LLNL-CONF-404514

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June 6, 2008

The 7th COMODIA International Conference on Modeling and Diagnostics for Advanced Engine Systems
Sapporo, Japan
July 28, 2008 through July 31, 2008

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Progress in Chemical Kinetic Modeling for Surrogate Fuels

(Chemical Kinetic Modeling for Surrogate Fuels)

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Key Words: Surrogate Fuels, Chemical Kinetic Modeling

ABSTRACT

Gasoline, diesel, and other alternative transportation fuels contain hundreds to thousands of compounds. It is currently not possible to represent all these compounds in detailed chemical kinetic models. Instead, these fuels are represented by surrogate fuel models which contain a limited number of representative compounds. We have been extending the list of compounds for detailed chemical models that are available for use in fuel surrogate models. Detailed models for components with larger and more complicated fuel molecular structures are now available. These advancements are allowing a more accurate representation of practical and alternative fuels. We have developed detailed chemical kinetic models for fuels with higher molecular weight fuel molecules such as n-hexadecane (C16). Also, we can consider more complicated fuel molecular structures like cyclic alkanes and aromatics that are found in practical fuels. For alternative fuels, the capability to model large biodiesel fuels that have ester structures is becoming available. These newly addressed cyclic and ester structures in fuels profoundly affect the reaction rate of the fuel predicted by the model. Finally, these surrogate fuel models contain large numbers of species and reactions and must be reduced for use in multi-dimensional models for spark-ignition, HCCI and diesel engines.

INTRODUCTION

Demands for higher combustion efficiency, reduced pollutant emissions and higher performance are continually being placed on internal combustion engine development. The chemistry of combustion of fuel and air has a critical influence on these engine performance issues. For example, the molecular structure of the fuel affects ignition timing in compression ignition engines. This timing needs to be maintained near top dead center (TDC) in the engine to attain maximum combustion efficiency. Another effect of molecular structure is that it controls the nature of the pollutant emissions from the engine. Fuels with high aromatic content usually produce more particulate emissions. Alternatively, fuels with high oxygenate content often produce more emissions of aldehydes. Also, the nature of the composition of pollutant emissions influences the efficiency of the aftertreatment system and affects its design requirements. Thus, it is important to develop accurate chemistry submodels for internal combustion engine codes so that chemical effects of the fuels on pollutant emissions, combustion efficiency, and performance can be properly predicted.

The development of chemical kinetic models for engine combustion involves a sequential process. First a detailed chemical model for the fuel must be developed and validated. These models usually have too many species and reactions to be used in multidimensional codes for simulating engine combustion. Thus, the computational requirements of the chemistry model must be reduced to a small enough size so that the overall calculation times of the engine code become reasonable.

The first step of developing detailed chemical kinetic models for practical fuels is a major task in itself. Gasoline, diesel and jet fuels are made up of hundreds to thousands of compounds. It is not practicable to simulate the chemistry of this many individual compounds using detailed chemical kinetic models. In order to make the modeling of practical fuel tractable, “surrogate fuel models” are being developed which contain a limited number of compounds that represent the chemistry of practical fuels [1-5]. To make a surrogate fuel model, detailed chemical kinetic models for each of the components in the surrogate fuel must be developed. Experimental data on the combustion of each of these components in fundamental laboratory devices like shock tubes, rapid compression machines and flow reactors must be acquired so that the detailed chemical kinetic models can be validated. Then the detailed models of individual components need to be combined into a surrogate fuel model which is validated by comparison to surrogate experimental data.

In this paper, we discuss how surrogate fuel components are selected. Then we focus on the first step of detailed chemical kinetic mechanism development for surrogate fuel components and the rapid progress that has been made in this area over the last few years. Finally, we briefly discuss the methods available for reducing the computational requirement of chemistry models and the future of chemical kinetic modeling for surrogate fuels.

SURROGATE SELECTION

There are several proposed ways to specify the number, identity, and quantity of the compounds in a surrogate fuel. One prevalent method is to specify compounds from each chemical class in a practical fuel. Figure 1 shows the major chemical classes for diesel fuel. Similar charts can be made for gasoline and jet fuel. These classes include n-alkane, branched alkane, cycloalkane, aromatic and others. “Others” include ring compounds that have both aromatic and paraffinic character, for example tetralin which is shown in the “other” class in Fig. 1. For each chemical class in Fig. 1, molecular structures are given as examples for that chemical class. For example for n-alkanes, n-hexadecane (a primary reference fuel for diesel fuel) is given as an example molecular structure. In references [1-3], key chemical compounds are identified that are relevant to gasoline, diesel and jet fuels. The molecular structures in Fig. 1 are ones that have been identified in reference [2] for diesel fuel. The amount of each compound can be specified by the amount of each chemical class in the fuel. The size of the “slice of pie” in Fig. 1 corresponds to the approximate amount of each chemical class in diesel fuel. The size of these slices can vary greatly depending on the source of the diesel fuel [2].

Another way to specify the type and amount of each surrogate component in the surrogate fuel, is to vary them to match physical and chemical properties of the target surrogate fuel [6]. In the case of jet fuel, the properties that are considered critical to match are H/C ratio, aromatic content, heat of combustion, smoke point, and the distillation curve [6]. For gasoline and diesel fuel, the octane number and cetane number are important ignition properties to be included to match in the target fuel properties. The process of comparison of the properties of the proposed surrogate with the practical fuels restricts the type and amount of individual components in the surrogate that can be considered. For example, the H/C ratio of the target fuel will place limits on the total amounts of aromatics which have low H/C ratios and total amount of paraffins which have high H/C ratios. Each additional fuel property specification further restricts the type and quantity of components that can be included in the surrogate.

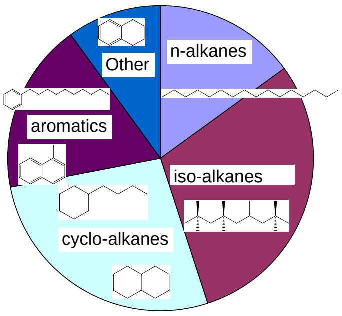

Fig. 1 Fuel surrogate palette for diesel fuel.

A third proposed way to choose the individual components in the surrogate is to perform component analysis on the target fuel [7] and use this analysis to specify the surrogate fuel. In this approach, the target fuel analyzed by nuclear magnetic resonance (NMR) spectroscopy and the relative amounts of primary, secondary, tertiary, quaternary, and aromatic carbons are determined. A surrogate fuel of individual components is assembled to match these molecular characteristics.

Additionally, improved methods are becoming available to characterize the composition of the fuel and aid in the specification of fuel surrogates. For example, two-dimensional gas chromatography and two-dimensional NMR allow a much better speciation of diesel and oil-sand derived fuels than previously possible [8, 9].

DETAILED MODELS FOR COMPONENTS

Much progress has been made in recent years in developing detailed chemical kinetic models for surrogate components [10-26]. The approach is to fill out the surrogate fuel palette (e.g. Fig. 1) for each fuel type (gasoline, diesel and jet fuel). Then, more fuel component models will be available for composing surrogate fuel models. In the following section, we discuss the progress in developing models for individual fuel components.

Recently, much attention has been focused on non-petroleum based fuels. These include liquid fuels derived from vegetable oils, animal fats, coal, oil-sands, shale-oil and natural gas. These alternative fuels expand the fuel surrogate palette even further. In the following section, we also discuss progress in fuel components for alternative fuels as well.

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. The component recommendations for surrogates include n-hexadecane for diesel fuel and n-decane and n-dodecane for jet fuel [2, 3, 6]. Recently, a chemical kinetic model for all n-alkanes from n-octane to n-hexadecane was developed [10, 27]. 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 [28-30]. Figure 2 shows comparison of results from the detailed chemical kinetic model for n-hexadecane [10] and measurements made in a stirred reactor [31]. The agreement between the modeling and the experimental results is good. n-Hexadecane is an important component for consideration for a diesel surrogate

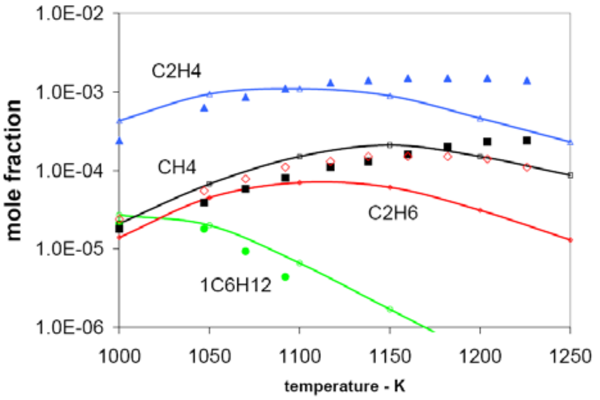

Fig. 2 Intermediate species for n-hexadecane oxidation in a stirred reactor [31]. Symbols are from the experiment and curves are from the model. (stoichiometric, 1 atm, 70 ms residence time)

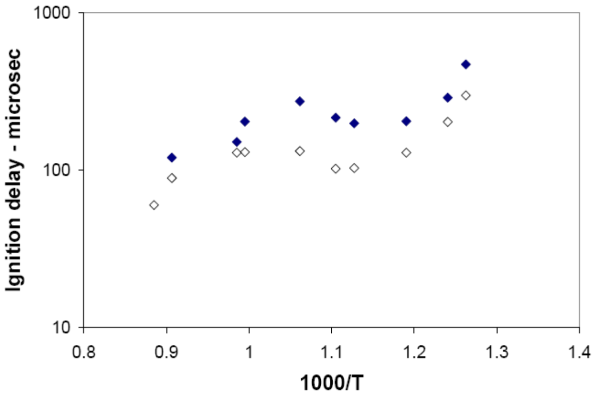

Fig. 3 n-Decane ignition in a shock tube (stoichiometric, 80 bar). Model: filled symbols, Experiments [32]: open symbols.

because it is a primary reference fuel for diesel engines. However, there is little experimental data in the literature on n-hexadecane. The detailed chemical kinetic model [10] includes chemistry for all the n-alkanes up to C16. There is also experimental data on ignition of n-decane, another large n-alkane (Fig. 3). The experiments were performed at engine-like conditions of 80 bar and at temperatures from 800 to 1100 K, including the negative temperature coefficient region [32]. The n-alkane model was further validated by comparing model predictions with these experimental measurements. The comparison showed good agreement (Fig. 3). The development of a chemical kinetic model for all n-alkanes up to n-hexadecane allows a broad choice of surrogate fuel components in n-alkane chemical class for use in surrogate fuel models.

Cyclo-alkanes

Cycloalkanes are an important chemical class, particularly in diesel fuel (Fig. 1) and jet fuel [3]. In gasoline fuel surrogates, methyl cyclohexane and cyclohexane have been recommended as components [1]. Methylcyclohexane has also gained attention as a recommended component in jet fuel surrogates [6, 33]. Additionally, cyclic alkanes are of interest because of their high concentration in oil-sand derived fuels and their potential influence on soot emissions from the combustion of these fuels in engines [34].

Recently, there has been much progress in the development of chemical kinetic models for cycloalkanes [12, 13, 19, 20]. These detailed chemical kinetic models are able to simulate the low and high temperature behavior of methyl cyclohexane and cyclohexane-air mixtures. Fig. 4 gives an example of a comparison of the results of a cyclohexane model [12] to experimental data from a rapid compression machine [35], which simulates temperature and pressure conditions at top dead center in an engine.

One of the key features of the chemical kinetic models that allow proper simulation of cycloalkane oxidation is the inclusion of the effect of the cycloalkane ring structure on reaction rate constants [13, 19, 36]. A reaction sequence that is key to predicting the correct reactivity is the addition of molecular oxygen to fuel radicals followed by an internal isomerization reaction. This sequence eventually leads to low temperature branching and heat release. Figure 5 shows the molecular structure of the transition state for the isomerization of a RO_2 radical. The cycloalkane ring is part of the structure of the transition state. The cyclic alkane ring structure increases the activation energy of the reaction compared to an acyclic alkane. This is due to the stiffness of the ring. However, the ring structure lowers the entropy change in the reaction so that the pre-exponential factor increases compared to the same reaction in an acyclic alkane. The comparison of the acyclic and cyclic RO_2 isomerization rate constants is shown in Table 1. The primary difference between the acyclic and cyclic reaction rate constants is that the RO_2 isomerization of the 6-membered ring is more favored in the cyclic case than in the non-cyclic case. The 6-membered ring leads preferentially to chain branching [13]. This means that cyclic alkanes have much more low temperature reactivity than would be expected, if its

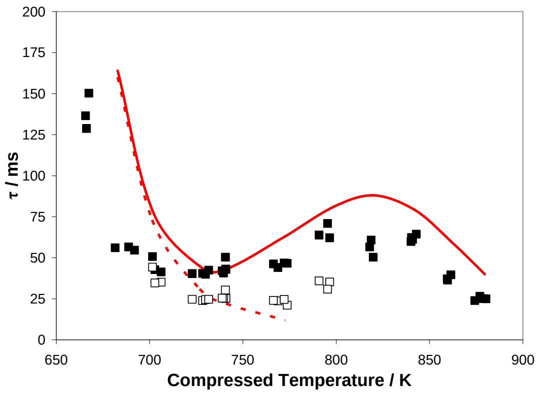

Fig. 4 Cyclohexane ignition in a rapid compression machine. End of compression pressures of 7 to 9 atm. Stoichiometric cyclohexane in simulated air mixtures The diluent gas consisted of $N_2/Ar/CO_2$. The dashed line and open squares correspond to the first stage ignition. Solid lines and filled squares correspond to the total ignition time. Model: lines, Experiments [35]: symbols.

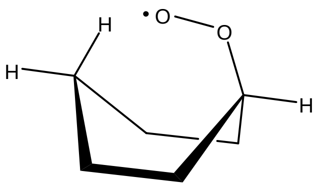

Fig. 5 RO_2 isomerization in cyclohexane.

cyclic structure was not taken into account. This work shows the importance of properly including the effect of molecular structure on reaction rates.

Toluene

Toluene is an important component in gasoline. It is the most common aromatic in gasoline and it can reach levels up to 35% [1]. Toluene is recommended as a component in gasoline surrogates in recent review by a surrogate fuel working group [1]. Recently, there have been significant improvements in the ability to simulate toluene oxidation [15, 37, 38]. Many of the reactions of toluene have been updated in the present work with rate constants recently reported in the literature. These include toluene decomposition reactions [39], reactions of toluene with OH, H, and O_2 [40] and reactions of benzyl with O_2 [41]. Abstraction of phenyl H's on toluene is also now included in the mechanism from Bounaceur *et al.* [26]. The updated mechanism has lead to improved agreement with toluene ignition delay times at shock tube conditions [15].

Methyl esters

One of the important renewable fuels is biodiesel. Biodiesel is frequently derived from vegetable oils from soy beans, canola (rapeseed), and other plants. These vegetable oils are usually converted into methyl esters so that they can be easily blended with conventional diesel fuel. Much of the methyl esters are derived from soybeans and canola and these fuels consist of only five components (Fig. 6). As a starting point, we have used methyl decanoate, a large methyl ester, as a surrogate for the methyl esters found in soy bean and rapeseed derived biodiesel. Methyl decanoate has a long n-alkane chain as in methyl palmitate found in soy and rapeseed-derived methyl esters (Fig. 6). The n-alkane chain in methyl decanoate is shorter than methyl palmitate and may lead to a lower reactivity than biodiesel. However, this effect can be compensated for by adding a large n-alkane to the methyl decanoate if needed to increase the reactivity of the biodiesel surrogate.

Table 1 Rate constants for RO_2 isomerization in acyclic alkanes and cyclic alkanes (cm-mole-sec units)

Ring size	**A**	**n**	**Ea**	**Rate, 750 K**
Curran *et al.* [42] non-cyclic RO_2:				
5	1.0e+11	0	26850	6.0e+3
6	1.25e+10	0	20850	4.2e+4
7	1.56e+9	0	19050	8.8e+3
Modified for cyclic RO_2:				
5	4.94e+11	0	31000	4.6e+2
6	1.86e+11	0	24080	1.8e+4
7	1.08e+10	0	24360	8.6e+2

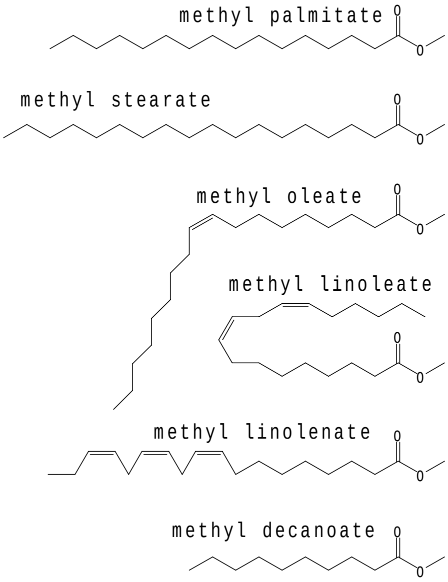

Fig. 6 Molecular structure of the components found in soybean and rapeseed oils methyl esters and of methyl decanoate [14].

Recently, a chemical kinetic mechanism for the low and high temperature oxidation methyl decanoate has been developed [14]. This development significantly enhances the capability for modeling biodiesel fuels. The results of the methyl decanoate model [14] are compared to rapeseed oxidation experiments in a jet stirred reactor (Fig. 7). The experiments were performed at 10 atm so that they are relevant to pressures found in internal combustion engines. It can be seen from the comparison of computed and measured results that the methyl decanoate model is a quite good surrogate for rapeseed-derived methyl esters.

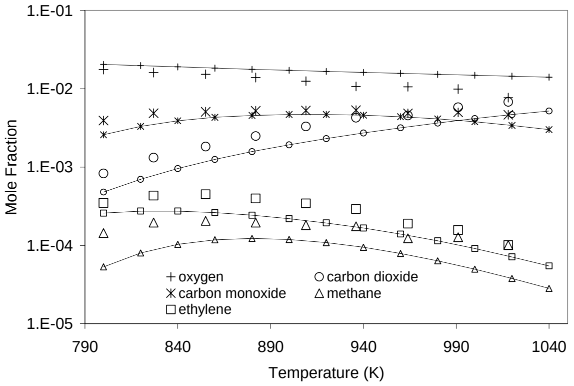

Fig. 7 Comparison of model predictions (methyl decanoate) with experimental measurements (rapeseed-based methyl esters) [43] in a jet stirred reactor at 10 atm (equivalence ratio of 0.5, fuel/O_2/N_2 mixtures, residence time of 1.0 sec).

Methyl esters form carbon dioxide at low temperatures directly from the methyl ester structure. [14, 44, 45]. The methyl decanoate model simulated the formation of CO_2 [14] at low temperature quite well (Fig. 7). When methyl esters are used as biodiesel, this direct formation of CO_2 wastes some of the oxygen in the fuel that can otherwise be used to prevent carbon in the fuel from leading to soot formation in the engine [44, 46].

SURROGATE MODELS

After mechanisms for individual components have been developed, these component mechanisms need to be combined to create a surrogate fuel model for gasoline, diesel, jet, or alternative fuels. Cross reactions between species contained in one component mechanism and not in the other component mechanism need to be considered. A number of surrogate models have been developed for gasoline [47-50] and diesel fuel [51]. In gasoline fuel comparisons, Gauthier *et al.* [52] found that experimentally measured ignition delay times for 60% isooctane, 20% toluene, and 17% n-heptane mixture gave good agreement with shock tube ignition delay times for a research gasoline. Figure 8 shows the results of using another gasoline surrogate, a five-component surrogate model (n-heptane, iso-octane, 1-pentene, toluene, and methyl cyclohexane), to simulate gasoline experiments in an HCCI engine [47]. Three different mixtures were tried (Table 2). In mixture 1, the relative amounts of each component were based on the approximate level of each of the chemical classes present in gasoline. In mixture 2, blended octane numbers were used to approximately match the octane number of the gasoline tested (90.8 RON and 83.4 MON). In mixture 3, the n-heptane concentration was increased to increase the reactivity of the mixture. Small differences were seen between the three mixtures, with mixture 3 behaving slightly better compared to the gasoline experiments (Fig. 8).

Table 2. Molar composition and octane numbers of the proposed surrogate fuel mixtures for gasoline.

% Molar Composition	Mixture 1	Mixture 2	Mixture 3
iso-Octane	60	40	40
n-Heptane	8	10	20
Toluene	20	10	10
Methyl cyclohexane	8	40	30
1-Pentene	4	0	0
RON (linear)	92.9	82.2	74.5
MON (linear)	90.6	80.0	72.7
RON (blend)	96.3	92.9	82.5
MON (blend)	92.9	84.9	76.3

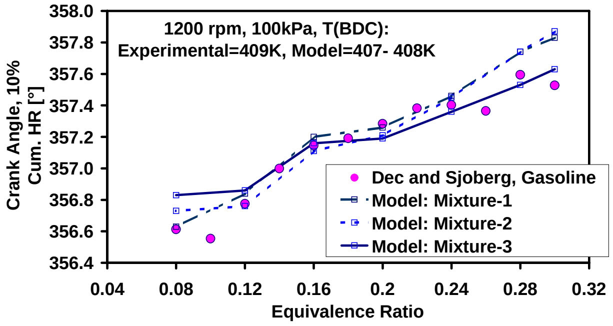

Fig. 8 Comparison of the predicted and measured crank angle for 10% burn at different equivalence ratios at constant intake pressure of 100 kPa and temperature of 409K. For qualitative comparison, T_{BDC} in modeling is adjusted to match that measured at an equivalence ratio of 0.16 [47].

In diesel fuel comparaisons, Bounaceur *et al.* [51] found that they could reproduce the experimental pressure history in a conventional diesel engine with surrogate models consisting of pure n-heptane or 70% decane and 30% alpha-methyl-naphthalene.

CHEMICAL MODEL REDUCTION

Detailed chemical kinetic models for surrogate fuels for gasoline, diesel, jet and various alternative fuels have large numbers of species and reactions with accompanying large computational requirements. Their direct use in computational codes for engine combustion would encounter excessive computational times unless some steps are taken. Methods to reduce the computational cost include mechanism reduction [53-57], use of low dimensional manifolds [58] and singular perturbation [59], chemistry tabulation [60, 61], sparse matrix solvers [62], multi-zone models [63], and others. Some of these methods can be combined.

One recently developed technique to reduce the size of chemical kinetic mechanisms is the directed relational graph method [53]. Using this approach Lu and Law were able to reduce a 561 species n-heptane mechanism and an 861 species iso-octane mechanism to 188 and 233 species respectively [64].

CONCLUSIONS

The development of surrogate fuel models for practical fuels like gasoline, diesel, jet fuel and alternative fuels has made considerable progress over the last few years. More detailed chemical kinetic models to represent components in these practical fuels are becoming available. The molecular structures of these component models can be used to represent almost all the chemical classes in practical fuels. Much work remains to extend the chemical kinetic models to higher molecular weights that are more representative of practical fuels and to extend the models to encompass a greater variety of chemical structures present in fuels. These component models can be then combined into fuel surrogate models which need to be reduced so that they can be effectively used in multidimensional engine simulation codes.

Acknowledgements

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

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