Recent Developments in Detailed Chemical Kinetic Mechanisms

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***Abstract*—Mechanism reduction must work for the mechanisms being used in current kinetics research. Recent mechanisms and their uses in combustion research are reviewed, attempting to quantify and limit the needs of new mechanism reduction techniques. These mechanisms also provide an ongoing challenge to reduction practitioners.**

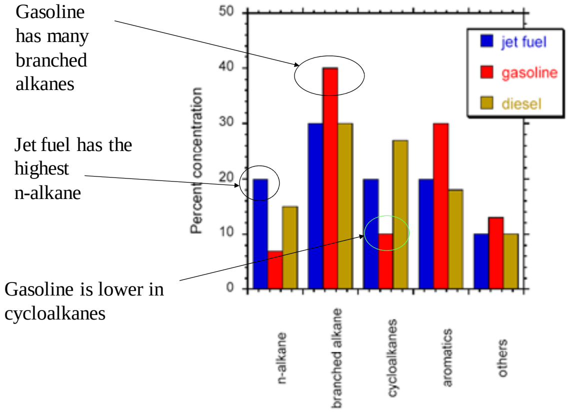
I. INTRODUCTION

Chemical kinetic reaction mechanisms have become essential parts of computational models for many types of practical combustion systems, ranging from flames and shock tubes to internal combustion engines, gas turbines and industrial furnaces. Most practical combustors have complex geometries, are essentially three dimensional and must be modeled with 2D or 3D fluid mechanics, and many such systems also feature other complex physics processes in addition to chemical kinetics. In the past, most of the computer resources would be given to the CFD simulation, with sharply reduced or simplified treatments of most or all of the major physics and chemistry submodels. However, in recent years, modeling approaches have become unwilling to sacrifice so much realism and accuracy in these submodels and have addressed problems in which one or more of these submodels provide important and complex interactions with the fluid mechanics.

In this paper, one class of those submodels is discussed in detail, that of the detailed chemical kinetics of practical hydrocarbon fuels. The focus will be not only on the complexity of the fuel combustion model but also on the features of some of the combustion problems of current importance and on the demands these problems place on the kinetics model. Systematic reduction of the kinetics submodels must retain the ability to reproduce those essential features that were in the original kinetic model.

II. SURROGATES FOR PRACTICAL FUELS

Current attention has been focused on developing kinetic mechanisms for practical, largely transportation fuels. A recent publication by the US DOE [1] on Basic Research Needs for Clean and Efficient Combustion of 21st Century Transportation Fuels noted that gasoline, diesel fuel, jet fuel, natural gas, and related transportation fuels consist of complex mixtures of hundreds or thousands of different chemical species, almost all of which have never had detailed kinetic mechanisms developed for them. The most common strategy to deal with this dilemma is based on the observation that most of the chemical components in these practical fuels can be placed into one of a small number of structural classes, such as n-alkanes, olefins, aromatics, branched alkanes, and cyclic alkanes. For example, one such analysis of samples of gasoline, jet fuel and diesel fuel is summarized in Figure 1.


Gasoline has many branched alkanes

Jet fuel has the highest n-alkane

Gasoline is lower in cycloalkanes

Fig.1. Compositions of some transportation fuels, sorted by structural classes

Over the years, kinetic mechanisms have been developed and validated for one or more hydrocarbon species from each of these classes, and in some classes, especially that of n-alkanes and branched alkanes, mechanisms from many different species have been developed. Some recent examples from our LLNL library include n-alkanes including n-heptane [2] and all of the n-alkanes from n-octane through n-hexadecane [3], branched alkanes including iso-octane [4], the 5 structural isomers of hexane [5] and the 9 structural isomers of heptane [6], cyclic paraffins including cyclohexane [7] and methyl cyclohexane [8], aromatics such as toluene [9], and large olefins such as di-isobutylene [10] and the isomers of hexene [11]. There are many other mechanisms from different researchers that have comparable features. Many other smaller examples of detailed mechanisms for species from most of these classes in the range of C_2-C_5 also exist within larger detailed mechanisms. These all provide an extensive "palette" from which to build mixtures of species, for all of which detailed kinetic mechanisms exist, to reproduce the structural features of any desired realistic practical hydrocarbon fuel. These representative fuels and the structural classes they represent are illustrated in Fig. 2.

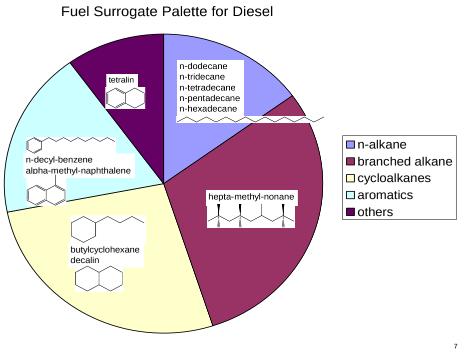


Fig. 2. Examples from each structural class for a sample of representative diesel fuel

Progress towards construction of surrogate mixtures for diesel fuel [12], gasoline [13] and jet fuel [14] have all shown that a good surrogate includes one or, even better, several representatives from each structural class which is present in the real fuel in significant amounts. Of course, the relative amounts of fuel in each class will be different for each type of practical fuel, to reflect the trends shown in Fig. 1. In addition, it is widely recognized that the average fuel molecule size in gasoline is smaller than the average fuel molecule size in jet fuel, and both are generally smaller than in diesel fuels.

III. MOLECULE SIZES AND MECHANISM SIZES

As the size of a fuel molecule increases, the number of chemical species and elementary reactions grows rapidly, so the detailed reaction mechanisms require more computer resources and solution time to integrate to find a problem solution. This growth in mechanism size is accompanied by a corresponding increase in the complexity of the kinetic problems that must be solved.

Both the increased size of the mechanism and complexity of the desired solutions place greater demands on mechanism reduction strategies. Some sample mechanism sizes are illustrated here:

Fuel	**# species**	**# reactions**
Hydrogen	7	25
Methane	30	200
Propane	100	400
Hexane	450	1500
n-heptane	550	2450
iso-octane	860	3600
PRF (n-heptane+ iso-octane)	990	4060
n-decane	940	3900
n-hexadecane	2116	8130
methyl decanoate	3030	8580
methyl stearate	2440	12750

IV. PROBLEM NEEDS FROM MECHANISMS

Many of the combustion phenomena that must be solved involve autoignition. Autoignition kinetics controls such phenomena as engine knock in spark ignition engines, ignition in diesel engines, and ignition is homogeneous charge, compression ignition (HCCI) engines. In each case, the reacting gases pass through a low temperature regime, an intermediate temperature regime, and finally a high temperature regime in which the final ignition occurs. The overall reaction pathway that controls all of these processes is the following:

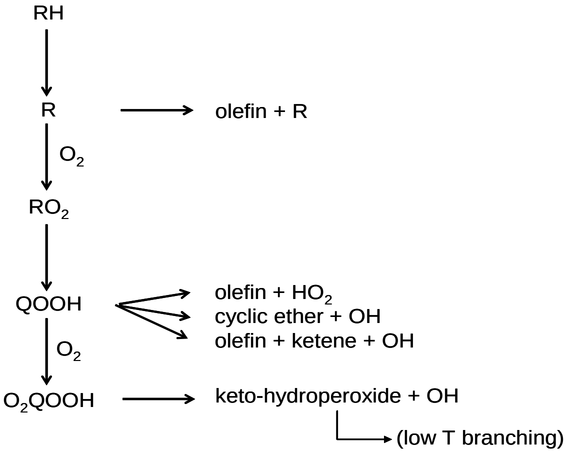


Fig. 3. Reaction pathways for low and high temperature regimes

Under these conditions, the gases go through a region of so-called negative temperature coefficient (NTC) of reaction, in which the overall rate of reaction and heat release can actually decrease with increasing reaction temperature. The kinetic sources of this phenomenon are quite subtle and require a detailed simulation of a rather complicated series of reactions generally referred to as the alkylperoxy radical isomerization reaction paths [15]. The kinetic description of this region has been shown to be the source of such features as octane and cetane numbers for hydrocarbon ignition [16] and reproduction of these features requires a model to include all of the key reaction sequences, most of which are strongly dependent on the molecular structure of the fuel molecule. It is very challenging to devise a mechanism reduction algorithm that can reproduce all of these features. The features are rather subtle and change the amounts of low temperature heat release by only a few degrees of temperature, but these small features make a large difference in the amounts of low temperature heat release that is observed and in the onset of ignition under practical conditions [17].

For example, a commonly used set of experiments that are used to validate hydrocarbon oxidation over a wide range of conditions are the shock tube experiments of Adomeit et al. [18,19] at Aachen in Germany. In these experiments, stoichiometric mixtures of fuel and air are ignited at elevated pressures (i.e., 13.5 and 40 bar). The ignition delay times depend on the initial temperature in a highly non-linear manner, as shown in Fig. 4.

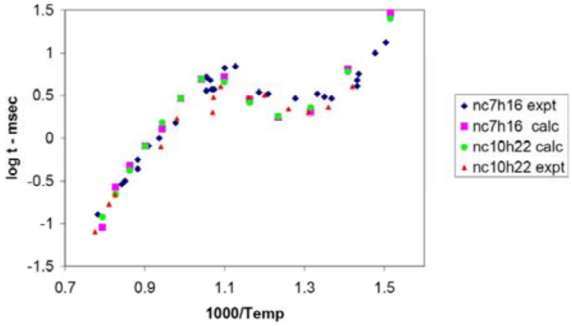


Fig. 4. Shock tube ignition delay times for n-heptane and n-decane, from experiments [18,19] and model [3].

This behavior may seem outrageously academic and unimportant, but it is actually the key to understanding and predicting octane and cetane numbers and predicting ignition in HCCI engines. For example, if two different fuels are used in a modern HCCI engine [20], the experimental and computed rates of heat release for those two fuels are shown in Fig. 5.

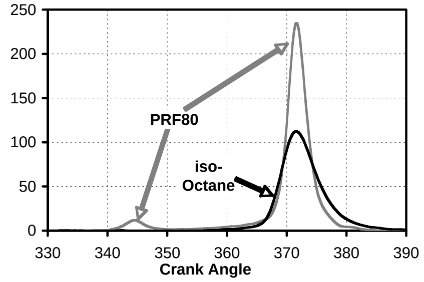
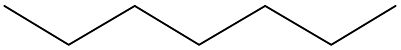
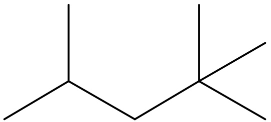


Fig. 5. Heat release rate as a function of crank angle in an HCCI engine for two fuels with different octane ratings.

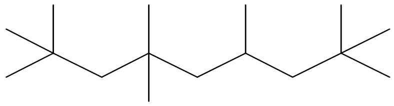
The fuel with lower octane, PRF80, releases heat at early times which advances ignition, while the iso-octane fuel, with a higher octane, does not have the same low temperature heat release and needs a higher intake temperature to ignite at the same temperature as the PRF80 fuel. This behavior is important to the engine designer and must be reproduced in the detailed and in the reduced reaction mechanism.

Current kinetic mechanisms also can describe the limits of ignition properties in gasoline and diesel engines. The metric commonly used in gasoline is the octane number, and the primary reference fuels for octane number are n-heptane and iso-octane, one of which, n-heptane, indicates easy ignition and an octane number of zero, and iso-octane, which is very difficult to ignite and has an octane number of 100. These fuels can be represented as follows





At the same time, the reference fuels for cetane number, which measures ignition quality under diesel conditions, are n-hexadecane for the easily ignited fuel, and heptamethyl nonane, the difficult to ignite component



The differences in ignition quality are due to structural differences that are, in turn, reflected in nuances in reaction rates that must be retained in a reduced mechanism that is derived from the fully detailed mechanism.

V. CONCLUSIONS

Historically, mechanism reduction has focused on larger scale phenomena in combustion phenomena, and on smaller hydrocarbon fuel molecules. Recent advances in kinetic modeling have provided a much more detailed description of hydrocarbon combustion, with much larger mechanisms, and requiring description of much more detailed and more refined experimental phenomena. Both of these trends create much greater demands on the process of mechanism reduction.

VI. ACKNOWLEDGMENTS

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