

Lubricity of Components of Biodiesel and Petrodiesel. The Origin of Biodiesel Lubricity[†]

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An alternative diesel fuel that is steadily gaining attention and significance is biodiesel, which is defined as the monoalkyl esters of vegetable oils and animal fats. Previous literature states that low blend levels of biodiesel can restore lubricity to (ultra-)low-sulfur petroleum-derived diesel (petrodiesel) fuels, which have poor lubricity. This feature has been discussed as a major technical advantage of biodiesel. In this work, the lubricity of numerous fatty compounds was studied and compared to that of hydrocarbon compounds found in petrodiesel. The effects of blending compounds found in biodiesel on petrodiesel lubricity were also studied. Lubricity was determined using the high-frequency reciprocating rig (HFRR) test. Dibenzothiophene, which is contained in nondesulfurized petrodiesel, does not enhance petrodiesel lubricity. Fatty compounds possess better lubricity than hydrocarbons, because of their polarity-imparting O atoms. Neat free fatty acids, monoacylglycerols, and glycerol possess better lubricity than neat esters, because of their free OH groups. Lubricity improves somewhat with the chain length and the presence of double bonds. An order of oxygenated moieties enhancing lubricity ($\text{COOH} > \text{CHO} > \text{OH} > \text{COOCH}_3 > \text{C=O} > \text{C-O-C}$) was obtained from studying various oxygenated C_{10} compounds. Results on neat C_3 compounds with OH, NH_2 , and SH groups show that oxygen enhances lubricity more than nitrogen and sulfur. Adding commercial biodiesel improves lubricity of low-sulfur petrodiesel more than neat fatty esters, indicating that other biodiesel components cause lubricity enhancement at low biodiesel blend levels. Adding glycerol to a neat ester and then adding this mixture at low blend levels to low-lubricity petrodiesel did not improve petrodiesel lubricity. However, adding polar compounds such as free fatty acids or monoacylglycerols improves the lubricity of low-level blends of esters in low-lubricity petrodiesel. Thus, some species (free fatty acids, monoacylglycerols) considered contaminants resulting from biodiesel production are responsible for the lubricity of low-level blends of biodiesel in (ultra-)low-sulfur petrodiesel. Commercial biodiesel is required at a level of 1%–2% in low-lubricity petrodiesel, which exceeds the typical additive level, to attain the lubricity-imparting additive level of biodiesel contaminants in petrodiesel.

Introduction

Biodiesel is an alternative diesel fuel obtained through the transesterification of vegetable oils or other materials largely comprised of triacylglycerols (also known as triglycerides), such as animal fats or used frying oils, with monohydric alcohols to give the corresponding monoalkyl esters.^{1,2} As a result of the transesterification reaction, biodiesel contains small amounts of glycerol, free fatty acids, partially reacted acylglycerols (monoacylglycerols and diacylglycerols), as well as residual starting material (triacylglycerols). These contaminating

trace materials are limited in biodiesel standards such as the American Society for Testing and Materials (ASTM) standard D-6751 and the European standard EN 14214, as well as other standards under development around the world. Table 1 lists these specifications in ASTM D-6751 and EN 14214.

The production and use of biodiesel have increased significantly in many countries around the world and it is in nascent status in numerous others. Biodiesel is technically competitive with conventional, petroleum-derived diesel fuel (petrodiesel) and requires virtually no changes in the fuel distribution infrastructure. Although biodiesel faces some technical challenges, such as reducing NO_x exhaust emissions, improving cold flow properties, and enhancing oxidative stability, the advantages of biodiesel, compared to petrodiesel, include the reduction of most exhaust emissions, biodegradability, a higher flash point, and domestic origin.^{1,2} It was also reported that neat biodiesel possesses inherently greater lubricity than petrodiesel, especially low-sulfur petrodiesel, and that adding biodiesel at low blend levels (1%–2%) to low-sulfur petrodiesel restores

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[†] Disclaimer: Product names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

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Table 1. Specifications Limiting Fatty Contaminants in Biodiesel Standards

specification	ASTM ^a Standard D-6751 (United States)			EN Standard 14214 (Europe)		
	test method	unit	limit	test method	unit	limit
acid number	D664	mg KOH/g	0.80 max	EN14104	mg KOH/g	0.50
free glycerol	D6584	% mass	0.02	EN 14105/EN 14106	% (m/m)	0.02
total glycerol	D6584	% mass	0.24	EN 14105	% (m/m)	0.25
monoglyceride content				EN 14105	% (m/m)	0.80
diglyceride content				EN 14105	% (m/m)	0.20
triglyceride content				EN 14105	% (m/m)	0.20

^a ASTM = American Society for Testing and Materials.

lubricity to the latter^{3–13} or aviation fuel.¹⁴ Such effectiveness was reported for even lower (<1%) blend levels^{15–17} or higher (10%–20%) levels.^{18,19} These results seem to imply that the alkyl esters that largely comprise biodiesel are responsible for this lubricity enhancement. On the other hand, individual fatty acid methyl esters were reported to have little effect.²⁰ However, adding free fatty acids or other selected oxygenated compounds to low-lubricity petrodiesel at additive levels enhances lubricity.^{21–26} Free fatty acids enhanced the boundary

lubrication behavior of sunflower oil formulations.^{27,28} Esters of vegetable oils with hydroxylated fatty acids such as castor and lesquerella oils improved lubricity at lower levels than the esters of nonhydroxylated vegetable oils.^{9,13} Oxidized biodiesel showed improved lubricity, compared to its non-oxidized counterpart.²⁹

The lubricity issue is significant, because the advent of low-sulfur petrodiesel fuels and, more recently, ultra-low-sulfur diesel (ULSD) fuels, as required by regulations in the United States, Europe, and elsewhere, has led to the failure of engine parts such as fuel injectors and pumps, because they are lubricated by the fuel itself. The poor lubricity of low-sulfur petrodiesel^{4,30–37} requires additives or blending with another fuel of sufficient lubricity to regain lubricity. The reason for the poor lubricity of low-sulfur petrodiesel is not the removal of the sulfur-containing compounds but rather that polar compounds with other heteroatoms such as oxygen and nitrogen are also reduced in low-sulfur petrodiesel.^{30,37,38}

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Methods that have been approved as standards for testing diesel fuel lubricity include the scuffing load ball-on-cylinder lubricity evaluator (SL-BOCLE) (ASTM D-6078) and the high-frequency reciprocating rig (HFRR) (ASTM D-6079, ISO 12156) lubricity tester. The HFRR method was selected in a round-robin evaluation of several lubricity-testing methods for an ISO standard.³⁹ It has been included in the European petrodiesel standard EN 590,⁴⁰ which utilizes the ISO 12156 method and, effective in 2005, the American petrodiesel standard ASTM D-975.⁴¹ The prescribed maximum wear scars are 460 μm in the EN 590 standard and 520 μm in the ASTM D-975 standard. Biodiesel standards currently do not contain lubricity specifications.

There has been further comparative discussion in the literature on the HFRR and SL-BOCLE methods,^{42–45} with some reports favoring SL-BOCLE, whereas tests using BOCLE indicated problems with additive evaluations.⁴⁶ On the other hand, the majority of data in the previously cited literature was acquired with the HFRR method and the HFRR data seem to discriminate between types of fuels and additives, although deviating reports exist.^{47,48} The HFRR method is more user-friendly and is also suitable for pressurization to study the lubricity of volatiles or fuels that are gases under ambient conditions.⁴⁹ The HFRR method has also been stated to be more severe than pump tests.⁵⁰ Wear scars of 460 μm (at 60 °C) were reported to indicate fuels with sufficient lubricity for practical use in a diesel engine, whereas fuels generating wear scars above this limit may or may not be acceptable.¹¹ Other fuel lubricity testing methods such as the ball-on-three-disks (BOTD) method were also discussed.^{48,51}

In this work, lubricity data for neat individual compounds that comprise biodiesel and some hydrocarbons that comprise petrodiesel, as well as blending and additive effects of fatty compounds in petrodiesel, were assembled using the HFRR lubricity test. The present work discusses and correlates structural features of

biodiesel and petrodiesel components influencing lubricity with the objective of defining the components and structural features that impart the best lubricity properties to a diesel fuel. Such data seem to be essential, because it can eventually aid in formulating “designer” fuels in which the fatty acid profile of biodiesel fuel is tailored toward optimizing various essential fuel properties. Such properties include not only the lubricity but also the cetane number as an indicator of ignition (and combustion) quality, cold flow, viscosity, and oxidative stability.

Also, for purposes of this work, the term “blend” will be used for concentrations of $\geq 1\%$ of a material in the main fuel and the term “additive” will be used for concentrations of $< 1\%$.

Experimental Section

All of the straight-chain esters (methyl, ethyl, *n*-propyl, *n*-butyl) were purchased from NuChek-Prep, Inc. (Elysian, MN) and had a purity of $> 99\%$, as confirmed by random checks (using nuclear magnetic resonance (NMR) spectroscopy and/or gas chromatography–mass spectrometry (GC–MS)) of some materials. Straight-chain and branched alkanes, as well as aromatic (including dibenzothiophene and dibenzofuran) and alkylated aromatic compounds, all of which had purities of $\geq 98\%$ (in most cases, $\geq 99\%$; verified by GC–MS analyses) were purchased from Aldrich Chemical Co. (Milwaukee, WI) and used as received. Petrodiesel fuels were obtained from Midwest Oil Co. (Peoria, IL) (No. 1 diesel fuel) and Chevron Phillips (ultralow-sulfur diesel (ULSD) fuels, with and without lubricity additive).

Lubricity determinations were performed at 25 and 60 °C (controlled to less than ± 1 °C), according to the standard method ASTM D-6079,⁵² with an HFRR lubricity tester obtained from PCS Instruments (London, England) via Lazar Scientific (Granger, IN). Controlling the humidity to 30%–50% is necessary for the HFRR test to give reproducible results,⁴⁶ which was accomplished here, according to the standard⁵² with a potassium carbonate bath (50% humidity). Other standards, such as ISO 12156, use the same experimental parameters as ASTM D-6079; however, they only allow for a test temperature of 60 °C. The principle and function of the HFRR apparatus, which is designed to evaluate boundary lubrication properties and, therefore, show only little impact of sample viscosity on the results,³⁸ have been described in the literature^{11,26,29,53} and therefore will not be discussed here. In addition to the usual wear scar data of the HFRR ball, we report the friction data (which involves the coefficient of friction⁵⁰) and film data (which involves the electrical resistance⁵⁰) recorded by the software during the experiments. Although most literature reports contain only the average wear scar value of the HFRR ball (in micrometers) calculated from the maximum values of the *x*- and *y*-axis of the wear scar and as is prescribed in standards, we report all *x*- and *y*-values, which reflect the approximate shape of the wear scar, as well as the averages. The average wear scar data at 60 °C are italicized in all tables, for ease of recognition.

With a few exceptions, lubricity tests were usually conducted only in duplicate, because of the large number of samples investigated and the cost and time associated with testing such a large number of samples. In addition to the high- and low-lubricity standards provided by the vendor for calibration,

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Table 2. High-Frequency Reciprocating Rig (HFRR) Data of Biodiesel and Petrodiesel Reference Materials

material	Wear Scar (μm)						Film (%)		Friction	
	25 °C			60 °C						
	X	Y	average	X	Y	average	25 °C	60 °C	25 °C	60 °C
low lube standard	661, 689	647, 655	654, 672	645, 659	625, 626	635, 643	16, 11	18, 22	0.528, 0.489	0.631, 0.754
high lube standard	335, 323	305, 300	320, 312	396, 428	397, 421	397, 425	57, 60	46, 36	0.209, 0.210	0.201, 0.220
DF1	436, 456	389, 390	413, 423	587, 635	527, 558	557, 597	30, 25	24, 15	0.260, 0.262	0.250, 0.262
ULSD	634, 629	592, 604	613, 617	666, 649	635, 623	651, 636	17, 21	12, 11	0.371, 0.360	0.383, 0.413
ULSD with additive	353, 365	253, 297	303, 331	352, 334	285, 265	319, 300	57, 53	72, 77	0.232, 0.244	0.216, 0.204
biodiesel	194, 208	111, 115	153, 162	158, 147	99, 120	129, 134	85, 92	95, 96	0.112, 0.115	0.123, 0.111

Table 3. HFRR Data of Components of Conventional Petroleum-Derived Diesel Fuel and Related Hydrocarbons

material	Wear Scar (μm)						Film (%)		Friction	
	25 °C			60 °C						
	X	Y	average	X	Y	average	25 °C	60 °C	25 °C	60 °C
hexadecane	459, 403	365, 365	412, 384	597, 589	546, 552	572, 571	37, 47	15, 15	0.255, 0.234	0.301, 0.309
1-dodecene	757, 733	735, 720	746, 727	669, 666	662, 644	666, 655	23, 25	48, 53	0.477, 0.430	0.466, 0.472
1-tetradecene	402, 408	345, 316	374, 362	524, 476	422, 421	473, 449	62, 66	56, 56	0.154, 0.148	0.150, 0.147
1-hexadecene	424, 339	309, 265	367, 302	513, 512	436, 441	475, 477	72, 81	41, 45	0.186, 0.166	0.187, 0.190
1-octadecene	539, 555	472, 493	506, 524	586, 576	560, 547	573, 562	24, 23	22, 22	0.293, 0.289	0.310, 0.305
HMN ^a	608, 615	611, 620	610, 618	671, 634	665, 649	668, 642	26, 27	10, 24	0.361, 0.377	0.539, 0.415
<i>trans</i> -Decalin	666, 650	647, 626	657, 638	652, 646	646, 625	649, 636	31, 23	21, 19	0.445, 0.423	0.502, 0.502
butylcyclohexane	678, 660	664, 667	671, 664	732, 693	685, 696	709, 695	27, 24	31, 31	0.443, 0.426	0.810, 0.508

^a HMN = 2,2,4,4,6,8,8-heptamethylnonane.

methyl oleate was also used, for calibration purposes. The wear scar (WS1.4) values for the high- and low-lubricity standards accompanying the HFRR apparatus were within the ranges of $403 \pm 34 \mu\text{m}$ and $633 \pm 55 \mu\text{m}$, as specified by the producer of these standards (Haltermann, Hamburg, Germany; see Table 2).

Results and Discussion

Lubricity was assessed using the ASTM D-6079 method at 25 and 60 °C. A variety of compounds were studied neat (including fatty esters, fatty alcohols, fatty acids, and hydrocarbons), as well as in blends or as additives with petrodiesel fuels. Table 2 gives the wear scar values of the reference fuels (ULSD, DF1, biodiesel). The effect of the lubricity additive in ULSD is clearly visible. Commercial biodiesel possessed, by far, the best lubricity of the reference fuels. The reasons for this behavior of biodiesel are discussed below. Table 3 lists the results for some neat hydrocarbons that partially comprise petrodiesel fuels. Table 4 presents such values for neat fatty compounds that can be found in biodiesel fuels. Table 5 reports the HFRR data of compounds with 10 C atoms (C_{10}). Table 6 contains the HFRR data of compounds with 3 C atoms (C_3) and varying OH, NH_2 , and SH groups. The HFRR data for additized petrodiesel fuels are presented in Table 7 (ULSD fuel without lubricity additive) and Table 8 (low-lubricity No. 1 diesel fuel).

As the data in Tables 2–8 show, there is some temperature dependence of the results, with wear scars, in most cases, being larger at 60 °C than at 25 °C. Maximum acceptable results for HFRR given in the literature are $380 \mu\text{m}$ at 25 °C and $460 \mu\text{m}$ at 60 °C,⁴⁴ with the latter parameter corresponding to the specification in the European standard EN 590, as mentioned previously. Generally, the range of wear scars for all samples tested here is greater at 60 °C than at 25 °C, thus allowing improved discernment of additization and influence of molecular structure on lubricity. Also, petrodiesel standards prescribe a test temperature of 60 °C and most published data were acquired at this

temperature. Generally, the friction values reported in the tables are reduced for samples of improved lubricity, although, at best, only a semiquantitative relationship may be possible. Friction values are usually slightly higher at 60 °C than at 25 °C.

The petrodiesel fuels used here (DF1 and low-lubricity ULSD) exhibit poor lubricity in neat form (see Table 2). The neat hydrocarbons listed in Table 3 also possess high wear scar values. The unsaturated compounds 1-tetradecene and 1-hexadecene show the lowest wear scar values of the compounds listed in Table 2, with the values for 1-dodecene and 1-octadecene being higher. Thus, for such hydrocarbons, this implies an effect of chain length and unsaturation on lubricity, which was also discussed in prior literature.⁴ This effect is present and probably even more pronounced for fatty compounds, as discussed below. The commercial biodiesel sample used for comparison in Table 2, on the other hand, shows excellent lubricity, as demonstrated by the low wear scar values.

The data in Table 4 lead to the following observations regarding the effects on lubricity of neat fatty compounds. Lubricity increases somewhat with chain length; however, the lubricity-enhancing effect of double bonds is greater than that of extended chain length. However, other authors stated that increasing unsaturation had a negative influence on fatty acids as wear reducers in vegetable oils.^{28,54} It was also reported that shorter chain lengths reduce molecular interaction with decreased temperature stability of the protective lubricant film.⁵⁵ The double-bond configuration does not have a significant role for the compounds studied here (methyl linoleate ($\Delta 9$, $\Delta 12$; all-cis) versus methyl linolelaidate ($\Delta 9$, $\Delta 12$; all-trans); see Table 4). The triacylglycerol of oleic acid (triolein) shows better lubricity than the corresponding methyl ester (methyl oleate). This contrasts with literature results in which methyl soyate

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Table 4. HFRR Data of Neat Fatty Compounds

compound	Wear Scar (μm)						Film (%)		Friction	
	25 °C			60 °C						
	X	Y	average	X	Y	average	25 °C	60 °C	25 °C	60 °C
methyl laurate	245, 249	208, 218	227, 234	467, 433	365, 383	416, 408	73, 74	56, 69	0.133, 0.133	0.157, 0.143
butyl laurate	254, 265	206, 220	230, 243	342, 372	301, 306	322, 339	85, 81	72, 64	0.128, 0.129	0.133, 0.133
methyl myristate	255, 245	211, 207	233, 226	368, 375	337, 329	353, 352	76, 78	77, 76	0.124, 0.123	0.130, 0.130
methyl myristoleate	292, 356	263, 240	278, 298	245, 278	200, 238	223, 258	80, 88	91, 90	0.125, 0.120	0.124, 0.119
methyl palmitate	nd ^a	nd ^a	nd ^a	375, 385	339, 339	357, 362	nd ^a	76, 77	nd ^a	0.125, 0.130
methyl palmitoleate	201, 196	142, 160	172, 178	266, 247	226, 208	246, 228	88, 89	86, 92	0.121, 0.119	0.112, 0.112
methyl stearate	nd ^a	nd ^a	nd ^a	387, 302	257, 252	322, 277	nd ^a	88, 87	nd ^a	0.114, 0.103
oleic acid	145, 151	91, 90	118, 121	0, 0	0, 0	0, 0	91, 91	98, 91	0.065, 0.069	0.086, 0.089
methyl oleate	219, 216	210, 205	215, 211	298, 357	281, 327	290, 342	89, 90	86, 72	0.118, 0.118	0.133, 0.139
butyl oleate	224, 232	185, 183	205, 208	311, 354	295, 335	303, 345	92, 90	84, 61	0.108, 0.108	0.119, 0.130
monoolein	nd ^a	nd ^a	nd ^a	146, 131	131, 114	139, 123	nd ^a	98, 98	nd ^a	0.051, 0.055
diolein	nd ^a	nd ^a	nd ^a	201, 179	170, 146	186, 163	nd ^a	94, 95	nd ^a	0.080, 0.064
triolein	147, 155	77, 75	112, 115	180, 173	106, 134	143, 154	99, 99	99, 97	0.041, 0.041	0.181, 0.211
linoleic acid	151, 152	97, 100	124, 126	0, 0	0, 0	0, 0	89, 87	100, 100	0.087, 0.084	0.057, 0.067
methyl linoleate	198, 213	146, 180	172, 197	260, 238	211, 199	236, 219	90, 86	94, 95	0.131, 0.132	0.12, 0.116
methyl linolenate	231, 250	194, 183	213, 217	201, 220	165, 149	183, 185	76, 75	94, 94	0.133, 0.135	0.108, 0.115
methyl 9,12-linoleaidate	220, 220	182, 180	201, 200	200, 198	150, 156	175, 177	89, 91	93, 94	0.093, 0.094	0.102, 0.112
methyl ricinoleate	184, 184	128, 120	156, 152	216, 193	165, 155	191, 174	93, 95	91, 92	0.077, 0.077	0.101, 0.096
oleyl alcohol	184, 214	175, 158	180, 186	332, 314	269, 263	301, 289	85, 87	47, 51	0.095, 0.087	0.123, 0.121
ricinoleyl alcohol	92, 100	90, 72	91, 86	180, 176	115, 147	148, 162	100, 100	95, 94	0.048, 0.049	0.064, 0.058

^a Not determined because the melting points were >25 °C (30 °C for methyl palmitate, 39 °C for methyl stearate, and 35 °C for monoolein). The melting points of palmitic and stearic acids are 51 and 71 °C, respectively.

Table 5. HFRR Data of C₁₀ Oxygenated Compounds and Diethylene Glycol Diethyl Ether

material	Wear Scar (μm)						Film (%)		Friction	
	25 °C			60 °C						
	X	Y	average	X	Y	average	25 °C	60 °C	25 °C	60 °C
methyl nonanoate	256, 237	180, 189	218, 213	370, 361	342, 318	356, 340	31, 32	64, 70	0.126, 0.131	0.138, 0.137
decanoic acid	nd ^a	nd ^a	nd ^a	92, 110	71, 72	82, 91	nd ^a	98, 98	nd ^a	0.103, 0.104
1-decanol	231, 262	195, 193	213, 228	324, 311	287, 265	306, 288	62, 72	59, 58	0.110, 0.110	0.126, 0.126
decanal	225, 250	217, 221	221, 236	277, 246	217, 215	247, 231	90, 87	84, 86	0.129, 0.129	0.134, 0.135
2-decanone	256, 321	273, 311	265, 316	402, 359	378, 366	390, 363	40, 46	41, 43	0.141, 0.146	0.159, 0.157
dipentyl ether	373, 411	376, 368	375, 390	488, 486	423, 445	456, 466	23, 27	34, 37	0.185, 0.180	0.169, 0.167
diethylene glycol diethyl ether	687, 695	681, 693	684, 694	739, 718	714, 709	727, 714	29, 32	35, 42	0.399, 0.402	0.506, 0.496

^a Not determined, because of the properties of decanoic acid (fr. 31.5 °C).

imparted somewhat better lubricity to a petrodiesel fuel than the parent vegetable oil.⁸ Neat free fatty acids possess significantly better lubricity (no wear scars visible at 60 °C for oleic and linoleic acids) than the corresponding fatty alcohols, the various acylglycerols, and glycerol (see Table 6). Generally, the carboxylic acid moiety is likely the most effective in enhancing lubricity. Apparently, sterically unhindered (i.e., exposed) electrons in the form of free electron pairs or double-bond electrons toward the end of a chain of C atoms are especially effective in enhancing lubricity, which is an effect discussed previously for components of petrodiesel.³⁸ It may be speculated that the corresponding orbitals overlap with orbitals in the metal atoms, similar to the formation of organometallic complexes (for example, π -complexes of alkenes), although the exact nature of this overlap would likely differ from the organometallic complexes. Studies of the tribochemical nature using fatty acids and esters, as well as related materials, have discussed the formation of organometallic species, such as metal carboxylates and organometallic polymers, although still little is known about the reactions that are occurring and this tribochemistry is subject to much speculation.^{50,56,57}

To further assess the influence of oxygenated moieties on lubricity, a series of neat compounds with 10 C atoms with different oxygenated functionalities was selected for further study (see Table 5), similar to previous work on the viscosity of fatty compounds.⁵⁸ Decanoic acid exhibited the best lubricity of the these compounds. However, the carbonyl compounds decanal and 2-decanone also showed good lubricity, performing better than decanol. The compound with the poorest lubricity in this series was dipentyl ether. The HFRR data (Table 5) of a compound with three ether linkages—diethylene glycol diethyl ether ($\text{C}_2\text{H}_5\text{—O—CH}_2\text{—CH}_2\text{—O—CH}_2\text{—CH}_2\text{—O—C}_2\text{H}_5$)—confirm that ether moieties do not provide significant lubricity-enhancing effects. Thus, the lubricity of neat esters is almost exclusively provided by the C=O moiety of the ester functionality, which is an observation that is also consistent with the lubricity provided by the aldehyde and ketone in this series. This result is confirmed by other authors, who stated that the most active compounds, in terms of lubricity enhancement, have more than one heteroatom with the

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Table 6. Effect of OH, SH, and NH₂ Groups on the Lubricity of C₃ Compounds by HFRR

material, C(R ₁)H ₂ –C(R ₂)H–C(R ₃)H ₂			Wear Scar (μm)						Film (%)		Friction	
R ₁	R ₂	R ₃	25 °C			60 °C			25 °C	60 °C	25 °C	60 °C
			X	Y	average	X	Y	average				
OH	OH	OH	0, 0	0, 0	0, 0	100, 91	75, 75	88, 83	100, 100	99, 100	0.047, 0.055	0.027, 0.025
OH	OH	H	172, 171	115, 138	144, 155	269, 336	255, 258	262, 297	87, 88	46, 67	0.100, 0.098	0.126, 0.131
OH	H	OH	237, 225	186, 173	212, 199	333, 371	242, 260	288, 316	57, 48	7, 12	0.075, 0.104	0.105, 0.111
OH	H	H	607, 581	540, 523	574, 552	nd ^a	nd ^a	nd ^a	8, 11	nd ^a	0.368, 0.350	nd ^a
H	OH	H	623, 638	614, 612	619, 625	nd ^a	nd ^a	nd ^a	22, 34	nd ^a	0.361, 0.367	nd ^a
OH	OH	SH	0, 92	0, 78	0, 85	374, 340	261, 216	318, 278	93, 93	0, 0	0.038, 0.037	0.136, 0.129
OH	SH	SH	544, 481	414, 337	479, 409	570, 531	419, 392	495, 462	0, 0	0, 0	0.124, 0.124	0.193, 0.190
SH	H	SH	481, 528	391, 416	436, 472	nd ^b	nd ^b	nd ^b	0, 0	nd ^b	0.224, 0.233	nd ^b
SH	H	H	548, 541	561, 552	555, 547 ^a	nd ^a	nd ^a	nd ^a	46, 45	nd ^a	0.203, 0.187	nd ^a
OH	OH	NH ₂	0, 0	0, 0	0, 0	64, 0	59, 0	62, 0	100, 100	97, 98	0.109, 0.117	0.041, 0.037
NH ₂	OH	NH ₂	nd ^c			361, 350	302, 308	332, 329	nd ^c	47, 47	nd ^c	0.114, 0.119

^a Not determined, because of the volatility of 1-propanol (bp 97 °C), 2-propanol (82 °C), 1,3-propanedithiol (bp 173 °C), and 1-propanethiol (bp 68 °C) at 60 °C. 1-Propanethiol largely evaporated, even during the 25 °C experiment, negatively influencing the wear scar data. ^b No 60 °C data for 1,3-propanedithiol, because of malodorous fumes resulting from higher volatility at this temperature. ^c Not determined, because of the melting point of 1,3-diamino-2-propanol (42–45 °C).

heteroatoms in exposed configuration,³⁸ which is a result that is confirmed by the lubricity displayed by the C₁₀ aldehyde.

In conjunction with the above discussion, the data in Tables 4 and 5 result in the following sequence of oxygenated moieties enhancing lubricity by HFRR at 60 °C: COOH > CHO > OH > COOCH₃ > C=O > C–O–C. At 25 °C, the values are closer together. Although the general sequence remains unchanged at 25 °C, there is little difference between the aldehyde, hydroxy, and methyl ester group at 25 °C. In this connection, it was reported that the correlation between wear scar diameter and actual pump performance is better for results obtained at 60 °C.⁵¹ Most compounds caused greater wear scars at 60 °C than at 25 °C, with the exception of the free fatty acids, oleic acid, and linoleic acid (see Table 4), the reason for which is not known. The lubricity enhancement caused by COOH and OH groups correlates with the known observation that ionic interactions of a metal substrate with a lubricating molecule due to hydrogen bonding and Debye orientation forces are considerably stronger than those based on dipole (van der Waals) forces.⁵⁹ Physisorption and/or chemisorption was thought to be the primary mechanism with rapeseed oil.⁵⁴ The lubricity of alkyl esters is lower than that of the hydrogen-bond-forming contaminants, because they do not give ionic interactions with the metal, because of their lack of free OH groups.

The number of lubricity-enhancing moieties in a molecule also has a role. Neat ricinoleyl alcohol displays better lubricity than oleyl alcohol (see Table 4). Glycerol, which contains only three carbons but three OH groups, possesses even stronger lubricity (see Table 6). Compounds with three carbons were selected to also assess the influence of N and S atoms (in the form of NH₂ and SH groups) on lubricity (see Table 6). The data in Table 6 show that lubricity decreases as the number of OH groups decreases. Thus, the neat propanediols performed well. However, the position of the hydroxy groups may have a role, as 1,2-propanediol shows slightly better lubricity than 1,3-propanediol. This may

be due to one end of the molecule being of hydrocarbon nature. Both 1- and 2-propanol exhibited high wear scar values (data collected only at 25 °C, because of their volatility). The presence of an SH group did not significantly affect lubricity, compared to the presence of only hydrogen. On the other hand, the amino compounds investigated here performed better than the thiols, with 1-aminoglycerol even giving lower wear scars than glycerol. This observation is compatible with reports in the literature that oxygen- and nitrogen-containing polar compounds are the species imparting lubricity to nondesulfurized diesel fuel and not the sulfur compounds.^{30,38} However, a study on sulfurized fatty acids in rapeseed oil stated that, at high loads, sulfurized octadecanoic acid performed better than octadecanoic acid.⁶⁰ Another study using C₁₈ compounds in sunflower oil reported a lubricity-improving effect in the order of carboxylic acid > amine > amide, with thiol exhibiting a negative effect.²⁷ The sequence of lubricity enhancement by HFRR using C₃ compounds is clearly oxygen > nitrogen >> sulfur.

Additization. In accordance with the prior literature, which has been discussed above, adding 1%–2% commercial biodiesel to the two low-lubricity petrodiesel fuels used here improved their lubricity (see Tables 2, 7, and 8). However, the addition of neat methyl oleate or methyl linoleate at a level of 1%–2% had only a marginal effect on the lubricity of the two low-lubricity petrodiesel fuels (see Tables 7 and 8). This result corresponds with work that reported a similar effect²⁰ but contrasts with other literature that describes an improvement of lubricity with low-level neat fatty esters.^{17,21} On the other hand, adding free fatty acids to the low-lubricity petrodiesel fuels improved lubricity considerably (see Tables 7 and 8), a result agreeing with previous reports.^{22,23,26}

These results prompted us to prepare samples in which, initially, 1% free fatty acid was added to the corresponding methyl ester and then this mixture was added at the 1% level to the low-lubricity petrodiesel fuels. Thus, the concentration of free fatty acid in the petrodiesel fuels is 0.01% (100 ppm) in these mixtures. The results in Tables 7 and 8 show a significant increase

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Table 7. Effect of Blending or Addition on HFRR Data of Ultralow Sulfur Petrodiesel Fuel^a

blend/additive	Wear Scar (μm)						Film (%)		Friction	
	25 °C			60 °C						
	X	Y	average	X	Y	average	25 °C	60 °C	25 °C	60 °C
1% biodiesel	223, 207	178, 179	201, 193	318, 318	266, 265	292, 292	92, 94	88, 90	0.169, 0.173	0.178, 0.171
2% biodiesel	191, 202	183, 185	187, 194	308, 297	254, 219	281, 258	95, 94	92, 93	0.158, 0.160	0.181, 0.182
1% methyl oleate	299, 238	240, 219	270, 229	618, 529	576, 501	597, 515	78, 84	36, 55	0.194, 0.179	0.264, 0.233
2% methyl oleate	245, 246	157, 155	201, 201	390, 375	377, 360	384, 368	89, 89	76, 74	0.170, 0.169	0.198, 0.204
5% methyl oleate	242, 249	222, 211	232, 230	386, 366	343, 351	365, 359	83, 88	71, 78	0.155, 0.156	0.179, 0.174
10% methyl oleate	225, 232	168, 173	197, 203	306, 310	272, 286	289, 298	90, 88	86, 88	0.154, 0.151	0.154, 0.157
0.01% oleic acid	235, 238	185, 211	210, 225	259, 254	208, 211	234, 233	90, 86	87, 86	0.119, 0.120	0.130, 0.128
1% oleic acid	232, 206	168, 172	201, 189	182, 193	174, 183	178, 188	91, 93	93, 93	0.116, 0.119	0.114, 0.114
2% oleic acid	213, 229	183, 188	198, 209	203, 198	165, 175	184, 187	88, 90	94, 93	0.121, 0.120	0.118, 0.113
1% monoolein	230, 216	137, 161	184, 189	146, 179	121, 142	134, 161	86, 86	99, 98	0.122, 0.122	0.120, 0.124
1% diolein	207, 225	159, 180	183, 203	280, 274	193, 228	237, 251	90, 90	92, 91	0.131, 0.132	0.141, 0.143
1% triolein	209, 220	160, 184	185, 202	393, 369	377, 370	385, 370	87, 90	70, 68	0.156, 0.153	0.197, 0.192
2% triolein	204, 193	143, 159	174, 176	299, 345	275, 282	287, 314	90, 92	85, 77	0.147, 0.143	0.163, 0.175
1% glycerol	nd ^c	nd ^c	nd ^c	646, 663	635, 635	641, 649	nd ^c	9, 8	nd ^c	0.378, 0.412
1% methyl oleate with 1% glycerol ^b	242, 239	220, 214	231, 226	483, 455	405, 427	444, 441	85, 88	56, 62	0.186, 0.181	0.209, 0.214
2% methyl oleate with 1% glycerol ^b	216, 246	171, 148	193, 197	398, 415	357, 375	378, 395	92, 89	69, 73	0.171, 0.162	0.211, 0.177
1% methyl oleate with 1% oleic acid ^b	232, 214	177, 182	205, 198	381, 363	331, 325	356, 344	89, 90	77, 81	0.154, 0.155	0.180, 0.171
2% methyl oleate with 1% oleic acid ^b	207, 200	184, 120	196, 160	290, 274	256, 198	273, 236	91, 90	89, 93	0.145, 0.146	0.139, 0.212
1% methyl oleate with 1% monoolein ^b	218, 230	170, 179	194, 205	345, 320	325, 286	335, 303	86, 84	80, 85	0.151, 0.151	0.174, 0.170
1% methyl oleate with 1% diolein ^b	256, 254	152, 185	204, 220	547, 502	518, 467	533, 485	85, 85	48, 57	0.167, 0.175	0.225, 0.212
1% methyl oleate with 1% glycerol & 1% oleic acid ^b	238, 232	177, 188	208, 210	371, 263	311, 231	341, 247	90, 90	82, 93	0.154, 0.153	0.167, 0.213
2% methyl oleate with 1% glycerol & 1% oleic acid ^b	209, 230	165, 199	187, 215	362, 280	318, 258	340, 269	90, 88	79, 86	0.141, 0.140	0.152, 0.139
1% oleic acid with 1% glycerol ^b	233, 237	187, 180	210, 208	203, 211	178, 169	190, 190	89, 90	93, 93	0.121, 0.119	0.116, 0.118
2% oleic acid with 1% glycerol ^b	218, 242	174, 195	196, 218	218, 227	169, 161	193, 194	89, 85	93, 94	0.120, 0.119	0.118, 0.118
1% methyl linoleate	292, 308	240, 258	266, 283	592, 588	554, 557	573, 573	83, 79	31, 24	0.193, 0.205	0.265, 0.275
2% methyl linoleate	226, 228	155, 185	191, 207	557, 572	514, 530	536, 551	93, 91	43, 35	0.176, 0.178	0.238, 0.247
1% methyl linoleate with 1% linoleic acid ^b	223, 242	152, 199	188, 221	491, 451	382, 374	437, 413	90, 89	57, 55	0.167, 0.163	0.191, 0.193
1% methyl linoleate with 1% glycerol ^b	nd ^c	nd ^c	nd ^c	587, 609	554, 550	571, 580	nd ^c	27, 23	nd ^c	0.260, 0.267
1% methyl linoleate with 1% monolinolein ^b	nd ^c	nd ^c	nd ^c	330, 304	271, 244	301, 274	nd ^c	87, 93	nd ^c	0.188, 0.183
1% methyl linoleate with 1% dilinolein ^b	nd ^c	nd ^c	nd ^c	543, 556	511, 509	527, 533	nd ^c	44, 50	nd ^c	0.239, 0.231
1% triolein with 1% oleic acid ^b	220, 242	169, 208	195, 225	389, 414	347, 352	368, 383	88, 89	69, 65	0.151, 0.148	0.172, 0.185
1% triolein with 2% oleic acid ^b	199, 263	178, 185	189, 224	346, 290	291, 242	319, 266	77, 84	77, 86	0.131, 0.137	0.155, 0.145

^a For data of the neat petrodiesel fuels, see Table 1. ^b Samples described in this fashion contain 1%–2% of the second- and third-named material in the first-named material. This mixture was then added to the petrodiesel fuel. Thus, the second- and third-named materials are present at 0.01%–0.02% (100–200 ppm) levels in the petrodiesel fuel. ^c Not determined.

in lubricity when adding these ester/free fatty acid mixtures to the petrodiesel fuels, compared to adding only the neat ester. This result also corresponds well with the aforementioned sequence of lubricity-imparting oxygenated moieties.

Similar results were achieved when adding methyl esters that contained 1% of the corresponding monoacylglycerols and then adding this mixture to petrodiesel (see Tables 7 and 8). Diacylglycerols were less effective than monoacylglycerols, which can be explained by the reduced number of OH moieties, as shown previously for C₃ compounds and the results for oleyl alcohol versus ricinoleyl alcohol. Both monoacylglycerols and diacylglycerols were proposed by other authors to be the actual lubricity-imparting agents in biodiesel.⁷

The 1% level of free fatty acid or monoacylglycerol in the methyl ester is above the specification stated in the

standards (see Table 1) but does clearly illustrate the effect. Only 1% of such a mixture imparts sufficient lubricity, which must be compared to the common 2% level of biodiesel usually applied. Thus, B2 (2% commercial biodiesel in petrodiesel) produced from biodiesel that contained 0.2% free fatty acid contains 0.004% (40 ppm) free fatty acid. The biodiesel may also contain 0.4% monoacylglycerols, leading to 0.008% (80 ppm) thereof in B2; thus, the concentration of lubricity-enhancing biodiesel contaminants present in B2 then is >0.01% (100 ppm), which is a level comparable to that studied here.

On the other hand, adding glycerol (see Tables 7 and 8) at similar levels had no beneficial effect on lubricity. This is likely due to the immiscibility of glycerol with petrodiesel. In conjunction with the lubricity-enhancing effect of monoacylglycerols, which produce, in neat form,

Table 8. Effect of Blending or Additization on HFRR Data of Low-Lubricity No. 1 Petrodiesel Fuel^a

blend/additive	Wear Scar (μm)						Film (%)		Friction	
	25 °C			60 °C						
	X	Y	average	X	Y	average	25 °C	60 °C	25 °C	60 °C
1% biodiesel	227, 258	202, 185	215, 222	323, 400	276, 339	300, 370	74, 70	85, 70	0.192, 0.191	0.179, 0.185
2% biodiesel	229, 239	160, 181	195, 210	273, 320	229, 271	251, 296	80, 80	93, 89	0.178, 0.183	0.160, 0.171
1% methyl oleate	300, 287	345, 254	323, 271	601, 570	537, 502	569, 536	69, 68	24, 28	0.209, 0.209	0.223, 0.223
2% methyl oleate	272, 286	184, 249	228, 268	571, 552	515, 500	543, 526	71, 70	33, 36	0.194, 0.198	0.208, 0.209
5% methyl oleate	268, 261	239, 228	254, 245	373, 367	348, 338	361, 353	77, 74	77, 75	0.182, 0.173	0.183, 0.185
10% methyl oleate	275, 270	275, 240	275, 255	363, 334	334, 336	349, 353	70, 83	77, 75	0.156, 0.165	0.172, 0.176
0.01% oleic acid	245, 226	199, 200	222, 213	250, 260	207, 223	229, 242	86, 78	87, 84	0.121, 0.127	0.131, 0.132
1% monoolein	234, 245	130, 143	182, 194	213, 199	136, 145	175, 172	90, 89	96, 97	0.127, 0.129	0.128, 0.129
1% diolein	225, 255	155, 225	190, 240	349, 306	276, 248	313, 277	85, 83	85, 87	0.157, 0.158	0.165, 0.168
1% glycerol	379, 418	351, 357	365, 388	658, 624	590, 555	624, 590	49, 48	9, 15	0.250, 0.256	0.283, 0.267
1% methyl oleate with 1% monoolein ^b	242, 247	224, 193	233, 220	276, 314	230, 198	253, 256	79, 78	92, 86	0.182, 0.181	0.171, 0.179
1% methyl oleate with 1% diolein ^b	269, 281	233, 271	251, 276	618, 557	543, 514	581, 536	79, 78	26, 30	0.212, 0.207	0.233, 0.222
1% methyl linoleate	317, 284	270, 250	294, 267	600, 602	558, 546	579, 574	68, 75	26, 27	0.222, 0.219	0.241, 0.239
2% methyl linoleate	226, 243	202, 224	214, 234	560, 559	500, 498	530, 529	90, 88	36, 39	0.202, 0.210	0.226, 0.227
1% methyl linoleate with 1% linoleic acid ^b	229, 221	197, 149	213, 185	370, 423	336, 371	353, 397	89, 89	73, 68	0.189, 0.192	0.175, 0.179
1% methyl linoleate with 1% glycerol ^b	225, 255	222, 240	224, 248	531, 556	473, 483	502, 520	86, 86	42, 40	0.217, 0.220	0.226, 0.234
1% methyl linoleate with 1% monolinolein ^b	219, 250	185, 200	202, 225	287, 233	322, 227	260, 275	91, 88	91, 88	0.211, 0.212	0.196, 0.190
1% methyl linoleate with 1% dilinolein ^b	253, 264	241, 238	247, 251	553, 611	501, 550	527, 581	77, 81	38, 30	0.214, 0.215	0.230, 0.239
1% triolein	248, 239	213, 211	231, 225	550, 554	502, 501	526, 528	81, 78	33, 33	0.198, 0.190	0.220, 0.220
2% triolein	297, 240	219, 167	258, 204	300, 333	268, 293	284, 313	77, 80	88, 84	0.176, 0.176	0.179, 0.188
1% triolein with 1% oleic acid ^b	241, 248	184, 199	213, 224	407, 359	328, 332	368, 346	85, 84	70, 79	0.165, 0.163	0.180, 0.174
1% triolein with 2% oleic acid ^b	239, 236	194, 195	217, 216	333, 312	308, 261	321, 287	84, 83	76, 78	0.143, 0.141	0.158, 0.159
1% 1-hexadecene	333, 337	306, 303	320, 320	620, 646	563, 568	592, 607	55, 61	17, 18	0.228, 0.231	0.242, 0.238
2% 1-hexadecene	408, 324	332, 277	370, 301	662, 641	569, 541	616, 591	45, 69	14, 17	0.236, 0.230	0.252, 0.234
1% dibenzothiophene	300, 322	251, 269	276, 296	630, 590	551, 514	591, 552	74, 69	14, 22	0.221, 0.233	0.263, 0.229
2% dibenzothiophene	419, 305	321, 261	370, 283	634, 611	565, 549	600, 580	46, 73	13, 25	0.214, 0.229	0.249, 0.224
1% dibenzofuran	371, 385	297, 309	334, 347	605, 584	544, 535	575, 560	59, 55	22, 21	0.218, 0.219	0.241, 0.237
2% dibenzofuran	278, 259	249, 232	264, 246	610, 626	570, 535	590, 581	73, 74	20, 21	0.224, 0.214	0.236, 0.232

^a For data of the neat petrodiesel fuels, see Table 1. ^b Samples described in this fashion contain 1%–2% of the second-named material in the first-named material. This mixture was then added to the petrodiesel fuel. Thus, the second-named material is present at 0.01%–0.02% (100–200 ppm) levels in the petrodiesel fuel.

greater wear scars than glycerol, at additive level, this result underlines that both hydrophilic and lipophilic moieties, as they are found in fatty compounds with polar end groups, are necessary to enhance lubricity.

Generally, the lubricity-imparting behavior of mixtures that consist of one or two types of biodiesel contaminants added to a neat methyl ester corresponded to the material that imparted the best lubricity (see Tables 7 and 8). Thus, the lubricity of materials such as free fatty acids and monoacylglycerols is not impeded by the other components in the mixtures that comprise biodiesel.

Therefore, free fatty acids and monoacylglycerols contained in commercial biodiesel, which are considered contaminants and are limited in biodiesel standards, are the materials that impart lubricity to the 1%–2% blends of biodiesel with low-lubricity petrodiesel. This result also explains the observation by other authors that the addition of methyl soyate to petrodiesel improved lubricity but the addition of the parent vegetable oil had less effect.⁸ The free fatty acids and monoacylglycerols in biodiesel (which arise during its production) caused the enhanced lubricity, compared to the vegetable oil, although the addition of neat triacylglycerols improves lubricity more than adding neat esters, as discussed previously. Other authors¹¹ have reported a “leap” in lubricity when adding rapeseed methyl ester at levels of 0.75%–1.00% to petrodiesel fuel, compared to lower

blend or additization levels. The present results not only show that such levels of biodiesel are needed to achieve additive levels of the free fatty acid and monoacylglycerol contaminants of biodiesel in the petrodiesel, but also that the “leap” likely indicates that a sufficient concentration of the contaminants has been achieved to impart lubricity.

The compounds with hydrogen-bonding ability are considered contaminants of biodiesel and are, accordingly, limited in biodiesel standards. These results explain why 1%–2% biodiesel, which is higher than the usual additive level, has been required to impart lubricity when adding biodiesel to low-sulfur petrodiesel fuel. The biodiesel must be added at a level sufficiently high for its hydrogen-bonding contaminants to attain the additive level in the low-sulfur petrodiesel fuel and become effective lubricity-enhancing additives.

The addition of a sulfur-containing compound in undesulfurized petrodiesel,⁶¹ as well as its oxygen congener dibenzofuran, to low-sulfur petrodiesel had little or no lubricity-enhancing effect (see Table 8). Related results have been reported.³³ Dibenzothiophene was also shown not to enhance viscosity when added to an aromatic hydrocarbon, in contrast to fatty esters.⁵⁸

(61) Song, C. Introduction to Chemistry of Diesel Fuels. In *Chemistry of Diesel Fuels*; Song, C., Hsu, C. S., Mochida, I., Eds.; Taylor and Francis: New York, 2000; pp 25–28.

Summary and Conclusions

The present results obtained with the high-frequency reciprocating rig (HFRR) lubricity tester give clear data concerning such factors as the influence of functional groups and additization on lubricity. The HFRR method proved to be sensitive to additives and their structure at the levels investigated here (down to 100 ppm).

The present results show that at least two features must be present in a molecule to impart lubricity. These features are the presence of a polarity-imparting heteroatom, preferably oxygen, with the nature (and number) of the oxygen moiety having a significant role, and/or a carbon chain of sufficient length, which also increases viscosity. If sufficient oxygenated moieties of lubricity-imparting capability are present, then even a short-chain compound (for example, glycerol) will possess excellent lubricity in the neat form, although a lack of miscibility with hydrocarbons such as petrodiesel will not impart lubricity when using this material as an additive. Lubricity is strongly dependent on the nature in which O atoms are bound in the molecule and, if they are present as lubricity-enhancing moieties, on the number of these moieties. The lubricity of neat esters is mainly caused by the presence of a carbonyl moiety,

with the ether linkage having a minor role. The functional group that enhances lubricity the most is COOH. The sequence of lubricity enhancement by oxygenated moieties in fatty compounds is similar, but not identical, to the sequence observed for the enhancement of kinematic viscosity,⁵⁸ showing differences between these properties. The lubricity of low-level blends (1%–2%) of biodiesel with low-lubricity petrodiesel is largely caused by free fatty acid and monoacylglycerol contaminants present in the biodiesel.

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Note Added in Proof: A very recent publication [Hu et al., Study on the Lubrication Properties of Biodiesel as Fuel Lubricity Enhancers. *Fuel*, in press] reports that monoacylglycerols and methyl esters especially enhance biodiesel lubricity, more so than free fatty acids and diacylglycerols, whereas triacylglycerols had almost no effect. These results are in partial accordance with the results presented here.

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