LLNL-CONF-411689

LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

Recent Advances in Detailed Chemical Kinetic Models for Large Hydrocarbon and Biodiesel Transportation Fuels

C. K. Westbrook, W. J. Pitz, H. J. Curran, O. Herbinet, M. Mehl

March 31, 2009

7th Asia-Pacific Conference on Combustion
Taipei, Taiwan
May 24, 2009 through May 27, 2009

Disclaimer

7th Asia-Pacific Conference on Combustion,
National Taiwan University, Taipei, Taiwan
24-27 May 2009

Recent Advances in Detailed Chemical Kinetic Models for Large Hydrocarbon and Biodiesel Transportation Fuels

C. K. Westbrook[1], W. J. Pitz[1], H. J. Curran[2], O. Herbinet[3] and M. Mehl[1]

[1]Lawrence Livermore National Laboratory, Livermore, CA 94551 USA

[2]National University of Ireland, Galway, IRELAND

[3]Universite de Nancy, Nancy, FRANCE

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 these two primary reference fuels for diesel, a new capability is now available to model diesel fuel ignition. Also, 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. Methyl decanoate and methyl stearate are large methyl esters that are closely related to biodiesel fuels, and kinetic models for these molecules have also been developed. These chemical kinetic models are used to predict the effect of the fuel molecule size and structure on ignition characteristics under conditions found in internal combustion engines.

1 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.

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 (Smith and Bruno, 2008).

Recently, we have made significant progress in the development of detailed chemical kinetic models for fuel components for large n-alkanes [4] 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 {Curran, 1998 #170;Curran, 2002 #165}, these models now comprise a complete set for primary reference fuels for gasoline and diesel. We have also made significant progress in developing reaction mechanisms for large methyl ester fuels, as part of a project to produce mechanisms for true biodiesel fuels. In this paper, we discuss the development of these new fuel component models.

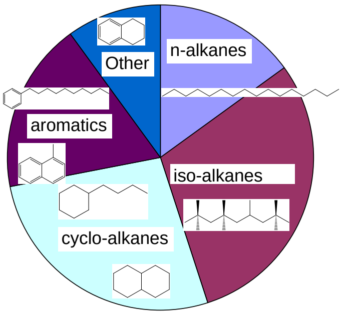

Fig. 1 Relative amounts of various chemical classes in diesel fuel.

2 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, 5]. Recently, the LLNL chemical kinetics team developed a chemical kinetic model for all n-alkanes from n-octane to n-hexadecane [4]. 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 [6-8]. Figure 2 shows comparison of results from the LLNL detailed chemical kinetic model for n-hexadecane [4] and measurements made in a stirred reactor [9]. The agreement between the modeling and the experimental results is good.

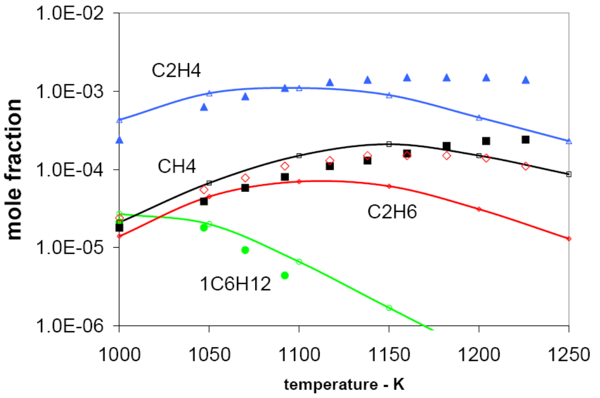

Fig. 2 Intermediate species for n-hexadecane oxidation in a stirred reactor [9]. Symbols are from the experiment and curves are from the model. (stoichiometric, 1 atm, 70 ms residence time)

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 few experimental data in the literature to provide for validation for a chemical kinetic model for n-hexadecane. In order to assess the ignition behavior for all n-alkanes, the ignition of C8 to C16 alkanes were computed over the low to high temperature range at 13 bar, a pressure relevant in an internal combustion engine (Fig. 3). 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.

These are large reaction mechanisms that include both high and low temperature submechanisms. The n-hexadecane mechanism includes more than 8000 reactions and 2100 species, while the n-decane mechanism has 3900 reactions and 950 species.

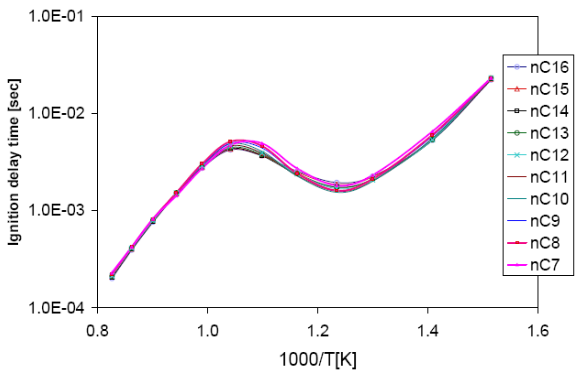

Fig. 3 Ignition behavior of a series of large n-alkanes (stoichiometric, fuel-air mixtures) [4].

3 Large iso-Alkanes

Although models have been developed for smaller branched alkanes such as isooctane [11], 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 fuel predictions and experiments. In Fig. 4, the autoignition properties of HMN are compared to n-alkanes and an iso-alkane, iso-octane. The n-alkanes and iso-octane fuels have been studied under relevant shock tube conditions, and the computed model results agree well with the experimental results 14,15]. It is seen that the ignition delay times of HMN lie between large n-alkanes and iso-octane at low 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 [12]. 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.

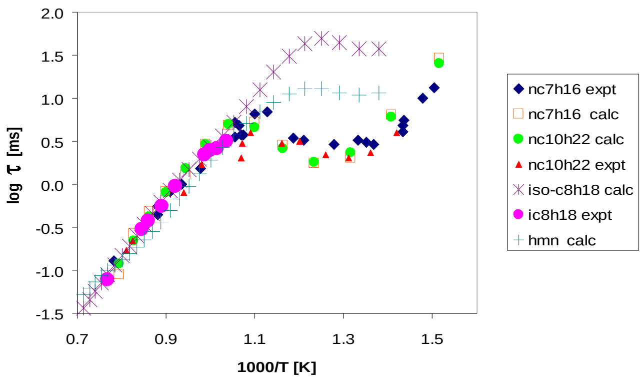

Figure 4. Autoignition of n-heptane, n-decane, iso-octane and 2,2,4,4,6,8,8-heptamethylnonane at 13 bar with stoichiometric, fuel/air mixtures. Computations: n-heptane (nc7h16)[13], iso-octane (ic8h18)[11], n-decane (nc10h22)[4], heptamethylnonane (hmn, present work). Experiments: n-heptane[14], iso- octane[15], n-decane[16]

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.

4 Biodiesel Fuels

Biodiesel fuels from soy oil and rapeseed oil consist of mixtures of C_{16} and C_{18} methyl esters, some with long straight chain n-alkyl radicals and others with straight chains with one, two or three double bonds. We chose to develop a methyl ester fuel mechanism of methyl decanoate, the n-C_{10} methyl ester, in order to develop kinetic rate rules that could be applied to these biofuels [17], and we are in the final stages of development of the much larger fuel methyl stearate. These molecules do not have the large degree of symmetry that are noted in n-alkanes, and the resulting reaction mechanisms for them are considerably larger, including nearly 8600 reactions and more than 3000 species in the case of methyl decanoate and more than 13000 reactions in the case of methyl stearate, the C_{18} methyl ester.

We found, somewhat surprisingly, that the autoignition properties of methyl decanoate, as shown in Fig. 5, are virtually identical to those of the n-alkanes that had been summarized above in Fig. 3. The conclusion of these results is that the long chain alkyl portion of each of these fuels are almost exclusively responsible for their rates of ignition. Also in [17], the methyl decanoate mechanism accurately reproduced the time-dependent OH radical concentrations in shock tube ignition experiments by Davidson et al. [18] using n-decane as the fuel.

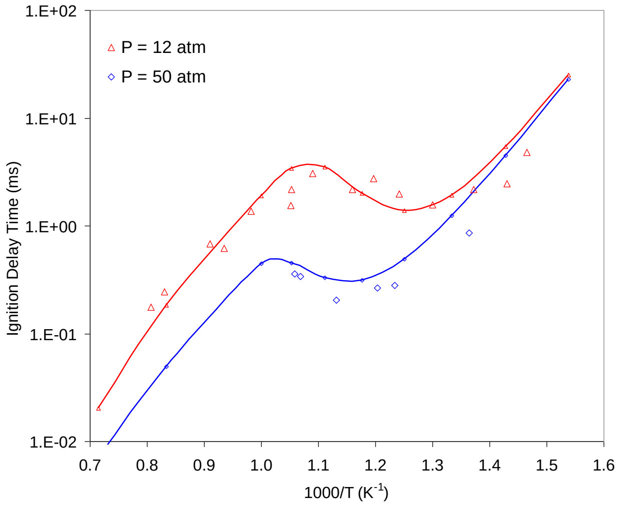

Fig. 5 Ignition delay times of n-decane and methyl decanoate (stoichiometric, fuel-air mixtures). Lines are computed, using the methyl decanoate mechanism from [17] and the symbols are experimental results for n-decane from Pfahl et al. [16].

5 Conclusions

The LLNL chemical kinetics group has developed significant capabilities to model the detailed chemical kinetics of components relevant to practical fuels like gasoline, diesel, jet, biodiesel and oil-sand derived fuels. These component models can be combined into fuel surrogate models to treat the combustion of practical fuels. These new capabilities enhance the ability to model the chemical kinetics of fuels in practical devices.

6 Acknowledgments

This work was supported by the U.S. Department of Energy, Office of Freedom CAR and Vehicle Technologies, Gurpreet Singh and Kevin Stork, program managers, and was performed under the auspices of the U.S Department of Energy by the Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

References

[1] Pitz, W.J., et al. *Development of an Experimental Database and Kinetic Models for Surrogate Gasoline Fuels*. in *SAE 2007 Transactions Journal of Passenger Cars - Mechanical Systems, SAE Paper 2007-01-0175*. 2007.

[2] Farrell, J.T., et al. *Development of an experimental database and kinetic models for surrogate diesel fuels*. in *SAE Paper 2007-01-0201, 2007 SAE World Congress*. 2007. Detroit, MI.

[3] Colket, M., et al. *Development of an experimental database and kinetic models for surrogate jet fuels*. in *45th AIAA Aerospace Sciences Meeting and Exhibit*. 2007. Reno, Nevada, paper no. AIAA-2007-0770: American Institute of Aeronautics and Astronautics.

[4] Westbrook, C.K., et al., *A Detailed Chemical Kinetic Reaction Mechanism for n-Alkane Hydrocarbons from n-Octane to n-Hexadecane.* Combustion and Flame, 2009. **156**(1): p. 181-199.

[5] Colket, M., et al. *Identification of Target Validation Data for Development of Surrogate Jet Fuels*. in *46th AIAA Aerospace Sciences Meeting and Exhibit*. 2008. Reno, Nevada, paper no. AIAA-2008-0972: American Institute of Aeronautics and Astronautics.

[6] Sjöberg, M. and J.E. Dec, *EGR and Intake Boost for Managing HCCI Low-Temperature Heat Release over Wide Ranges of Engine Speed*. 2007.

[7] Flowers, D.L., S.M. Aceves, and A. Babajimopoulos. *Effect of Charge Non-uniformity on Heat Release and Emissions in PCCI Engine Combustion*. in *Society of Automotive Engineers Paper 2006-01-1363*. 2006.

[8] Akihama, K., et al. *Mechanism of the smokeless rich diesel combustion by reducing temperature.* in *Society of Automotive Engineers paper 2001-01-0655*. 2001.

[9] Ristori, A., P. Dagaut, and M. Cathonnet, *The oxidation of n-hexadecane: experimental and detailed kinetic modeling.* Combustion and Flame, 2001. **125**(3): p. 1128-1137.

[10] Zhukov, V.P., V.A. Sechenov, and A.Y. Starikovskii, *Autoignition of n-decane at high pressure.* Combustion and Flame, 2008. **153**(1-2): p. 130-136.

[11] Curran, H.J., et al., *A Comprehensive Modeling Study of iso-Octane Oxidation.* Combustion and Flame, 2002. **129**: p. 253-280.

[12] Pitz, W.J., et al., *Modeling and experimental investigation of methylcyclohexane ignition in a rapid compression machine.* Proceedings of the Combustion Institute, 2007. **31**(1): p. 267-275.

[13] Curran, H.J., et al., *A Comprehensive Modeling Study of n-Heptane Oxidation.* Combustion and Flame, 1998. **114**(1-2): p. 149-177.

[14] Ciezki, H.K. and G. Admeit, *Shock-Tube Investigation of Self-Ignition of n-Heptane-Air Mixtures Under Engine Relevant Conditions.* Combustion and Flame, 1993. **93**: p. 421-433.

[15] Fieweger, K., R. Blumenthal, and G. Adomeit, *Self-ignition of S.I. engine model fuels: A shock tube investigation at high pressure.* Combustion and Flame, 1997. **109**(4): p. 599-619.

[16] Pfahl, U., K. Fieweger, and G. Adomeit, *Self-Ignition of Diesel-Relevant Hydrocarbon-Air Mixtures under Engine Conditions.* Proc. Combust. Inst., 1996. **26**: p. 781-789.

[17] Herbinet, O., Pitz, W.J., and Westbrook, C.K., “Detailed Chemical Kinetic Oxidation Mechanism for a biodiesel surrogate”, **Combust. Flame 154**, 507-528 (2008).

[18] Davidson, D.F., Herbon, J.T., Horning, J.T., and Hanson, R.K., International Journal of Chemical Kinetics, 33(12), 2001, 775-783.