

Boundary Lubrication of Biofuels and Similar Molecules

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ABSTRACT

The cluster of excellence “Tailor-Made Fuels from Biomass” (TMFB) at RWTH Aachen University seeks to identify and investigate new potential biofuels and their production routes. To ensure a safe handling in common-rail systems the lubricity of future biofuels is part of the investigations. To further deepen the understanding of the behaviour of such fluids in the regime of boundary lubrication a group of twelve potential biofuels and systematically derived fluids was investigated by a modified version of the standardised High Frequency Reciprocating Rig test procedure for Diesel lubricity. Insufficient lubricity is observed for most biofuels whereas linear molecules with polar head groups provide good or very good lubrication. For all studied groups longer molecules provide better lubricities. The position of the functional group significantly influences the overall lubricity and impact of the carbon chain length.

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INTRODUCTION

The cluster of excellence “Tailor-Made Fuels from Biomass” (TMFB) at RWTH Aachen University seeks to identify and investigate new potential biofuels and their production routes, see [figure 1](#). Due to the highly complex and interdisciplinary nature of this task, the cluster consists of researchers from various fields of science and engineering.

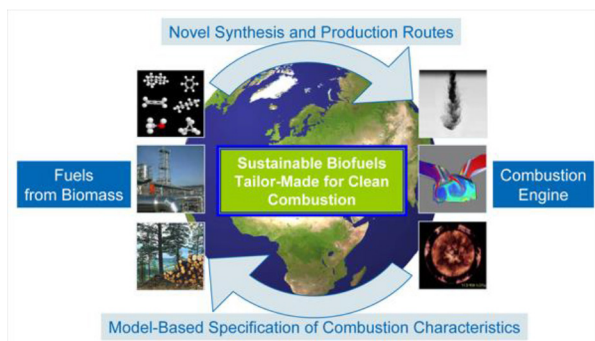


Figure 1. The cluster of excellence Tailor-Made Fuels from Biomass

To ensure a safe handling of the fuel in a combustion engine and its periphery the tribological properties of the potential biofuel candidates are investigated. This part of the cluster’s research is performed at the Institute for Fluid Power Drives and Controls (IFAS), see [1, 2].

Biofuel Lubricity

The injection nozzles of most modern diesel engines are supplied by a common rail system. Due to the high amount of boundary lubrication present in the related pumps the “lubricity” of the handled fuel is a vital characteristic for the system’s longevity. The following

definition given by Appeldoorn and Dukek can be used for a general understanding of the topic: “If two liquids have the same viscosity and one gives lower friction, wear or scuffing it is said to have a better lubricity”. [3] However, for the sake of precision in this paper “lubricity” is used synonymous with the measure of the standardised lubricity testers that will be introduced later on.

To investigate the lubricity of diesel fuel two laboratory scale tests have been developed and standardised: The High Frequency Reciprocating Rig (HFRR) and the Scuffing Load Ball on Cylinder Lubricity Evaluator (SLBOCLE), see [4, 5]. Both test methods are applied within the tribological research on biofuels at IFAS, see [6]. The research presented in this paper will focus on measurements based on the HFRR test which will be introduced in more detail later.

A large number of molecules could function as biofuels. Therefore an efficient model based prediction of fuel properties is an important aspect of the cluster’s research. In case of the lubricity Mausch and Fatemi developed a quantitative structure-property relationships (QSPR) model for the HFRR method, see [2, 7]. Although QSPR-models can serve as fast screening tools, their prediction power can be limited and strongly depends on the quality and quantity of measurements used for the model set-up. Furthermore, to evaluate the plausibility of the selected molecule properties the underlying processes and parameters of boundary lubrication need to be understood.

The majority of tribological research on boundary lubrication and fluid-surface interactions focusses on the performance of antiwear (AW), extreme pressure (EP) additives or friction modifiers. For example long linear acids such as stearic acid can act as lubricating additives. This is ascribed to the formation of a boundary layer of perpendicularly adsorbed molecules on the metal surface. Crucial for the adsorption is the polarity of the functional group, see figure 2.

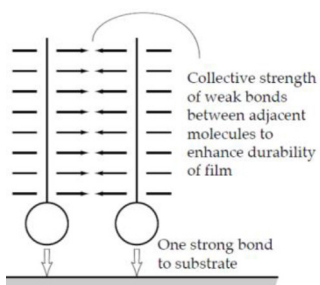


Figure 2. Boundary layer of linear molecules [8]

Naturally the structure of most biofuel candidates derive from requirements related to combustion or their biomass origin. Hence, most TMFB molecules do not resemble typical lubricants or lubrication additives like stearic acid. In figure 3 three of the most promising biofuel candidates are depicted.

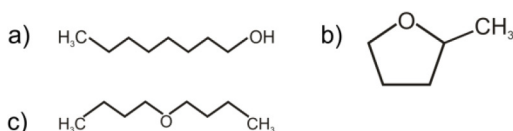


Figure 3. Molecule structures of selected biofuel candidates: a) 1-Octanol, b) 2-Methyltetrahydrofuran and c) Di-n-Butylether

Please note that subsequently 2-methyltetrahydrofuran will be addressed as 2-MTHF and di-n-butylether as DnBE. Because of their molecular structure, the boundary layer formed by these molecules and the resulting lubricity cannot be assessed easily. The measurement series presented in this paper seeks to study two aspects of biofuel lubricity. On the one hand the influence of the molecule's polarity is investigated by variation of the functional group. And on the other hand these results are compared to the influence a change in the carbon chain length has for a given functional group. These findings may subsequently be used to further improve fast screening methods such as the presented QSPR model.

METHOD

The following two subsections will firstly introduce the standardised lubricity test method used for the experimental investigations. Subsequently the fluids applied to this method are introduced.

The High Frequency Reciprocating Rig

As mentioned above the HFRR test has been standardised to investigate the lubricity of diesel fuel. The basic set-up of the HFRR test is depicted in figure 4.

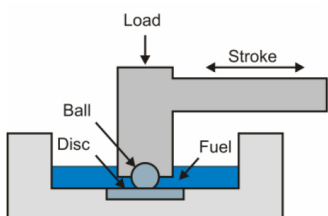


Figure 4. Standardised set-up of the HFRR

A 6 mm 100Cr6 steel ball is attached to an arm, which is capable of a reciprocal movement. This upper specimen is pressed against a 100Cr6 steel disc by a load of 200 g (1.962 N) while submerged in the investigated fluid. The ISO-12156 sets the test duration to 75 minutes and the fluid temperature to 60 °C. During each test the ball is forced to slide on the surface of the disc with 50 Hz and a stroke of 1 mm. Because of the known sensitivity of wear towards air temperature and humidity the HFRR norm limits the range for both properties. The test procedure leads to wear on the surfaces of both specimens. The figure 5 depicts such a wear scar on the ball specimen after a test with 1-octanol.

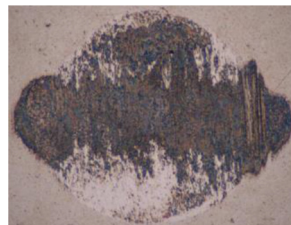


Figure 5. Wear scar on a HFRR ball (1-octanol)

The amount of wear is highly dependent of the fluid in the contact between the ball and the disc. Hence, the wear scar diameter (*WSD*) of the ball specimen can be used to judge the lubricating abilities of the fluid. To determine this measure the maximal dimensions of the wear scar in direction of the oscillation (*Y*) and perpendicular to it (*X*) are determined by an optical microscope and then averaged, see (1).

$$WSD = \frac{X+Y}{2} \quad (1)$$

The ISO-12156-1 adjusts the determined scar dimensions with regard to the water vapour pressure at the start and end of the test procedure. For this a linear correction formula is used and the resulting measure is the *WSI.4* [4]. In Europe the lubricity of commercial diesel must not exceed a wear scar diameter (*WSI.4*) of 460 µm, see [2]. Although the disc specimen has a lower hardness earlier investigations have shown that a high correlation of the wear scar dimensions exists, see [1, 10].

All later presented experiments were performed according to a slightly modified version of the standardised test procedure. The influence of the atmospheric conditions on the lubricity results of the biofuel candidates is unknown. In addition, Lapuerta et al. have shown that for similar fluids the established correction factor is not well suited [11]. Therefore no correction formula is applied to the *WSD* results. Each fluid is investigated at least three times and the mean *WSD* of the upper specimens will be used as the principal measure for the lubricating abilities of the fluid. Another deviation from the standardised test procedure is that the amount of fluid used is increased from 2 ml, as given in the norm, to 10 ml to minimise the risk of complete evaporation of the lubricant during the test. All tests are performed on a HFRR machine manufactured by PCS Instruments.

Investigated Fluids

The three biofuel molecules shown in [figure 3](#) are promising diesel surrogates. Among these 1-octanol was chosen as the basis of a systematic variation because of its linear structure and favourable rheological properties [6]. According to the boundary layer model for linear molecules shown in [figure 2](#) the nature of the functional group will directly influence the strength of the bonding of the molecule to the surface. To investigate this, the hydroxyl group of 1-octanol ($\text{CH}_3(\text{CH}_2)_6\text{COH}$) was altered while the length of the linear carbon chain was kept constant. By doing so the following molecules were derived: octanoic acid ($\text{CH}_3(\text{CH}_2)_6\text{COOH}$), 1-octanal ($\text{CH}_3(\text{CH}_2)_6\text{CHO}$), 2-octanone ($\text{CH}_3(\text{CH}_2)_5\text{COCH}_3$) and n-octane ($\text{CH}_3(\text{CH}_2)_6\text{CH}_3$). In this set the n-alkane will serve as a non-polar reference. To characterise the polarity [table 1](#) provides the dipole moments of the studied functional groups.

Table 1. Dipole moments of the functional groups [12]

Functional group	Group dipole moment [D]
Alkyl ($-\text{CH}_3$)	0.00
Hydroxyl ($-\text{OH}$)	1.70
Carbonyl ($-\text{CO}-$)	2.49
Aldehyde ($-\text{CHO}$)	2.49
Carboxyl ($-\text{COOH}$)	1.63

Because of their similar linear structure the overall dipole moments of the studied fluids depend mainly on the polarity of their functional groups. However, in [table 3](#) the overall dipole moments for the fluids are given as well.

The chain length of adsorbed linear molecules is known to influence the lubricated system. This is usually ascribed to the intensification of dispersion forces that follows from the increased number of carbon atoms in the elongated structure. This in turn leads to an increase of the coherence of the boundary layer [8]. Studt reports that for linear acids and alcohols a minimal chain length is necessary for effective lubrication [13]. To examine this aspect, the set of derived C_8 molecules was extended to include the corresponding C_{12} molecules. [Table 2](#) lists all fluids that were investigated. The test results of these molecules will serve as a foundation for the discussion of the molecular structure which includes a comparison to the other two biofuel candidates (2-MTHF and DNBE). In addition to the biofuel molecules shown in [Figure 3](#), [Figure 6](#) depicts the molecular structures of the linear molecules from [table 2](#).

Although the standard HFRR test is designed for the investigation of fuels in the regime of boundary lubrication an influence of hydrodynamic lift cannot be ruled out completely when fluids with different dynamic viscosities are tested, see [14]. A disturbing influence is most likely to occur for fluids that deviate significantly from the range set for standardised diesel. To enable a discussion of the lubricity results with regard to this property the [table 3](#) lists the dynamic viscosities of all investigated fluids. With the exception of 1-dodecanol and 2-MTHF the presented values for the dynamic viscosities are calculated from the data and formula given by Yaws, see [15]. The value for 2-MTHF is taken from Drumm [17].

Table 2. Investigated fluids [12]

No.	Fluid	CAS No.	Formula
1	n-Octane	111-65-9	C_8H_{18}
2	n-Dodecane	142-96-1	$\text{C}_{12}\text{H}_{26}$
3	1-Octanol	111-87-5	$\text{C}_8\text{H}_{18}\text{O}$
4	1-Dodecanol	112-53-8	$\text{C}_{12}\text{H}_{26}\text{O}$
5	1-Octanal	124-13-0	$\text{C}_8\text{H}_{16}\text{O}$
6	1-Dodecanal	124-07-2	$\text{C}_{12}\text{H}_{24}\text{O}$
7	2-Octanone	111-13-7	$\text{C}_8\text{H}_{16}\text{O}$
8	2-Dodecanone	6175-49-1	$\text{C}_{12}\text{H}_{24}\text{O}$
9	Octanoic acid	112-54-9	$\text{C}_8\text{H}_{16}\text{O}_2$
10	Dodecanoic acid	143-07-7	$\text{C}_{12}\text{H}_{24}\text{O}_2$
11	2-MTHF	96-47-9	$\text{C}_5\text{H}_{10}\text{O}$
12	DnBE	112-40-3	$\text{C}_8\text{H}_{18}\text{O}$

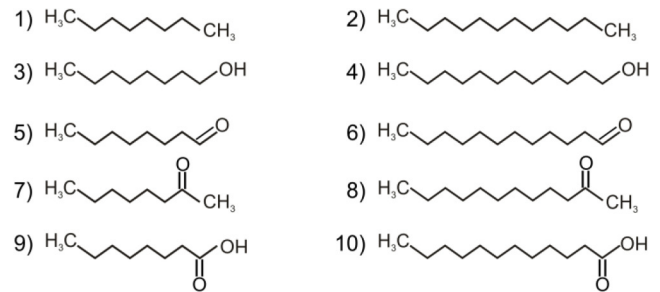


Figure 6. Molecular structures of the investigated linear molecules

Table 3. Dynamic viscosities [15, 17] and dipole moments [16] of the studied lubricants

Fluid	Viscosity(60°C) [mPas]	Dipole [D]
n-Octane	0.35	0
n-Dodecane	0.82	0
1-Octanol	2.40	1.649
1-Dodecanol	4.56	1.691
1-Octanal	0.66	2.32
1-Dodecanal	0.72	2.578
2-Octanone	0.55	2.461
2-Dodecanone	0.69	-
Octanoic acid	2.17	1.7
Dodecanoic acid	5.45	1.64
2-MTHF	0.33	-
DnBE	0.41	1.169

EXPERIMENTAL RESULTS

The shape and appearance of the ball wear scars differ with lubricity. For good lubricants ($WSD < 250 \mu\text{m}$) the wear scar is an elliptical area that has a brown or black colour which is not continuous but stained or patchy. As depicted in [Figure 7](#) only this colour change marks the 'worn' area on the ball since no grooves or other wear marks are visible. Under close examination the discoloured patches appear as debris that has been attached to the ball surface like paint or a coating. This speculation is fostered if the bright area in the upper middle of the octanoic acid wear scar is considered. The colour and texture of the