THE INFLUENCE OF FUELS CHEMICAL COMPOSITION ON ITS LUBRICITY – NEW VIEWS ON THE MECHANISM OF PROTECTION LAYER CREATION DURING TRIBOLOGICAL PROCESS

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Abstract

The aim of this paper is to examine the current views on the mechanism of the formation of a protective film by mineral fuels and biocomponents (FAMEs and alcohols). As the experimental data show, the ability of fuels / biofuels to form a protective film under different conditions is very important to the efficient operation of fuel pumps. The mating parts of pumps are protected against wear and seizure because of the interactions between the metal surfaces and the lubricant (fuel / biofuel) at the molecular level. The tribochemical research focuses on the tribochemical reactions of lubricating additives because the base fuel is frequently treated as a solvent only. Today, most fuels for CI engines contain FAME, a biocomponent that may differ in the chemical structure depending on the type and properties of the vegetable oil used. The current trend is to produce fuels from biomass hydrocarbons, which are blended with mineral diesel fuel. It has been found that the chemical structure of biohydrocarbons is responsible for changes in the lubricity of the blends. Lubricity is determined using a standard high frequency reciprocating rig (HFRR) test because of one parameter, i.e. the wear of the ball.

The results of the authors' previous studies were used to create a new model of the protective film formation by fuels containing biocomponents (oxygenates) and biohydrocarbons. The model makes it possible to describe the tribochemical processes quantitatively. The quantitative analysis is based on the parameter α_i, which is the measure of reactivity of lubricating additives and/or biocomponents related to the properties of the mating parts and the operating conditions in a tribological system. The new approach to the mechanism of the protective film formation, based on the quantitative description of tribochemical reactions, enables us to begin research on new criteria for the lubricity of fuels containing lubricating additives and biocomponents.

Keywords: Mechanical Engineering, Fuel, Oils & Lubrication

1. Introduction

A fuel supplied to the combustion chamber of an engine is not only a source of energy but it also serves as a lubricant for the fuel pump and the injector. Now that the content of sulphur in fuels is substantially lower, lubricity has become a very important property of fuels, especially those for compression-ignition (CI) and jet engines. Sulphur-containing compounds from sulphur-rich crude oil once acted as natural lubricating additives; today, they are removed during the oil refining process.

Natural sulphur compounds are replaced with oxygen-containing organic compounds, such as lauryl acid or similar long-chain oxygenates. These additives are usually added to a fuel at a low concentration ranging from 10 to 100 ppm. The compounds are responsible for the formation of protective films at surfaces of mating elements in pumps and injectors.

The classic theories of the boundary layer formation assume that polar molecules of lubricating additives usually undergo adsorption at the surface of the lubricated elements and the thin film of the adsorbed molecules offers protection against friction. This durable film prevents the surfaces of the mating elements (metal – metal) from direct contact and their mechanical wear. [9] According to these theories, fuel components, other than lubricating additives, act as solvents and they do not participate in the formation of the protective film.

The above theory is not consistent with the numerous empirical data available on hydrocarbon-containing mineral fuels as well as fuels with oxygen-containing biofuels. Currently, the most common biofuels used for CI engines are Fatty Acids Methyl Esters (FAMEs) containing polar molecules introduced into mineral diesel fuels at a concentration of about 7% (V/V) – 70 000 ppm. The concentration is 1000-fold higher than the effective concentration of a lubricating additive. This is the reason why FAME is treated as a biocomponent of diesel fuel and not as an additive. However, the problem lies not only in the concentration. For example, in many cases, the amount of 100 ppm of lauryl acid offers better protection against wear for the mating parts in a fuel pump than 70 000 ppm of esters. This effect cannot be explained using the classic theory presented briefly above. The main problem with tribochemical research is that:

- macroscopic mechanical effects are interpreted directly at the molecular level,
- all the methods of metal surface analysis at the molecular and submolecular levels are applied after friction occurs; the effects detected are only the durable effects of friction, which cannot be responsible for the protective film formation.

In such a case, another theory, developed by Kajdas and Kulczycki [3, 4, 6, 7], can be useful to study the mechanism of the protective film formation by mineral fuels with biocomponents and by biofuels.

2. The determination of the coefficient of reactivity α_i for fuel components / additives

This new theory described in Refs. [3-7] assumes that molecules of fuel / biofuel contributing to the formation of a protective film undergo two processes:
- chemical reactions,
- interactions with a solid body, e.g. mating elements of the fuel pump.

This concept requires measuring the activity of components / additives responsible for the protective film formation. It is thus essential to determine the coefficient of reactivity α_i for the selected components / additives, which is assumed a function of the mechanical actions at the macroscopic level and the chemical and physical processes at the molecular level resulting in changes of internal energy in a tribological system.

$$\alpha_i = [(L - L_0) / (\Delta u - \Delta u_0)] \, d\Delta u/dL, \qquad (1)$$

where:

L – work done on the system,

Δu – change of internal energy; the index 0 marks the reference values for the work and the change of internal energy.

The mechanical work done on a tribological system can be described precisely using easily measured parameters such as the friction coefficient, sliding velocity, load and time. It is problematic, however, to determine the change of internal energy. It was found by Kulczycki [5] that the value of:

$$C = [1/(\Delta u - \Delta u_0)] \, d\Delta u/dL, \qquad (2)$$

is constant for a number of lubricants containing similar additives. Results from four-ball tests were used to formulate the following empirical relationships [5]:
- for anti-war processes (load increases continuously – 45 N/s): $\alpha_{AW} = (8.6 \times 10^{-5} v_{40} - 10^{-2}) P_{lat} + 0.2 - 7.3 \times 10^{-4} v_{40}$; where P_{lat} – work done on a system until seizure occurs, v_{40} – kinematic viscosity of the lubricant tested at 40 °C; $C = (8.6 \times 10^{-5} v_{40} - 10^{-2})$,

- for EP processes (standard test where load increases gradually): $\alpha_{EP}=0.48 – 1.3 \times 10^{-4}P_w$; where P_w – welding load; $C = 1.3 \times 10^{-4}/\mu v t$, where μ – friction coefficient, v – sliding velocity and t – test duration.

C is a function of a variable used to describe a tribological process. C is usually a function of the applied load P and, for different lubricating additives or reagents in general, its value is constant as a number of lubricants tested undergo the same mechanism of a tribochemical process. It can be concluded that C is a harmonic function of the applied load expressed by a wave function:

$$C = 1/A \exp[-E_a/(RT + \varepsilon)] \, [(e_0) \cos (k_2L + k_3)] \, s \, t, \qquad (3)$$

where:

L – mechanical work done on the tribological system, necessary to reach a critical stage, e.g. seizure,

T – temperature of the boundary layer, which can be constant during a tribological process or can increase with increasing load (T is the function of P),

ε – energy, other than heat (RT), introduced into the reaction space,

e_0 – density of energy flux emitted in the form of electrons by the surface of the solid body (perpendicular to the surface),

t – time,

s – the area of the surface of the solid body, which emits electrons,

RT – heat generated as a result of friction,

A, k_2, k_3 – constant values.

The exponential part of Eq. (3) is connected with the chemical kinetics of triboreactions while its trigonometric part is related to the emission of electrons / photons by a metal / solid body surface. The energy flux density is different at various angles and can be expressed as follows:

$$e_\gamma = e_0 \cos \gamma, \qquad (4)$$

where γ is the function of P and e_0 is the density of energy flux perpendicular to the surface of the solid body. The observations reveal anisotropic electron emission for the cathodes and, accordingly, a relationship between anisotropy and the temperatures of the cathodes. The influence of the load and, consequently, the generated temperature on anisotropy was partly confirmed by Hrach [1].

Thus, relationship (1) can be expressed as:

$$\alpha_i = [(L – L_0)/A \exp[-E_a/(RT + \varepsilon)] \, [(e_0) \cos (k_2L + k_3)] \, s \, t. \qquad (5)$$

From the analysis of function (5), it is evident that the coefficient of reactivity represents the response of the tribological system to the influence of the surroundings. The response is in the form of triboreactions of the fuel components and the energy transfer from the protective film to the solid body.
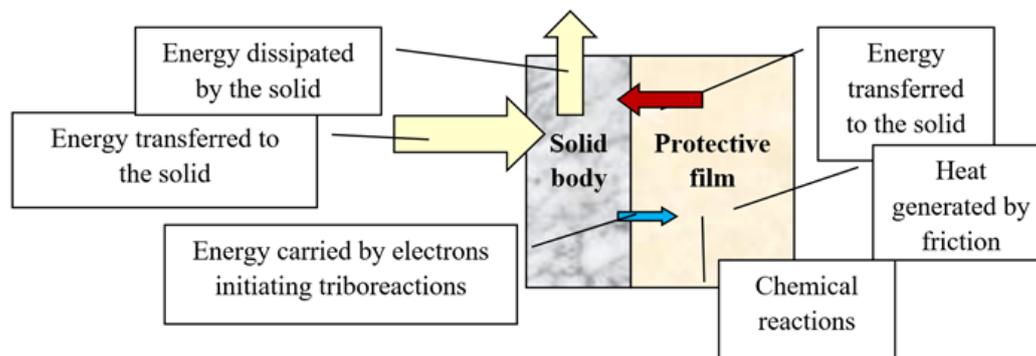
Fig. 1. The diagram of the processes expressed by the coefficient of reactivity α_i

The diagram in Fig. 1 shows that energy is transferred from the surface of the solid body into the protective film and that the distance of energy migration is much greater than the thickness of the monomolecular film on the solid surface. To be precise, this distance is greater than the distance of possible migration of low energy electrons emitted by the solid surface. It can be concluded that the emitted electrons should be absorbed by molecules that transfer this energy over relatively long distances and pass it to the molecules of the reagents. These special molecules can be clusters [2, 10]. Clusters are likely to transfer the energy drawn from the surroundings out of the friction zone so that the protective film is not damaged. The ability of clusters to transfer energy depends on their chemical structure or rather the chemical structure of the fuel components. As clusters have limited energy transfer ability, molecules of the additive can consume part of the energy carried by clusters, which will result in endothermic reactions. In Eq. (5), ε should be treated as mechanical energy transferred, like heat (RT), probably by means of clusters, from the metal surface to the inner part of the protective film. Although the mechanism described by Eq. (5) has been confirmed to a certain extent by numerous literature data, it still needs empirical verification. This model points out how important the thickness of the protective film is as a measure of the lubricating properties of fuels; it can be used to explain the influence of biocomponents on the lubricity of biofuels.

3. The methods for the determination of lubricity

The lubricity of diesel fuel is usually determined using an HFRR test. The standard test conditions are as follows:
– test duration – 75 min,
– frequency of the upper ball – 50 Hz,
– stroke length – 1000 μm,
– bulk temperature of the fuel – 60 °C,
– load – 200 g.
  Basic terms:
– lubricity of a diesel fuel – property of a fuel related to the wear of the upper ball,
– mean wear scar diameter (MWSD),
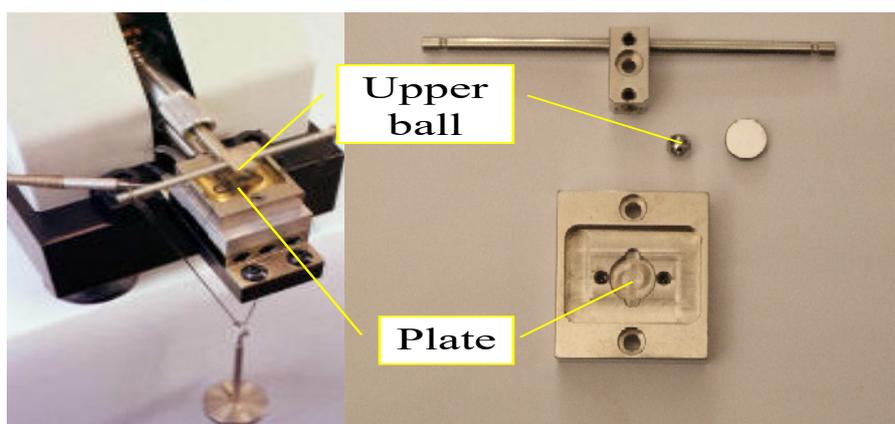– wear scar diameter calculated for a pressure of 1.4 kPa (WS 1.4).

Fig. 2. The elements of the HFRR system

The only parameter used to determine the lubricity of diesel fuels is the wear of the upper ball, which, according to the standards, should be less than 460 μm.

During standard tests, the coefficient of friction and the thickness of the protective film are measured and recorded; these parameters, however, are not taken into account when determining the lubricating properties of fuels.
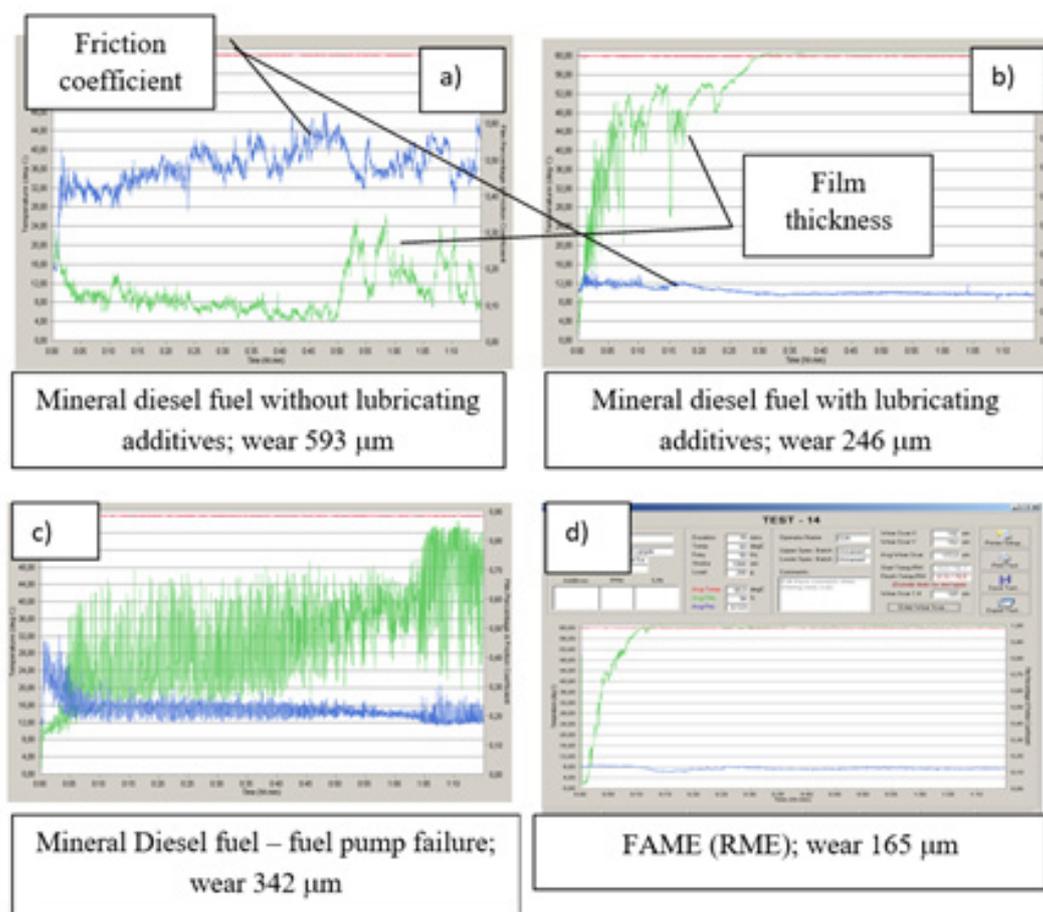
Fig. 3. Results of the HFRR tests for selected fuels

From the above figures, it is clear that the thickness of the protective film provides very important information about the film formation. This parameter is more significant than wear when, for example, the lubrication of fuel pumps is described. From the comparative analysis of Fig. 3a) and 3b), it is clear that the addition of about 100 ppm of a lubricating additive causes a change in the thickness of the protective film. This seems to be a good illustration of the above concept that clusters participate in the formation of the protective film.
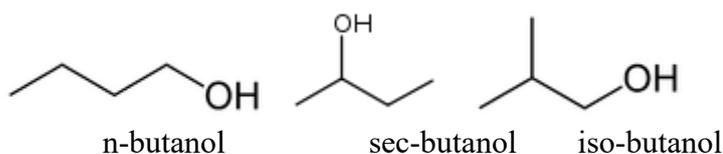
4. The influence of biocomponents on the lubricity of biofuels

Two types of biocomponents were used to assess the influence of their chemical structure on the formation of the protective film and the protection of the mating elements against wear:

- Fatty Acid Methyl Esters (FAMEs) obtained from different vegetable oils and isomers of butanol (MB) differing in the composition. FAMEs prepared from vegetable oils differed in the chemical structure.

$$R – C(O) – O – CH_3 \quad \text{Fatty Acid Methyl Ester.}$$

FAMEswere test as biofuels and were added to mineral diesel fuel containing lubricating additive.

n-butanol   sec-butanol   iso-butanol

- The blends of butanol isomers (MB) and mineral diesel fuel contained a lubricating additive at various concentrations. The results obtained for the two types of biocomponents are presented in Tab. 1 and 2.

Tab. 1. The influence of the chemical structure of FAMEs on the lubricating properties of fuels determined using HFRR tests [11]

Fuel	FAME content in the diesel fuel [% (V/V)]	Friction coefficient	Wear WS 1.4 [μm]	Thickness of the protective film [%]
Diesel fuel	0	0.20 ± 0.01	310 ± 15	86 ± 10
Rapeseed Methyl Ester	5	0.16 ± 0.01	194 ± 10	93 ± 10
	10	0.16 ± 0.01	169 ± 15	89 ± 10
	15	0.16 ± 0.01	156 ± 17	92 ± 9
	20	0.15 ± 0.01	192 ± 13	85 ± 9
	25	0.15 ± 0.01	200 ± 15	86 ± 9
	30	0.14 ± 0.01	242 ± 22	82 ± 8
	100	0.14 ± 0.01	217 ± 19	94 ± 9
Soybean Methyl Ester	10	0.16 ± 0.01	197 ± 14	94 ± 10
	100	0.12 ± 0.01	102 ± 13	94 ± 10
Sunflower Methyl Ester	10	0.14 ± 0.01	192 ± 14	94 ± 10
	100	0.12 ± 0.01	159 ± 16	96 ± 11
Castor Methyl Ester	10	0.15 ± 0.01	163 ± 15	89 ± 10
	100	0.09 ± 0.01	125 ± 16	93 ± 10
Linseed Methyl Ester	10	0.15 ± 0.01	163 ± 17	96 ± 11
	100	0.09 ± 0.01	132 ± 19	94 ± 10

Tab. 2. The influence of the chemical structure of the blends of butanol and a mineral diesel fuel on the lubricating properties of fuels determined using HFRR tests [8]

Fuel	Protective layer thickness [%]	Friction coefficient	Wear WS 1.4 [μm]
Diesel fuel ON	84.6	0.172	363
ON + 5% MB1	65.7	0.239	409
ON + 10% MB1	71.6	0.183	423
ON + 15% MB1	71.8	0.208	357
ON + 20% MB1	63.7	0.212	442
ON + 5% MB2	57.6	0.188	431
ON + 10% MB2	71.1	0.187	359
ON + 20% MB2	69.4	0.184	391
ON + 5% MB3	69.4	0.184	387
ON + 10% MB3	86.1	0.210	318
ON + 15% MB3	73.7	0.177	382
ON + 20% MB3	57.7	0.177	417
ON + 5% MB4	76.5	0.176	373
ON + 10% MB4	73.6	0.176	395
ON + 15% MB4	70.5	0.177	400
ON + 20% MB4	76.4	0.175	374

The blends of butanol isomers (MB) are as follows:

MB1: 50% (V/V) butan-1ol [n-butanol] + 50% (V/V) 2-metylobutan-1-ol [isobutanol],

MB2: 100% (V/V) 2-metylopropan-1-ol [isobutanol],

MB3: 40% (V/V) butan-1ol [n-butanol] + 20% (V/V) butane-2-ol [sec butanol] + 40% (V/V) 2-metylopropan-1-ol [isobutanol],

MB4: 60% (V/V) butan-1ol [n-butanol] + 20% (V/V) butane-2-ol [sec butanol] + 20% (V/V) 2-metylopropan-1-ol [isobutanol].

The analysis of obtained results leads to conclusion, that FAME effectively increases thickness of protective layer and this effect does not depend significantly on FAME chemical structure and

on decreasing of lubricating additive concentration proportionally to FAME concentration in blends Additive is diluted by FAME).

Butanol generally decreasing thickness of protective layer and the level of decreasing depends significantly on concentration of various isomers in blends MB; moreover decreasing of film thickness is not proportional to MB concentration – it is not the result of additive dilution.

All these conclusions lead to hypothesis that biocomponents: FAME and alcohols take a part in protective layer formation, but the mechanism is not as former classic assumed – adsorption of polar molecules on metal surfaces. The obtained data rather confirm the new idea of the mechanism of protective layer formation by fuels and biofuels; it means the molecules of biocomponents take a part in energy transfer inside the protective layer, including transfer to the molecules of lubricating additives.

FAME and alcohols are compounds of quite different chemical structure than hydrocarbons of mineral fuels. Developed currently synthetic hydrocarbons containing biofuels blend with mineral diesel fuel give similar results as observed in case FAME ad alcohols. Synthetic hydrocarbons addition change significantly blends lubricity determined by HFRR test – not only by WS1.4 wear, but by film thickness as well. This effect depends on hydrocarbon chemical structure. All these data confirm described above hypothesis.

5. Conclusions

The mechanism of protective layer formation by fuels and biofuels is still under discussion. Former ideas of protective layer formation, based on lubricating additives adsorption and reaction with metal surface do not agree with many experimental data. One of important problem discussed currently is the role of components/biocomponents (other than additives) of fuels in protective layer formation. The new idea of the mechanism of these components/biocomponents participation in protective layer formation – presented in this paper, better explains the experimental data.

This new idea of the mechanism of protective layer formation is quantitatively described by proposed new measure of fuels lubrication properties. The coefficient of reactivity α_i may play the role of such measure. Concluding it was found that this new quantitative description of tribochemical reactions enable to begin the work on the new criteria of fuels containing lubricating additives and biocomponents lubricity.

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