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Proposal Title: Generation of Comprehensive Surrogate Kinetic Models and Validation Databases for Simulating Large Molecular Weight Hydrocarbon Fuels

Institution Proposal Number:

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Topic Number: MURI Topic #12  
Topic Title: Science-Based Design of Fuel-flexible Chemical Propulsion/Energy Conversion Systems

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Project Summary/Abstract

Title: Generation of Comprehensive Surrogate Kinetic Models and Validation Databases for Simulating Large Molecular Weight Hydrocarbon Fuels

MURI Topic number 12, Submitted to AFOSR by
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Funding request: Three years: $4.5M; Two Additional years: $3.0M; Five years (total): $7.5M

Research Problem: Accurate description of petroleum derived and alternative fuel combustion chemistry in forms that will permit use in efficient numerical design tools is critical to assessing effects of fuel property changes on existing hardware performance and to developing future propulsion systems. Detailed modeling of real fuels is prohibitively complex given variability, numbers, and types of components found in the fuels and lack of fundamental physical, thermochemical, kinetic, and transport data. An alternative is to develop rules and methodologies to accurately reproduce combustion related gas phase chemical kinetic, transport, and physical properties of real fuels (C/H ratio and structural composition, heat content, evaporation and ignition properties, burning and heat release rates, and NOx and sooting characteristics) using "surrogate" mixtures of a small number of components. Of most significance is that experimental data to validate kinetic and transport effects for each fuel component, their mixtures, and real fuels in the same fundamental venues and over the wide ranges of conditions (equivalence ratio, pressure, temperature, dilution, and transport time scales) found in propulsion systems are largely deficient. Rules for selecting surrogate components and matching their mixture properties against real fuels are not well defined or fully tested. Detailed chemical kinetic, thermochemical, and transport parameters for large molecular weight hydrocarbon components (10<C<18) and their reaction fragments are limited. Finally, though new methods of minimizing and optimizing detailed kinetic mechanisms have progressed substantially, dimensional sizes of the results for large molecules and mixtures remain too large for implementation directly into CFD codes for parametric engineering design calculations.

Technical Approaches: Based on a new principle to control kinetic and transport timescales of aliphatic and aromatic fuel mixtures, a small number of surrogate components are selected that can match gas phase combustion properties of real fuels. A cross-validated and comprehensive experimental database will be generated consisting of ignition delay, speciation, flame speed, ignition and extinction limits, and sooting characteristics for each component, their mixtures, and for real fuels. Single pulse shock tube and variable pressure flow reactor experiments will produce data for highly dilute reaction conditions, while rapid compression machine, laminar premixed and non-premixed flames, and turbulent combustor experiments will yield data for higher fuel/oxidizer concentrations approaching those in real systems. Detailed kinetic models will be developed and validated based on computational theory and comprehensive hierarchical mechanism development approaches, guided by computational mechanism construction and utilizing in-house codes for mechanism behavior analysis. New kinetic reduction tools including diffusion and temperature coupling will be developed and used together with existing tools to produce minimized/optimized detailed kinetic mechanisms for use in CFD computations.

Anticipated Outcome: New validated principles to select surrogate fuel components; a cross-validated comprehensive experimental validation database for selected high carbon number components over ranges of physical parameters found in existing and advanced propulsion applications; detailed kinetic models for single components and their mixtures coupled with laminar transport that describe autoignition, heat release rate, laminar premixed and non-premixed flame, and sooting properties; rules and methods to match properties of surrogate mixtures with real fuels; tools to produce reduced kinetic models compatible with CFD applications.

Impact on DOD Capabilities: Enhanced efficacy of evaluating fuel property effects on existing propulsion system performance, and in advancing existing and new propulsion concepts.
Statement of Work

We propose to generate a surrogate fuel model, cross-validated critical experimental data, detailed and reduced kinetic mechanisms, analytical tools and experimental methods to accurately predict the complex gas phase combustion behavior of real fuels using a limited number of chemical components. Surrogate fuel model formulations will be based upon a blend of C₈₋C₁₆ components to which others can be added to improve the simultaneous emulation of chemical kinetic, transport, and physical property characteristics of real propulsive fuels.

The specific objectives are as follows:

(1) **Select and refine surrogate component candidates**

The sensitivity of radical production/inhibition rate to the molecular structures of aromatic species and of flame structure to the formation and diffusion of small fuel fragments and radicals are proposed as guiding principles for selecting surrogate fuel components. The following candidates are identified: one or more saturated hydrocarbons: n-decane, n-dodecane (Detailed kinetic models for normal alkanes up to C₁₆ are hierarchically similar); iso-cetane; one cycloalkane (methylcyclohexane); two alkylated aromatics: (n-propylbenzene; 1,3,5 trimethylbenzene); and 1-methylnaphthalene. Experimental data for component mixtures based on selected formulation methodologies will be compared with data using real fuels in the same experimental configurations to test and validate component selections and mixture formulation methodologies.

(2) **Develop transport, thermochemical and elementary kinetic databases and validated detailed kinetic models for each surrogate component**.

This research will estimate thermochemical and elementary chemical kinetic parameters to supplement existing databases, (e.g. at NIST, by W. Tsang and at DOD/DOE laboratories) as well as those under development (e.g. PRIME) through theoretical ab-initio calculations utilizing the GAUSSIAN suite of programs to characterize potential energy surfaces, and multi-channel RRKM packages (ChemRate, MultiWell, and VARIFLEX), as well as with codes developed in-house at Princeton for estimating rate coefficients. Transport data for large hydrocarbon molecules will be estimated by using Lennard-Jones collision diameters and potential energy well depths calculated from critical pressure and temperature properties. Comprehensive detailed models for fuel components will be constructed hierarchically based on literature data and the thermochemical/kinetic parameter assessment and modeling experience of the research team in prior model developments for large carbon number hydrocarbons (n-alkanes C₇₋C₁₆, iso-octane, benzene, toluene, xylanes, methylcyclohexane and 1-methylnaphthalene), small hydrocarbons, hydrocarbon oxygenates, and CO/H₂/O₂. Automatic mechanism generation will be used to complement the team’s long-term experience in developing comprehensive mechanisms hierarchically. Soot and NOₓ submodel components will be taken from the literature, validated against experiments, and adapted to the present studies.

(3) **Evolve a robust, fundamental, experimental validation database to characterize autoignition, heat release rate, premixed and non-premixed laminar flame properties and sooting for each component species, representative mixtures of components and real fuels**.

New experimental data from fundamental venues are essential for constructing and validating accurate detailed kinetic mechanisms and transport coupling characteristics. Data will be obtained for each surrogate fuel component, increasingly complex mixtures of components, and for real fuels themselves over ranges of pressures and temperatures that collectively represent conditions found in practical propulsive applications. Literature resources are sorely deficient of the needed data. This major task will provide new and extensive experimental data for: a. Ignition delays, species histories, and heat release rates; b. Flame speeds, ignition and extinction limits, Markstein length, flame structure and transport properties; and c. Sooting characteristics (over wide ranges of physical parameters in terms of fuel/oxygen equivalence ratio, pressure, initial temperature, and dilution) for each surrogate component, representative surrogate component mixtures and several real gas turbine fuels using the following experimental venues:
Princeton University (PU)

Variable Pressure Flow Reactor (VPFR) Experiments  Chemical characterizations in the VPFR will include as many identifiable stable reaction intermediates as possible for pure components and increasingly complex surrogate mixtures using continuous extractive, convection quenched sampling, analyzed on-line using paramagnetic oxygen, non-dispersive infrared (NDIR), continuous Fourier Transform Infrared (FTIR), and off-line using gas chromatograph (GC)/FTIR, GC/Mass Spectrometric (MS)/Flame Ionization Detection (FID) analytical methods.

VPFR experiments will determine “reactivity” characteristics as a function of initial reaction temperature. These experiments define the low temperature reactivity, heat release, significant characterization of intermediates evolved in the low temperature kinetic regime, the hot ignition temperature, and characterization of intermediates evolved near and above the hot ignition temperature. Experimental conditions will be: 2-12.5 atm pressure, fixed reaction residence time, equivalence ratio conditions of 0.5, 1.0, 1.5, $\infty$ heavily diluted in nitrogen, and for initial reaction temperatures from 550 - 950 K.

Other VPFR experiments will characterize “species-time history” profiles. These experiments define the reactant, intermediate, and product species evolutions as a function of initial fuel reactant parameters, and equivalence ratio, in low and intermediate temperature kinetic regimes (above the hot ignition temperature). Species time-history profiles will be obtained at the pressure and equivalence ratio conditions described above, at constant initial reaction temperatures spanning the low, intermediate, and high temperature regimes.

Experiments will also be performed with several real fuels using the above configurations. Chemical characterizations will be limited to major species indicative of reaction time scales.

Premixed Flame and Ignition Experiments  High pressure spherically outward propagating flame experiments will be conducted to measure flame speeds, flammability limits, and Markstein numbers at elevated pressures (1-30 atm) and initial temperatures over a broad range of equivalence ratios. Spectrally dependent radiation modeling and potential flow analysis will be used to correct previously ignored sources of error to yield radiation-free and geometry-independent flame speeds. Temperatures, major species and OH distributions will be determined by Rayleigh scattering, planar laser induced fluorescence (PLIF), and tunable diode laser absorption spectroscopy (TDLAS) using counterflow flames (at 1-6 atm). A two-dimensional numerical model with detailed kinetics and transport properties will be developed to assess multi-dimensional transport and the validity of similarity solutions in counterflow flames.

Non-Premixed Flame and Ignition Experiments  OH distributions will be measured by TDLAS and PLIF. The impact of transport properties of fuel and fragments on ignition time and ignition kernel development will be investigated by comparing ignition results of premixed and non-premixed flames, and, numerically, by transport perturbation analyses. This work will be coordinated with CWRU.

Case Western Reserve University (CWRU)

Rapid Compression Machine Experiments  Rapid compression machine (RCM) experiments will provide information on chemical kinetics leading to autoignition for high fuel/oxidizer concentrations, elevated pressure (10-50 atm) and low-to-intermediate temperatures (600-1100 K). Experiments will include individual components and multi-component blends of increasing complexity, and real fuels; all over a range of equivalence ratios and dilutions. Measurements will include ignition delay and species concentration histories during the induction period prior to autoignition.

Pre-mixed Flame Experiments  Counterflow premixed twin-flame experiments to determine fundamental flame properties, including laminar flame speeds and stretch-induced extinction limits, using Particle Image Velocimetry will be conducted from sub-atmospheric pressures to 6 atm and for fuel lean to fuel rich equivalence ratios.

Non-Premixed Flame Experiments  Counterflow flame experiments to determine fundamental flame properties, including forced ignition limits, stretch-induced extinction limits, and scalar
profiles, from sub-atmospheric pressures to 6 atm will be performed in coordination with PU. Raman scattering will be employed for major species and temperature measurements.

**Pennsylvania State University (PSU)**

*Autoignition experiments* High pressure flow reactor (HPFR) experiments will be conducted to determine the autoignition times for individual surrogate components, their mixtures, and real fuels. These experiments will be conducted over a range of equivalence ratios at elevated pressures (5-30 atm) and temperatures (600-950K). Prevaporized fuels will be studied under turbulent flow conditions (Reynolds number ~ 5×10^5 to 3×10^6) to simulate actual jet engine operating conditions. Chemiluminescence from OH and CH as well as laser-based diagnostics will be used to characterize observations. For selected conditions, work will be closely coordinated with RCM experiments at CWRU to validate measured autoignition times.

*Sooting Characteristics* The High Pressure Modular Gas Turbine Combustor (MGTC) will be used to determine and compare sooting characteristics of surrogate and practical fuels over a range of preheated air temperatures as high as 800K, at pressures up to 20 atmospheres, and for a range of fuel/air equivalence ratios. Quantitative measurements of soot volume fraction will be made using both laser extinction and laser-induced incandescence techniques. A recently developed extension of the threshold sooting index for characterizing sooting tendency will be applied to predict sooting characteristics of proposed surrogate fuel mixtures. Preferential vaporization on experimental observations will also be assessed.

**University of Illinois, Chicago (UIC)**

*Single Pulse Shock Tube Experiments* Single pulse shock tube (SPST) experiments will determine ignition delay and examine pyrolytic and oxidative chemistry for highly diluted concentrations of oxidizer and individual surrogate components, component mixtures of increasing complexity and real fuels under both inert and oxidizing conditions at high pressures (10-40 atm) and temperatures (800-2500K), and for a range equivalence ratios (0.5-4) and residence times (0.5-3.0 msec). Prevaporization methods of mixture preparation will be augmented by an aerosol preparation technique to permit experiments with low vapor pressure surrogate components, mixtures, and real fuels. Gas samples will be analyzed using GC and GC/MS techniques to determine stable species concentrations of hydrocarbon and oxygenated reactants/intermediates/products as a function of reaction conditions and residence times. Species profiles will also be provided for some pyrolysis conditions.

(4) Derive comprehensive, validated kinetic models for component mixtures relevant to real fuel emulation over the full thermodynamic parameter space

Comprehensive, detailed validated models for component mixtures will be developed using hierarchical development techniques that describe the kinetic and transport coupling of individual components observed in the above suite of validation experiments as well as for other venues and conditions that appear in the literature. Specifically, the predictions of detailed kinetic models for mixtures using the methodologies and rules formulated in (6) below will be compared against experimental data obtained in the above venues with several real fuels. The full mechanisms will be validated against generated experimental as well as literature data.

(5) Identify critical performance targets for surrogate mixture behavior important to altitude relight, high speed propulsion, augmentor performance, and gas turbine environments

Based on experimental data and new principles for the selection of surrogate fuel components, the team members will work with an advisory group composed of industrial and government laboratory researchers to further refine the critical performance targets that define the conditions of pressure, temperature, equivalence ratio, and transport coupling over which detailed descriptions of surrogate fuel mixtures must emulate real fuel behavior.

(6) Develop methodologies to reproduce real fuel targets with mixture formulation models

There is flexibility provided by varying the component fractions of mixtures formed using the surrogate candidates proposed above to adjust the surrogate C/H ratio, structural composition, energy density, heat release rate, the respective types of aromatics that compose the aromatic
content, and hence the autoignition characteristics, and sooting properties to emulate those of a real fuel. Methodologies that adjust surrogate component mixture properties to match those of a particular propulsive real fuel will be tested by comparing experimental characteristics of surrogate mixtures against real fuels with known C/H ratio, energy density, etc. in the same fundamental experimental venues as discussed in task (3) above. Chemical reactivity characteristics, and high temperature ignition characteristics, sooting characteristics, and laminar premixed and non-premixed properties of the predicted mixture and a real fuel will be compared. Comparison of evolution of major reaction products and intermediates will also be made.

(7) **Apply existing and new dimensional reduction methods to produce reduced models that can be used in numerical design tools**

In addition to applying other existing dimensional reduction methods, we will specifically investigate the following reduction approaches: (a) An augmented CSP method will be developed to include both temperature and diffusion coupling with species reactions, and to identify the timescales of reaction groups, heat release, and diffusion transport; coupled or isolated species groups; and unimportant reactions and species. A minimized elementary mechanism is obtained by removing the unimportant reactions, species or species groups; (b) A Combined pre-established and In Situ High Dimensional Model Representation (CIS-HDMR) normalized fitting model will be developed replace the integration of reduced mechanism generated by CSP analysis to achieve significant dimensional reduction of kinetic mechanisms and improvement of computation efficiency.