

## Molecular Characterization of Lubricant Degradation Produced in a Tribological Wear Test Using TOF-SIMS Imaging MS

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We have studied the effects of friction, produced in the course of a tribological wear test, on unsaturated fatty acids and saturated methyl esters used as lubricants in diesel fuel. The fatty acid and methyl ester additives provide necessary lubricating properties, and there is evidence of a protective tribochemical film that forms on metal contact surfaces when using fatty acid enriched biodiesel fuels. Prior investigation [1] has revealed that the presence of methyl esters alone reduces the frictional coefficient by 30%, while the addition of fatty acids can further reduce the frictional coefficient by up to another 50%. X-ray photoelectron spectroscopy (XPS) analysis of wear test specimens has indicated the evolution of a slightly dielectric tribo film in low wear areas. The dielectric tribo film was marked by increased hydroxyl and carbonyl functionality as well as decreased ester functionality compared to the initial surface.

The present study focuses on the application of time-of-flight SIMS (TOF-SIMS) to determine the molecular evolution of lubricants used in biodiesel fuel and the potential metal-organic reaction products leading to formation of a tribo film. The test specimens were produced on a reciprocating cylinder-on-flat tribometer with conditions intended to simulate the piston-cylinder contact geometry and dynamics that are typical of an internal combustion engine. A conventional diesel fuel (i.e. no addition of fatty acid methyl ester) was used for the present testing so as to isolate the molecular evolution of the fatty acid lubricants under the test conditions. The lubricants consists of C<sub>18</sub> fatty acids, with one or two unsaturations, at a concentration of 800 part-per-million (ppm).

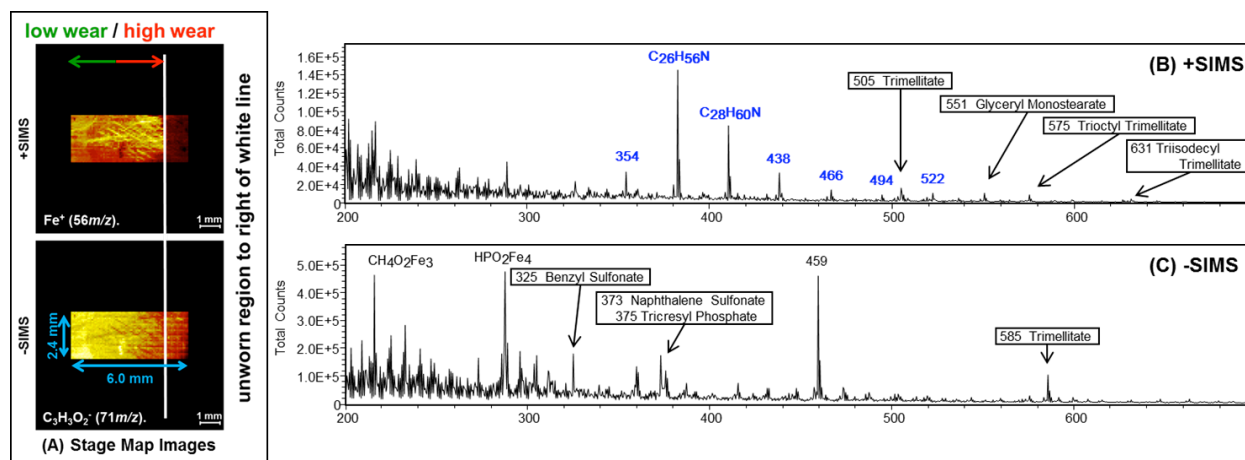
The TOF-SIMS analysis was performed using a PHI *nanoTOF II* instrument equipped with a Bi cluster liquid metal ion gun (LMIG). The TRIFT mass spectrometer of the *nanoTOF II* provided an advantage for this study in that the wear track topography is effectively decoupled from the molecular characterization and imaging. High resolution molecular identification and imaging was accomplished using the HR<sup>2</sup> imaging mode of the *nanoTOF II*'s newly designed LMIG which achieves a spatial resolution ( $\Delta z$ ) of approximately 400 nm at a mass resolution ( $m/\Delta m$ ) of approximately 10,000 using a high analytical beam current. The HR<sup>2</sup> imaging mode was an indispensable resource for high resolution molecular identification and imaging.

There were no intact fatty acid lubricants observed on the wear test specimens, even outside the wear track area. The larger molecular decomposition fragments of the fatty acid lubricants were observed in the low wear regions of the wear track. Rearrangement products of the fatty acid lubricants were observed at the greatest concentrations localized to the high wear regions of the wear track. The fatty acid lubricants appear to transform in the presence of heat and oxygen to a mellitate-like intermediate in the process of forming the protective tribo film. Other rearrangement products, ostensibly formed with traces of sulphur and phosphorous that were clearly observed in the metal, include benzyl, cresyl, and naphthyl sulfonates and phosphates. The presence of the mellitates along with the benzyl, cresyl, and

naphthyl side groups indicates a high degree of reduction and cyclization that evolved from the initial fatty acid lubricant additives.

References:

[1] J.M. Martin *et al*, Friction **1** (2013) p. 252.



**Figure 1.** (A) Stage raster mosaic map images of the tribological wear track area in the positive ion polarity (top; Fe<sup>+</sup>, 56 m/z) and the negative ion polarity (bottom; C<sub>3</sub>H<sub>3</sub>O<sub>2</sub><sup>-</sup>, 71 m/z). The total map area is 6.0 x 2.4 mm<sup>2</sup>, and the image is binned down to 256 x 256 pixels. High wear and low wear regions are indicated, and the region to the right of the white line is outside the wear track. (B) Positive ion polarity mass spectrum in the range of m/z = 200 – 700 from the entire image area. Peaks indicated with blue labels are a series of neutral C<sub>2</sub>H<sub>4</sub> losses ( $\Delta m = -28.0316$ ) with the highest m/z peak arising at C<sub>36</sub>H<sub>76</sub>N<sup>+</sup>. Various mellitate species appear at higher mass-to-charge ratios. (C) Negative ion polarity mass spectrum in the range of m/z = 200 – 700 from the entire image area. The mellitate, sulfonate, and phosphate moieties are identified.