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The Stribeck curve as a suitable characterization method of the lubricity of biodiesel and diesel blends

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ABSTRACT

The adequacy of Stribeck curves for the characterization of the lubricity of biodiesels, B20 blends and diesel fuel is demonstrated. Ball-on-disk tests in the speed range 2–1570 mm/s were performed to obtain the Stribeck plots and the results are compared to those from the conventional HFRR (high frequency reciprocating rig) ball-on-disk method (ASTM (American Society for Testing and Materials) D6079). Contrarily to the HFRR method, in the Stribeck tests very clear ball wear marks are seen without significant wear of the flat counterbody. These characteristics provide more confidence in the lubricity assessment of fuels. Moreover, in the Stribeck method higher lubricity at 60 °C is revealed for all biodiesels and the respective blends, related to the formation of protective oxide tribolayers. When evaluated by the HFRR test method, such temperature effect on the lubricity performance is not identified. From the point of view of the energy loss of the system, or friction response, lubricity is also better depicted by the Stribeck test method. The friction coefficient plots reveal that the major difference among the fuels occurs in the low velocity range, or in the start–stop stage of moving components, where the poorest lubricity is attained with the neat diesel fuel and the best lubricity with the animal fat biodiesel.

1. Introduction

It is well known that a third to a half of the total energy produced in the world is consumed by friction [1]. Studies on friction are thus of great importance in a plethora of systems, including friction in pumping and injection systems of direct injection internal combustion engines, where fuel plays the lubricant role. Given the current environmental requirements, substitutes to fossil fuels in diesel engines are becoming increasingly explored, the most popular being biodiesels whose advantages are broadly described in recent reviews [2–5]. The most common route for biodiesel production starts from plant and animal oils undergoing a transesterification reaction with an alcohol in the presence of a catalyst, resulting in mixtures of long-chain fatty acid esters, and glycerol as main byproduct [4–6]. As biodiesel is diesel miscible, blends are often used, providing an increase in the diesel lubricity, increasing their energy efficiency [3,4,6,7]. Biodiesel fuels demonstrated improved lubricity in about 30% comparing to low sulphur diesel, even with low amounts (1%) of addition to diesel [6]. With respect to friction behaviour, 5% of added biodiesel decreases the friction coefficient by about 20% [8]. The lubricity behaviour of biodiesels is attributed to the characteristics of the fatty acid ester molecules (carbon chain length, degree of unsaturation and branching of the chains) [9], and to the presence of free fatty acids, glycerides [10,11] and glycerol [11,12]. Monoglycerides are the most effective components, followed by the free fatty acids and diglycerides, whereas triglycerides almost have no effect [10]. The individual fatty acid ester molecules are less lubricious than free fatty acids due to the absence of free OH groups [11].

The assessment of the biodiesel lubricity is usually performed in tribological tests by measuring the size of the wear mark in an HFRR (high frequency reciprocating rig) test [4,5,7–14]. In this method, wear is the parameter that defines lubricity and friction is less taken into account, despite their equivalent importance in any dynamic system undergoing contact and motion. There are also alternative methods of lubricity assessment, namely the SLBOCLE

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(scuffing load ball on cylinder lubricity evaluator) test, which measures the load to achieve a given value of the coefficient of friction [15]. The four-ball test was also applied to relate the lubricity of biodiesels with their tribological performance [16,17]. All these tests are somewhat limited in evaluating the friction behaviour in conditions of lubrication that mechanical systems may undergo, namely BL (boundary lubrication) at stop–start stage, through mixed BL-EHL (boundary-elastohydrodynamic lubrication), up to hydrodynamic regime in steady state operation.

Actually, the above tests mainly measure the lubricant performance of the fuel in BL condition. In a broader range of lubrication regimes, the Stribeck curve is a classical method to characterize the frictional behaviour in oil lubricated systems [18–21]. Recently, ball-on-disk tests were performed to obtain Stribeck curves of biodiesels that allow discriminating the contributions of boundary and elastohydrodynamic lubrication phenomena to friction [22]. Friction data of boundary lubrication regime were compared to nanoscale measurements using atomic force microscopy, disclosing that the friction phenomena is mostly related to cohesive forces arising from complex molecular phenomena, other than to viscosity [23]. In an investigation on the influence of oscillation frequency in the lubrication regime with soybean-based biodiesel, a so-called modified Stribeck curve was used to demonstrate that the friction behaviour is associated to the transition from boundary to hydrodynamic lubrication within the biodiesel film [24].

The present work intends to stress the advantage of the Stribeck curve method in characterizing the lubricity of fuels, comparing to the conventional HFRR test. Vegetable and animal derived biofuels, worldwide commercialized as standard reference materials, "high-lubricity" and "low-lubricity" diesels, and B20 blends are studied. The influence of temperature on lubricity is investigated by carrying out tests at 20 °C and 60 °C. Results attest that the wider range of information taken from the Stribeck curve provides a great reliability level in the lubricity data.

2. Materials and methods

The biodiesel materials used in the tests are those developed by NIST (National Institute of Standards and Technology – USA) in partnership with INMETRO (Instituto Nacional de Metrologia, Qualidade e Tecnologia), worldwide commercialized as standard reference materials under the name SRM (Standard Reference Materials) 2772 (soybean biodiesel [25]) and SRM 2773 (animal fat biodiesel [26]). According to the certificates [25,26], the biodiesels are a mixture of FAMEs (fatty acid methyl esters). Table 1 presents the FAME's content, the mass fraction of sulphur, mono, di and triglycerides, free glycerine and total glycerine, and the physicochemical characteristics. From this table, the main differences among the biofuels are: (1) soybean biodiesel presents a higher content of unsaturated, long chain carbon FAMEs (C18:2 and C18:3), compared to the animal fat; (2) no sulphur is mentioned in the soybean biodiesel; (3) there is a slight high amount of total and free glycerine, also mono, di and triglycerides, in the animal fat biodiesel.

Besides the pure biodiesels, pure diesel fuel and blends of 20% in volume of biodiesel in diesel (B20) were also tested. The diesel (SRF Cetane CK Fuel-low, Chevron Philips) is a standard fuel for cetane number calibration of diesel engine fuels, composed of saturated (63%), aromatics (35%) and olefins, with low sulphur content (0.03% wt). The kinematic and dynamic viscosities and the density at 20 °C and 60 °C, of the pure fuels and of the B20 blends, these estimated according to Ramírez-Verduzco et al. [27], are presented in Table 2. Two additional fuels (fluid "A" and fluid "B", PCS Instruments) were also used as references of high lubricity ("A", a diesel fuel with 0.4 wt % sulphur) and low lubricity ("B", an isoparaffinic hydrocarbon) according to ASTM D6079 standard. The respective viscosities and the densities measured at 20 °C are also shown in Table 2.

Table 1
Characteristics of the biodiesel fuels.

	SRM 2772 (vegetable)	SRM 2773 (animal)
Mass fraction of the FAME's [g/kg]		
Capric acid C10:0	NM	0.2
Myristic acid C14:0	0.76	9.2
Lauric acid C12:0	NM	0.47
Pentadecanoic acid C15:0	0.104	0.305
Palmitic acid C16:0	107	184
Palmitoleic acid C16:1	1.32	23.3
Heptadecanoic acid C17:0	1.03	NM
Stearic acid C18:0	43	87.8
Oleic acid C18:1	233	343
Trans-vaccenic acid C18:1	NM	0.78
Vaccenic acid C18:1	14.3	19.4
Linoleic acid C18:2	523	226
Linolenic acid C18:3	78.2	25
Nonadecanoic acid C19:0	NM	0.42
Arachidic acid C20:0	3.7	2.28
Arachidonic acid C20:4	NM	2.53
Heneicosanoic acid C21:0	NM	0.077
Behenic acid C22:0	3.7	1.66
Tricosanoic acid C23:0	NM	0.13
Mass fraction of other components		
Sulphur [mg/kg]	NM	7.4
Free glycerin [mg/kg]	164	12
Monoglycerides [mg/kg]	3620	4110
Diglycerides [mg/kg]	1960	2970
Triglycerides [mg/kg]	1230	1350
Total glycerin [mg/kg]	1520	1660
Physicochemical properties		
Acid number [mg/g]	0.17	0.2
Oxidation stability of FAME's at 110 °C [h]	4.41	4.46

NM: not mentioned; uncertainty values less than 6%.

The wear materials were balls and disks made of SAE (Society of Automotive Engineers) 52100 steel appropriate for bearing applications. All samples were cleaned before the tests following the sequence: immersion in toluene for 8 h, 30 min in ultrasonic cleaner, rinsing in acetone and isopropyl alcohol, drying in dry air flux, storing in desiccator under vacuum until the start of the test. Table 3 presents the test parameters of the Stribeck curve and the HFRR methods [28].

The wear scars in the balls were examined by optical microscope (Olympus BX51M) and measured by Image Pro software, and the tri-dimensional images were obtained by means of a PGI 830 Taylor Hobson profilometer coupled to the TalyMap Gold software that also allows analyses of bi-dimensional profiles, these used to calculate the Ra roughness with a cut-off length of 25 μm. The semi-quantitative compositional analyses in the wear scars were performed by EDS (energy dispersive X-ray spectroscopy) coupled to a scanning electron microscope (Fei, Quanta 600).

Table 2
Kinematic and dynamic viscosities and density of the biodiesels, the diesel, the B20 fuels and the lubricity reference fluids used in the tests.

Fuel	Kinematic viscosity [mm^2/s]		Dynamic viscosity [10^{-3} Pa s]		Density [g/m^3]	
	20 °C	60 °C	20 °C	60 °C	20 °C	60 °C
Diesel	3.93	1.79	3.33	1.47	0.85	0.82
Soybean FAME	6.43	2.85	5.67	2.43	0.88	0.85
Animal fat FAME	7.15	3.04	6.26	2.57	0.88	0.85
B20 soybean FAME	4.31	1.95	3.73	1.64	0.87	0.84
B20 animal fat FAME	4.39	1.98	3.79	1.65	0.86	0.83
"A" fluid	5.16	NM	4.37	NM	0.85	–
"B" fluid	3.60	NM	2.83	NM	0.79	–

NM: not measured.

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