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Review

A perspective on the origin of lubricity in petroleum distillate motor fuels☆

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ABSTRACT

Lubricity, or a substance's effect on friction and wear between two surfaces in relative motion, is affected by both chemical and physical mechanisms present at a sliding contact. The inherent lubricity of distillate motor fuels stems from surface-active compounds found in petroleum, principally heavy aromatic compounds such as polycyclic aromatic hydrocarbons (PAH) and nitrogen heterocyclic polyaromatic hydrocarbons (NPAH) containing three or more fused rings. These compounds are less abundant in motor gasoline and more abundant in diesel fuel due to differences in the boiling ranges of these distillate fuels. PAH and NPAH compounds can form chemical bonds with metal surfaces and reduce the friction of metal surfaces in sliding contact. Reducing the coefficient of friction lowers the peak stress amplitude at the sliding contact, thereby mitigating the effects of plasticity-induced wear mechanisms and delaying the transition to abrasive wear. Hydrotreatment of distillate motor fuels to remove sulfur also hydrogenates heavy aromatic compounds, leading to a reduction in fuel lubricity and increased wear of fuel injectors and pumps. The addition of linear alkyl polar compounds can improve fuel lubricity in severely hydrotreated petroleum distillate motor fuels. Boundary lubrication by linear alkyl polar compounds is distinct from lubrication by native heavy polar aromatic compounds found in petroleum. Mechanical testing is typically employed to measure fuel lubricity due to the complex interactions between the surface-active compounds and wear mechanisms at work in a sliding contact, and the lack of a single SI unit like viscosity that describes the sum of interactions between the fluid, material, and mechanical forces at a sliding contact.

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1. Introduction

Lubricity is “a qualitative term describing the ability of a fluid to affect friction between, and wear to, surfaces in relative motion under load” [1]. Of two fuels with the same viscosity, the one that produces less friction, wear, or scuffing is considered to have better lubricity [2]. It is important to note that lubricity is not an intrinsic fluid property. The ability of a fluid to affect friction and wear depends on its composition, the mechanical forces present at the point of contact, and the material properties of the surfaces in relative motion. Changes to any of these variables may alter the apparent lubricity of a petroleum distillate motor fuel. The lubricity of petroleum-based fuels may be adversely affected by processing, and it is useful to identify the surface-active compounds responsible for the inherent lubricity of these fuels and their role at the sliding contact, particularly as increasing demands are placed on the composition of petroleum-based fuels by regulatory and operational requirements.

Distillate motor fuels (i.e., motor gasoline, aviation turbine fuel, and diesel fuel) accounted for 60% of global petroleum use from 2008 through 2010 [3]. Continued growth in demand for these fuels, combined with heightened concern over air pollution, has led to increasingly stringent clean fuel standards that limit sulfur content in distillate motor fuels. Sulfur can poison catalysts used in emission control systems; moreover, the combustion of sulfur compounds releases harmful sulfur oxides (SO_x) into the atmosphere. Ultra-low sulfur diesel (ULSD) fuel sold in North America today may contain no more than 15 ppm sulfur [4]; in Europe, the limit is even lower, at 10 ppm sulfur [5,6]. Government-sponsored studies in the United States [7] and the United Kingdom [8] have recommended reducing future sulfur levels in aviation turbine fuel to 15 ppm and 10 ppm, respectively. More recently, the United States Environmental Protection Agency mandated the reduction of sulfur content in motor gasoline from 30 ppm to 10 ppm by 2017 [9,10]. In the past, lowering the sulfur content of aviation turbine fuels and diesel fuels resulted in accelerated wear and premature failure of fuel pumps and injectors, an unanticipated effect of processing on fuel lubricity.

The sulfur content of crude petroleum varies widely, ranging from less than 0.05% to over 14% by mass [11]. To meet current clean fuel standards, excess sulfur present in crude petroleum must be removed during refining. Hydrodesulfurization, a thermochemical process where sulfur compounds are converted catalytically to hydrogen sulfide gas in the presence of hydrogen gas [12], is often used by petroleum refineries to reduce the sulfur content of finished distillate motor fuels [13]. Hydrotreatment also removes the trace compounds present in petroleum that improve fuel lubricity [14], often thought to contain oxygen or nitrogen heteroatoms, as was found to be the case for both aviation turbine fuels and diesel fuels.

Adding lubricity improving compounds to commercial aviation turbine fuels has been shown to be an effective solution in the past; however, the practice of using the fuel as a part of cooling systems found in high performance aircraft subjects these additives to thermal stresses that may degrade their effectiveness. High performance engines can push petroleum distillate motor fuels to their limits during routine operation. Indeed, there are indications that this situation will become more pronounced in the future.

Advanced aircraft routinely use the fuel as a heat sink (a process called regenerative cooling or heat transfer), but the capacity of the fuel to serve this function is quickly approaching a limit imposed by the chemical stability of the fuel. Current thinking is to remove lubrication subsystems from such aircraft entirely, to save energy overhead, and to shift the lubricant function entirely onto the fuel. The fuel will then serve as propellant, heat sink and lubricant. The drive to improve performance is not limited to aviation, and similar demands on fuel lubricity can also be found in current automobile designs.

The use of common rail fuel injector technology, originally developed for diesel engines, has become increasingly prevalent in gasoline engines in recent years. High-performance gasoline direct injection (GDI) engines have been gaining market share since their introduction in the 1990s, and accounted for 30.4% of all new cars sold in the United States during 2012 [15]. Common rail fuel injector pumps are sensitive to fuel lubricity [16], and the removal of sulfur in motor gasoline through hydrotreatment may also remove trace compounds present in petroleum that impart lubricity to the distillate fuel. To understand the potential effects of fuel processing on the lubricity of thermally stressed aviation turbine fuels as well as wear of GDI engine components, it is useful to consider the origin of inherent lubricity in petroleum-based fuels by examining lubricity in the context of surface-active compounds across different distillate cuts.

2. Literature review

During the 1960s, hydrotreatment of aviation turbine fuel to remove sulfur was observed to increase wear of jet engine components [2,17]. Subsequently, the ball-on-cylinder lubricity evaluator (BOCLE) test was devised to measure the lubricity of aviation turbine fuels [18]. Further testing of hydrotreated aviation turbine fuels showed that the addition of corrosion inhibitors containing fatty acid dimers (e.g., dimerized linoleic acid) restored lubricity [19,20]. Long-chain polar compounds, such as fatty acids, are known to be effective boundary lubricants [21]. The principal wear mechanism in the BOCLE test is thought to be chemical oxidation [22]; however, it is unclear whether the same mechanism is responsible for the wear of jet engine components observed in the field.

In the 1990s, adoption of ultra-low sulfur diesel fuel in Sweden was observed to cause rapid wear and failure of rotary fuel injection pumps [23]. Around the same time, the US military reported a sharp rise in rotary fuel injection pump failures in compression ignition engines when diesel fuel was replaced with aviation turbine fuel [24]. The high-frequency reciprocating rig (HFRR) test was adopted as an industry standard to measure diesel fuel lubricity [25], because it offered better discriminability between high and low lubricity diesel fuels compared with the BOCLE test [26]. The difference in discriminability between the BOCLE test and the HFRR test is thought to be due to the wider range of wear mechanisms observed in the latter (e.g., abrasive plowing and adhesive galling) [27].

The lubricity of motor gasoline has been found to be significantly lower compared with diesel fuel in HFRR tests [28,29]. HFRR testing of pure hydrocarbon compounds found in gasoline showed that lubricity is a function of fluid viscosity and not its alkane, alkene, and aromatic concentration [30]. Wear was found to increase proportionally with the coefficient of friction, but no correlation was found between viscosity and lubricity in commercial gasoline samples [31].

3. Theory

3.1. Surface-active compounds in boundary lubrication

All surfaces are “rough” on the microscopic scale. Friction between two bodies in physical contact is dominated by interactions between the high points, or asperities, on the contacting surfaces [32]. In boundary lubrication, the thickness of the lubricating film is approximately the same as the surface roughness of the surfaces in contact. Boundary lubricants prevent direct contact between asperities, thereby lowering friction and wear at the sliding interface.

Surface-active compounds are often added to fuels to improve their lubricity. Systematic studies of boundary lubricants began in the 1940s, leading to the development of numerous additive compounds for lubricants and greases [33,34] ranging from fatty acids and their derivatives to inorganic glass-forming compounds (e.g., zinc dialkyldithiophosphates used as extreme pressure additives) [35]. Fatty acids and their derivatives readily adhere to metal oxide surfaces to form a protective thin film and are often added to fluids as friction modifiers [36]. The polar head group