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# Fuel Chemistry Models for Simulating Gasoline Kinetics in Internal Combustion Engine Applications

Zhenwei Zhao, Marcos Chaos, Andrei Kazakov, Ponnuthurai Gokulakrishnan, Michele Angioletti, Frederick L. Dryer

fldryer@princeton.edu

http://www.princeton.edu/~combust

Princeton University



Mechanical & Aerospace Engineering Department



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## Introduction

- **Motivation:** develop chemical kinetic sub-models that can properly describe the important attributes of gasoline direct injection (GDI), and homogeneous charge compression ignition (HCCI) combustion processes.
- Practical fuels, such as gasoline, are mixtures of very large numbers of different hydrocarbons — extensive efforts have been focused on studying the kinetic behavior of single component or simple mixtures of components that can represent gasoline.
- PRF mixtures (primary reference fuels; *n*-heptane and *iso*-octane) are at the foundations of rating gasoline octane number; however, PRF physical/chemical properties can behave significantly different in homogenous charge, spark ignition engines than gasoline itself.
- More complex mixtures of individual species representing different molecular groups have been suggested as surrogate fuels for gasoline. As a result of the number of initial molecular types, the dimensional character of surrogate kinetic models becomes large and the additional mechanism parameters become quite uncertain.
- The kinetic validation process itself becomes significantly more complex as fewer experimental data are available for validating the mechanism performance for the additional pure components as well as the mixtures.
- In this work, we have been driven by the above issues to consider approaches that limit the number of species to three, including the original PRF components. To this end we use PRF+toluene mixtures (heretofore named PRF+1) as surrogate fuels for gasoline combustion research.
- Experiments have been performed on PRF+1 mixtures with appropriate C/H ratios to match real gasoline in order to achieve an optimal mixture composition. Concurrently a minimized/optimized chemical kinetic model has been developed to best match the behavior of PRF+1 mixtures at pure toluene, *n*-heptane, and *iso*-octane content, as well as at the optimal PRF+1 composition. The present work provides additional contributions to improve the database on pure components, mixtures, and gasoline autoignition and oxidation kinetic behavior for optimizing and validating models by comparisons with predictions

## Toluene selection and C/H ratio

- The overall C/H ratio of complex surrogates has typically not been scrutinized so as to align with the C/H ratio of the gasoline of interest.
- Gasoline C/H ratios vary considerably by source, even though the Gasoline Octane Number (RON), Motored Octane Number (MON), and Road Octane number, of the various gasoline compositions may be nearly the same.
- The C/H mass ratio of PRF mixtures is functionally dependent on octane number. Mass ratio values lie between 5.213 (PRF 0) and 5.296 (PRF 100). Those for gasoline samples are typically considerably larger.
- The adiabatic equilibrium flame temperature of a fuel/air mixture is not only a strong function of the mixture equivalence ratio, but also of the C/H mass ratio of the fuel (see Fig. 1). It is important, thus, to match this parameter, in addition to others that reflect autoignition properties by selecting a proper additive to PRF components.
- Toluene is a simple aromatic that appears in gasoline and that can be used in test mixtures both to match C/H ratios and adjust over autoignition properties. Of possible alternatives to add to PRF components, it has also received the most detailed kinetic modeling attention.
- Toluene oxidation exhibits no negative temperature coefficient (two-stage ignition) kinetic behavior. The octane behavior of a PRF+1 mixture that replicates C/H ratio can be independently adjusted by changing the ratio of *n*-heptane and *iso*-octane without varying the toluene molar fraction.
- The presence of toluene in PRF mixtures, however, scavenges radical species that are produced in the reaction of alkanes at low and intermediate temperatures, and therefore suppresses negative temperature coefficient behavior of a PRF+1 mixture relative to the PRF mixture without toluene. Toluene has a higher hot ignition temperature than either PRF component, and thus addition of toluene to PRF mixtures will also affect hot ignition characteristics.

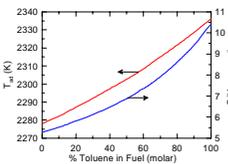
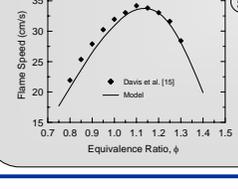
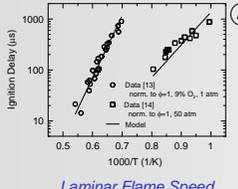
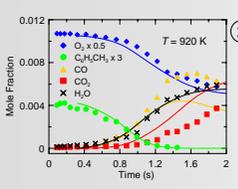
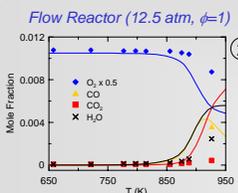


Figure 1. Calculated equilibrium reaction temperature for a PRF 87 mixture with added toluene to adjust the overall PRF+1 C/H mass ratio.

## Model Formulation

- Initial formulation started from a baseline *iso*-octane mechanism (Curran et al. [1]) — Minimized and optimized using methods similar to those in [2] — the model was shown to reproduce well autoignition and oxidation characteristics of pure *iso*-octane
- A suitable combination of minimized versions for *iso*-octane and *n*-heptane (derived from [3]) was identified, and the resulting combined mechanism was tested and optimized to reproduce pure component (PRF=0 and PRF=100) combustion characteristics as well as those for a PRF 90 (including laminar flame speeds).
- No suitable toluene submodel was identified that could properly couple with the Min/Opt PRF model. Research conducted previously in our laboratory has demonstrated the inability of several public-domain toluene oxidation reaction models (i.e., [4-7]) to predict high-pressure oxidation data taken in the VPFER.
- We have developed an in-house sub-mechanism for toluene oxidation, on current (and, still, incomplete) level of conceptual understanding of the oxidation of aromatic single ring species. The redevelopment process included several steps:
  - Basic mechanism structure for main species (toluene, benzyl, benzaldehyde, benzene, and their derivatives). Appropriate reaction rate coefficients were assigned based on an extensive up-to-date literature review.
  - Thermochemistry was taken from the Burcat [8] and LLNL databases, where possible.
  - Cyclic C<sub>5</sub> sub-mechanism added based on implementations by Alzueta et al. [9] and Djurjic et al. [10]. Updated cyclopentadienyl radical thermochemistry from Roy et al. [11] and Kiefer et al. [12] were adopted.
- The resulting set was then integrated with the PRF Min/Opt model (linking it to C<sub>2</sub>, C<sub>3</sub>, and C<sub>4</sub> intermediates and final products) producing the PRF+1 mechanism reported here (adding an additional 22 species and 102 reactions for a total of 469/1221 species/reactions).

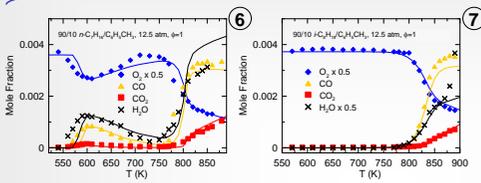
## Pure Toluene



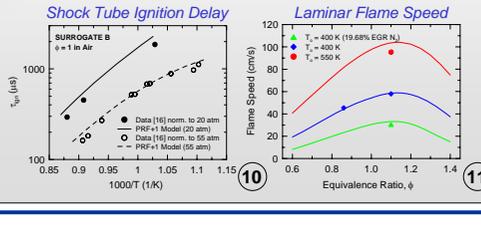
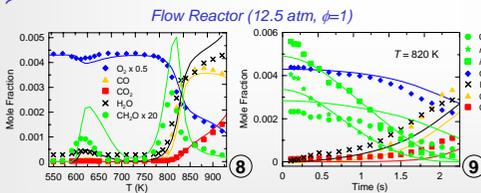
## Validation

- Figure 2 shows model-predicted toluene/O<sub>2</sub> reactivity against VPFER data. The model clearly captures the lack of NTC chemistry shown experimentally although it predicts a slightly higher reactivity as temperature increases.
- Figure 3 compares predictions of species time histories for the conditions shown in Fig. 2 at 920 K. Major species profiles are well reproduced. The agreement for intermediates (benzene, formaldehyde, not shown) is somewhat less satisfactory and further work needs to be done to determine alternative channels for these species. It should be pointed out, however, that the present agreement is a dramatic improvement over that found using the models of Refs. 4-6.
- Agreement with the latest low- and high-pressure toluene/air ignition data [13, 14] is excellent (Fig. 4).
- Flame speeds of toluene/air mixtures are faithfully reproduced by the model at all equivalence ratios (Fig. 5).

## Binary Mixtures



## Ternary Mixtures



- Figures 6 and 7 show PRF+1 model prediction against *n*-heptane/toluene and *iso*-octane/toluene reactivity data collected in the VPFER. As with the ternary mixtures shown below, very good agreement is observed for major species and the NTC region is properly reproduced (Fig. 6). In addition, although not shown, characteristic reaction time scales and dependences on equivalence ratio are properly captured by the model.
- Figures 8-11 show comparison of model predictions against data from different experimental systems for ternary mixtures (i.e. PRF+toluene). Figures 8, 9, and 11 show data collected in our laboratory for a mixture emulating a gasoline with ON=84.
- Of especial importance are the data shown in Fig. 10. These data appeared in the open literature after the development of the present model, and although the model was not optimized against this set, very good agreement can be observed.

## Summary

- A toluene oxidation submechanism has been produced that can properly reproduce available experimental data.
- The toluene model has been combined with a PRF model to generate a minimized and optimized model (PRF+1) to simulate gasoline combustion kinetics.
- The PRF+1 model performs well against experimental data from shock tubes, laminar flames, and new flow reactor data collected as part of the present effort.
- Comparison in all of the various experimental configurations are significant improvements over other models presently in the literature, especially for mixtures involving toluene.

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