A COSMO-RS based QSPR model for the lubricity of bio- and petrodiesel components*

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The development of a new, optimized fuel is a process in which various necessary fuel properties have to be taken into account. For an inclusion of candidates not synthesized yet into the design process, for each relevant property a fully predictive model relying on nothing but the molecular structure is mandatory. One of the most important aspects for the design of a fuel is its lubricity. In this study the predictive method COSMO-RS for the calculation of thermodynamic mixture-properties is adopted for deriving a quantitative structure-property relationship (QSPR) for the lubricity of fuel components. COSMO-RS calculates molecular descriptors (sigma-moments) based on quantum chemical calculations. These descriptors are adapted to describe the underlying phenomena causing the film formation ability and lubricity of the fuel. The lubricity is assessed via high frequency reciprocating rig (HFRR) measurements taken from literature. The molecular descriptors and experimental data are evaluated via statistical methods in order to find the most influential molecular descriptors.

keywords: QSPR, COSMO-RS, lubricity, HFRR, screening, fuel design

1 Introduction

1.1 Lubricity and molecular modeling

Due to world-wide increasing carbon dioxide emissions and a rising energy demand in contrast to the limited availability of fossil energy resources, renewable raw materials are attaining increasing interest as sources for new fuels. The design of new fuels which ought to be optimized according to efficiency and emissions has to take numerous fluid properties into account, e.g. viscosity, heat capacity, ignitability, burn-

ing velocity, and, last not least, lubrication performance. A multi-criteria optimization for fluids requires predictive models for all properties. Especially if possible candidates include those not even synthesized yet, models based on nothing but the molecular structure are mandatory.

In this study we present a model for the lubricity, quantified by high frequency reciprocating rig (HFRR)¹ measurements, utilizing the 'Conductor-Like-Screening-Model'² (COSMO) and a sigma-moment-QSPR³ approach based on the 'Conductor-Like-Screening-Model-for-Real-Solvents'⁴ (COSMO-RS). The latter provides us with

descriptors for the screening charge density of a given molecule taken from quantum mechanical density functional theory calculations.

Increasing computational power boosts the usage of quantumchemical (QM) calculations related to engineering tasks⁵. In principle QM calculations are capable of generating very accurate results. Their use for engineering tasks is generally limited due to two main reasons.

First, calculations taking more than just a few small molecules into account are too time consuming to be performed on a high level. Low level methods include severe simplifications which influences on the desired target value have to be checked very carefully⁶. QM methods are well established for calculations in the gas phase as the molecules can be calculated separately. Calculations involving liquid phases with considerable intermolecular interactions have to be treated in a special way⁷.

One of the methods approximating the energetic behavior of a molecule in liquids is COSMO. It places the molecule in an ideal screening conductor which replaces the ambient liquid and scales the resulting energy and surface charge by a function of the permittivity of the liquid. Additionally, temperature effects have to be taken into account when modeling thermodynamic effects. This has to be done in subsequent steps. For the aforementioned COSMO this can be done by COSMO-RS.

The second main limitation is that the problem has to be well defined on a molecular scale. Engineering tasks are per definition very application-oriented, so that target functions are often quite diffuse and consist of collective terms including a diversity of effects, e.g. in our case one has to deal with poorly quantifiable terms like 'lubricity' or 'scuffing' which rather belong to

'industrial tribology' than to the science of friction and wear. For instance Appledorn⁸ gives the following definition of lubricity in the context of fuels: "if two liquids have the same viscosity, and one gives less friction, wear or scuffing, it is said to have better lubricity". This broad definition does not distinguish between friction-modifying, wear-resistance and anti-scuff ability of a fluid. They do not coincide in many cases. Regardless of a serious lack of an precise scientific definition, engineers developed different test rigs to assess this 'unknown' quality striving to predict the wear rate in fuel injection systems^{9,10}. On the other hand, the diversity of phenomena behind boundary lubrication and its underlying mechanisms of adsorption/reaction layers are far away from being well enough understood to fill the gap between the QM scale and durability of fuel-lubricated injection systems.

From the modeling point of view, it is a very challenging task to combine the different phenomena. A physically rigorous connection to the shape of molecular orbitals is by far not obvious (if possible at all) and stretches across huge time and length scales. In general, the more practical a given problem is, the more difficult it gets to establish a physically sound model with sufficient power to predict the desired property, due to effects not known to a quantifiable degree.

Therefore QSPR approaches are used to take advantage of ones chemical and physical intuition (or huge databases) for choosing numerous molecular descriptors which are supposed to influence the desired quantity. Besides convenient obtainable descriptors (molecular weight, molecular volume, etc.), descriptors can be gained from quantum mechanical computations (multipole moments, HOMO-LUMO-gap, electron density distribution, etc.). This is

done mostly by performing a simple multi-linear regression of a measured target value believed to represent the desired property to the descriptors. Consequently those methods are also used to generate molecular descriptors to correlate lubrication related phenomena.

1.2 QM-based QSPR for lubrication related problems

QSPR-models using molecular descriptors have recently found an applicability in lubrication related phenomena, e.g. Koshima¹¹ used a QSPR describing anti-shudder performance of different fluids in lock-up clutches as a function of hydrogen bond strength, dipole moment and values for different functional groups.

As stability of lubricants is essential to its practical use, Jayadas¹² investigated orbital energies and net electric charges of polar headgroups for the prediction of corrosion characteristics of biodegradable lubricants.

Huang¹³ found that the trend predicted from molecular descriptors like HOMO-LUMO-GAP, net electric charge of bonding atoms and the superdelocalizability is in good accordance with tribological tests gained from different measurement techniques for 3-(N,N-dibutyldithiocarbamate-yl)maloic acid and 3-(N,N-dibutyldithiocarbamate-yl) propionic acid when assuming a direct interaction with a naked metallic surface.

A QSPR-model for the direct prediction of the wear scar diameter gained from HFRR measurements (WSD) for mixtures of hydrocarbons has recently been presented by Lodrigueza¹⁴. The usage of 28 descriptors is recommended for good results, which leads to a coefficient of deter-

mination of $R^2 = 0.6656$ for 214 diesel-mixtures. For screening purposes this method is not applicable as it relies on characteristic absorbance values obtained from mid-infrared spectroscopy. The same applies to a neural network based prediction of diesel fuel lubricity presented by Korres et.al.¹⁵. Although it achieves a very good correlation coefficient of $R^2 = 0.94$ for a test set, the input variables for their model are conductivity, density, viscosity, sulfur content, and 90% recovery temperature which have to be measured.

In general the exact structural composition of the surface in real applications is mostly unknown. Solely the bulk composition is usually known and the fact that the surface consists of blank, oxidized and hydrolized patches. The amount of surface fractions of each of those types is probably a process variable, e.g. the exposure time being sufficient for oxidation, the amount of water in the lubricant/atmosphere¹⁶, etc. This lack of information limits a rigorous modeling, even for the standardized fuel lubricity measurements.

Since we aim at introducing some physical knowledge into our QSPR model instead of using it purely as a statistical data mining tool, we have to make assumptions concerning the physical effects governing lubricity, as explained in the following section.

2 Theoretical basis

Aiming for a model that predicts the lubricity requirements in injection pumps we have chosen the HFRR method which was selected in a 'round-robin' evaluation of several lubricity-testing methods for an ISO standard for diesel fuel¹⁰. In a HFRR measurement a 2 ml test sample is main-

tained at a temperature of 60°C. In the sample a 6 mm steel ball with an external load of 200 g oscillates on a plate at 50 Hz with a stroke length of 1 mm for 75 minutes. The contact is fully immersed in fuel. This test is able to differentiate between different additive molecular structures⁹.

Knothe^{17,18} studied the effect of molecular structure on lubricity of petrodiesel and biodiesel components as well as molecules consisting of ten and three carbon atoms with different functional groups experimentally. Their experimental results are used as the initial point for the development of our prediction model. Our 'lubricity' is the inversal length of a wear scar taken from HFRR measurements.

In order to establish a structure property relationship regarding lubricity, the existing models for the impact of molecular structure on friction, wear and scuffing in boundary lubrication have to be taken into account. This is important to derive the essential information from electron charge density adapted to specific lubrication applications. Regarding friction there are various models which are based on the theory of reversible adsorption, describing the effect of different additive molecular structures on the friction coefficient. Beltzer et al.¹⁹ present a model for the effect of additive molecular structure on friction. They discuss the adsorption of linear molecules with polar functional groups on a hydroxylated iron oxide and state that adhesive interactions between the adsorbate and the surface, as well as the lateral interaction between the neighboring adsorbate molecules are the two major interaction energies determining the friction-modifying properties. The polar functional group is said to be bound to the surface with an adhesive hydrogen bond. According to the type of adjacent functional groups, these

can establish a repulsive or cohesive dipole-dipole interaction. Additionally there is a Van-der-Waals dispersion force between nonpolar chain tails. These interactions also determine the shape of the adsorption isotherm which is closely connected to examined friction force^{19,20}. Rowe²¹ proposed a model for the prediction of wear based on adsorption theory in which the wear volume is described as a function of molecular characteristics which involve diameter and area associated with the molecule, energy of adsorption, and fundamental time of vibration of the molecule in the adsorbed state. Beerbower²² reviewed the models of Rowe and included additional relations for assessment of molecular parameters in this model.

Our basic assumption is a tight relation of the inversal wear scar diameter (WSD) to the change of the chemical potential of an adsorbing compound. This change has been shown to be closely related to the so called 'sigma-moments' obtained from the QM-based model 'COSMO-RS'³. Nevertheless, HFRR lubricity of various types of compounds can be a complex result of different parallel and subsequent effects in different scales, like multi molecular film formation²³, fractionation of polar and highly viscous compounds near the surface²⁴, polymerisation²⁵, alteration of the chemical composition of the surface during wear, catalytic effects of the surface²⁶, reaction layers, chemisorption and formation of metal soaps²⁷ and layering transition^{29,30}, just to mention a few. Even though our model does not describe those effects explicitly, there is still hope be useful due to a somewhat included reactivity; e.g. as far as the surface screening charge distribution determines the affinity to other molecules. The higher this affinity the higher the chance of a reaction.

2.1 COSMO-RS and corresponding sigma moment QSPR

COSMO-RS utilizes the surface screening charge distribution (SSCD) of a molecule obtained with the COSMO-method to calculate thermodynamic properties⁴. The SSCD for a molecule is calculated in a cavity placed in an ideally conducting continuum. These are calculated from quantum-mechanically computed electron densities (BP-RI-DFT with TZVP-basis set³¹) inside the cavity. The cavity is built of slightly modified Van-der-Waals spheres around the atoms³². This approach is referred to as 'COSMO' resulting in a so called COSMO-file for a molecule². To take temperature effects into account, the ensemble of interacting molecules is considered as an ensemble of pair-wise interacting surfaces with the screening charge density distribution taken from the aforementioned COSMO-file⁴. The chemical potential of a molecule in a given mixture can be calculated subsequently from statistical thermodynamics³³. By the difference of the pseudo-chemical (non-ideal) potential of a molecule in different phases, partition coefficients can be calculated by simple thermodynamics if the molecular composition of the phases and the structure of the molecules are known. This is especially suitable for screening purposes³⁴. If the exact structure is not known, the calculation of partition coefficients is still possible using a COSMO-RS based QSPR³⁵, known as 'sigma-moment-COSMO-RS', but experimental data is needed once to parameterize the model (as for every QSPR method). Further the model has also been successfully used to predict adsorption coefficients on poorly defined matrices like e.g. ac-

tive carbon³ or soil³⁶. For heterogeneous solid surfaces in fuel applications like those of iron-oxide or carbon coatings this approach is promising. The histogram plotting the surface $p^X(\sigma)$ per screening charge over the SSCD is called σ -profile, which is characteristic for a certain molecule X. As a distribution function can be determined by its statistical moments (If those exist and the moment generating function converges) this can also be done for the σ -profile. As shown by Klamt⁷, the partition or adsorption coefficient K can be written as a function of its sigma-moments M_i^X and characteristic coefficients $c_{S,S'}^i$ for the partitioning (or adsorbing) phases S and S':

$$-RT \ln K = c^{S,S'} + \sum_i c_i^{S,S'} M_i^X$$

The sigma-moments of the molecule X are calculated from its convoluted σ -profile $p^X(\sigma)$ and a sigma function $f_i(\sigma)$:

$$M_i^X = \int p^X(\sigma) f_i(\sigma) d\sigma$$

The sigma functions are simple polynomic functions $f_i(\sigma) = \sigma^i$ with $i \geq 1$ (for $i = 0$ one obtains the total COSMO surface which is also often included in a QSPR regression). The first order moment is the total charge which vanishes for molecules, the second order moment is a measure for the ability of a solute to interact with a polarizable continuum. Higher order moments lack simple physical analogues⁷. To take hydrogen bonding capabilities of a molecule into account, for SSCD exceeding a given threshold σ'_{hb} special functions $f_{acc/don}(\sigma) = \pm\sigma - \sigma'_{hb}$ are used to provide 'hydrogen bonding moments' $M_{acc/don}$ if $\pm\sigma > \sigma'_{hb}$. The threshold value σ'_{hb} for $M_{acc/don,2}$, $M_{acc/don,3}$ and $M_{acc/don,4}$ is $\sigma'_{hb} = 1.0 \text{ e/nm}^2$, $\sigma'_{hb} = 1.2 \text{ e/nm}^2$, and $\sigma'_{hb} = 1.4 \text{ e/nm}^2$, respectively. Addition-

ally these are combined with a parabolic smoothing around the edges. In the applied implementation of COSMO-RS, COSMOtherm, the screening surface charges in electron per Angström ($e/\text{\AA}^2$) are multiplied by 100 to gain more handy values in the order of one. The resulting σ -moments computed by COSMOtherm C21 0108³⁷ are taken here as is.

3 Modeling

The HFRR lubricity data is taken from the investigations of Knothe^{17,18} on lubricity of petrodiesel and biodiesel components. In contrast to the conventional method, in our model the measured average wear scar diameter on the plate is used as input value for the correlation. Since the ball is harder, according to our observation very often only a kind of mild polishing on the ball can be detected for high lubricity fuels. This makes the interpretation of the real boundaries of the wear scar unfeasible. The main reason for taking the plate values however, is the intended inclusion of lubricants like e.g. oleic acid, which leaves no recognizable wear scar on the ball. Knothe gives a zero value for the ball wear scar, but a finite one for the plate. In general the wear scar diameter on the disc is an indirect measurement of WSD on the ball³⁸ and can be obtained using equations of Kalin³⁹ if needed.

In addition to the aforementioned sigma moments as descriptor we included several additional descriptors. E.g. the effect of chain length is investigated theoretically and experimentally in different applications for friction and wear²⁷. It is shown that tribological properties of homologous series of hydrocarbons, carboxylic acids and alcohols correlate with their chain length.

This has been ascribed to larger dispersion forces²⁰ which increase with an increasing molecular surface (proportional as a first approximation).

To include dispersion interactions we included the COSMO surface A_{COSMO} and, additionally, the COSMO volume V_{COSMO} as descriptors into the regression. The element-specific radii used to calculate volume and surface are strongly related to van-der-Waals radii, but multiplied with a factor of roughly 1.2 to match experimental free energy of solvation data with COSMO³²). Furthermore as the HFRR lubricity can be promoted by a partially hydrodynamic lubrication²⁸, we included the COSMO-RS predicted viscosity ν .

The sigma moments are a representation of the molecular SSCD-distribution. Initially the COSMO-RS-QSPR was developed for partition and adsorption phenomena for a given compound between unchanging phases. In our case one of the phase changes (i.e. our test fluid). To include possible effects by this change of the reference state we included the change of chemical potential $\Delta\mu$ from the COSMO state (molecule in ideal conductor) to the COSMO-RS state (molecule soluted in itself).

Deviations from ideal linear molecular shapes reduce the lubrication performance of an adsorbate. For instance when comparing tribological characteristics of various isomers of octadecanoic acids including a linear and a branched configuration, the linear molecule reveals an enhanced friction coefficient. For carboxylic acids, branched molecules seem to make a good surface coverage difficult²⁰. For the lubricity of hydrocarbon fuels, the HFRR-lubricity of linear alkanes are shown to be usually better than the lubricity of branched ones²⁹.

The shape of the molecule is not regarded

by COSMO-RS. As even the full, not to a QSPR-model simplified COSMO-RS is barely able to distinguish between the thermodynamics of branched and not branched molecules due to the loss of spatial information in the sigma profiles, we include a rough shape parameter 'sphericity' which can be also interpreted as inversal linearity. Sphericity relates the surface of a body X to the surface of a sphere of the same volume⁴⁰:

$$\Psi = \frac{\pi^{\frac{1}{3}}(6V_X)^{\frac{2}{3}}}{A_X}.$$

Finally we get the following multilinear correlation for the inversal wear scar in mm:

$$\frac{1}{WSD} = \sum_i c_i M_i^X + c_a A_{\text{COSMO}} + c_b V_{\text{COSMO}} + c_c \nu + c_d \Psi + c_e \Delta\mu$$

With six σ -moments, three hydrogen bond acceptor- and three hydrogen bond donor-moments, a total of 16 coefficients is available to perform the QSPR calculation. The QSPR coefficients for a certain property can be determined from a multilinear regression of the σ -moments with a sufficient number of experimental data from HFRR test. However, a multilinear regression is usually performed with a much lower number of descriptors than data points available to avoid overparameterization, so we reduced the number of parameters subsequently due to their significance ranked by their individual t -values⁴¹. This was done as long as the coefficient of determination R^2 (both, adjusted and not adjusted) had a value above 0.9.

The σ -moments are calculated via the COSMO-RS implementation COSMOthermX C21 0108³⁷. If available, the COSMO-files are taken from the COS-

MOlogic database (2008). Non-available molecules are assembled via Gaussview 5.0.8⁴⁴ and computed on a BP-RI-DFT level with a TZVP basis set using TURBOMOLE³¹. The generation of conformers was performed using COSMOconf 2.1. For the computation of the σ -moments solely those with a minimal COSMO-energy were regarded.

4 Results and Discussion

The above mentioned criteria reveal the following equation (resulting correlation depicted in Fig.1) for the lubricity in mm^{-1} of a molecule X:

$$\begin{aligned} \frac{1}{WSD} = & 1.836 \frac{1}{\text{mm}} + 1.600 \cdot 10^{-2} \frac{1}{\text{\AA}^2 \cdot \text{mm}} \left(\frac{\text{\AA}^2}{e} \right)^4 \cdot \\ & M_4^X - 1.342 \cdot 10^{-1} \frac{1}{\text{\AA}^2 \cdot \text{mm}} \left(\frac{\text{\AA}^2}{e} \right) \cdot M_{\text{acc}2}^X - 1.623 \cdot \\ & 10^{-1} \frac{1}{\text{\AA}^2 \cdot \text{mm}} \left(\frac{\text{\AA}^2}{e} \right) \cdot M_{\text{don}2}^X - 7.416 \cdot 10^{-4} \frac{1}{\text{\AA}^2 \cdot \text{mm}} \cdot \\ & A_{\text{COSMO}}^X - 9.726 \cdot 10^{-1} \frac{1}{\text{mm}} \Psi \end{aligned}$$

PLACE HERE: Fig.1: Prediction of the lubricity of petrodiesel and biodiesel components using five descriptors.

As 5 descriptors seem quite many for 28 observations, we further reduced parameters down to only one significant descriptor (and a constant for y-axis intercept) which leads to:

$$\frac{1}{WSD} = 9.474 \cdot 10^{-1} \frac{1}{\text{mm}} + 3.889 \cdot 10^{-3} \frac{1}{\text{\AA}^2 \cdot \text{mm}} \left(\frac{\text{\AA}^2}{e} \right)^4 \cdot M_4^X.$$

This simple equation still allows a rough categorization into good, average and poor lubricants as shown in Fig.2

PLACE HERE: Fig.2: Prediction of the

lubricity of petrodiesel and biodiesel components using one descriptor.

As in general the physical meaning of the sigma moments is not obvious and difficult to relate to known physical properties, one should be careful when interpreting the correlations mentioned above. Nevertheless some remarks shall be made here. The last remaining (fourth) sigma moment weights the strongly polar regions in a huge amount as it is built from the convolution of the sigma profile and the SSCD to the power of four. Even small but strongly polar regions of the molecular COSMO-surface produce high fourth moments. From that statement 'the more polar the better' seems reasonable. But as the sixth moment does not remain, which rates very small polar regions even higher, it seems that a larger and quite polar region is better for the lubrication ability than 'hot-spot' charges. This interpretation is backed up by the negative sign of the remaining hydrogen bonding moments in the first presented equation using five descriptors, which is even giving a penalty for too polar regions, i.e. alcohols perform worse than they should according to their polarity and their high 4th sigma moment. Not surprising is the remaining shape parameter in the regression, as the shape has a significant influence (see e.g. Tartaglino²⁹) and in our case, the less deviation from linear structure the better. At the end the total COSMO-surface remains as a significant parameter, in accordance to e.g. Sivebaek³⁰ who modeled and measured increasing lubricity with increasing chain length for hydrocarbons. In our model the sign points in the opposite direction. This might be needed to compensate the implicit inclusion of the surface in the remaining sigma moments. Additionally

the SSCD is lowered for a molecule with a given polarity if a molecule gets bigger.

According to Fig. 1 and Fig. 2 three different groups of lubricants can be distinguished by their wear protection, namely poor lubricants (I), average lubricants (II) and good lubricants (III). As 'poor lubricants' we have chosen those with $\text{WSD}^{-1} < 1.05 \text{ mm}^{-1}$. This relates to $\text{WSD}_{\text{average,plate}} > 950 \text{ } \mu\text{m}$ or rather to $\text{WSD}_{\text{average,ball}} > 460 \text{ } \mu\text{m}$ which is the maximum permissible wear scar for diesel fuel according to DIN EN ISO 12156-1. This group consists of typical petrodiesel components i.e. different, oxygen free carbohydrates. These are most susceptible to the reduction of the model to just one descriptor. The σ -profile is in general very similar for different, pure carbohydrates. As depicted in Fig.3 this is also the case for the ones regarded in this study. The screening charge densities are centered around zero charge, rarely exceeding $\pm 0.5 \text{ e/nm}^2$. As the surface screening charge distribution is nearly identical, the sigma moments derived from the sigma profile can barely distinguish one pure carbohydrate from another. For those molecules adding size and shape descriptors is essential and in this cases the shape parameters are particularly relevant. In our model there is nearly no distinction between alkenes, so the biggest deviation is for 1-dodecene with a predicted lubrication of $\approx 1 \text{ mm}^{-1}$ but a much lower measurement value of $\approx 0.85 \text{ mm}^{-1}$. We expected this molecule to perform better than the saturated hydrocarbons, alongside with the other alkenes in the set, located in the better region around 1 mm^{-1} , but slightly worse than those due to its shorter chain length. This is especially surprising as 1-tetradecane is the best lubricant in this group, this deviation might be due to measurement artifacts or, obvi-

ously, a lubrication mechanism unknown to us. According to Knothe¹⁷ the purities of the lubricants under investigation vary between $\geq 98\%$ and $\geq 99\%$. As especially for pure hydrocarbons a few ppm of good lubricating substances (e.g. fatty acids) raise the lubricity considerably^{42,43}, the HFRR measured WSD values might be shifted. The deviations mentioned could be artifacts caused by impurities.

PLACE HERE: Fig.3: Screening charge surface distribution for poor lubricants, i.e. regarded alkanes, alkenes.

Average lubricants ($1.05 \text{ mm}^{-1} < \text{WSD}_{\text{average,plate}}^{-1} < 1.40 \text{ mm}^{-1}$) in this study consist mostly of monofunctional, saturated and non-saturated methyl- and butylesters and one alcohol (oleyl-alcohol). As can be taken from their surface screening charge histogram depicted in Fig.4 all molecules in this group show a higher polarity in comparison to the poor lubricants depicted in Fig.3.

PLACE HERE: Fig.4: Screening charge surface distribution for average lubricants, i.e. esters and alcohols.

Although the group of average lubricants already fulfill the minimal lubricity requirements, there are even better lubricants. We grouped together those 'good lubricants' with lubricities better than $1.40 \text{ mm}^{-1} \text{WSD}^{-1}$ ($\hat{=}\text{WSD}_{\text{average,plate}} < 715 \text{ }\mu\text{m} \hat{=}\text{WSD}_{\text{average,ball}} < 230 \text{ }\mu\text{m}$). In addition to two monofunctional esters, this group consists of multifunctional esters (see Fig.5). The lubricity of monofunctional esters in this group is underestimated by our model and methylolinolenat is the main outlier from our 'groups'. As this molecule shows no significant deviation in its molec-

ular structure compared to the other esters in the data set, there seems to be no obvious reason for its better lubrication ability. Further on the fatty acids of the test set can be found here which are known in literature for their excellent lubrication and wear protection abilities⁴³, and even our model reduced to one descriptor predicts the same.

PLACE HERE: Fig.5: Screening charge surface distribution for good lubricants, i.e. esters and fatty acids.

Apart from this model working quite well for typical petro- and biodiesel components as summarized by Knothe¹⁷, an application to his data set of C_{10} oxygenated compounds, diethylene glycol diethyl ether, C_3 compounds and carbonates was not fully successful, neither in combination with the petro- and biodiesel components nor as a separate model. Whereas carbonates and monofunctional ethers can be described well, multi functional-components are problematic. Most of the latter consist of a chain of three carbon atoms and functional groups of the form $\text{CH}_2\text{R}_1 - \text{CHR}_2 - \text{CH}_2\text{R}_3$ with different combinations of the remaining OH, SH, and NH_2 . As the COSMO-RS surface screening charge histogram does not include any geometric information, it is most likely that the bonding probability due to adjacent groups as they are present in the C_3 components is underestimated. Such an effect is a known weakness of COSMO-RS and has been mentioned for acetic-acid which forms stable dimers due to two cooperative hydrogen bonds⁷. Cooperative effects can therefore not be described by this model. Thus a failure of our approach for such components is not surprising. Hence one should apply the presented model to multi-functional com-

ponents with care only.

In the following, more general limitations of our approach will be discussed. One of them is quite obvious, that the structure of the molecule has to be known for the lubricants. In fact, it usually is known when starting the HFRR or similar lubrication measurement. But due to unknown possible reaction paths, the exact structures of reaction products may be unknown and diverse, therefore these cannot be modeled. Particularly vegetable oils are known for their low thermal, oxidative and hydrolytic stability and for different types of esters lubrication dominating reactivities have been described previously^{45,46}. In the end HFRR-lubricity results are, like many other tribological tests, influenced by many different mechanisms discussed before and this allows a direct interpretation of a QSPR model only with certain assumptions and reservations. The presented QSPR model focusses solely on COSMO / COSMO-RS calculations which (as any QSPR approach) can easily be enhanced by several additional descriptors. Beneath a more profound shape parameter than the 'sphericity' used here, a promising descriptor might be the binding energy per unit area for a given lubricant with a characteristic surface (e.g. iron oxide). It is pointed out by Persson et.al.⁴⁷ that the barrier for nucleating the squeeze-out of the final, wear preventing, molecular monolayer depends on the binding energy per unit area of the adsorbed film. To maintain the predictivity of the model, this binding energy could be computed by quantum chemical density functional theory. However, as the relative arrangement of the adsorbate to the adsorbing surface is not known a priori, reasonable assumptions about possible configurations and their respective statistical weight have to be made.

5 Conclusion

We present a fully predictive, COSMO-RS-based QSPR model, describing lubrication abilities of mono-functional bio- and petrodiesel components based on the surface screening charge density distribution of a molecule. This is represented by chosen statistical moments of its histogram, called σ -moments. As target lubricity property we have chosen reciprocal plate wear scar diameter data from literature. For typical petro- and biodiesel components the model allows a good categorization into good, mediocre and poor lubricants. For lubricants with very similar screening charge distributions like alkanes, additional parameters are needed. The applied shape parameter seems feasible but worthy to be improved. But, even when no shape parameter is included, just one σ -moment allows a rough categorization of the aforementioned groups. However, as the bio- and petrodiesel correlations are successful, a transfer to multi-functional molecules should be done carefully as the model fails to describe the lubricity of specific C₃ and C₁₀ components. Subsuming, the models allow a good estimation for screening purposes, but outliers are possible. Consequently experiments validating promising screening results are still necessary but the experimental effort can be significantly reduced to promising candidates.

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ties.

Abbreviations

BP-RI-DFT - Becke-Perdew resolution of identity density functional theory

COSMO - conductor-like screening model

COSMO-RS - conductor-like screening model for realistic solvation

HFRR - high frequency reciprocating rig

HOMO - highest occupied molecular orbital

LUMO - lowest unoccupied molecular orbital

SSCD - surface screening charge distribution

TZVP - triple zeta valence polarization

QM - quantum chemical

QSPR - quantitative structure-property relationship

WSD - wear scar diameter

References

- [1] ASTM D-6079-99, 1999 ASTM Annual Book of Standards, American Society for Testing and Materials, West Conshohocken, PA.
- [2] Klamt A., Schürmann G., COSMO: A New Approach to Dielectric Screening in Solvents with Explicit Expressions for the Screening Energy and its Gradient, *J. Chem. Soc. Perkin Trans.* **1993**; **2**, pp. 799-805 DOI: 10.1039/P29930000799
- [3] Mehler C., Klamt A., Peukert W., Use of COSMO-RS for Prediction of Adsorption Equilibria, *AIChE Journal* **2002**; **48(5)**, pp 1093-1099, DOI: 10.1002/aic.690480518
- [4] Klamt A., Eckert F., COSMO-RS: A novel and efficient method for the a priori prediction of thermophysical data of liquids, *Fluid Phase Equilibria* **2000**; **172(1)**, pp. 43-72, DOI: 10.1016/S0378-3812(00)00357-5
- [5] Sandler SI., Quantum mechanics: a new tool for engineering thermodynamics, *Fluid Phase Equilibria* **2003**; **210(2)**, pp. 147-160, DOI: 10.1016/S0378-3812(03)00176-6
- [6] Schwabe T., Grimme S., Theoretical Thermodynamics for Large Molecules: Walking the Thin Line between Accuracy and Computational Cost, *Accounts of chemical research* **2008**; **41(4)**, pp. 569-579, DOI: 10.1021/ar700208h
- [7] Klamt A., Cosmo-RS: From Quantum Chemistry to Fluid Phase Thermodynamics and Drug Design, ISBN-13: 978-0444519948, 2005
- [8] Appledorn JK., Dukek WG., Lubricity of Jet Fuel, SAE Technical Paper 660712, **1966**
- [9] Bovington C., Caprotti R., Meyer K., Spikes HA., Development of laboratory tests to predict the lubricity properties of diesel fuels and their application to the development of highly refined diesel fuels, *Tribotest* **2006**; **2(2)**, pp. 93-112 DOI: 10.1002/tt.3020020202
- [10] Lacey PI., Howell SA., Fuel lubricity reviewed, SAE Technical Paper Series 982567, **1998**
- [11] Koshima H., Tsubouchi T., Ichihashi T., Hisaeda Y., Antishudder Performance of Low-Molecular-Weight Alkenylsuccinimides, *Tribology Online* **2008**; **3(6)**, pp. 328-332, DOI:10/2474.trol.3.328
- [12] Jayadas N.H., Prabhakaran Nair K., Elucidation of the Corrosion Mechanism of Vegetable-Oil-Based Lubricants, *Journal of Tribology* **2007**; **129**, pp. 419-423, DOI: 10.1115/1.2464133
- [13] Huang W., Tan Y., Chen B., Dong J., Wang X., The binding of anti-wear additives to iron surfaces: quantum chemical calculations and tribological tests, *Tribology International*, **2003**; **36(3)**, pp.163-168 DOI: 10.1016/S0301-679X(02)00130-5
- [14] Lodrigueza EA., Method for Prediction of High Frequency Reciprocating Rig Wear Scar Diameter for Hydrocarbon Mixtures **2008**, United States Patent Application Publication, Pub. No.: US 2008/0090302 A1

- [15] Korres DM., Anastopoulos G., Lois E., Alexandridis A., Sarimveis H., Bafas G., A neural network approach to the prediction of diesel fuel lubricity, *Fuel* **2002**; **81**, pp. 1243-1250, DOI: 10.1016/S0016-2361(02)00020-0
- [16] Shaver DB., Giannini RM., Lacey PI., Erwin J., Effects of Water on Distillate Fuel Lubricity, SAE Technical Paper Series 982568, **1998**
- [17] Knothe G., Steidley KR., Lubricity of components of biodiesel and petrodiesel. The origin of biodiesel lubricity. *Energy & Fuels* **2005**; **19(3)**, pp. 1192-1200, DOI: 10.1021/ef049684c
- [18] Knothe G., Evaluation of ball and disc wear scar data in the HFRR lubricity test, *Lubrication Science* **2008**; **20**, pp. 35-45, DOI:10.1002/lc.51
- [19] Beltzer M., Jahanmir S., Effect of molecular structure on friction; *Lubrication Science* **1998**; **1(1)**, pp. 3-26, DOI: 10.1002/lc.3010010103
- [20] Jahanmir S., Beltzer M., An adsorption model for friction in boundary lubrication, *ASLE transactions* **1985**; **29(3)**, pp. 423-430, DOI: 10.1080/05698198608981704
- [21] Rowe CN., Role of Additive Adsorption in the Mitigation of Wear, *ASLE Transactions* **1969**; **13(3)**, pp. 179-188 , DOI: 10.1080/05698197008972294
- [22] Beerbower A., A Critical Survey of Mathematical Models for Boundary Lubrication, *ASLE Transactions* **1970**; **14(2)**, pp. 90-104 DOI: 10.1080/05698197108983231
- [23] Ratoi M., Anghel V., Bovington C., Spikes HA., Mechanisms of oiliness additives, *Tribology International* **2000**; **33(3-4)**, pp. 336-345, DOI:10.1016/S0301-679X(00)00037-2
- [24] Guangteng G., Spikes HA., Fractionation of liquid Lubricants at Solid Surfaces, *Wear* **1996**; **200(1-2)**, pp. 336-345, DOI: 10.1016/S0043-1648(96)07268-7
- [25] Furey MJ., Kajdas C., Kemplinski R., Applications of the Concept of Tribopolymerisation in Fuels, Lubricants, metalworking, and minimalist Lubrication, *Lubrication Science* **2002**; **15(1)**, pp. 73-82, DOI: 10.1002/lc.3010150106
- [26] Hsu SM., Gates RS., Boundary Lubrication and boundary lubricating films, in: B. Bhushan, *Modern tribology handbook*, vol. I, CRC Press, Boca Raton, 2001, pp. 455-492
- [27] Bowden FP., Tabor D., *Friction and Lubrication of Solids*, Clarendon Press, Oxford, 2008
- [28] Wei, D. P. , Spikes, H. A. and Korcek, S.(1999) 'The Lubricity of Gasoline', *Tribology Transactions*, 42: 4, 813 - 823,
- [29] Tartaglino U., Sivebaek IM., Persson BNJ., Tosatti E., Impact of molecular structure on the lubricant squeeze-out between curved surfaces with long range elasticity, *The journal of chemical physics* **2006**; **125**, 014704, DOI: 10.1063/1.2210008
- [30] Sivebaek IM., Samoilov VN., Persson BNJ., Squeezing molecular thin alkane lubrication films between

- curved solid surfaces with long-range elasticity: Layering transitions and wear, *Journal of Chemical Physics* **2003**; **119(4)**, pp. 2314-2321, DOI:10.1063/1.1582835
- [31] Ahlrichs, R., Bär M., Häser M., Horn H., Kölmel C., Electronic Structure Calculations on Workstation Computers: The Program System TURBOMOLE, *Chem. Phys. Letters* **1989**; **162(3)**, pp. 165-169, DOI: 10.1016/0009-2614(89)85118-8
- [32] Klamt A., Jonas V., Bürger T., Lohrenz J.C.W., Refinement and Parametrization of COSMO-RS, *J. Phys. Chem. A* **1998**; **102**, pp. 5074-5085, DOI: 10.1021/jp980017s
- [33] Klamt A., Krooshof GJP., Taylor R., COSMOSPACE: Alternative to Conventional Activity-Coefficient Models, *AIChE Journal* **2002**; **48(10)**, pp. 2332-2349, DOI:10.1002/aic.690481023
- [34] Spiess AC., Eberhard W., Peters M., Eckstein MF., Greiner L., Büchs J., Prediction of partition coefficients using COSMO-RS: Solvent screening for maximum conversion in biocatalytic two-phase reaction systems, *Chemical Engineering and Processing* **2008**; **47(6)**, pp. 1034-1041, DOI: 10.1016/j.cep.2007.02.007
- [35] Wichmann K., Diedenhofen M., Klamt A., Prediction of Blood-Brain Partitioning and Human Serum Albumin Binding Based on COSMO-RS Sigma-Moments, *J. Chem. Inf. Model.* **2007**; **47(1)**, pp. 228-233, DOI: 10.1021/ci600385w
- [36] Klamt A., Diedenhofen M., Prediction of Soil Sorption Coefficients with COSMO-RS, *J. Chem. Environmental Toxicology and Chemistry*, **2002**; **21**, pp. 2562-2566
- [37] Eckert F., Klamt A., *COSMOtherm, Version C2.1*, Release 01.08', COSMOlogic GmbH & Co. KG, Leverkusen 2008
- [38] Lacey PI., Shaver DB., Evaluation of the Wear Mechanisms Present in the HFRR, *2nd International Colloquium, Esslingen*, January 1999
- [39] Kalin M., Vizintin J., Use of equations for wear volume determination in fretting experiments, *Wear* **2000**; **237(1)**, pp. 39-48, DOI: 10.1016/S0043-1648(99)00322-1
- [40] Wadell H., Volume, shape and roundness of quartz particles, *Journal of Geology* **1935**; **43**, pp. 250-280
- [41] Press WH., Teukolsky, SA., Vetterling WT., Flannery BP. *Numerical Recipes in C++*, Cambridge University Press; 2002, New York
- [42] G. Anastopoulos, E. Lois, F. Zannikos, S. Kalligeros, C. Teas, HFRR lubricity response of an additized aviation kerosene for use in CI engines, *Tribology International* 35:599-602 (2002); DOI: 10.1016/S0301-679X(02)00050-6
- [43] Kajdas C., Maizner M., Boundary Lubrication of Low-Sulphur Diesel Fuel in the Presence of Fatty Acids, *Lubrication Science*, **2006**; **14(1)**, pp. 83-108, DOI: 10.1002/ls.3010140107
- [44] Frisch MJ. et. al., *Gaussian 09*, Gaussian, Inc., Pittsburgh PA, 2009

- [45] Adhvaryu A., Erhan SZ., Epoxidized Soybean Oil as a Potential Source of High Temperature Lubricants, Industrial Crops and Products **2003; 15(3)**, pp. 247-254, DOI: 10.1016/S0926-6690(01)00120-0
- [46] Zeman A., Sprengel A., Niedermeier D., Spth M., Biodegradable Lubricants - Studies on Thermo-Oxidation of Metal-Working and Hydraulic Fluids by Differential Scanning Calorimetry (DSC), Thermochim. Acta. **1995; 268**, pp. 9-15, DOI: 10.1016/0040-6031(95)02512-X
- [47] Persson, B.N.J., Mugele, F., Squeeze-out and wear: Fundamental principles and applications, Journal of Physics: Condensed matter **2004; 16**, R295–R355

Figures

Figure 1: Fig.1: Prediction of the wear resistance of petrodiesel and biodiesel components using five descriptors

Figure 2: Fig.2: Prediction of the wear resistance of petrodiesel and biodiesel components using one descriptor

Figure 3: Fig.3: Screening surface charge density distributions of poor lubricants (Group III) and their related lubricity in 1/mm

Figure 4: Fig. 4: Screening surface charge density distributions of mediocre lubricants (Group II) and their related lubricity in 1/mm

Figure 5: Fig.5: Screening surface charge density distributions of good lubricants (Group I) and their related lubricity in 1/mm