promoted the development of a uniform system for fuel quality monitoring, taking under serious consideration the lubricating properties of gasoline fuels. Recent important efforts that take place from the other side of Atlantic Ocean to specify the diesel lubricity according to ASTM standards, should awake the research interest in a depth analysis of the wear characteristics of gasoline fuels.
8. HFRR test is applicable, under the conditions prescribed, to determine the effect of the compositional and physico-chemical characteristics of gasoline fuels on their lubricity. A number of laboratory-scale research must be available to predict the effects of fuel lubricity on injection system wear, as the case of diesel lubricity [14].
9. Further hydroprocessing in order to minimize sulphur concentration till 2005 at 50 ppm in the E.U. countries according to the directives of E.U and AUTO OIL II program, will support previous phenomena of processing diesel and aviation fuels that resulted in deep removal of polar constituents and nitrogen compounds. This development will probably enhance further the loss of lubricating ability of gasoline.
10. Latest research reports correlate the lubricity of the fuel that was used and the failure of the engines, as a large number of diesel engine failures have been reported to the immediate past [15]. This means that limits must be obtained to determine when a gasoline fuel is of a proper quality and where engine failures took place.
11. Further study of the effect of the tribological data on gasoline lubricity must be held. Time data including the variance of the film and the coeffiecient of friction, as well as estimation of the worn part of the specimens using SEM and appropriate profilometers could provide useful informations about the wear mechanisms for each type of gasoline fuel and their effects on lubricity measurements.

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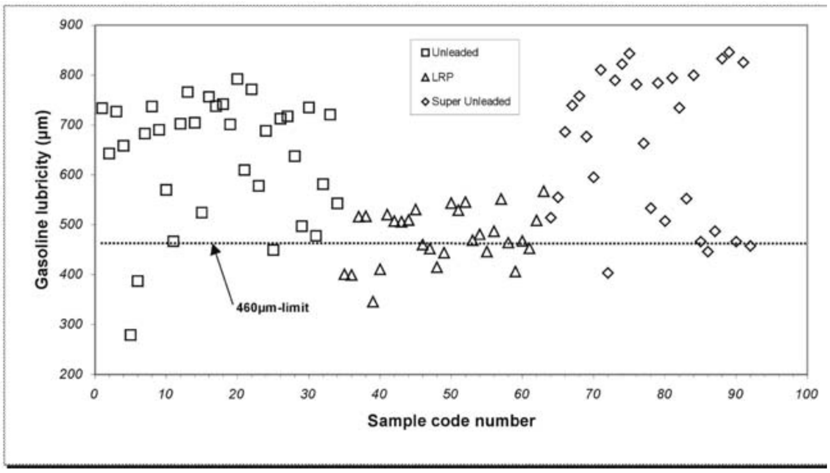


Figure 1. Lubricity values for the three gasoline types.

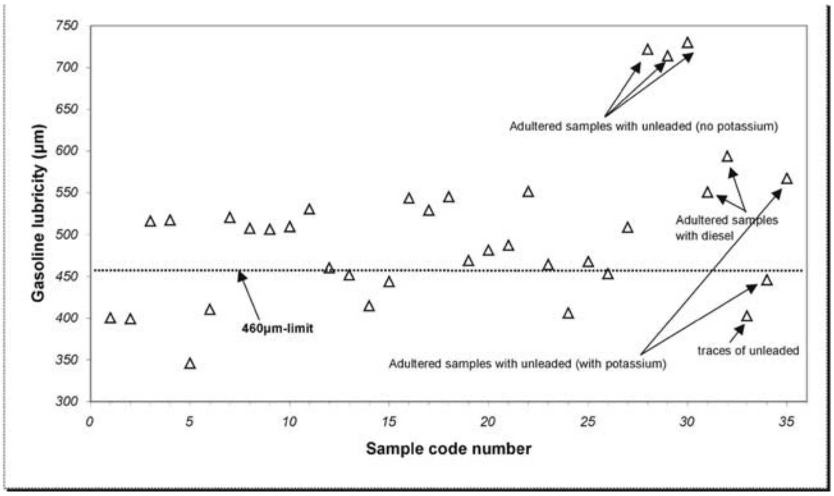


Figure 2. LRP gasoline lubricity values and adulterated samples.

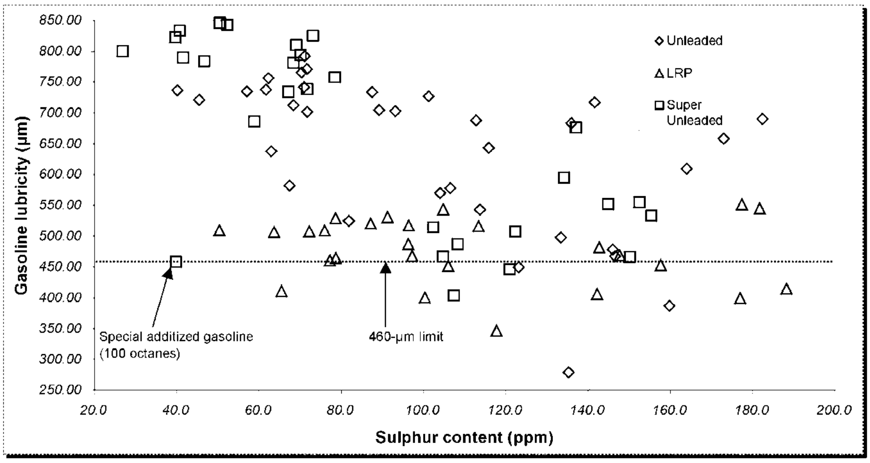
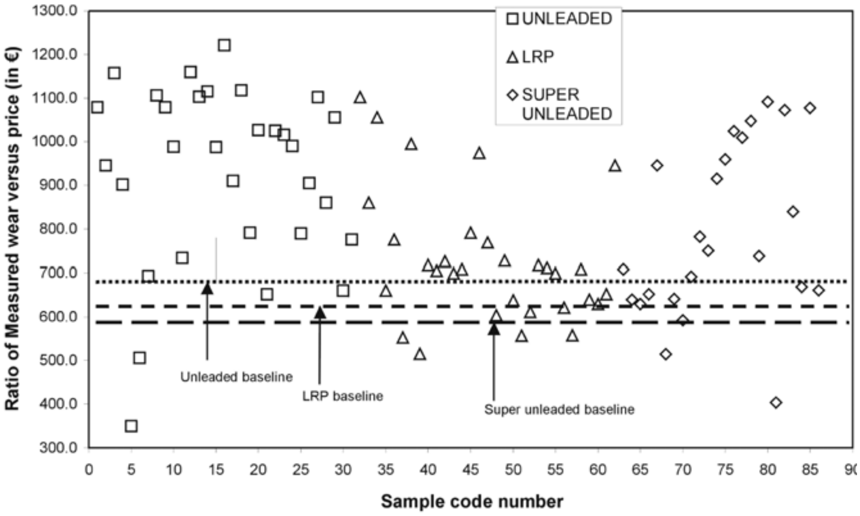


Figure 3. Effect of the sulphur concentration on lubricity.



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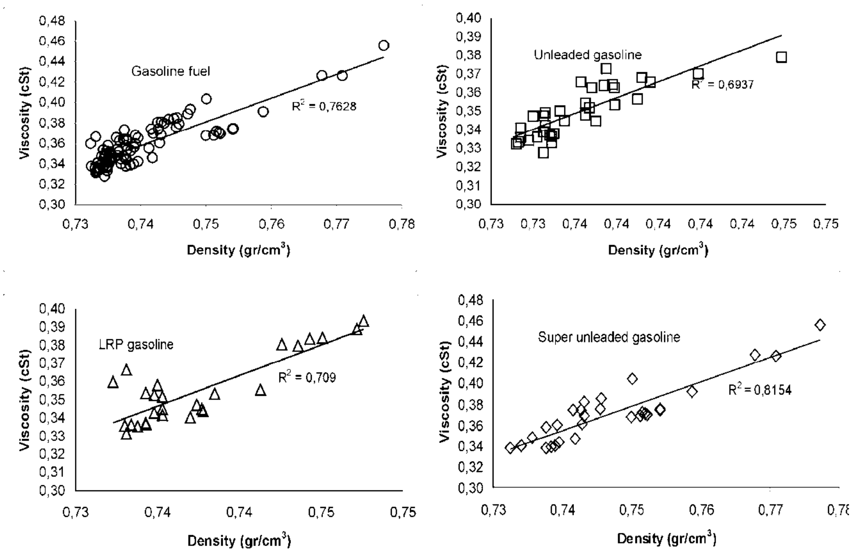

Figure 6. Graphs indicating linear correlation between viscosity and density at 15^0 C.

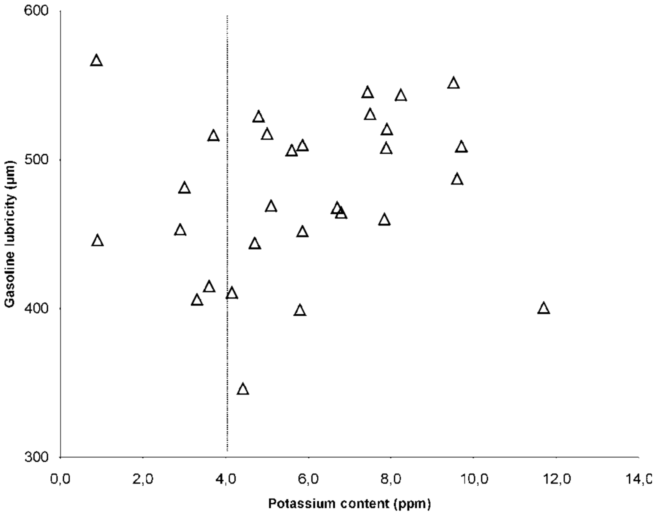

Figure 7. Potassium content and gasoline lubricity.

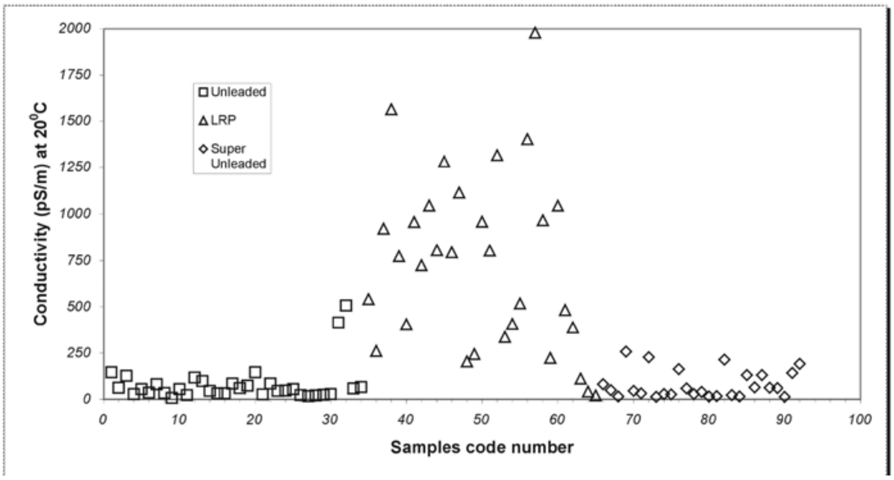

Figure 8. Conductivity values at 20^{0}C for each type of gasoline fuel. Effect of the potassium concentration.

GASOLINE LUBRICITY	TOTAL	UNLEADED	LRP	SUPER UNLEADED
Mean	595,2	639,0	477,9	661,3
Standard deviation	140,8	123,6	54,6	149,5
Standard error	141,5	125,5	53,7	151,7
Mean square deviation	140,773	123,6	54,6	149,473
Variance	19817,2	15266,5	2986,4	22342,0
Kurtosis	-1,162	0,813	-0,376	-1,561
Skewness	0,125	-1,143	-0,462	-0,288
Minimum	279,2	279,2	346,2	403,8
Maximum	846,0	792,6	567,2	846,0
Sum	54761,6	21724,9	13860,4	19176,3
Number	92	34	29	29
Confidence limit (95,0%)	28,766	41,531	19,890	54,401
Mean + C. L. (95%)	624,0	680,5	497,8	715,7
Mean - C. L. (95%)	566,5	597,4	458,1	606,8

Table 1. Data of descriptive analysis for gasoline lubricity.

EFFECT ON GASOLINE LUBRICITY	TOTAL	UNLEADED	LRP	SUPER UNLEADED
AROMATICS	0,355*	0,102	-0,020	0,414*
BENZENE	0,405**	0,223	0,148	0,762**
CONDUCTIVITY	-0,408**	-0,079	-0,309	-0,210
DENSITY	0,275**	-0,231	-0,183	0,346
MTBE	0,400**	0,465**	0,140	0,265
NITROGEN	-0,438**	-0,574**	-0,069	-0,427*
OLEFINS	-0,410**	0,109	0,004	-0,540**
OXYGEN	0,350**	0,475**	0,143	0,108
POTASSIUM	_	_	0,005	_
SATURATES	-0,263**	-0,434*	-0,056	0,014
SULPHUR	-0,510**	-0,505**	-0,255	-0,687**
TOLUENE	0,479**	0,643**	0,169	0,534**
VAPOUR PRESSURE	0,116	0,365*	0,151	0,021
VISCOSITY	-0,008	-0,395*	-0,441**	0,067
XYLENE	0,272**	0,057	0,050	0,068
WATER	0,467**	0,333	0,100	0,574**

** Correlation is significant at the 0,01 level (2-tailed).
* Correlation is significant at the 0,05 level (2-tailed).

Table 2. Data of correlation analysis between lubricity and physicochemical properties.