544c Design of New Lubricant Formulations through Mechanistic Modeling

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Lubricants play a critical role in sustaining machinery with moving parts. Typical lubricants such as motor oils and greases are often used at elevated temperatures and are highly susceptible to oxidative degradation. Degraded lubricants have reduced functionality and contribute to shorter part lifetime and increased wear. The link between such tribological failures and the economy is clear; conservative estimates state that up to 1% of the GDP of developed nations (over $100 billion for the US alone) could be saved through increased attention to friction and wear. Frictional energy losses in automotive engines alone count for over $12 billion in wasted fuel costs. Given these, there is clearly a strong motivation for continued improvement in lubricant formulations. This presentation outlines our efforts in unraveling the fundamental chemistry of the oxidative degradation process as a means to developing more robust lubricant formulations.

Automated mechanism generation is an essential tool to be able to create mechanistic models of lubricant degradation chemistry. Thus far, modelers have only used pathways-based or “lumped” methods in modeling the oxidative degradation of lubricants. These approaches have provided tremendous insight into the major pathways for lubricant degradation. However, lubricants are a complex mixture of different hydrocarbons, and degradation products introduce new functionalities into the lubricant formulation that may have a significant impact on the performance of the lubricant or secondary degradation routes. In order to account for different reactivities of individual molecules and the role of secondary reactions, it would be valuable to have a mechanistic model of lubricant degradation chemistry. It is prohibitive to generate these models by hand. We have developed an approach based on the principles of graph theory that represents chemical species and reactions mathematically so that large reaction mechanisms can be generated automatically via computer. Only the input chemicals and allowed reaction types need to be specified, and the full reaction network is created. The reaction network may then be coupled with reactor design equations which model autoxidation conditions in real systems, thus allowing features of lubricant degradation to be predicted.

The major types of elementary steps underlying oxidative degradation are well known in the literature. These steps provide the starting point for defining the reaction families used in mechanism generation. In particular, the following reaction families have already been formulated: hydrogen abstraction, oxygen addition, radical recombination, bond fission, b-scission, and numerous hydrogen shift and disproportionation reactions. Additionally we have found, consistent with prior observations, that a bimolecular peroxide decomposition process is very important in producing alkoxy radicals. Rate constant correlations have been developed for gas-phase chemistry for the majority of these reaction families, and their extensibility to condensed phase chemistry has been tested. Application of automated mechanism generation to synthetic model lubricants will be discussed.