Challenges for mechanism reduction

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***Abstract*—Detailed chemical kinetic mechanisms are becoming increasingly complex. They are growing in the number species and reactions due to large size of components in practical fuels. They also are growing due to the need to develop surrogate fuel models that contain many fuel components. Additionally, these models have to reproduce complex chemical and physical behavior important for combustion in practical devices. These requirements represent severe challenges to mechanism reduction needed for CFD codes.**

I. Introduction

Much progress has been made in mechanism reduction. It is now routine to reduce detailed chemical kinetic mechanisms for hydrocarbons (e.g. methane, propane, n-heptane) that are valid for ignition from low to high temperatures [1].

However, detailed chemical kinetic mechanisms are becoming increasingly complex. The number species and reactions in mechanisms are growing because of the need to address components in practical fuels that have a large number of atoms. A recent chemical kinetic model for a series of n-alkanes and iso-alkanes from LLNL contains 7200 species and 31400 reactions [2]. They also are growing due to the requirements to develop mechanisms for not just a single fuel component, but multiple fuel components to represent practical fuels like gasoline and diesel fuels. In a recent publication on surrogate fuels for diesel, a 8-component surrogate fuel for diesel is proposed to simulate multiple characteristics of real diesel fuels including composition, ignition behavior, vaporization, and density [3]. The corresponding chemical kinetic mechanism for this surrogate will also be huge because of the large number of components and their large size having 9 - 21 carbon atoms each in each component. These mechanisms must to be severely reduced in size to accommodate the needs of computational fluid dynamic (CFD) codes in combustion.

II. Complex Behavior to be Simulated

A. Complex chemical behavior of fuels

One of challenges of developing reduced mechanisms is ensuring that they can reproduce the complex chemical behavior of real fuels. The simulation of low temperature behavior is important because low temperature combustion controls ignition in diesel and homogeneous charge compression ignition (HCCI) engines. Fig. 1 shows the complex behavior of ignition delay in a rapid compression machine that simulates ignition at internal combustion (IC) engine conditions. The ignition delay increases as the temperature increases in the so-called negative temperature coefficient (NTC) region. It is essential for detailed and reduced models to simulate this behavior to accurately model ignition in engines.

The NTC behavior is also observed in species concentrations as the temperature is increased. Fig. 2 has experimental and computed results from the LLNL model [4] in a jet stirred reactor for stoichiometric mixtures of n-heptane. Reduced models for IC engine applications need to be able to reproduce this behavior to provide accurate predictions.

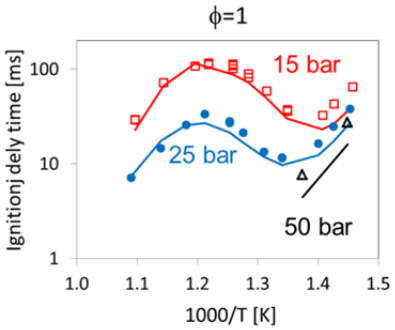

Fig. 1. Measured and computed ignition delay times for stoichiometric mixtures of methyl cyclohexane [5].

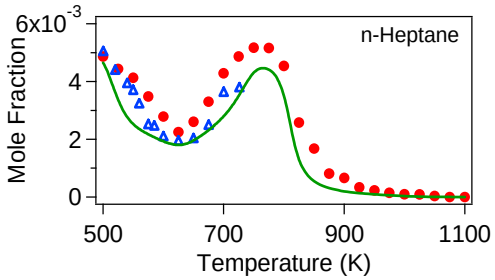

Fig. 2 Measured and computed fuel concentration for temperatures over the NTC region in a jet stirred reactor for stoichiometric n-heptane [6].

The capability to predict soot emissions from combustion devices is also essential. The formation of soot precursors is an important step in many soot models used in CFD engine simulation codes. Detailed and reduced mechanisms should be able to accurately simulate the formation and consumption of important soot precursors like benzene. Fig. 3 shows a comparison of the computed and measured benzene concentrations in a low-pressure flame using the LLNL methyl cyclohexane (MCH) mechanism [7].

Detailed and reduced models should reproduce the chemical behavior of target fuels that often contain hundreds of components. In the case of diesel fuel, Mueller et al. [3] proposed that components in the surrogate mixture model

should represent the molecular structure characteristics of 11 different carbon types and match their relative proportion in the target fuel as well has possible. In this case, this required the inclusion of 8 different fuel components that represented the chemical classes of n-alkanes, iso-alkanes, cycloalkanes, 1-ring aromatics, 2-ring aromatics, and naphtho-aromatics. The inclusion of all these fuel components makes the development of a highly reduced models challenging.

Biofuels present an additional challenge because they have further molecular structures that need to be included in detailed and reduced models. When they are mixed with conventional fuels, the models must include all the molecular structures required for hydrocarbons as well as that of the biofuel. Additionally, biofuels are often saturated (i.e. include double bonds). Three of the five types of methyl esters in most biodiesels have double bonds in the carbon chain, and these three components are present in the highest concentration [8]. These double bonds allow addition of radicals to the double bond, an additional reaction class to be included in the model. Also, the presence of double bonds in a carbon chain on a methyl ester allow the formation of resonantly stabilized radicals that are long-lived and need to be additionally considered in detailed and reduced models.

B. Complex physical behavior of fuels

Not only does the chemical behavior of fuels need to be simulated, but physical behavior is well. In the case of fuel vaporization, additional fuel components should be included to model the distillation properties of the fuel. In a reacting fuel spray, low boiling point components will evaporate prior to high boiling point components. The lighter n-alkanes that vaporize first ignite more slowly than the higher molecular components that vaporize readily at higher temperatures. To be able to include this effect in a surrogate fuel model, additional components in the same chemical class (e.g. n-alkanes) need to be included that span the boiling point range of fuel.

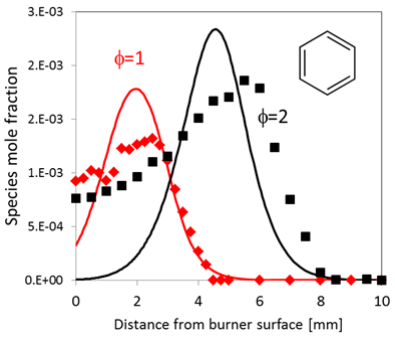

Fig. 3 Measured and computed benzene concentrations in a low pressure MCH flame for stoichiometric and rich mixtures [7].

III. Discussion

To simulate the behavior real fuels, the chemical and physical behavior of the fuel must be taken into account. The molecular structures present in real fuels need to be included in the detailed and reduced models, and chemical behavior such as low temperature chemistry needs to be accurately represented. In order to predict soot emissions, the production and consumption of soot precursor species should be modeled accurately. In addition to the chemical properties, the surrogate mixture model should be able to simulate the physical properties such as the vaporization characteristics of the target fuel. This is particularly important for diesel and biodiesel fuels which contain high boiling point components so that some relatively low boiling point species will evaporate in a reacting spray before other higher boiling point compounds. Including all these fuel components and representing these complex behaviors in a reduced model is challenging. These reduced models are used in multidimensional CFD codes that have many submodels which compete for computer resources. The requirements of surrogate fuel models with more than 10 components means that the mechanisms must be highly reduced to limit the impact of the chemistry solver requirements on the overall reacting flow simulation. This severe reduction of the detailed models makes it difficult to simulate the complex chemical behavior of the real surrogate fuel. Currently, the reduced models for surrogate fuels with many components are partially reduced “by hand” rather than in a fully automatic way because of the severe reduction requirements. One of the challenges of mechanism reduction is to fully automate this reduction process.

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