

# **H1. *Invited*: Development of Surrogate Chemical Kinetic Mechanisms for Practical Fuels**

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Chemical kinetic mechanisms are needed to simulate the chemistry of practical fuels like gasoline, diesel and jet fuel to enable combustion models for real devices such as spark-ignition, homogeneous-charge-compression-ignition (HCCI), diesel and jet engines. In this talk, the development of a surrogate mechanism for gasoline is presented showing the issues that were encountered. The surrogate mechanism is targeted for modeling of combustion in an HCCI engine. A lot of interest is focused on HCCI engines because of their high efficiency and low emissions of NO<sub>x</sub> and soot. However, there are technical barriers that need to be solved such as control of combustion phasing, high-load operation, and emissions of CO and hydrocarbons. Combustion models for practical fuels can help solve these problems for HCCI engines.

The results for the surrogate gasoline model compare well with experiments on HCCI engines for combustion phasing when the fuel/air equivalence ratio is varied. Prediction of HCCI combustion phasing is critical since combustion of 50 percent of the fuel needs to occur when the piston is near top dead center in the engine to attain the desired efficiency benefits of HCCI. The surrogate gasoline model does not predict well the combustion phasing when the intake pressure is raised and the intake temperature is lowered. In this case, experiments show the onset of low temperature chemistry in the engine that is not observed in model when simulating the experiments. More investigation of the effect of the temperature-pressure history in the engine on the model simulations needs to be performed.

In order to construct surrogate mechanisms for practical fuels, sub-mechanisms for individual components for the surrogate fuel need to be developed. In the presentation, the development of a diisobutylene mechanism to represent olefins in gasoline and the development of a methylcyclohexane mechanism to represent cyclic alkanes in gasoline and diesel fuel will be discussed. In the diisobutylene mechanism, the 1-pentene and 2-pentene isomers of 2,4,4-trimethyl pentene were considered as fuels. The trends in ignition delay times measured in a shock tube were opposite that expected based on the relative rate constants for the decomposition of the two isomers.

In the presentation, technical barriers to the development of mechanisms for practical fuels will be discussed. These barriers are related to the use of tools for the calculation of thermodynamic properties and reaction rate constants, and tools for automatic mechanism generation and mechanism reduction. There are also difficulties in keeping track of large amounts of data and metadata for reaction mechanisms and making it available to the research community. Additionally, better solvers are needed when large surrogate mechanisms are applied to premixed flame and counterflow flame problems.

## H2. An Experimental and Chemical Kinetic Modeling Study of Surrogate Diesel Fuels

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Typical biodiesel fuels consist of mixtures of saturated and unsaturated methyl esters containing carbon chains with twelve or more atoms in length [1]. Although methyl butanoate (MB) and ethyl propanoate (EP) do not have the high molecular weight of a biodiesel fuel, they do have the essential chemical structural features, namely the  $RC(=O)OCH_3$  structure (where R is an alkyl or alkenyl radical) with the advantage that the resultant reaction mechanism is smaller and more manageable in size than that for a larger hydrocarbon. In addition, as both MB and EP both have the same molecular formula a comparative study of the influence of molecular structure is of interest.

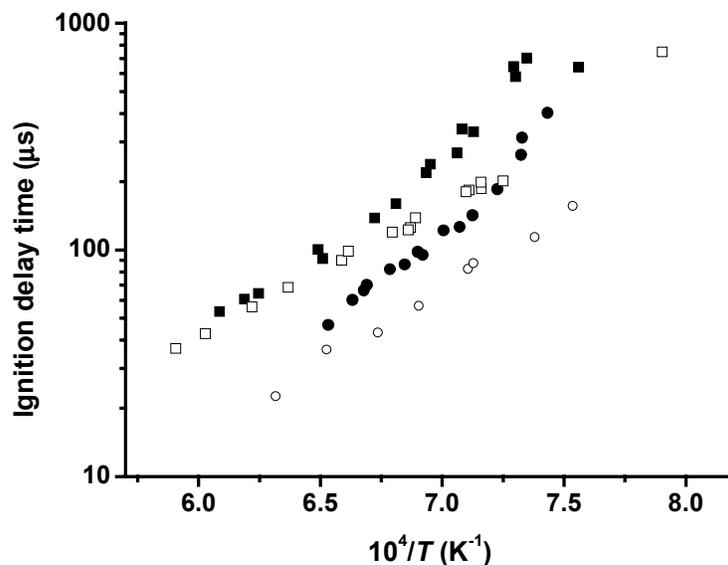


**Fig. 1:** Molecular structure of surrogate biodiesel fuels.

Numerous engine combustion studies have been performed using ester fuels and their constituents [3]. Until recently, the few fundamental studies suitable for comparison with chemical kinetic models are restricted to the pyrolysis regime. These studies were performed in a static reactor by Parsons et al. [4—6] in 1956, and by Hoare et al. [7] in 1967 but their results were more qualitative than quantitative in nature. The only known detailed chemical kinetic models [8, 9] have been used to simulate the data outlined above. More recently, Marchese et al. [10] performed flow reactor studies using methyl butanoate at 12.5 atm, over a temperature range of 500—900 K and equivalence ratios of 0.35 to 1.6. The mechanism of Fisher et al. was tested against the experimental data and good agreement was observed.

In order to further validate the chemistry of methyl butanoate oxidation, experiments were performed behind reflected shock waves using 1.0% fuel, at  $\phi = 1.0$  in the temperature range 1325—1650 K, at pressures of 1 and 4 atm. In addition, ethyl propanoate was studied under identical physical conditions in order to compare the chemical reactivity of both fuels. It was found that ethyl propanoate showed a higher reactivity than methyl butanoate. The detailed kinetic mechanism published previously by Fisher et al. was used to simulate the ignition delay times for MB. Initial simulations showed that the mechanism was faster than experimental measurements. However, after treating the unimolecular fuel decomposition reactions using a chemical activation formulation based on RRKM theory, good agreement was observed between the model and experiment. Moreover, the reason for the increased reactivity of ethyl propanoate

relative to methyl butanoate is explained via a low activation energy, six-center unimolecular reaction of ethyl propanoate producing propanoic acid and ethylene.



**Fig. 2:** 1.0% fuel in Ar,  $\phi = 1.0$ , ■ MB 1 atm, □ EP 1 atm, ● MB 4 atm, ○ EP 4 atm

#### References:

1. Graboski, M.S., McCormick, R.L., *Prog. Energy Combust. Sci.* 24:125—164, (1998).
2. Miyamoto, N., Ogawa, H., Nurun, N.M., Obata, K., Arima, T., Society of Automotive Engineers, SAE-980506, (1998).
3. Knothe, G., Bagby, M.O., Ryan, T.W. III, *JAOCs*. 75(8):1007—1013 (1998).
4. Parsons, B. I., and Danby, C. J., *J. Chem. Soc.* 1795—1798 (1956).
5. Parsons, B. I., and Hinshelwood, C., *J. Chem. Soc.* 1799—1803 (1956).
6. Parsons, B. I. *J. Chem. Soc.* 1804—1809 (1956).
7. Hoare, D. E., Li, T.-M., and Walsh, A. D., *Proc. Combust. Inst.*, 11:879—887 (1967).
8. Archambault, D., Billaud, F., *J. Chim. Phys.* 96:778—796 (1999).
9. Fisher, E. M., Pitz, W. J., Curran, H. J., Westbrook, C. K., *Proc. Combust. Inst.* 28:1579—1586, (2000).
10. A. J. Marchese, M. Angioletti, F. L. Dryer, *30<sup>th</sup> Intl. Symposium on Combustion*, Work in Progress Poster 1F1-03, University of Illinois at Chicago, July 25—30, 2004.

### H3. The Development and Validation of a Surrogate Mechanism for Real Fuels

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Surrogates for real fuels reported in the literature are normally composed of mixtures of paraffins, iso-paraffins, cycloparaffins, olefins, and aromatics selected to match relevant performance metrics of the fuels. The present paper provides mechanisms for the fuel components that can be used in surrogate formulations. In developing the mechanisms particular attention was given to paraffin mechanisms, since paraffins dominate the composition of aviation and diesel fuels. The building block was a normal heptane mechanism compiled from sub-mechanisms in the literature and extended to normal decane, normal dodecane, methyl cyclohexane, and iso-octane. Around 250 new reactions were added and also rates of more than 50 reactions in the base set were modified to fit the data from a large number of premixed flames. Reactions involving paraffins, olefins, and alkyl radicals in the same reaction class were assigned generic rates. Rates of reactions involving alkynes, allylic radicals and other unsaturated species were carefully estimated by consulting findings in the literature for same or similar reactions with adjustments of statistical factor and activation energy. Improvements have also been made in predicting the formation of the first aromatic ring, which was found to be closely related to reactions of the allyl radical; these allylic reactions determine the concentration levels of all olefins, most higher unsaturated species, and benzene. The resulting mechanism, named the Utah Surrogate Mechanism, consists of 208 species and 1087 reactions and gave overall satisfactory agreements between the measured and predicted species concentration profiles for a number of flames including a premixed kerosene flame, where the kerosene was modeled by a five-compound mixture of isooctane, methyl cyclohexane, normal dodecane, toluene, and benzene. The mechanism was also used to model other important fuel components and surrogate fuels including three fuel-rich premixed flames (iso-octane, n-heptane, n-decane) at atmospheric pressure and a premixed heptane flame with an equivalence ratio of 1.0. The simulated concentrations of products and intermediates were found to be in satisfactory agreement with the experimental data in these premixed flames. For example, the predicted concentrations of 34 out of 47 species measured in the fuel-rich normal heptane and normal decane flames are within 20% of the experimental data. The mechanism was also validated with two fuel-rich premixed benzene flames to test its applicability to the combustion of aromatic species, in addition to seven fuel-rich premixed flames of smaller hydrocarbons including one methane flame, three acetylene flames, and three ethylene flames; these flames were run at various pressures. Examples of the numerical accuracy of the Utah Surrogate Mechanism in predicting the critical soot precursors of acetylene and benzene are presented in Figures 1 and 2.

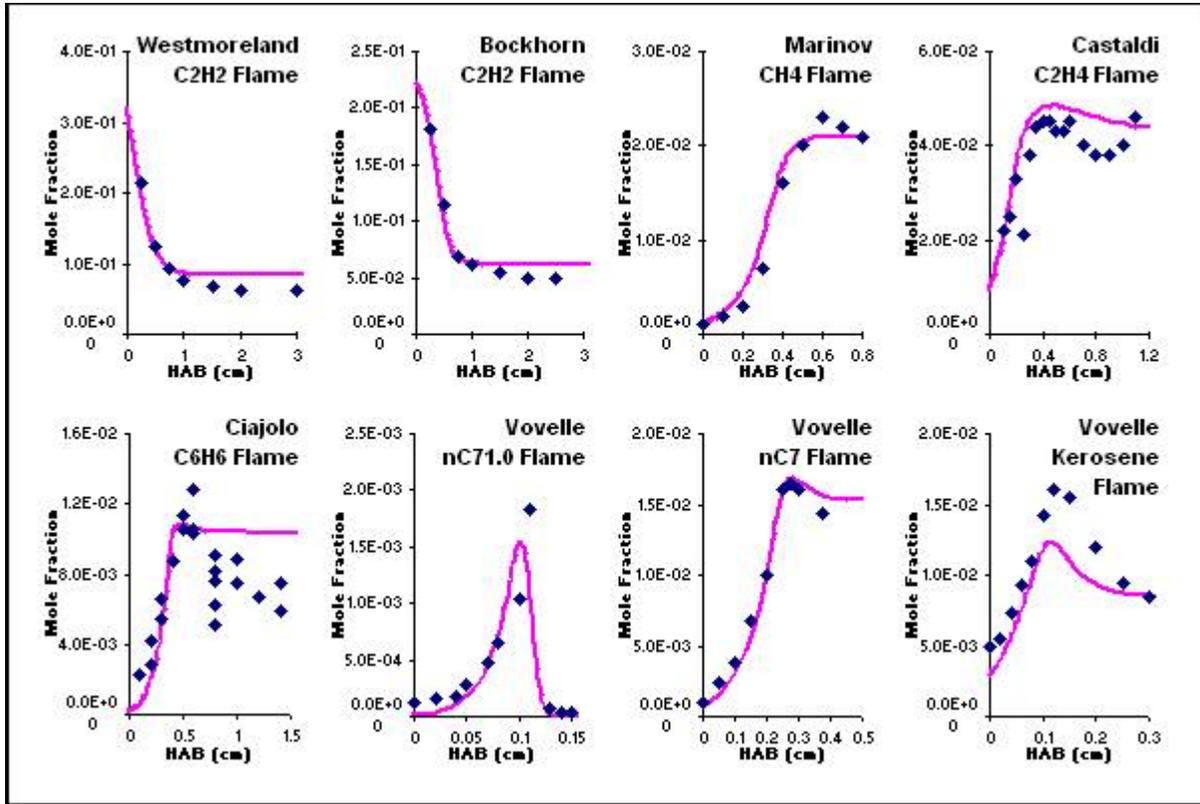


Figure 1: Comparisons of the predicted and measured concentration profiles of acetylene in premixed flames.

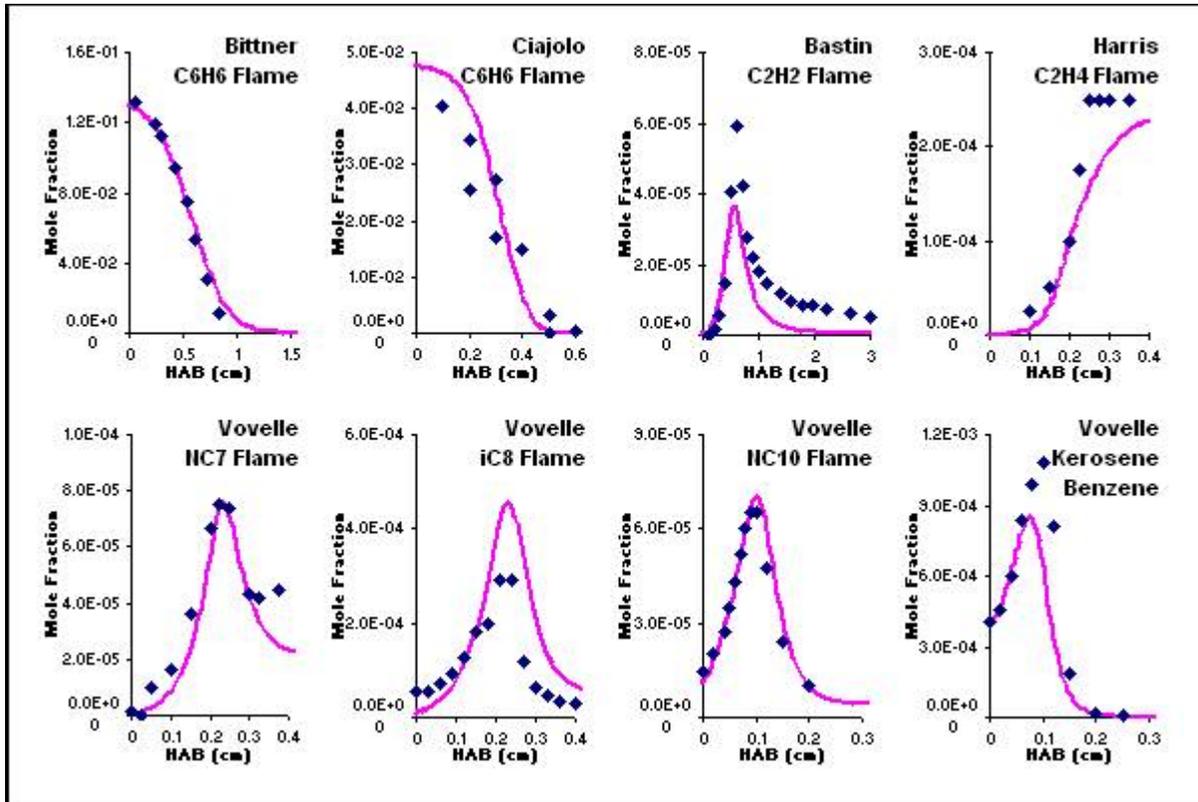


Figure 2: Comparisons of the numerical and measured concentration profiles of benzene in premixed flames

## H4. The Decomposition of N-Pentyl and N-Hexyl Radicals under Combustion Conditions

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Linear alkanes are the main components of most organic fuels. Alkyl radicals are the first decomposition products. This is followed by their oxidation and/or decomposition. The relative contributions of the two processes dictate the subsequent behavior of the combustion system. Most existing databases have concentrated on fitting data of pertinence to the former. Such databases are therefore not pertinent for rich environments. In this presentation we describe our current work at assigning rate constants for the decomposition and isomerization processes involving linear alkyl radicals. Work on linear pentyl and hexyl radicals will be described. The former is the first of the larger alkyl radicals for which isomerization is important. These radicals and their reactions must be part of all databases containing more than 6 carbon atoms.

Practically all the existing data on alkyl radical decomposition bear on smaller alkyl radicals. There does exist considerable information on the reverse radical addition reaction. Through detailed balance rate expressions for the decomposition processes can be obtained. Our procedure involves collecting all existing data pertinent to reactions in both directions, estimating the thermodynamic properties of relevant molecules and radicals using standard procedures and deriving a set of self consistent rate expressions for beta bond scission. Existing data on isomerization process involve studies at lower temperatures. They result in rate expressions that have very low A-factors. We have carried out experimental studies using n-alkyl iodides in single pulse shock tube experiments. Results for the pentyl and hexyl iodides leads to a determination of the contributions from 1-4 and 1-5 hydrogen migration. They are compatible with lower temperature results only if contributions from tunneling in the lower temperature regime is taken into account.

Rate constant over extended temperature and pressure ranges have been determined on the basis of the solution of time dependent master equation. Our shock tube experiments in the 2 to 6 bar range are in the  $k/k_{\infty}$  range of 0.3. Over the entire temperature and pressure range of pertinence to combustion applications (0.3 to 100 bars), deviations from high pressure behavior does not exceed an order of magnitude and reaches a maximum in the 1000 K range and probably cannot be ignored. There are problems in fitting results in standard format. The Arrhenius plots at constant pressure does not show consistent deviations from the high pressure value. Instead, as a result of the low reaction threshold, rate constants begin to return to high pressure values as the temperature is further increased. This pathological behavior means that even a modified Arrhenius plot is not able to capture the expected behavior.