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Detailed chemical kinetic models for large n-alkanes and iso-alkanes found in conventional and F-T diesel fuels

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Abstract

n-Hexadecane and 2,2,4,4,6,8,8-heptamethylnonane represent the primary reference fuels for diesel that are used to determine cetane number, a measure of the ignition property of diesel fuel. With the development of chemical kinetics models for both primary reference fuels, a new capability is now available to model diesel fuel ignition. Additionally, we have developed chemical kinetic models for a whole series of large n-alkanes and a large iso-alkane to represent these chemical classes in fuel surrogates for conventional and future fuels. These chemical kinetic models are used to predict the effect of the aforementioned fuel components on ignition characteristics under conditions found in internal combustion engines.

Introduction

Detailed chemical kinetic models are needed to simulate the combustion of current and future transportation fuels. These fuels, such as gasoline, diesel and jet fuel, are commonly composed of hundreds to thousands of compounds. In order to represent them, compounds are typically chosen from each of the chemical classes present in the target fuel. For example, the chemical classes in diesel fuel are shown in Fig. 1. Also shown are the carbon skeletal structures of compounds to represent those classes. The chemical kinetic models of the components are then combined to make surrogate fuel mechanisms to represent the real fuels [1-3]. Cross reactions between the components need to be added as well.

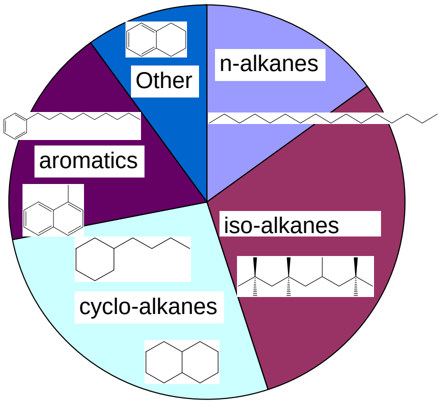

Figure 1. Relative amounts of various chemical classes in diesel fuel.

Some of these chemical classes such as n-alkanes and iso-alkanes are also representative of future fuels, such those derived using Fischer-Tropsch (F-T) processes. F-T can be used to synthesize diesel and other transportation fuels from sources of biomass, coal and natural gas. F-T diesel fuels are expected to be similar to F-T jet fuels which are commonly comprised of iso-alkanes with some n-alkanes [4].

Recently, the LLNL chemical kinetics group has made significant progress in the development of detailed chemical kinetic models for fuel components for large n-alkanes [5] and iso-alkanes. These components include n-hexadecane and 2,2,4,4,6,8,8-heptamethylnonane which are the primary reference fuels for diesel. Together with our previously developed primary reference fuels [6, 7], these models now comprise a complete set of primary reference fuels for gasoline and diesel. In this paper, we discuss the development of these new fuel component models.

Large n-alkanes

There is a current need to extend chemical kinetic models to address large alkanes because they are included in recommendations for components in surrogates for diesel and jet fuels [2, 3]. The component recommendations for surrogates include n-hexadecane for diesel fuel and n-decane and n-dodecane for jet fuel [2, 3, 8]. Recently, we developed a chemical kinetic model for all n-alkanes from n-octane to n-hexadecane [5]. This model allows the simulation of both low and high temperature chemistry of these n-alkanes. The inclusion of low temperature combustion in the model is important for simulation of new modes of combustion in engines such as homogeneous charge compression ignition (HCCI), premixed charge compression ignition (PCCI), and smokeless rich combustion [9-11]. Figure 2 shows

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comparison of results from the detailed chemical kinetic model for n-hexadecane [5] and measurements made in a stirred reactor [12]. The agreement between the modeling and the experimental results is good.

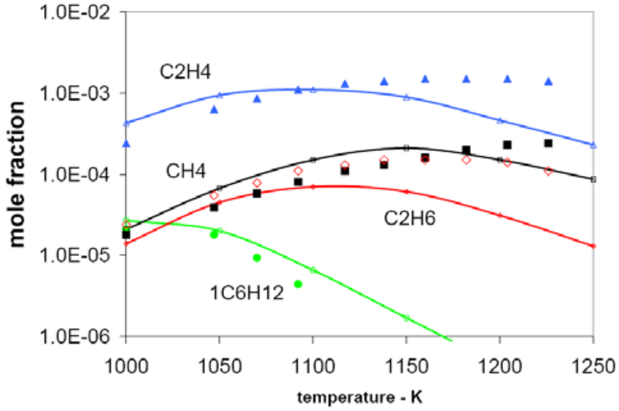

Figure 2. Intermediate species for n-hexadecane oxidation in a stirred reactor [12]. Symbols are from the experiment and curves are from the model. (stoichiometric, 1 atm, 70 ms residence time)

n-Hexadecane is an important component for consideration for a diesel surrogate fuel because it is a primary reference fuel for diesel engines. There are little experimental data in the literature to provide for validation for a chemical kinetic model for n-hexadecane. However, there are experimental data (Fig. 3) on ignition of n-decane, a large n-alkane included in the n-hexadecane mechanism. The n-decane experiments were performed at engine-like conditions of 80 bar and at temperatures from 800 to 1100 K, including the negative temperature coefficient region [13].

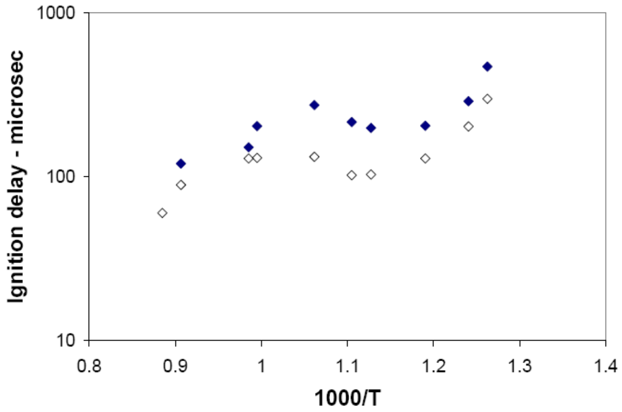

Figure 3. n-Decane ignition in a shock tube (stoichiometric, 80 bar). Model: filled symbols, Experiments [13]: open symbols.

Predictions of n-decane ignition by the C_8-C_{16} mechanism compared well with experimental measurements (Fig. 3). In order to assess the ignition behavior for all n-alkanes, the ignition of C_8 to C_{16} alkanes were computed over the low to high temperature range at 13 bar, a pressure relevant in an internal combustion engine (Fig. 4). The calculations show that all the large n-alkanes exhibit nearly the same ignition behavior regardless of carbon length. Therefore, a small n-alkane like n-octane can be used to represent the ignition behavior of a much larger n-alkane like n-hexadecane. Using n-octane to represent the ignition of n-hexadecane would allow the use of a chemical kinetic model of much smaller size and require much less computer resources. Finally, the development of a chemical kinetic model for all n-alkanes up to n-hexadecane allows a broad choice of surrogate fuel components in the n-alkane chemical class for use in surrogate fuel models.

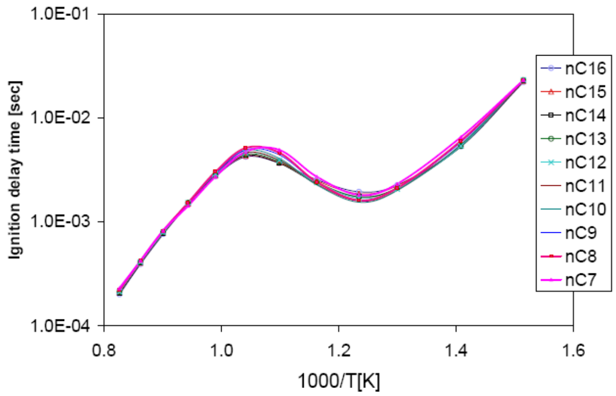

Figure 4. Ignition behavior of a series of large n-alkanes (stoichiometric, fuel-air mixtures, 13.5 bar) [5].

Large iso-alkanes

Although models have been developed for smaller branched alkanes such as isooctane [7], additional efforts are required to properly capture the kinetics of the larger branched alkanes. Recently, we have developed a chemical kinetic model that can be used to represent 2,2,4,4,6,8,8-heptamethylnonane (HMN), a large iso-alkane and a primary reference fuel for diesel. The same reaction rate rules used in the iso-octane mechanism were incorporated in the HMN mechanism. Both high and low temperature chemistry was included so that the chemical kinetic model would be applicable to advanced internal combustion engines using low temperature combustion strategies. The chemical kinetic model consists of 1114 species and 4468 reactions.

Currently, there are no experimental data available on neat HMN in the literature to validate the predictions of the chemical kinetic model. Instead the results of the HMN chemical kinetic model were compared to other alkane model predictions and experimental measurements. In Fig. 5, the autoignition properties of HMN are compared to n-alkanes and an iso-alkane, iso-octane. It is seen that the ignition delay times of HMN lie between large n-alkanes and iso-octane at low

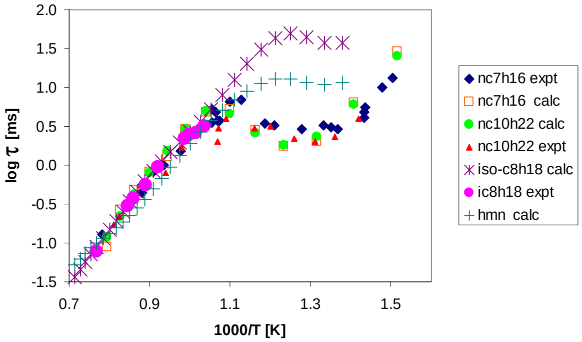

Figure 5. Autoignition of n-heptane, n-decane, iso-octane and 2,2,4,4,6,8,8-heptamethylnonane at 13 bar with stoichiometric, fuel/air mixtures. Computations: n-heptane (nc7h16) [6], iso-octane (ic8h18) [7], n-decane (nc10h22) [5], heptamethylnonane (hmn, present work). Experiments: n-heptane [15], iso-octane [16], n-decane [17].

temperatures and are nearly the same as the other fuels at high temperatures.

This low temperature ignition behavior can be explained in terms of the alkylperoxy (RO_2) isomerization reactions that control the overall, low-temperature reaction rate. The RO_2 isomerization reactions with the highest rate constants have six membered transition states and generally occur between CH_2 groups. This type of RO_2 isomerization reaction also leads to a subsequent addition of O_2 followed by another isomerization and finally chain branching with the production of two OH radicals. It is this chain branching that contributes greatly to low temperature reactivity [14]. The CH_2 groups in HMN interact through six-membered ring RO_2 isomerization reactions that lead to a greater extent of chain-branching than seen for iso-octane which has only one CH_2 group.

The chemical kinetic models for n-hexadecane and HMN represent a significant advance in modeling of fuels for diesel engines because they are the primary reference fuels used to determine the cetane number used to rate ignition properties of diesel fuels. Also, these two components are the ones recommended by Farrell et al. [2] as components in a four component surrogate mixture to represent diesel fuel.

Summary

We have developed significant new capability to model the detailed chemical kinetics of components relevant to diesel, jet, and F-T derived fuels. These component models can be combined into fuel surrogate models to treat the combustion of practical fuels.

Acknowledgments

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