Study of the Effect of Gasoline Components on Lubricity

- Effects of Aromatic, Water, and Ethanol Content on Gasoline Lubricity -

Nitiwat Chiampradit 1) Takashi Nomura 2) Masayuki Ichiyanagi 1) Yasumitsu Isobe 2)
1) Toyota Daihatsu Engineering and Manufacturing Co., LTD.
99 Moo 5, Ban-ragad Bang-Bo, Samutprakarn, 10560 Thailand
2) Toyota Motor Corporation 1, Toyota-cho, Toyota Aichi, 417-8572 Japan

Received on November 28, 2016

ABSTRACT: Due to each country’s energy policy, various types of gasoline such as ethanol blended gasoline, high/low aromatic content gasoline, etc. are sold in the market. As the production of engines and their part supply chains become more globalized, it is important to develop engines that can be compatible with various types of gasoline. To maintain engine durability, it is necessary to clarify the effects of these gasoline components on engine durability. To understand the friction of metal to metal contact, which are directly connected to engine durability, we examined synthetically the relationship between gasoline components and lubricity.

KEY WORDS: Material, Lubrication/tribology, Gasoline lubricity, HFRR, wear [D3]

1. Introduction

Due to each country’s energy policy and each refinery’s capability, there are various types of gasoline in the market today. The amount of components such as ethanol, aromatics, water, and sulfur vary by each fuel type.

In the automotive area, to ensure the durability of global vehicles, it is important to develop engines that are compatible with various types of gasoline. Lubricity is one of the most important properties to consider, because in gasoline direct injection systems, fuel lubricity is required to avoid metal to metal contact (1).

Past studies have shown the global usage of biofuels adds more uncertainty over the gasoline lubricity discussion. For example, in studies involving ethanol containing gasoline, the results vary from a large change in lubricity (2) to a slightly improved results (3), to no significant impact when ethanol is used from 20 to 85%-v/v in gasoline blend (4). Further gasoline component studies have shown no significant dependence of chemical structure on lubricity when comparing each single component (5).

To understand the friction of metal to metal contact, which are directly connected to engine durability, we examined synthetically the relationship between gasoline components and lubricity of mixture solvent in actual gasoline.

This study consisted of 4 parts:
Study 1: The effect of aromatic content, by using a simulated gasoline made by a mixture of toluene as the mono-aromatic component and iso-octane as the paraffin component.
Study 2: The effect of water content, by adding water to market gasoline at the maximum amount before phase separation.
Study 3: The effect of ethanol content, by blending market gasoline with reagent anhydrous ethanol.
Study 4: The effect of water and ethanol content; through a combination of Study 2 & 3.

2. Experiment and procedure

2.1. Test Equipment

A High Frequency Reciprocating Rig (HFRR) lubricity tester has been used for determining the lubricity of diesel fuels, therefore, in this study, we prepared a specimen holder and the gasoline bath designed for gasoline evaluation using a HFRR (6).

Fig. 1 shows a diagram of the HFRR and a sample of a wear scar. This tester is a ball-on-disc type, (5), which uses a steel ball sliding over a steel disc immersed in a liquid sample. In this study, stainless steel SUS440C was used for the ball and disc material, which is same material used for fuel system parts. The wear scar diameter (WSD), which is the average length of the minor and major axes of the scar generated by the ball, is used for evaluating the lubricity of the sample. In general, as the lubricity of the liquid sample increases, the WSD decreases (7).

Fig. 1 Diagram of the HFRR and example of wear scar after test
2.2. Tested samples

The liquid samples were prepared with various aromatic, water and ethanol content. The contents of the tested samples are shown in Tables 1 - 4.

For the study of the effect of aromatic content, we prepared simulated gasoline made by a mixture of toluene as the mono-aromatic component and iso-octane as the paraffin component. We blended toluene with iso-octane in ratios from 0 to 100 by vol%. In order to control the water content, we performed a dehydration treatment on the components before mixing.

For the study of the effect of water content, E0 market gasoline was used with the addition of water to the gasoline until the maximum amount was reached before phase separation. Water amount targets were 50 ppm, 100 ppm and 200 ppm.

For the study of the effect of ethanol content, the tested gasoline blended with anhydrous ethanol. Ethanol content target was 10, 20, 30, 40, 60, 80 and 100 % by volume.

For the study of the effect of the combination of water and ethanol, (combination of Study 2 & 3). We mixed base gasoline with ethanol at 20 % and 85 % by volume, and then water was added into the base gasoline.

2.3. Test Procedure and Test Parameter

A gasoline lubricity evaluation has not been established yet, however, the consensus in literature (3) is that the basic procedure developed for the diesel lubricity evaluation can be used. Thus, the evaluation method is based on the diesel HFRR test method defined by ASTM D6079. The difference between the standardized test condition for gasoline and diesel is the type of specimen holder that used in each test. For the diesel evaluation, a rectangular specimen holder with a maximum fluid capacity of 4mL and exposed fluid area of 6 cm$^2$ is used. While for the gasoline evaluation, a cylindrical specimen holder with a 20 mL fluid capacity and 7 cm$^2$ exposed fluid areas is used. Also we adjusted some the other test conditions to align with the gasoline properties by using a 10mL capacity specimen holder, and a temperature at 25 °C while conducting these evaluations. Furthermore, material of the ball and disc was changed from steel to SUS440C stainless steel.

WSD was determined by an average of three measurements.

A comparison of the HFRR test conditions for gasoline and diesel are shown in Table 5.
3. Results and discussion

Results of the relationship between WSD and each parameter are shown in fig. 3-6.

3.1. Study 1: The effect of aromatic content

Fig. 3 shows the influence of aromatic content. When the aromatic content increases to 20% by volume the WSD decreases, and from this result we could conclude up to that volume that there is a positive correlation of aromatic content and lubricity.

3.2. Study 2: The effect of water content

Fig. 4 shows the influence of water content in E0 gasoline. This result shows as the amount of water increases, lubricity will decrease.

3.3. Study 3: The effect of ethanol content

Fig. 5 shows the influence of anhydrous ethanol content. This result shows that regardless of the ethanol content in the gasoline, the WSD maintained a low, stable value.

3.4. Study 4: The effect of water content and ethanol

Fig. 6 shows the result of the effect of both water and ethanol in gasoline. This result shows that as the water content increases, the WSD also increases. However, when the ethanol content was increased, the effect of water content on WSD was reduced. E85 gasoline showed remarkable results.
4. Wear mechanism theory

The interaction between the friction surface and the lubricant can be explained by the Stribeck curve. The Stribeck curve divides lubrication into three regimes based on the lubrication parameter: [1] Boundary Lubrication, [2] Mixed Lubrication and [3] Hydrodynamic Lubrication.

During HFRR evaluation, a wear scar was formed on both the steel ball and disc. This phenomenon indicated that metal to metal contact occurred. Therefore, the lubrication regime was determined to be boundary and mixed lubrication.

In general, metal surfaces are covered with oxides and organic contaminants, and are chemically stable on the surface. However, when solid contact occurs under boundary lubrication, these surface films are dynamically removed and the bare metal surface is exposed, as shown in Fig. 7. This is called the nascent surface. (8)

In HFRR testing, a liquid sample exists between the steel ball and disc. Components from this liquid sample can interact with the metal when nascent surface is exposed.

The presented mechanism of a lubricant film formation by adsorption and reaction on the nascent surface is described below.

4.1. Study 1: The effect of aromatic content

Previous studies have shown the active component of steel is the transition metal, and iron has a partially un-occupied d-orbital. Aromatics such as toluene have a benzene ring, which has a π-electron and exhibit high adsorption activity. On the other hand, saturate hydrocarbons such as iso-octane without any functional groups are hard to adsorb on the nascent surface. The effect can be explained by components having π-electrons are easily adsorbed by the donation of the electrons to the iron d-orbital. (8)

It suggests that this strong adsorption to the surface can occur through the donation of an electron and can form a chemical film (lubricant film) as shown in Fig. 8, which results in a reduction of friction between the surfaces.

4.2. Study 2: The effect of water content.

In general, gasoline contains aromatic components such as toluene, which can form a lubricant film through chemical adsorption to the surface, however when water is added to the gasoline, lubrication effectiveness decreased in this study.

From the polarity and surface tension of each component as shown in Table 6 and Fig. 9, it can be seen that water has a both a higher surface tension and a highly polar covalent bond compared to gasoline components.

| Component | Surface tension ($10^3$ N/m) | Polarity (Type of Bond) |
|------------|-------------------------------|-----------------------|
| Ethanol    | 22.55                         | C-H : Non polar covalent bond |
|            |                               | C-O : Moderately polar covalent bond |
|            |                               | O-H : Highly polar covalent bond |
| Water      | 72.75                         | O-H : Highly polar covalent bond |
| Toluene    | 28.40                         | C-H : Non polar covalent bond |

This suggests that the polarity from the water interfered with adsorption on nascent surface of the π-electron from the aromatic components. The water replaces lubricant film, as shown in Fig. 10. Therefore, formation of the lubricant film is more difficult if the water amount in the gasoline increases, which in turn leads to a decrease in lubricity.
4.3. Study 3: The effect of ethanol content

In general, ethanol contains hydrocarbon groups similar to other gasoline components and has polarity because of a functional group.

This shows that ethanol has capability to form a lubricant film quickly through chemical adsorption. So the nascent surface is not exposed as shown in Fig. 11. Further, it is miscible with the gasoline. As a result, the anhydrous ethanol content does not influence lubricity.

4.4. Study 4: The effect of water and ethanol content

In the mechanism shown in Study 2, the effect of water content, we described the fact that water has both a higher surface tension and a highly polar covalent bond compared to gasoline components, and then therefore the water replaces lubricant film.

In general, ethanol can bond with water due to the polarity group (O-H) and the other side of ethanol being a hydrocarbon group (CH₃-).

Ethanol must bond with the water which reduces the influence of water on lubricity as shown in fig. 12-13.

5. Conclusion

According to the test results and the presented mechanisms, we can conclude that

1) Aromatic content and water content effect the lubricity of gasoline. Lower aromatic content and higher water content causes a reduction lubricity.

2) The lubrication of metal to metal contacts are in the boundary and mixed lubrication regimes. In this study we proposed that the boundary lubrication was the dominate regime, and the wear in this regime is largely affected by high surface tension and highly polar components which interfere in the formation of a lubricant film on the friction surface.

From this study, the influence of gasoline components on lubricity was understood so that can enable an improvement in engine durability.

“This paper is written based on a proceeding which is presented at JSAE 2016 Annual Congress Autumn.”
References

(1) Marangoni, D., Fuel Lubricity, Industrial Lubrication and Tribology, pp. 108-118, Vol 50, No.3, (1998)
(2) Rovai, F., Tanaka, D. and Sinatora, A.; Wear and Corrosion Evaluation of Electric Fuel pumps with Ethanol/Gasoline blends, SAE Technical Paper 2005-01-2196, (2005)
(3) US EPA. Use of Reformulated Gasoline in Nonroad Engines, EPA 420-F-95-007, April 1995.
(4) Agudelo, J.; Delgado, A.; Benjumea, P., The Lubricity of ethanol-gasoline fuels blends, Rev.Fac.Ing.Univ.Antioquia, No. 59, pp. 9-16, (2011)
(5) Knothe, G. Evaluation of ball and disc wear scar data in the HFRR lubricity test. Lubrication Science, Vol 20, No.1, pp. 35-45, (2008)
(6) Wei D. P, Spikes, H., Koreck, S. The lubricity of gasoline, Tribology transactions, Vol 52, No.4, pp 813-823, (1999)
(7) Luiz Guiherme R. Lopreato. Gasoline lubricity: An Exploratory Evaluation, SAE Technical Paper 2012-36-0502, (2012)
(8) Shigeyuki Mori. Boundary lubrication from the viewpoint of surface chemistry, JTEKT Engineering journal No.1008, pp2-11, (2010)