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The Impact of Alternative Fuels on Combustion Kinetics

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Technical Section

Technical Objectives

The research targets the development of detailed kinetic models to quantitatively characterize the impact of alternative fuels on the performance of Navy turbines and diesel engines. Such impacts include kinetic properties such as cetane number, flame speed, and emissions as well as physical properties such as the impact of boiling point distributions on fuel vaporization and mixing. The primary focus will be Fischer-Tropsch liquids made from natural gas, coal or biomass. The models will include both the effects of operation with these alternative fuels as well as blends of these fuels with conventional petroleum-based fuels. The team will develop the requisite kinetic rules for specific reaction types and incorporate these into detailed kinetic mechanisms to predict the combustion performance of neat alternative fuels as well as blends of these fuels with conventional fuels. Reduced kinetic models will be then developed to allow solution of the coupled kinetics/transport problems. This is a collaboration between the Colorado School of Mines (CSM) and the Lawrence Livermore National Laboratory (LLNL).

Technical Approach

The CSM/LLNL team plans to build on the substantial progress made in recent years in developing accurate detailed chemical mechanisms for the oxidation and pyrolysis of conventional fuels. Particular emphasis will be placed upon reactions of the isoalkanes and the daughter radicals, especially tertiary radicals, formed by abstraction from the isoalkanes. The various components of the program are described below.

Model Generation In general, the mechanism generation phase consists of two components. The first step will be to identify appropriate surrogate mixtures that account for the chemical functionalities expected to be present in the alternative fuels of interest. The appropriate surrogate mixture for the Fischer-Tropsch liquids will likely be some combination of n-alkanes and methyl branched alkanes in the diesel boiling point range. Fortunately, several research groups have developed surrogate blends for conventional fuels. Thus our team can focus explicitly on identification of the appropriate model compounds to represent the specific (new) functionalities expected in the alternative fuels (e.g., isoparaffins for the Fischer-Tropsch fuels). Combustion performance depends not only on the intrinsic kinetics of the fuel, but also on the nature of the preparation of the fuel/air mixture. The physical properties of the fuel (e.g., boiling point, volatility, viscosity) dramatically impact the vaporization characteristics, which in turn directly affect the local equivalence ratio, thereby influencing the kinetics. Thus choice of surrogate fuels requires that careful attention be paid to these properties as well. The LLNL is very experienced in development of surrogate blends, and they will lead this aspect of the research program.

The second step is to extend existing mechanisms for conventional fuels by including reactions to describe the kinetics of the surrogate mixtures of Fischer-Tropsch fuels. The reactions and rates

constants will be based on previous work on n-alkanes and iso-alkanes [1-4] with improved rate constants from CSM.

Mechanism Reduction Comprehensive mechanisms properly account for the kinetics over wide ranges of process conditions. The corresponding disadvantage of these mechanisms is that their very large size makes it virtually impossible to couple with transport models. Thus some type of mechanism reduction approach is required to shrink the mechanism to a size commensurate to solving the coupled kinetics/transport problem. For example, for high-temperature combustion events, one might be able to safely ignore all of the complexities that arise from low-temperature ignition. Mechanism reduction approaches are an active area of research and we plan to take advantage of this on-going work.

Model Validation Validation of the models is an essential component of the program. We are aware of the new initiative at the Naval Academy that will be examining the impact of various fuels on combustion performance in both turbines and diesel engines. We propose that a tight coordination between our modeling efforts and those experiments will help validate our models. In particular, early experiments with alternative fuels would be especially useful to determine the magnitude of the differences observed relative to conventional Navy fuels. Such information would provide important guidance to our team in terms of which aspects of our program are most important. We recognize that connecting the detailed models of alternate fuels to actual engine and turbine performance requires substantial extrapolation. The validation attempts may well identify issues that are best addressed in experiments designed to isolate a specific aspect of the combustion event. Such experiments are beyond the scope of this research.

Progress Statement Summary

We have been developing the kinetic models for two iso-dodecane molecules, using the same kinetic modeling formalisms that were developed for the gasoline and diesel primary reference fuels. These mechanisms, and the thermochemical and transport coefficient submodels for them, are very close to completion at the time of this report, and we expect them to be available for kinetic simulations early in the coming year. They will provide a basis for prediction and selection of desirable F-T molecules for use in jet engine simulations, where we should be able to predict the ignition, combustion and emissions characteristics of proposed fuel components. These mechanisms include the reactions and chemical species needed to describe high temperature phenomena such as shock tube ignition and flammability behavior, and they will also include low temperature kinetics to describe other ignition phenomena such as compression ignition and knocking.

Progress

During the past years, our hydrocarbon kinetics modeling group at LLNL has focused a great deal on fuels typical of gasoline and diesel fuel. About 10 years ago, we developed kinetic models for the fuel octane primary reference fuels, n-heptane [1] and iso-octane [2], which have 7 and 8 carbon atoms and are therefore representative of typical gasoline fuels. N-heptane represents the low limit of knock resistance with an octane number of 0, while iso-octane is very knock resistant with an octane number of 100. High knock resistance in iso-octane was attributed largely to the large fraction of primary C-H bonds in the molecule, including 15 of the 18 C-H bonds, and the high bond energy of these primary bonds plays a large role in this knock resistance. In contrast, in the much more ignitable n-heptane, 10 of its 16 C-H bonds are much less strongly bound secondary C-H bonds, leading to its very low octane number. All of these factors, as well as a similarly complex kinetic description of the equally important role of the transition state rings that transfer H atoms within the reacting fuel molecules, were quantified and collected into large kinetic reaction mechanisms that are used by many researchers in the fuel chemistry world.

Much more recently, our group carried out a very similar kinetic modeling study of the diesel primary reference fuels, consisting of n-hexadecane [4] and 2,2,4,4,6,8,8-heptamethyl nonane (HMN) [3]. Just as for the gasoline PRFs, the highly branched reference fuel is highly ignition resistant, and in this case for HMN, its cetane number, measuring ease of ignition under diesel conditions, is very low (15). Just as the long, straight-chain molecule n-heptane is the highly reactive, easily ignited gasoline primary reference fuel, the cetane number is 100 for the easily ignited n-hexadecane, which is also a long, straight-chain n-alkane.

All of these studies show that the molecular structure of a fuel molecule have a big influence on its ignition and other combustion properties. Since the present project is focused on jet fuels and more specifically on fuels produced via the Fischer-Tropsch process, we selected several sample hydrocarbons for kinetic modeling analysis that address important features that we expect in such fuels. Typical jet fuels have carbon numbers between those for gasoline and diesel fuel, so we have selected sample fuels with 12 carbon atoms. One very common feature of F-T fuels is that they are relatively long chain molecules with multiple methyl radicals as side chains. We have had considerable experience with 2-methyl alkanes and 3-methyl alkanes, so we felt that we understood many of the kinetic features of such molecules, so to examine additional factors, we chose two C12 molecules with multiple side methyl chains. However, we decided to arrange these side methyl radicals in two very distinct ways, in order to extract as much kinetic insight as possible.

The two C12 molecules selected for our kinetic modeling analysis are both constructed on a C7 backbone, so they are both formally named "heptane". Since both have 5 side methyl radicals, both are named "pentamethyl heptane". The differences between them is that the 5 side methyl radicals are located at very different positions on the heptane backbone, resulting in two fuel molecules that we expect to exhibit very contrasting kinetic behavior.

These two molecules are 2,2,4,6,6-pentamethyl heptane and 2,3,4,5,6-pentamethyl heptane. These can be shown structurally as:

2,2,4,6,6-pentamethyl heptane (iso-dodecane a)

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      C         C         C
C - C - C - C - C - C - C
      C                   C
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2,3,4,5,6-pentamethyl heptane (iso-dodecane b)

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      C   C   C   C   C
C - C - C - C - C - C - C
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Both molecules have the same overall molecular name of $C_{12}H_{26}$ but their structures are clearly quite different. In the case of iso-dodecane a, 21 of the total 26 C-H bonds are primary bonds; arguing from experience with iso-octane and HMN, we would expect this isomer of iso-dodecane would be quite ignition resistant, in fact quite similar to both of those other reference fuels. In the case of iso-dodecane b, 5 of the C-H bonds are tertiary bonds, which are the most easily abstracted possible. However, 21 of the C-H bonds are again primary C-H bonds, so this molecule is virtually impossible to predict for its ignition behavior. In an important sense, these two fuels represent two limiting structural classes for jet fuel molecules that might be produced in F-T processing. It is also quite possible that both are more

branched than should be expected in realistic F-T processes, but kinetic modeling of both of them will provide important and very useful kinetic modeling information that will be immensely useful in simulations of actual F-T jet fuels that eventually are produced in significant amounts.

We have been developing the kinetic models for both of these iso-dodecane molecules, using the same kinetic modeling formalisms that were developed for the gasoline and diesel primary reference fuels. These mechanisms, and the thermochemical and transport coefficient submodels for them, are very close to completion at the time of this report, and we expect them to be available for kinetic simulations early in the coming year. They will provide a basis for prediction and selection of desirable F-T molecules for use in jet engine simulations, where we should be able to predict the ignition, combustion and emissions characteristics of proposed fuel components. These mechanisms include the reactions and chemical species needed to describe high temperature phenomena such as shock tube ignition and flammability behavior, and they will also include low temperature kinetics to describe other ignition phenomena such as compression ignition and knocking.

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