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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Contents

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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 fluids 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

of these additive compounds preferentially adsorb onto surface oxides [37], leading to the formation of an organic film composed of nonpolar linear hydrocarbon chains (Fig. 1). The addition of synthetic amide compounds [38], fatty acids [39,40], and biodiesel fuel [38,41,42] have been reported to improve the lubricity of ULSD fuel as measured by the HFRR test. Similar improvements in fuel lubricity were reported for aviation turbine fuels with ester additives [43] and for motor gasoline with detergent additives [30]. Linear alkyl polar compounds are effective in improving fuel lubricity when they are present in a distillate motor fuel above a minimum concentration of 10–100 ppm [39,40].

While boundary lubricant additives are effective in improving the lubricity of distillate motor fuels, few occur naturally in crude petroleum. For instance, carboxylic acids in petroleum are typically naphthenic (cycloalkane) or naphthenoaromatic compounds [44], not fatty acids. Moreover, the surface-active compound must also be distillable in the appropriate temperature range for motor fuels. Gas chromatography with mass spectrometric detection (GC/MS) analysis of F-76 naval diesel fuel drawn from six geographic regions around the world failed to detect carboxylic acids in any of the samples [45]. Although sulfur compounds have been studied extensively for their ability to form self-assembled monolayers on gold surfaces [46], HFRR testing of model sulfur compounds in diesel fuels showed either a decrease in lubricity [39] or no effect [47] as a function of sulfur concentration. More specifically, benzothiophenes and related compounds have been noted to increase a fluid's load-carrying capability without affecting its lubricity [47,48].

Barbour et al. explicitly note that minor oxygen- and nitrogen-containing compounds act to improve lubricity in petroleum distillate fuels [47]. The compounds were concentrated in the most polar fraction, as separated through column chromatography. The finding is consistent with prior findings by Wei and Spikes, who measured a decrease in HFRR wear scar diameters using 8-hydroxyquinoline and 1,4-hydroquinone as model compounds in a known hydrotreated fuel [39]. Interestingly, Appeldoorn and Tao noted a synergistic effect between trace oxygen and water with heavy aromatic hydrocarbons in improving

lubricity of aviation turbine fuels [49], while others have noted a decrease in lubricity as a function of water content in diesel fuels [50,51]. Relative humidity is known to have an effect on HFRR wear scar diameter measurements [52]. It is possible that competing chemical interaction between trace oxygen and water with heavy aromatic hydrocarbons and nascent metal surfaces to form oxygen-containing compounds may be responsible for the conflicting reports.

Heavy aromatic compounds were first observed to improve lubricity in aviation turbine fuels [49] and later in diesel fuels [39,47]. Polycyclic aromatic hydrocarbons (PAHs) and nitrogen heterocyclic polyaromatic hydrocarbons (NPAHs) occur naturally in crude petroleum [53]. Aromatic compounds have delocalized π-orbitals that can interact with conduction electrons in metallic surfaces (Fig. 2), as evidenced by the effect of aromatic solvents on surface plasmons [54] and surface-induced aromatic stabilization of large π-conjugated molecules on metallic surfaces [55]. Studies on graphene–metal interactions have shown strong chemisorption between graphene and nickel surfaces through donation/back-donation bonding [56]. Moreover, substitutional nitrogen doping of graphene increases the binding energy between graphene and nickel [57]. PAH and NPAH compounds present in petroleum may improve the lubricity of distillate motor through their effect on several wear mechanisms.

3.2. Effect of boundary lubricants on wear mechanisms

Mechanical wear is a complex phenomenon involving many physical and chemical processes, operating over a wide range of sliding velocities and contact pressures [58]. The rate of material removal due to the combined effect of all of these processes is known as the wear rate, and is affected by the presence of boundary lubricants. Observation of mechanical wear between steel surfaces in relative motion, subject to the effects of surface-active compounds present in a distillate motor fuel, constitutes the basis of fuel lubricity testing today. Table 1 summarizes
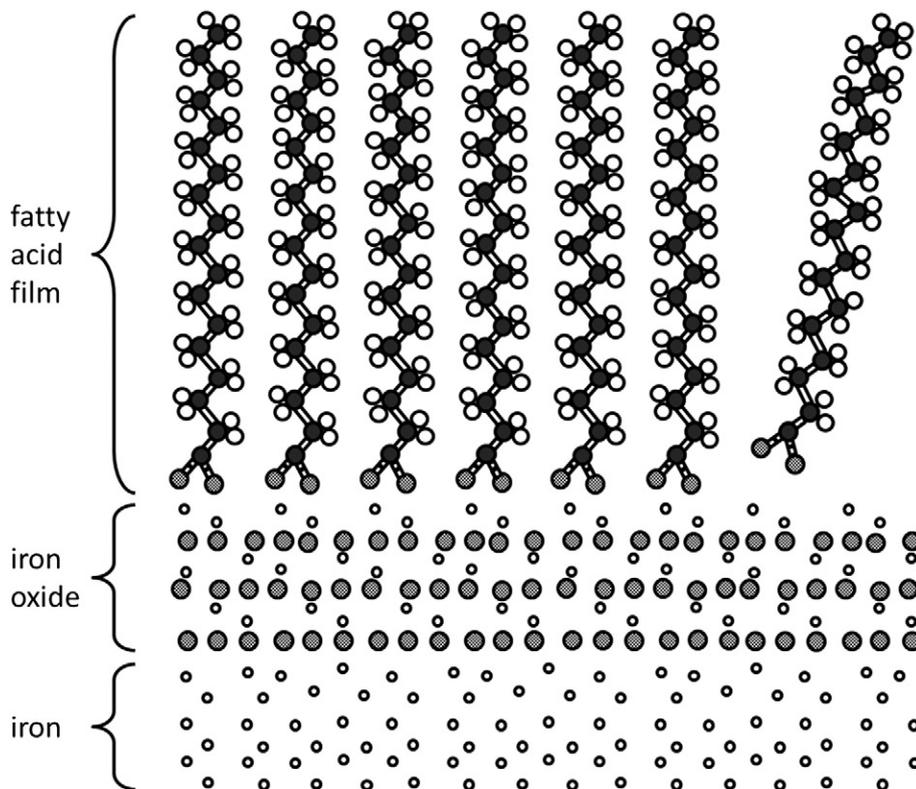
Fig. 1. Adsorption of deprotonated stearic acid on iron (III) oxide (Fe_2O_3, hematite) and formation of boundary lubricant film. The fatty acid film prevents direct contact between the high points, or asperities, of two contacting surfaces.
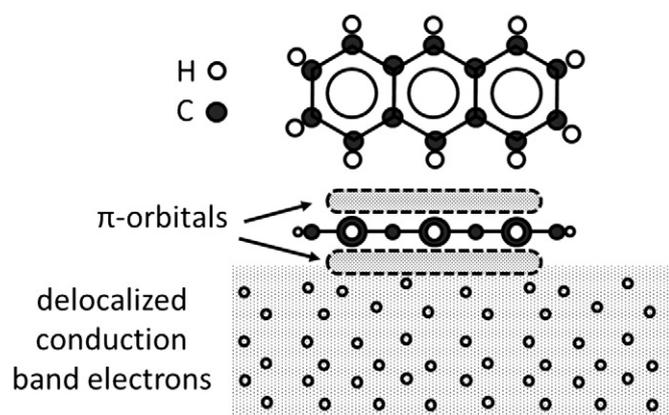
Fig. 2. Adsorption of anthracene, a polycyclic aromatic hydrocarbon (PAH) compound, on a metal surface. The aromatic π-orbitals above and below the planar molecule can interact with delocalized conduction band electrons in the metal and form a chemical bond between the PAH compound and the surface.

the differences between the BOCLE, HFRR, and other lubricity tests commonly encountered in the literature.

3.2.1. Oxidative wear

Most metals oxidize in air. For some metals, the formation of a native oxide film passivates their surfaces and protects them from further oxidation (e.g., aluminum, titanium). This is not the case for iron, which oxidizes to form various oxides that readily crack, spall, and detach from the metal due to differences in the metal and oxide unit cell volumes [59]. Oxygen diffuses readily through native iron oxide films; therefore, the underlying iron or steel surface remains susceptible to further oxidation and subsequent mass loss. Mechanical removal of iron oxides due to asperity collisions during sliding contact can increase the rate of mass loss, leading to oxidative wear of iron and steel surfaces.

The oxidative wear rate of steel may be reduced through chemical or mechanical means. In the case of stainless steels, alloying iron with chromium results in the formation of a chromium oxide film that adheres strongly to the metal surface and passivates the surface by blocking oxygen diffusion. Iron oxides can become mechanically compacted into a debris film during sliding contact, which protects the underlying metal from rapid oxidation and prevents metal-to-metal welding between asperities [60]. In a lubricated contact, the

formation of an oxide film is an important factor in boundary lubrication. Linear alkyl polar compounds, such as fatty acid derivatives and amides, assemble into a protective film in the vicinity of an oxide surface. The boundary lubricant film reduces the coefficient of friction at the sliding contact and prevents direct mechanical contact with the underlying oxide. The presence of dissolved water and oxygen in the fuel can accelerate the formation of surface oxides and alter the apparent effectiveness of these lubricity additives when oxidative wear is the dominant wear mechanism.

3.2.2. Plasticity dominated wear

The yield stress of a metal establishes its elastic and plastic response to a mechanical load. Below its yield stress, a metal specimen is elastic or "springy," returning to its original dimensions when external forces are removed. When external forces exceed its yield stress, a metal specimen becomes permanently deformed or plastically strained and does not return to its original dimensions when external forces are removed.

When two metal surfaces come into contact, the mechanical forces acting on the interface can cause plastic deformation of the metal at asperity contacts. The extent of plastic deformation is dependent on the magnitude of the load and the material response of the metal. Accumulation of plastic strain leads to work-hardening and reduction in ductility in most metals and their alloys. Over time, plastic deformation can lead to the loss of material or wear through adhesion and delamination.

3.2.2.1. Adhesive wear. Plastic deformation of a metal surface can disrupt surface oxide films, much like the cracking of caramelized sugar atop crème brûlée when an external load is applied with a spoon. Breakdown of surface oxide films can cause cold welds to form between asperities in a sliding contact, with a concomitant increase in friction and wear [61]. The cold weld formed between asperities can be stronger than the underlying metal, leading to the transfer of material from one surface to the other if the two surfaces are in relative motion [62]. This was shown to be the case in an autoradiographic study of sliding metallic contacts [63], which showed that a small amount of metal is transferred from a radioactive surface to a non-radioactive surface when the two are brought into sliding contact. Adhesive wear is sometimes described as "galling" or "scuffing" in the tribology literature.

Interestingly, fatty acids do not protect a freshly cut metal surface from wear [64]. In the absence of surface oxides, chemisorption of heavy PAH and NPAH compounds may protect nascent metal surfaces from adhesive wear by preventing cold welds from forming. Heavy PAH and NPAH compounds containing three or more aromatic rings

Table 1
Standardized test parameters for the four-ball anti-wear, ball-on-cylinder lubricity evaluator (BOCLE), scuffing-load BOCLE, and high-frequency reciprocating rig (HFRR) tests. Test balls used in the tests are hardened AISI E-52100 steel (Rockwell hardness "C" scale 58–66), which is also known as SAE-AMS 6440 steel as specified in ASTM D6079-11. Alternate standards with similar test geometries are given for reference; the values in the table are for the ASTM standard test methods.

	Four-ball	BOCLE	SL-BOCLE	HFRR
ASTM standard	D4172-94	D5001-10	D6078-04	D6079-11
ISO standard	20623:2003			12156-1:2006
Test geometry	ball-on-ball	ball-on-cylinder	ball-on-cylinder	ball-on-flat
Test motion	rotating ball	rotating cylinder	rotating cylinder	reciprocating ball
Ball diameter	12.7 mm (0.5 in)	12.7 mm	12.7 mm	6.00 mm
Ball material	hardened AISI E-52100 steel	hardened AISI E-52100 steel	hardened AISI E-52100 steel	hardened AISI E-52100 steel
Counterface material	hardened AISI E-52100 steel	hardened SAE 8720 steel	hardened SAE 8720 steel	annealed AISI E-52100 steel
Cylinder diameter	not applicable	50 ± 1 mm	50 ± 1 mm	not applicable
Fluid volume		50 ± 1 ml	50 ± 1 ml	2 ± 0.20 ml
Stroke length	not applicable	not applicable	not applicable	1 ± 0.02 mm
Frequency	1200 ± 50 rpm	240 ± 0.5 rpm	525 ± 0.5 rpm	50 ± 1 Hz
Fluid temperature	75 ± 1.7 °C	25 ± 1 °C	25 ± 1 °C	60 ± 2 °C
Relative humidity		10 ± 0.2%	50 ± 2%	30% to 85%
Applied load	40 ± 2 kg	500 g	1 to 5 kg	200 ± 1 g
Test duration	60 ± 1 min	30 min ± 0.1 min	1 min/increment	75 ± 0.1 min
Sliding velocity	0.80 ± 0.03 m/s	0.63 ± 0.01 m/s	1.38 ± 0.03 m/s	0.100 ± 0.003 m/s
Sliding distance	2900 ± 130 m	1130 ± 23 m	82.5 m/incr.	450 ± 13 m
Number of cycles	72×10^3	7.2×10^3	525/incr.	225×10^3

are similar in structure to graphene, which has been reported to reduce friction and wear significantly when deposited between sliding steel surfaces [65]. In past studies, PAHs and NPAHs have been shown to be effective boundary lubricants in diesel fuel [39,47].

3.2.2.2. Delamination wear. Contact between asperities of two solid bodies causes subsurface compressive stress fields to form near the points of contact. The magnitude of the compressive stress field is a function of the external load, material elasticity, and contact geometry [66]. Friction between asperities in sliding contact introduces a tensile component near the trailing edge of the contact spot [67]. The magnitude of the tensile stress is proportional to the coefficient of friction at the sliding contact [68]. Cyclic compressive and tensile loading of asperities leads to the formation of subsurface voids and cracks in metals over time [69]. The accumulation of subsurface damage results in the formation and delamination of wear particles [70]. Delamination wear is also known as "spalling" or "surface fatigue wear."

The presence of a boundary lubricant film at the point of contact can reduce the tensile stress developed near asperities in sliding contact. The number of fatigue cycles to failure in steel is exponentially proportional to the cyclic stress amplitude [71]. In a ball-on-cylinder lubricity experiment, the addition of stearic acid (octadecanoic acid) to pure *n*-hexadecane can reduce the friction coefficient by a factor of two and the wear rate on steel in sliding contact by up to two orders of magnitude [72]. Either linear alkyl polar compounds or heavy aromatic compounds can reduce the extent of delamination wear by decreasing the coefficient of friction at the sliding contact.

Delamination wear creates work-hardened metallic wear particles and nascent metal surfaces. Entrainment of hardened wear particles can lead to abrasive wear at the sliding contact, while the presence of nascent metal surfaces can accelerate oxidative wear in the presence of dissolved water or oxygen in the fuel. Nascent metal surfaces on the wear particles are chemically active [73], and may also react with both synthetic and naturally occurring lubricity compounds found in petroleum, removing them from solution.

3.2.3. Abrasive wear

Abrasive compounds, commonly found in grinding wheels and sandpaper, are typically employed in manufacturing to remove material rapidly. Similarly, hard asperities can remove material from a soft surface through plowing or cutting. Hard particles can become embedded in a soft surface and cut into the opposing surface in a sliding contact. While hard particle contaminants (i.e., rust and dirt) are removed from distillate motor fuels through filtration, hard particles may be generated in situ at a sliding contact from other wear mechanisms (e.g., oxides and work-hardened spalls). Abrasive wear is often described as "gouging" or "scoring", as the process leaves very distinct grooves in the wear scar.

Boundary lubricants offer little to no protection in the presence of abrasive particles. An atomic force microscopy study of abrasive wear using a diamond tip as a model asperity on annealed 3004-O manganese-aluminum alloy showed that the presence of stearic acid decreased the coefficient of friction and increased the cut depth [74].

Wear scars measured in the HFRR lubricity test show clear signs of abrasive wear [75], as seen in Fig. 3. This is curious, given the fact that the steel ball is hardened (Rockwell hardness "C" scale 58–66) and the stationary steel surface is not (Vickers hardness "HV 30" 190–210, corresponding to Rockwell hardness "C" values between 11 and 15). It is likely that the HFRR test provides better discriminability for diesel fuel lubricity because the abrasive wear scar measured on the hardened steel ball is produced by work-hardened wear particles from the counterface steel surface, which are in turn produced through plasticity dominated wear mechanisms. There is a strong correlation ($r^2 > 0.987$) between the average size of the wear scar on the ball and the corresponding wear scar size on the counterface surface [76]. When the counterface steel surface is also hardened, the HFRR test fails to discriminate between high and low lubricity fuels [27]. The data suggest that
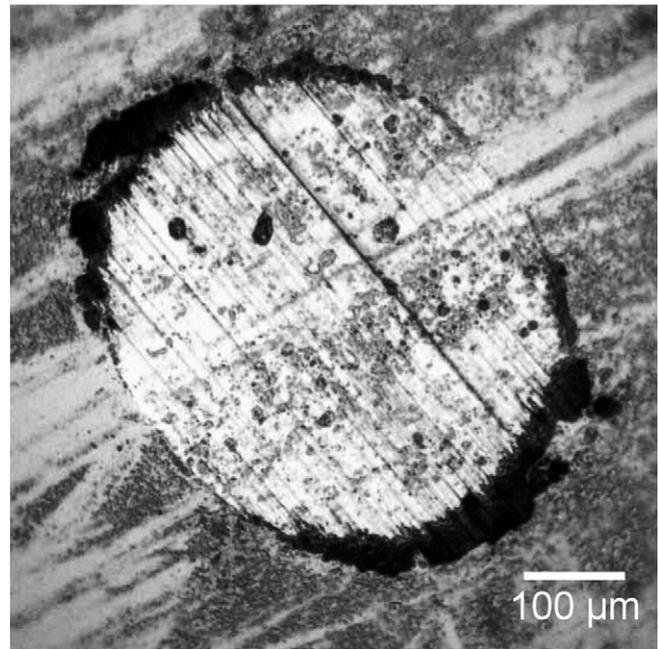
Fig. 3. Optical micrograph of an abrasive wear scar on hardened 52100 steel ball surface after linear reciprocate sliding contact with annealed 52100 steel surface [71].

while the wear scar that is measured in the HFRR test is formed through abrasive wear, other wear mechanisms must also be present for the lubricity test to be effective.

3.2.4. Wear map of common lubricity tests

Normalized pressures and velocities of four common lubricity tests were calculated from parameters reported in Table 1 and superimposed on a wear mechanism map (Fig. 4) based on empirical data from steel pin-on-disk contact experiments [58]. The normalized pressure is calculated by dividing the nominal force by the product of the nominal contact area and the room temperature hardness of the contact. Nominal contact areas for the test geometries were calculated using analytical solutions for elastic Hertzian contacts [77]. Room temperature hardness values are calculated from the nominal test load and indenter geometry
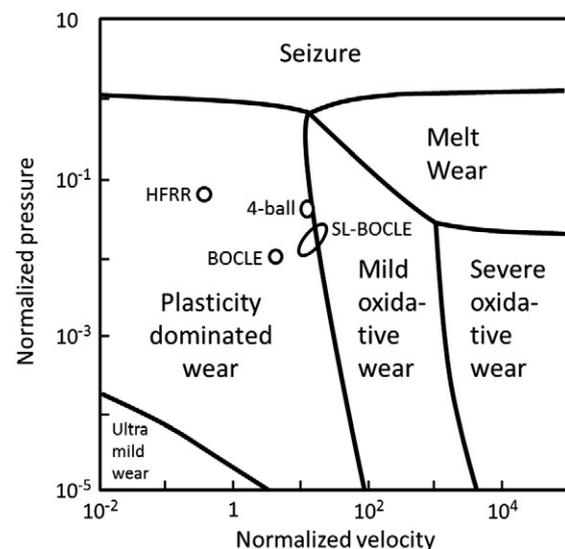
Fig. 4. Normalized pressures and velocities of common lubricity tests superimposed on an empirical wear-mechanism map for steel using a pin-on-disk configuration [54]. The pressure and velocity axes are dimensionless. See text for discussion of the nondimensionalization calculations.

[78]. Where hardness values of the ball and counterface surface differ, the lower value is used for the room temperature hardness of the wearing surface. A standard conversion table was used to estimate the Rockwell "C" hardness of the annealed steel flat disk used in the HFRR lubricity test [79]. The normalized velocity is calculated by dividing the product of the sliding velocity and asperity contact radius by the thermal diffusivity of steel. The differences in normalized pressures and velocities may lead to different conclusions on the lubricity of a fuel sample, depending on the test that is used to make the measurement.

While all mechanisms described previously may contribute to wear at a sliding contact, the wear map shows the dominant wear mechanism as a function of contact pressure and sliding velocity based on empirical data. Interestingly, the wear map supports the notion that the key mechanism underlying the HFRR test is plasticity dominated wear (i.e., adhesive and delamination wear). While the BOCLE test is also in the plasticity dominated wear region, differences in the test geometry and number of cycles lead to a more significant role for oxidative wear in the BOCLE test. More specifically, wear particles produced during the BOCLE test may be lost from the contact surface as the steel cylinder rotates through the fuel reservoir. This is not the case in the HFRR test; the wear particles produced during the linear reciprocating sliding motion may become embedded in the contact area and contribute to abrasive wear. The increase in wear rate due to abrasive wear and rapid removal of material may obscure the role played by adhesive and delamination wear in the HFRR test.

4. Discussion

4.1. Petroleum distillate cuts

Motor fuels distilled from crude petroleum are separated by their initial and final boiling temperatures, with gasoline having the lowest initial boiling temperature, followed by aviation turbine fuel with the next highest initial boiling temperature and diesel fuel with the highest boiling temperature. Fig. 5 shows representative distillation curves for motor gasoline [80], aviation turbine fuel [81], and diesel fuel [80]. Note that these curves have been measured by the advanced distillation curve metrology [82–84] rather than the conventional ASDM D-86

technique [85]. Dashed lines showing the maximum final boiling temperature specified by industry standards are also shown for reference. The literature suggests that the lubricity of distillate motor fuels may be positively correlated with their boiling range, with motor gasoline having the worst lubricity [30], diesel fuel having the best lubricity [39], and aviation turbine fuel falling between the other two distillate motor fuels in lubricity. While the difference in viscosity between the different distillate fuels accounts for some of the differences in lubricity, the presence of certain surface-active compounds such as PAHs and NPAHs has been shown to improve lubricity in petroleum distillate fuels [39,47]. Given the common origin of these distillate motor fuels, it is logical to surmise that the inherent lubricity of distillate fuels has its origin in naturally occurring compounds found in crude petroleum. If this is true, the relative abundance of high boiling point heavy polar aromatic compounds should also show a positive correlation with distillate fuel boiling range.

4.2. Vapor pressure of PAH and NPAH compounds

Fig. 6 illustrates the critically evaluated vapor pressure range of six representative NPAH compounds drawn from an on-line database maintained by the Thermodynamics Research Center (TRC) at NIST [86,87]. Based on the vapor pressure of the NPAH compounds, it is evident that in a distillation process, one finds a larger concentration of heavy aromatic compounds in diesel fuel, with somewhat smaller quantities present in aviation turbine fuel, and only trace amounts found in motor gasoline. This is consistent with the idea that heavy polar aromatic compounds provide inherent lubricity to petroleum distillate motor fuels.

Heavy aromatic compounds constitute a small fraction of the total aromatics content in distillate motor fuels. Bernabei et al. measured the total aromatics concentration and PAH content in aviation turbine fuels, and found that PAHs were between 0.5% and 6.5% of the total aromatics content [88]. Due to the difference in initial and final boiling temperatures between distillate cuts of aviation turbine fuels and diesel fuels, the PAH and NPAH fraction of total aromatics content in diesel fuel should be higher than the value observed for aviation turbine fuel.

Fig. 5. Representative distillation curves (measured by use of the advanced distillation curve method) of motor gasoline, aviation turbine fuel, and diesel fuel distilled from petroleum. Dashed lines indicate the maximum final boiling temperature for the three distillate motor fuels. The combined uncertainty in temperature and distillate volume fraction is smaller than the plotting symbols for single prototype diesel fuel and motor gasoline samples. The uncertainty is of the magnitude of the plotting symbols; the range bars for the aviation turbine fuel reflect the expanded uncertainty due to variation in distillation curves across 18 different samples.

Fig. 6. Vapor pressure of nitrogen heterocyclic polyaromatic hydrocarbon (NPAH) compounds (e.g., acridine, 1-azaanthracene, 2-azaanthracene, phenanthridine, benzo[f] isoquinoline, and benzo[h]isoquinoline) as a function of distillation temperature. Distillation temperature ranges for motor gasoline, aviation turbine fuel, and diesel fuel are shown for comparison.

4.3. Effect of heavy aromatic compounds on distillate fuel lubricity

Hydrotreatment of petroleum distillate fuels is known to reduce their aromatic content through hydrogenation [89]. The removal of sulfur compounds through hydrodesulfurization also hydrogenates heavy aromatic compounds, and the severity of hydrotreatment is proportional to the reduction in fuel lubricity, as evidenced by the progressive increase in HFRR wear scar diameter as a function of hydrotreatment cycles in diesel fuels [90]. Fig. 7 illustrates the increase in HFRR wear scar diameter (decrease in lubricity) as a function of decreasing total aromatics concentration of diesel fuels through hydrotreatment. An increase in the average wear scar diameter, indicative of poor lubricity, occurs after the first hydrotreatment step. The critical total aromatics concentration appears to be between 25% and 30% (volume/volume) for most of the diesel fuels, except for the sample from the UK with a critical concentration around 35% (volume/volume). Wei and Spikes reported a similar change in wear scar diameter between 25% and 30% relative aromatic content, with the fluid composition measured using infrared spectroscopy [39].

A survey of 112 low-sulfur diesel fuel and aviation turbine fuel samples from US military depots found that fuels containing more than 1.25% (mass/mass) heavy aromatic compounds, as measured through supercritical fluid chromatography, resulted in adequate lubricity under HFRR testing [91]. All fuels with poor lubricity (average HFRR wear scar diameters exceeding 520 μm) contained less than 1.25% (mass/mass) heavy aromatic compounds; however, the converse relationship is not true. Fuels containing less than the critical concentration of heavy aromatic compounds may have adequate lubricity due to the addition of boundary lubricant compounds other than PAHs and NPAHs.

4.4. Estimate of lubricity as a function of fuel composition

Friction and wear between two solid bodies in contact are affected by a multitude of factors, including the presence of boundary lubricants and the chemical and physical mechanisms active in material removal. Due to the complexity of the problem, fuel lubricity is assessed through mechanical testing that replicates one or more wear mechanisms likely to be encountered in actual fuel injectors and pumps. Current lubricity tests, based on wear scar measurement or surface scuffing loads, are
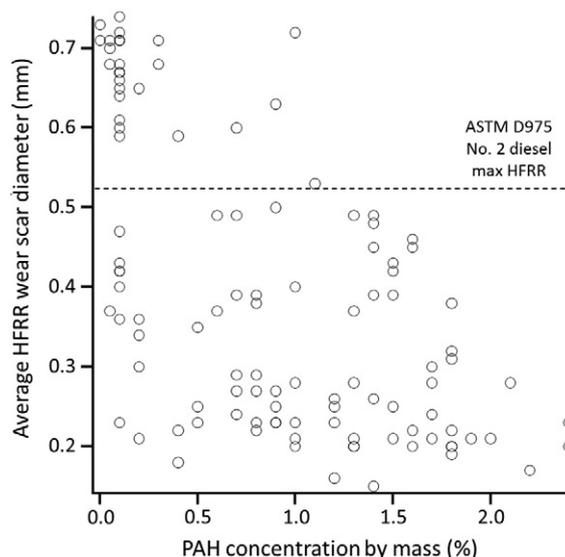
Fig. 8. Effect of tricyclic PAH concentration on aviation turbine fuel and diesel lubricity after Westbrook and LePera [91]. Average HFRR wear scar diameter is plotted as a function of heavy aromatics concentration by volume as measured through supercritical fluid chromatography. The dashed line shows the maximum average HFRR wear scar diameter allowed for No. 2 diesel fuel.

unable to provide data needed for a deeper understanding of boundary lubrication by PAH and NPAH compounds. Mechanical testing requires specialized machines and trained operators to measure the wear scar or determine the scuffing load. Moreover, they offer little guidance for additive treat rates or fuel blending ratios to ameliorate poor lubricity in distillate motor fuels (Fig. 8).

Wear scar data from the literature show that lubricity as measured through HFRR testing is not a linear function of the heavy aromatic compound concentration; instead, there is a critical concentration below which the wear rate rises significantly. Further study of the critical concentration of PAH and NPAH compounds needed to improve lubricity in motor distillate fuels would provide additional insight into the type of boundary lubricant film formed by these compounds. Significantly, the critical concentration of the heavy aromatic compounds needed to prevent wear may be affected by the fuel composition and operating temperature. The critical concentration of linear alkyl polar additive compounds needed to improve lubricity should also be measured independently of and in conjunction with PAH and NPAH compounds to determine if any synergistic or antagonistic effects are present. Control of humidity and oxygen content are likely to be important in such studies, as the oxidation of freshly exposed metal surfaces may play an important role in determining whether linear alkyl polar additive films or heavy aromatic films are formed at the sliding contact.

A recent patent on the prediction of HFRR wear scar diameter in distillate motor fuels on the basis of mid-infrared spectroscopy data suggests that lubricity may be measured directly from fluid composition [92]. The patent incorporates a multi-linear regression model based on the infrared absorbance due to functional groups present in the fuel, focusing on those found in aromatic compounds and specifically polynuclear aromatics. Similar analysis and modeling of distillate motor fuels using ^{1}H and ^{13}C nuclear magnetic resonance spectroscopy is presently underway at NIST.

5. Conclusions

The inherent lubricity of distillate motor fuels originates from heavy polar aromatic compounds found in petroleum. Polycyclic aromatic hydrocarbons and nitrogen heterocyclic polyaromatic hydrocarbons are capable of forming protective boundary lubricant films on freshly

Fig. 7. Effect of hydrotreatment on diesel fuel lubricity after Lacey and Erwin [81]. Average HFRR wear scar diameter is plotted as a function of total aromatics concentration by volume as measured through UV spectroscopy. The arrow shows the change in the wear scar value for the U.K. F-76 naval diesel fuel after initial hydrotreatment.

exposed metal surfaces through chemisorption, lowering the friction and wear at sliding contacts. The reduction in friction probably has a significant effect on plasticity dominated wear mechanisms (i.e., adhesive and delamination wear) by reducing the peak stress amplitude at the sliding contact, which has an exponential effect on the number of fatigue cycles to failure in steel.

The concentrations of PAH and NPAH compounds in distillate motor fuels are inversely proportional to final distillation temperatures: heavy polar aromatic compounds are least abundant in motor gasoline and most abundant in diesel fuel. Linear reciprocating wear experiments show that both motor gasoline and aviation turbine fuel have worse lubricity than diesel fuel. To prevent wear in sliding contacts lubricated with motor gasoline, addition of lubricity improving additives may be necessary.

Acknowledgments

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