

Analysis of the Influence of Gasoline Adulteration on Lubricant Degradation and Internal Combustion Engine Performance

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Abstract

In internal combustion engines, studies of the effects of fuel adulteration focus on problems that occur in the fuel system and pollutants, but little attention is paid to the lubricant. This analysis evaluates, in addition to the problems in the supply system, the early degradation of the lubricant from the physical and chemical changes it undergoes when using adulterated gasoline in an internal combustion engine. In this work, a 160cc Honda stationary engine mounted on a bench and connected to an alternator through a transmission belt was used. Fuels adulterated with ethanol, kerosene and thinner were used in proportions of 5%, 10%, 15% and 20%. The cycles were 40 hours each, which is equivalent to approximately 2,000 km covered. To measure the engine time and rotation, a tachometer/hourmeter was used, where the time of each cycle was recorded. PQA tests, infrared spectrometer (sulfation, nitriding, oxidation and TBN) were performed, in addition to changes in engine behavior in relation to rotation. The results showed changes in rotation according to the concentration and type of contaminants. Engine wear was small for the 2,000 kilometers covered. The sulphation, nitriding, oxidation and TBN levels were altered indicating the degradation of the lubricating oil.

Introduction

The development of the oil industry took place in the mid-19th century, with the need for fuel for lighting. At the end of this century, the demand for gasoline increased very rapidly due to the growth of transport [1].

Light petroleum distillates, with low resistance to detonation, formed the gasoline composition and the addition of ethyl and methyl alcohols inhibited this detonation characteristic. But in 1921, Midgley and Brown found that lead-tetra-ethyl was more effective in inhibiting detonation, becoming, from that moment, the main additive to gasoline (GONÇALVES ET ALL, 2006) [1].

In Brazil, the addition of lead to gasoline was banned in 1989, being the first country to ban its use. This ban came with the growing concern for the environment and the damage caused by lead to human beings, as it is toxic and damages vehicle catalyts. Today only lead is used in aviation gasoline (ANP, 2014). [2]

In Brazil, Ethanol is mixed with gasoline, respecting specific recommendations. Fuel obtained from sugarcane is known as an ecologically correct fuel, as it contributes to the reduction of carbon dioxide in the atmosphere through photosynthesis in sugarcane fields. (PETROBRÁS, 2011).[3]

There are two types of fuel alcohol, the one used in flex engines, which is hydrated ethyl alcohol, which has the characteristic of being clear and colorless. The alcohol added to gasoline, on the other hand, is anhydrous ethyl alcohol, which receives the addition of orange dye (GONÇALVES and PADOVESE, 2010). [4]

Vehicles powered exclusively by ethanol represent a 60% reduction in the production of carbon monoxide, 25% in the production of hydrocarbons and 11% in nitrogen oxide compared to vehicles that use only gasoline as fuel (LEÃO, 2002). [5].

Ethanol has another advantage, its vaporization heat is higher than gasoline, that is, while gasoline needs 390kJ/kg to vaporize, ethanol needs 910kJ/kg. This means that when fuel is injected into the intake manifold, the fuel mixture cools the air, making the mixture cooler. Lower temperature means higher density, and higher density means more mixing inside the chamber. Which brings us to greater power. (PASSOS, 2015). [6]

The octane of ethanol is 110 octane, much higher than that of gasoline, which is why it is used to increase the octane of "C" gasoline (PASSOS, 2015).[6]

In Brazil, ethyl alcohol mixed with gasoline has been used since 1935, at the time on a 5% scale, only in 1980 this percentage rose to 20–22%, reaching 27% today (GONÇALVES and SILVA, 2011) [7,8].

Due to the variation in prices between gasoline and ethanol, there is the possibility of illegal adulteration in order to obtain profits from the sale of fuel. There is also the possibility of changing the percentage of ethanol in the mixture allowed by Brazilian agencies. (OUTA et al, 2020).[9]

The most common components, such as contaminants in gasoline used as fuel, are thinner, kerosene and ethanol itself.

This work starts from the contamination of gasoline fuel to verify its effect on the performance of the internal combustion engine and its useful life.

Fuels

There are two types of gasoline sold in Brazil, the Common "C" and the Premium. Regular gasoline can be with or without additives, with additives being named "additived" and without additives named "common". Thus, the distributors offer gasoline with different names that meet the specifications or even exceed the parameters of the category that are covered (PETROBRÁS, 2015a) .[10]

Petrobrás sells common gasoline "C", GRID gasoline with additives, and Podium, which is Premium gasoline (PETROBRÁS, 2015a) .[10]

"C" gasoline: gasoline that has up to 50 ppm of sulfur in its composition and has a minimum octane rating of 87 units. This gasoline has the addition of ethanol in the proportion of $27\% \pm 1\%$.

Additivated Gasoline: it has a different color from ordinary gasoline, in the case of Petrobrás' additive, it is greenish and has the same octane rating as gasoline "C". Its composition contains friction-reducing additives, detergents and dispersants that help preserve the engine and improve performance and efficiency. It also has the addition of ethanol in the proportion of $27\% \pm 1\%$.

Premium Gasoline: has a minimum octane rating of 91 units, which is higher than that of regular and additive gasoline. Its sulfur content is 50 ppm. This gasoline is suitable for imported vehicles and high performance vehicles. This gasoline has the addition of ethanol in the proportion of $25\% \pm 1\%$. Petrobrás gasoline in the Premium category is Podium, which has a minimum octane rating of 95 units and a sulfur content of up to 30 ppm. Podium Petrobrás gasoline is the highest octane gasoline on the planet, higher than European super premium gasoline.

This increase in the percentage of ethanol mixed with gasoline occurred after tests carried out by the entities representing the manufacturers of cars, motorcycles and auto parts at the request of the government. In these tests, the percentages of 22%, 25%, 27.5% and 30% were evaluated. To verify the feasibility of increasing the percentage, the Ministry of Mines and Energy (MME) asked Petrobras to assess the impacts of this increase in its laboratories (PORTAL_BRASIL, 2015) .[11-12].

After the test results and the decision for the increase, the National Association of Automotive Vehicle Manufacturers (Anfavea) requested the Federal Government that for Premium gasoline (high octane) the percentage of $25\% \pm 1\%$ be maintained, to meet the imported high-performance vehicles, until all tests on these vehicles were finalized (PORTAL_BRASIL, 2015) .[11,13-14] .

2. 1. ADULTERATION

Any and all changes in the composition of gasoline through the addition of ethanol in percentages different from those established by the ANP (National Petroleum Agency) and various solvents, such as benzene, thinner, turpentine, kerosene, diesel, etc., is what is called of gasoline adulteration (TAKESHITA, 2006) .[16]

The act of adulterating gasoline began when the market was opened to the fuel sector, after a long period of monopoly and which had its worsening with the reduction of the subsidy for hydrated and anhydrous ethanol, in addition to freeing up the purchase of solvents at the same time, through importation, which made the cost much lower than that of gasoline. This opening was intended to give the consumer more choice when buying fuel, thus giving an incentive to competition (TAKESHITA, 2006) .[16,17]

The adulteration of fuels has grown a lot, despite being an illegal activity, and the main drivers of this practice according to (TAKESHITA, 2006) [16] are:

1. a considerable price difference between gasoline and solvents;
2. Ease of acquiring solvents in the market, without restrictions on sales;
3. The difficult detection of adulteration by simple inspections, since the solvents are diluted in gasoline;

4. The high value of taxes levied on gasoline, and much lower taxes levied on solvents, generate a small profit margin;
5. The values of gasoline and kerosene, which it is easy to see that, in addition to taxes, the values per liter are very different, or rather, kerosene is much cheaper.

Gasoline can be adulterated by many products, but all must be miscible with it and flammable, so that they do not leave residues of their presence. Kerosene is heavier than gasoline and its octane rating is lower, thus generating engine acceleration failures (holes), combustion chamber carbonization and detonation at low rpm. (Albuquerque et al, 2009) [18].

It is common to find adulterated gasoline with the addition of kerosene, ethanol above the normalized percentage, attenuant (thinner, turpentine), benzene, etc.

This addition of gasoline adulterating products, either by excess of the existing one or by another one that is not present in its formula, causes changes in the physical-chemical properties of gasoline (TAKESHITA, 2006) .[16]

TAKESHITA [16], carried out a study of the influence of solvents on the physical and chemical parameters of gasoline, but at the time his work did not include any analysis of changes in lubricants.

Chowdhury et al [19] proposed a type of sensor to detect combustible tampering . This sensor was based on micro gas chromatography (μ GC) for portable, fast and accurate analysis of diesel fuels adulterated with kerosene. Separation columns were fabricated using microelectromechanical systems (MEMS) technology. The columns were 1 m long and consisted of an embedded matrix of columns. Two different stationary phase coatings were examined to explore the effectiveness of the proposed technique.

Moreira et all (2003) [20] carried out a review organizing information from the literature on the subject with an emphasis on identifying and optimizing suitable methods for monitoring adulteration. In this review, he presented detailed discussions on the role of physicochemical, chromatographic and spectroscopic methods in the characterization of gasoline and diesel.

Majhi et all (2012) [21] studied three different types of gasoline samples adulterated with 5, 7 and 10% kerosene. These samples were analyzed for the following characteristics to detect adulterants in commercial gasoline: chromatographic analysis, atmospheric distillation (ASTM D 86-1996) and filter paper test. The first two methods were scientific approaches to detecting gasoline adulterants and the third is useful at retail outlets. This method was emphasized to detect kerosene from the public distribution system (PDS) as an adulterant in commercial gasoline; according to the authors, gasoline is frequently adulterated with PDS kerosene in Asian countries due to its low cost.

Onojake et all (2013)[22] collected ten samples of premium motor alcohol at different dispensing points and analyzed to determine the extent to which adulteration of this petroleum product affects automotive engines. According to the results, the octane numbers of the study ranged from 60.10 to 93.30, the

specific gravity ranged from 0.7523 to 07885, the Reid vapor pressure ranged from 0.28 to 0.60 kgf / cm² and atmospheric distillation temperatures rangee from 189 to 251 degrees Celsius. The results of this study demonstrated that most products are significantly adulterated, which is undesirable for spark-ignited engines as it can cause detonation, insufficient engine power, a slow rate of deflagration experienced by most consumers, and constant beats.

Most contamination studies do not account for engine and lubricant degradation.

Materials And Methods

To carry out the tests, a four-stroke Honda engine, OHV, single-cylinder of 163 cm³, maximum power of 5.5 CV/3,600 rpm and net power of 4.8 CV/3,600 rpm was used. The maximum torque of 1.10 kgf.m/3,600 rpm and net torque of 1.05 kgf.m/2,500 rpm. The oil capacity in the crankcase is 0.6 liters

and the fuel (gasoline) capacity is 3.1 liters. The idle rotation is $1.400^{+200}_{-150} \text{ rpm}$. This engine model does not have a lube filter.

I was used the manufacturer recommended lubricant (genuine Honda SAE 10W-30 SJ JASO MA semi-synthetic).

This engine was mounted on a bench where it was coupled to an alternator through pulleys and belt, to simulate the daily workload, as shown in Figure 1.

To verify if the alternator was performing the function of simulating a workload, a rotation test was carried out with and without the alternator, that is, the engine was put to work coupled and without being coupled to the alternator.

As the engine was purchased new, specifically for this project, it was necessary to go through the break-in process, according to the owner's manual (HONDA, 2015) , [23]with a 20-hour operation. At the end of the break-in, the engine was overhauled, with the removal of the used lubricant, which was discarded, and disassembled for internal cleaning. After the overhaul, with the engine mounted, the specific cycles for the work were started.

In order for the lubricant to have the same demand in all tests, with the different mixtures of fuel and contaminants, the rotation was predetermined and fixed.

The determination of a rotation around 2000 rpm is due to the fact that this is the rotation where the vehicle has a moderate fuel consumption and a good performance.

To achieve this rotation, regulation of the idle speed through its screw was used. The engine was started up with clean gasoline and the adjustment was made, which was not changed until the end of all the tests.

3.1 BENCH INSTRUMENTATION

The workbench has an hourmeter and tachometer clock, and the reading was taken alternately, that is, with the engine off, the clock shows the hours accumulated so far and when you press the selector button, it shows the partial hours worked. When the engine is running, the watch shows the engine speed and pressing the selector switches it to the split hours worked.

The hourmeter/tachometer clock operates on the energy induced by the spark plug cable. This clock has two wires and to be installed, just wind one of the wires around the spark plug cable, making five turns and the other wire must be connected to the motor frame, which is the negative.

Figure 2 shows the detail of the assembly of the hourmeter wire on the engine spark plug cable.

The hourmeter makes it possible to configure the type of engine to which it is connected, that is, whether the engine is two or four strokes and the number of cylinders the engine has. In this case it was configured as a four-stroke, one-cylinder engine only.

3.2 TEST STEPS – CYCLES

The duration of each cycle was defined based on the regulatory speed of an average city, which is between 40 and 50 km/h. Honda's stationary engine is similar to a motorcycle engine, where lubricant changes must be made every 4,000 km. According to the motor vehicle manuals, this change interval of 4,000 km is based on a normal use system, but if the use is severe, this interval should be half this mileage, ie 2,000 km.

Thus, as the engine is on a bench, coupled to an alternator, the severe work regime was adopted. Based on these data, converting kilometers into hours, we find 40 hours, which was the duration of each cycle. Equation (1) presents the calculation made to find out how many hours there should be in each cycle.

$$\text{hours} = \frac{2000\text{km}}{50\text{km/h}} = 40\text{h} \quad (1)$$

The tests were with “clean” gasoline and with a contaminant, namely kerosene, ethanol and thinner, in percentages of 5, 10, 15 and 20% in each cycle, totaling sixteen tests, four with each contaminant.

All fuel measurements were made using a test tube, pipette and beaker. These glassware were used in order to make the volumes as accurate as possible.

The cycles lasted for 40 hours.

The engine was filled with lubricant and fuel and started to run. After completing the forty-hour cycle, the engine was turned off and the lubricant sample removed, as shown in Figure 3.

The samples were taken right after turning off the engine, so the engine was still hot and the sample would also be very homogeneous.

A 20 ml disposable syringe and hose were used, and the sample taken was approximately 300 ml, so that all tests could be performed.

After taking the sample, the engine crankcase was drained and the engine was disassembled for a very thorough internal cleaning, removing the rest of the used lubricant from the crankcase and cleaning the cover of this crankcase.

The rest of the lubricant used, after taking the sample, was packed in plastic containers and then discarded in workshops that carry out oil changes and give the proper destination to this lubricant, thus contributing to the non-contamination of the environment.

For this procedure, it was necessary to remove the motor from the bench, place it on a table and start disassembly. The next step is to remove the pulley, using a pulley puller and only then start the disassembly of the crankcase cover, which is fixed with eight screws.

For this disassembly and cleaning procedure, absorbent paper was used, avoiding the use of cloth because this releases fragments or lint that is harmful to the engine. Then, the engine was assembled again, filled with new lubricant and gasoline with a new percentage of contamination, the partial hour meter was reset and a new cycle started.

This cleaning and sampling procedure was the same for all cycles and all contaminants.

After all the cleaning, the engine was reassembled, the pulley was installed again and the engine returned to the bench. At this time, it was filled with new lubricant (not in use) and the fuel tank was filled with a new percentage of mixture.

3.3 ANALYSIS

When running the engine, the hourmeter/tachometer begins to measure the running time with the predetermined amount of fuel and also marks the engine speed.

When starting the engine, it was waited 10 minutes to ensure that the engine had stabilized working conditions, such as ideal temperature, thus guaranteeing the same parameter for all tests.

After 10 minutes, a film of about 90 seconds of the tachometer was made. Then, all rotation values were recorded, second by second, until reaching sixty readings. With these values, rotation graphs were plotted

for analysis.

3.3.1-PQA (Particle Quantifier Analyzes)

For this test, the ferrous particle monitor from Kittiwake Developments Ltda was used as shown in Figure 4.

This Monitor examines the sample through an inductive field, which when detecting the presence of magnetic materials presents the result in the form of a dimensionless index called the PQ index. This index is directly related to the amount of ferromagnetic materials contained in the oil, very useful information in the construction of trend graphs.

After a sample homogenization step, using a pipette, 2 ml of lubricant was placed in each container of the PQA Monitor, which then receives the lid and identification.

3.3.2 -Spectrometer of infra-red

Infrared spectrometry was performed according to the specifications (SPECTRO SCIENTIFIC, 2013[24] and SPECTRO SCIENTIFIC, 2014) [25]. With the apparatus we obtained the measurements of Oxidation, Sulfatation, Nitriding and TBN (Total Acid Number).

Results And Discussions

The graph in figure 5 is linked to the alternator and running with the engine at idle.

It was possible to verify that the alternator was playing its role, even if the load was not very large.

Making an analogy with current drivers, it can be said that this alternator was for the engine, like a driver who walks without straining the equipment, without reaching high speeds and abrupt accelerations, even because this type of driving makes the engine more economic.

Thus, it is possible to verify that the rotation gave a difference between with and without load of 160 rpm, both between the averages, maximums and minimums presented in the graph.

4.1 CONTAMINATION WITH 5%, 10%, 15% AND 20%

For these percentages of contamination, engine speed, PQA, viscosity, and infrared spectrometer were analyzed.

The contaminants used in this step were kerosene, ethanol and thinner as describe in the Table 1.

Table 1 - Abbreviations of used in the experiments

Abbreviation	Description
ON	New unused oil
GO	Gasoline without contaminants
K5	Gasoline with 5% kerosene
K10	Gasoline with 10% kerosene
K15	Gasoline with 15% kerosene
K20	Gasoline with 20% kerosene
E5	Gasoline with 5% ethanol
E10	Gasoline with 10% ethanol
E15	Gasoline with 15% ethanol
E20	Gasoline with 20% ethanol
T5	Gasoline with 5% thinner
T10	Gasoline with 10% thinner
T15	Gasoline with 15% thinner
T20	Gasoline with 20% thinner.

Figure 6 shows the behavior of the engine rotation when it was put into operation with gasoline adulterated with ethanol.

The engine rotation using gasoline contaminated with ethanol, presented the same behavior of a dual-fuel car engine, as the percentage of ethanol increased, the rotation also increased, providing the engine with greater power. Thus, the engine behaved as expected.

The engine's rotation when fueled with ethanol presented very sharp peaks and valleys, which can be explained by the use of a spark plug for a gasoline engine that cannot generate a good burn of such a high percentage of ethanol.

Ethanol makes the mixture cooler and thus requires a spark plug for this situation.

Another characteristic of the mixture being cold is that when it is injected into the engine, it comes into contact with the intake air and cools it. This improves the density of the fuel-air combination, resulting in a bigger mass of fuel and more power for the engine.

Figure 7 shows the graph of engine RPM when filled with gasoline adulterated with kerosene.

With this type of contaminant, it is easy to see that the rotation of the engine fueled with clean gasoline has a very regular behavior, the variations presented are within the acceptable rotation variation for this type of engine.

When the engine is filled with gasoline contaminated with kerosene, it is possible to see that the engine starts to fail. In the graph this failure is represented by changes in rotation, moments of sharp peaks followed by deep valleys compared to gasoline.

This engine behavior is in line with what the literature reports, in relation to the behavior of an engine using gasoline adulterated with kerosene, which presents acceleration failures, which technicians call acceleration "holes", which is when the engine fails.

These holes can also be explained by kerosene's octane, which ranges from 15 to 25, causing the octane of contaminated gasoline to decrease dramatically, even to the point of hitting pins at times.

With this contaminant, the engine tries to work in the rotation of clean gasoline, but the calorific value of the mixture does not allow it. Analyzing the graph, it can be seen that at some point the lines of the mixtures, in all percentages, cross the line that represents clean gasoline, but they cannot stabilize.

Figure 8 shows the graph of engine speeds when filled with gasoline adulterated by thinner.

This contaminant was the most problematic for the engine, which had a very different functioning, especially when using gasoline with 20% thinner, when the engine failed a lot. This behavior was more clearly observed when the engine was still cold, because after heating the engine, the heat helped to burn the mixture.

The graph shows that with lower percentages, 5%, 10% and 15%, the engine speed fluctuated a lot, being very similar to that of kerosene, with well-defined ups and downs.

The difference that was clear in the graphics is that with kerosene, the rotation increased a little, which did not happen with the thinner, where the rotations were very close to the rotation of clean gasoline, but with the rotation oscillating a lot.

When fueled with 20% thinner, the rpm did not go up and was on the same level as clean gasoline, however, the ups and downs of the rotation weighed heavily on the engine. The graphic does not do justice to the real functioning of the engine. With this percentage, the engine failed a lot and at times it looked like it was going to shut down.

4.1.1 Particle Counting - PQA

This analysis presents a quantitative and not a qualitative result.

Figure 9 shows the values found for all contaminants in all proportions.

There is an increase in wear represented by the increase in the magnetic particle content (PQA). However, there is no significant variation in the values presented, since these quantities do not represent a worrying wear value. Significant values that require attention, must be over 60.

4.1.2 Oxidation

Figure 10 shows the oxidation graph for all contaminants at all percentages.

The use of the engine, both with gasoline without contaminants and with adulterated gasoline, caused the lubricant to oxidize, but it remains in the acceptable range. Ethanol is less harmful to the lubricant given its oxidation.

4.1.3 Total Base Number - TBN

Figure 11 shows the TBN graph for all percentages of contamination.

The TBN did not show significant variations, which could be harmful to the engine, for any of the contaminants.

4.1.4 Sulfation

Sulphation shows the degree of acid formation that the lubricant exhibits at the time of measurement.

Figure 12 shows the sulphation result for all samples.

The use of the engine caused the sulphation of the lubricant, but at levels considered acceptable.

4.1.5 Nitriding

This analysis reflects the conditions of combination of Nitrogen and Oxygen in the air inside the engine, when subjected to high temperatures and pressure. Figure 13 illustrates the result obtained.

The use of the engine with gasoline contaminated with ethanol and thinner “slightly” increased the nitriding as its content as a contaminant increased. Kerosene had practically no effect on the nitriding of the lubricant, and only in large amounts does it change the value of nitriding in small amounts.

Conclusion

Oxidation in an engine generates sludge, lacquer, resin, soot, etc., all products that are extremely harmful to it. The sludge is like black cream that can clog the ducts where the lubricant circulates to lubricate the engine. Due to its consistency, it makes the movement of the internal parts of the engine difficult, causing it to lose performance. According to the tests presented, there is no damage to the engine's operation, but if it is expanded to frequent operation with these types of contaminants, the engine's useful life will be reduced.

TBN indicates how much alkaline reserve you have to fight the oxidation generated by the acids formed during combustion. The results presented show the negative influence of these contaminants on the internal combustion engine.

Sulphation is undesirable, whatever its level of evolution. It starts by consuming the lubricant additives and then it starts to chemically corrode the interior of the equipment on the entire surface that the lubricant comes into contact with. The detrimental effect of contaminants on the sulfation of the lubricant during use is also notorious.

There was no significant wear on the engine when using it with adulterated fuel, but new tests must be carried out with a greater load and test time. New work is also being done in order to verify the pollutant emissions when using these contaminants in the same proportions. The spark plug is also a good indicator of the damage these contaminants cause. In the new tests, this spark plug is being monitored and will be qualitatively measurable.

In view of the analyses, this work showed that gasoline contaminations had poor results in the engine's functioning. For all contaminations, there was a higher than normal carbonization of the spark plug.

Rotation analyzes showed clear results and within what the literature suggests. Significant changes were found in engine speed with all contaminants and within expectations. With ethanol the rotation increased and with kerosene and thinner the engine had an irregular operation and with many failures, bad behavior for the engine that loses power and increases consumption.

Declarations

6. ACKNOWLEDGMENTS

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7 DATE AVAILABILITY

The data used to support the study can be available upon request to the corresponding author.

8 CONFLICTS OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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Figures

Figure 1

Bench mounted engine (a) details, (b) bench where the engine was mounted



Figure 2

Mounting the hourmeter wire on the spark plug wire

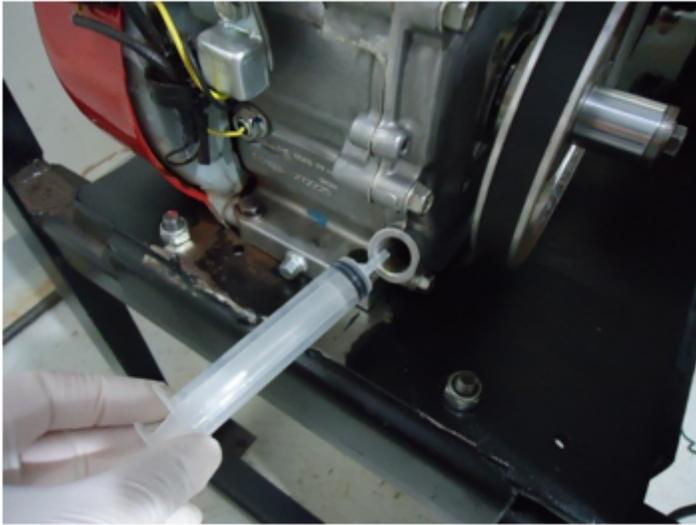


Figure 3

Lubricant sample collection



Figure 4

PQA Ferrous Particle Monitor

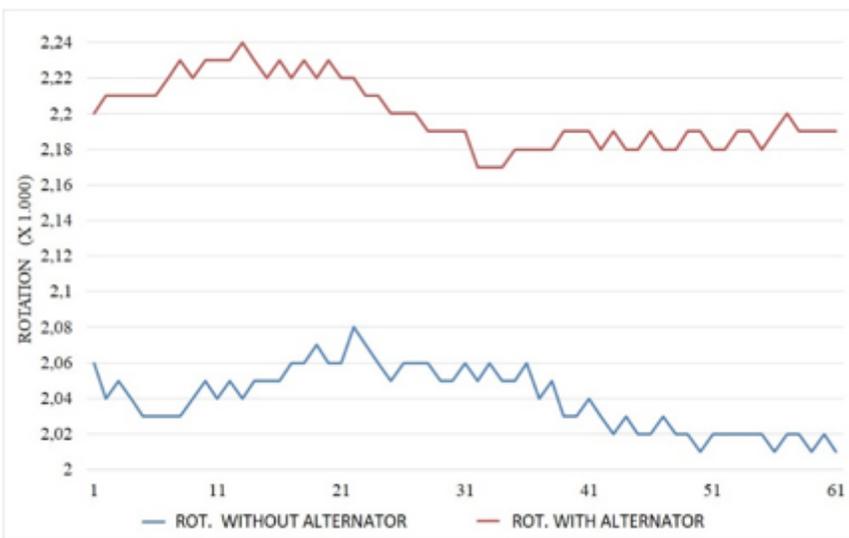


Figure 5

Engine rotation with and without connecting to the alternator

Figure 6

Rotation with ethanol contamination

Figure 7

Rotation with kerosene contamination

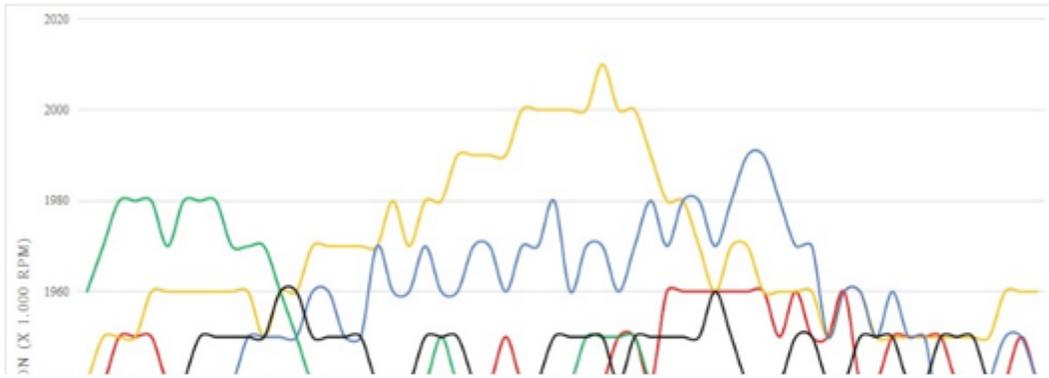


Figure 8

Rotation with thinner contamination

Figure 9

Particle counting

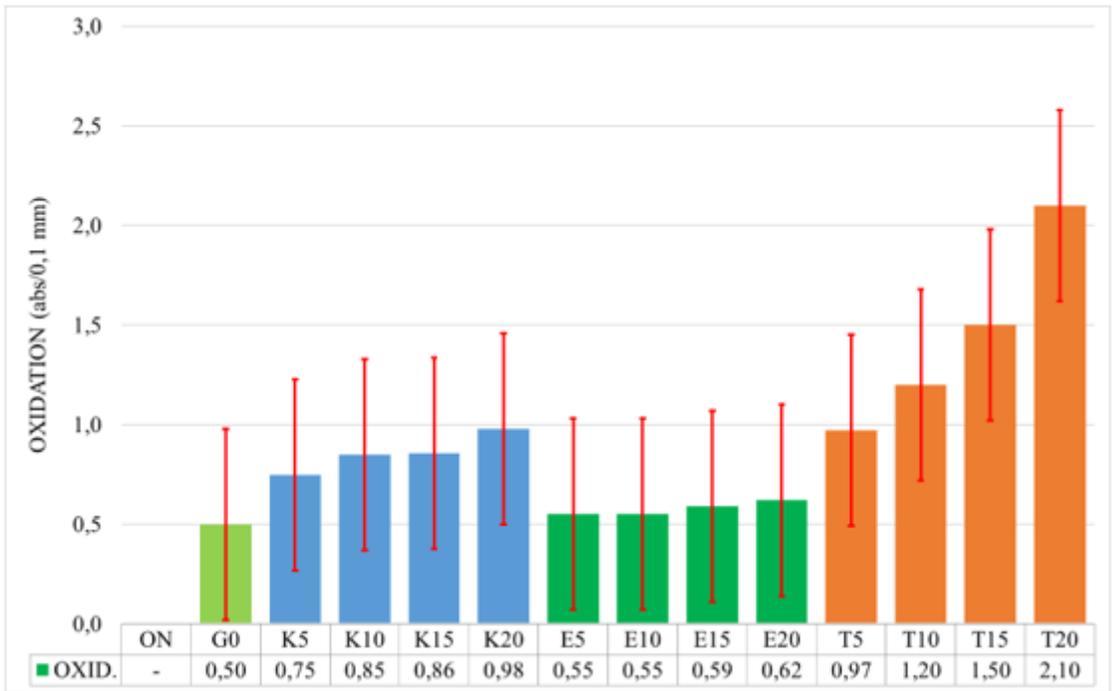


Figure 10

Oxidation

Figure 11

Total Base Number

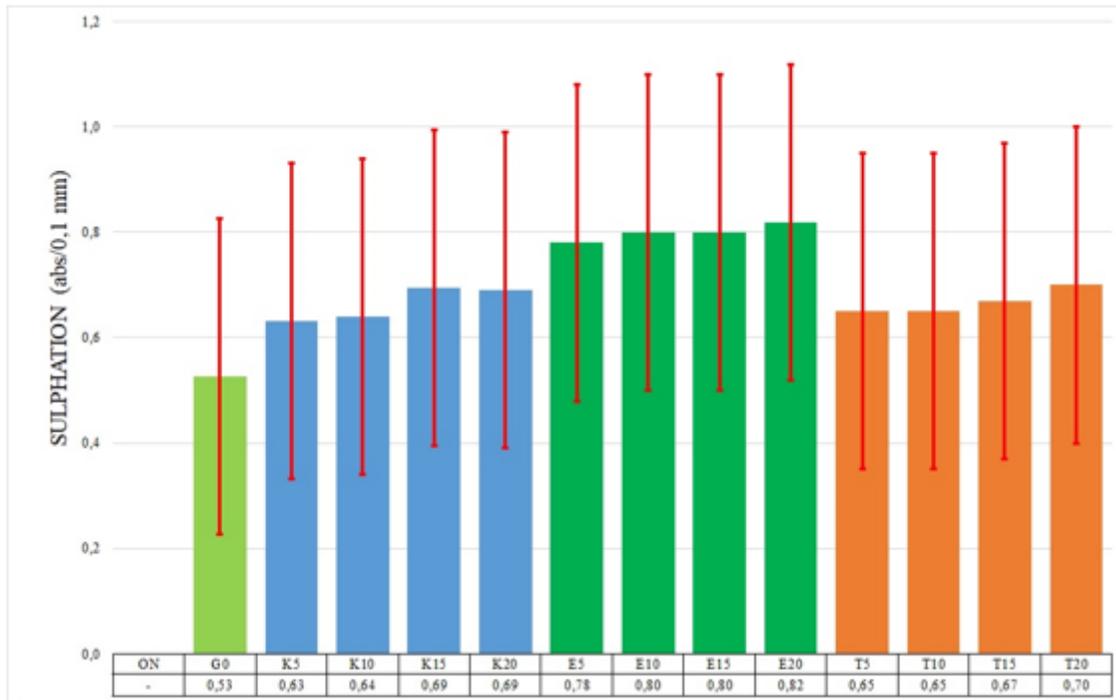


Figure 12

Sulphation

Figure 13

Nitriding