

Development of Reduced Kinetic Models for Petroleum-Derived and Alternative Jet Fuels

Stephen Dooley¹

Department of Chemical and Environmental Science, University of Limerick, Ireland

Sang Hee Won², Francis M. Haas³, Jeffrey Santner⁴, Yiguang Ju⁵, Frederick L. Dryer⁶

Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey 08544, USA

Tanvir I. Farouk⁷

Department of Mechanical Engineering University of South Carolina, Columbia, SC, USA

The surrogate fuel concept to replicate the detailed gas phase combustion behaviors of conventional and alternative jet aviation fuels in numerical combustion models is extended and tested in specific examples of synthetic jet fuels derived from coal and natural gas, and also to the pressure and equivalence ratio dependences of the combustion responses of conventional Jet-A fuel. The formulation of surrogate fuels for Syntroleum S-8, Shell SPK and Sasol IPK, is described. Assuming these compositions, a detailed chemical kinetic model construction previously elaborated upon is extended and tested against reference data sets of shock tube ignition delay and laminar burning velocity. Calculations with the detailed kinetic model, containing 3147 species correctly represent the experimentally measured reactivity of the target fuels for shock tube ignition delay. The model also captures trends in the ignition delay for a reference Jet-A as a function of pressure and equivalence ratio.

The earlier reported detailed model is expanded to encompass a range of n-alkane carbon numbers up to C₁₆ and iso-cetane. The expanded model is validated against available shock tube ignition delay in detailed form and against laminar burning velocity datasets using a series of numerically reduced models of decreasing dimension for n-hexadecane, iso-cetane, and their mixtures.

Though the detailed model reproduces the general kinetic behavior for the ignition delays of each jet fuel, the predicted values are generally longer than experimental results. A series of reduced models of the order of 100 species in size, are produced for simulation of flame environments. Calculations for laminar premixed flames for each jet fuel are similar with burning velocities for IPK flames marginally lower than those for the conventional Jet-A which in turn are marginally lower than those for S-8.

The requirement for severely reduced, but high fidelity chemical kinetic numerical schemes that retain predictive capacities for the combustion behaviors of real liquid transportation fuels is addressed through the introduction of a strategy to produce “compact” models of the order of 35 species. The strategy utilizes calculations of the detailed model construct as a fundamental and scientific standard, to which engineering approximations achieved through adjusting reaction rates and omitting or diverting the fate of select reaction pathways at high carbon numbers are applied. The strategy is tested for the exemplar real fuel test case of the S-8 ignition delay and laminar

¹ Senior Research Scientist, Dept. of Chemical & Environmental Sciences, University of Limerick, AIAA Member.

² Associate Research Scholar, Department of Mechanical and Aerospace Engineering, Princeton University, AIAA member.

³ Technical Staff, Department of Mechanical and Aerospace Engineering, Princeton University, AIAA member.

⁴ Graduate Student, Department of Mechanical and Aerospace Engineering, Princeton University, AIAA member.

⁵ Professor, Department of Mechanical and Aerospace Engineering, Princeton University, AIAA Associate Fellow.

⁶ Professor Emeritus and Senior Scientist, Department of Mechanical and Aerospace Engineering, Princeton University, AIAA Associate Fellow.

⁷ Assistant Professor, Department of Mechanical Engineering, University of South Carolina, Associate Fellow.

burning velocity data sets. The calculations of a compact model comprising only 36 species is demonstrated to retain quantitative fidelity to the calculations produced using the benchmark detailed model. Thus, a procedure to couple the real fuel description through combustion property target characterization, to the production of compact models for use in computational fluid dynamic platforms is demonstrated.

I. Introduction

Surrogate mixtures that emulate the combustion behaviors of a real aviation fuel have been extensively investigated by various approaches in the last decade¹⁻¹⁴ as this concept is viewed as a key enabling suggestion toward high fidelity numerical combustion models for real liquid transportation fuels. In the case of jet aviation fuel, it has recently been demonstrated that successful surrogate mixtures for the emulation of combustion kinetic behaviors can be formulated by matching select physical and chemical properties of a targeted fuel¹²⁻¹³ to those of simple mixtures of 2-4 pure component hydrocarbons. These studies have utilized the Derived Cetane Number (DCN), hydrogen to carbon molar ratio (H/C ratio), average molecular weight (MW) and the Threshold Sooting Index (TSI) as fundamental fuel formulation metrics to qualify the combustion phenomena of transportation fuels that are predominantly chemical kinetic in nature. Using this methodology, two surrogate mixtures have been formulated targeting a specific jet fuel, Jet-A POSF 4658, and another mixture has been proposed for the synthetic paraffinic aviation fuel, S-8. The similarity in combustion behaviors of the Jet-A, to those of mixtures of n-decane, iso-octane, and toluene (n-decane/iso-octane/toluene 42.7/33.0/24.3 mole %) ¹² and n-dodecane, n-propyl benzene, and 1,3,5-trimethyl benzene, in addition to iso-octane (n-dodecane/iso-octane/1,3,5 trimethyl benzene/n-propyl benzene 40.41/29.48/7.28/22.83 mole %) ¹³ was experimentally determined and found to be very similar. Later, a simpler mixture of n-dodecane/iso-octane (n-dodecane/iso-octane 51.9/48.1 mole %) ¹⁴ was also determined to have combustion properties closely consistent to the S-8 fuel it was formulated to mimic.

To achieve such high fidelity numerical models the predictability offered by fundamental knowledge of chemical thermodynamics and chemical reaction kinetics must be carefully and scientifically assembled into a numerical representation dimensionally small enough to be amenable to coupling with computational fluid dynamics algorithms. Given the very many (~tens of thousands of) chemical reactions and discrete chemical species (thousands) resulting from such a scientific framework, this task is arduous and has become a community-wide goal.

Stemming from the opportunity presented by these¹²⁻¹³ and related efforts¹⁻¹¹, we have recently begun to explore the state of the community effort to accurately and efficiently predict the gas phase combustion behaviors of existing and future jet aviation fuels¹⁴. We have reported provisional detailed and reduced kinetic model constructions that satisfy experimental measurements of homogeneous ignition delay and laminar flame propagation velocity for the pure components that comprise the surrogate fuels formulated for the target Jet-A fuel referred to above¹⁴. The performance of the detailed kinetic model construct, and the performance and dimensional size of reduced kinetic models was established for; n-dodecane, n-decane, iso-octane, n-propyl benzene, 1,3,5 trimethyl benzene, toluene and the mixtures of these components (referred to above) that have been demonstrated experimentally to be high fidelity surrogate fuels for a conventional jet aviation fuels. This work arrived at a summary position in quantitatively identifying the state-of-art in kinetic model size vs. kinetic model fidelity concerned with describing the gas phase combustion behaviors of conventional jet aviation fuel by fundamental scientific means. Specifically, in order to numerically reproduce real Jet-A ignition delay within a factor-of-two of experiment, current minimal model sizes are 144 species for temperatures > 1100 K at 20 atm, and 233 species for > 500 K at 20 atm, where both limits allow atmospheric pressure laminar burning velocity to be reproduced to within ~8% of experimental determinations. This information is summarized in detail in Figures 1-4 for the test case of Jet-A POSF 4658, showing the example cases of two surrogate fuel compositions¹⁴.

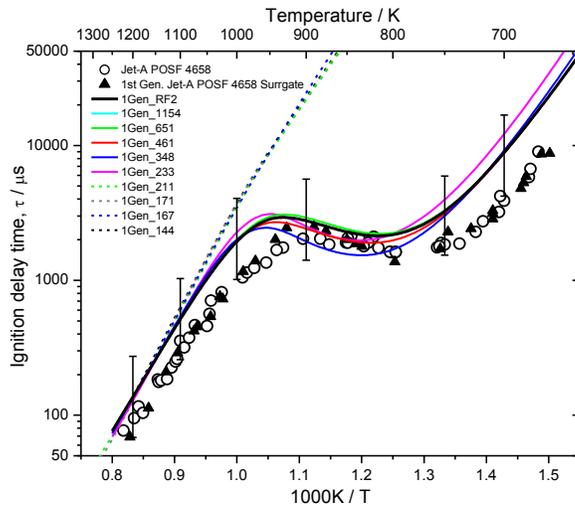


Figure 1. Shock tube ignition delay times for stoichiometric fuel in air mixtures of Jet-A POSF 4658 (hollow circles, 16-25 atm¹²) and the 1st generation (n-decane/iso-octane/toluene 42.7/33.0/24.3 mole %) Jet-A POSF 4658 surrogate fuel (solid triangles, 17-23 atm¹²). Lines are simulations with the kinetic models of this study, where “1Gen_144” refers to a reduced model produced for the 1st generation composition containing 144 species, and so forth¹⁴. Error bars show a factor-of-two threshold to the computations of the detailed model.

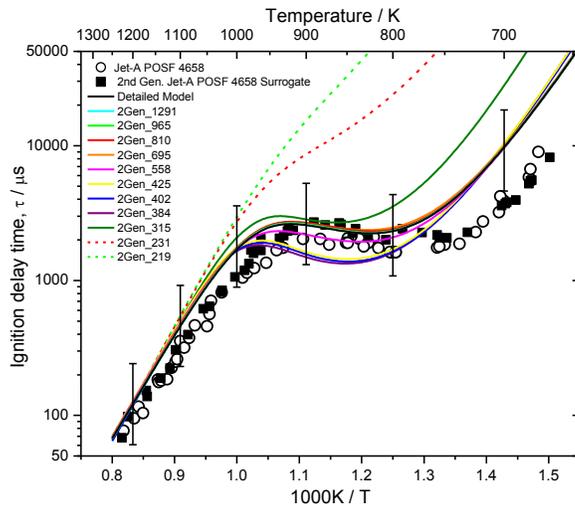


Figure 2. Shock tube ignition delay times for stoichiometric fuel in air mixtures of Jet-A POSF 4658 (hollow circles, 16-25 atm¹²) and the 2nd generation (n-dodecane/iso-octane/1,3,5-trimethyl benzene/n-propyl benzene 40.41/29.48/7.28/22.83 mole %) Jet-A POSF 4658 surrogate fuel (solid circles, 17-23 atm¹³). Lines are simulations with the kinetic models of this study, where “2Gen_219” refers to a reduced model produced for the 2nd generation composition containing 219 species, and so forth¹⁴. Error bars show a factor-of-two threshold to the computations of the detailed model.

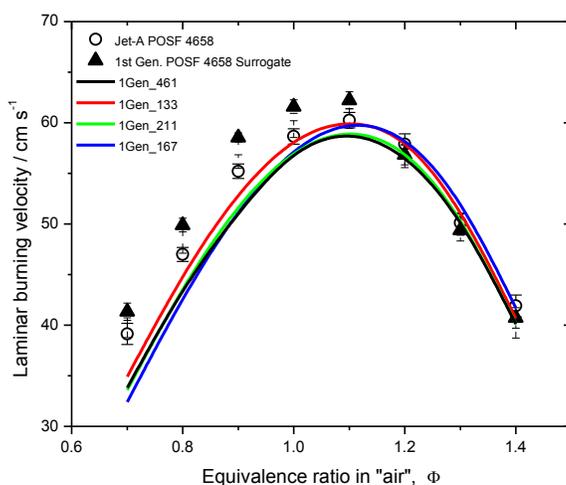


Figure 3. Jet-A POSF 4658 and 1st generation (n-decane/iso-octane/toluene 42.7/33.0/24.3 mole %) Jet-A POSF 4658 surrogate fuel laminar burning velocities at 1 atm and 400 K¹³ (symbols) and computations with reduced models of this study (lines), where “1Gen_167” refers to a reduced model produced for the 1st generation composition containing 167 species, and so forth¹⁴. Burning velocities are obtained by the non-linear extrapolation technique as discussed in Hui & Sung Fuel 109 (2012) 191–200¹⁵, [personal communication C. J. Sung 2012 University of Connecticut].

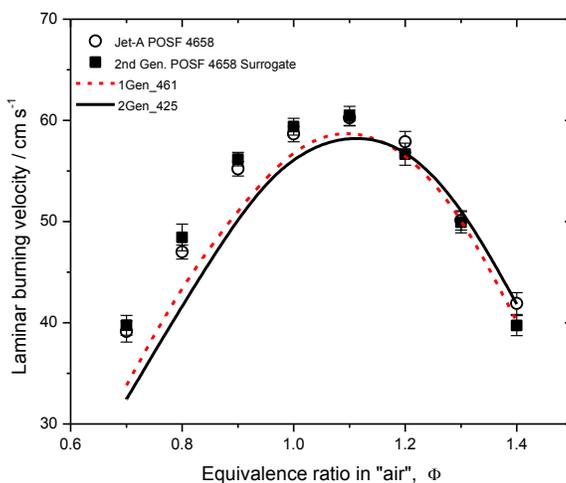


Figure 4. Jet-A POSF 4658 and 2nd generation¹³ (n-dodecane/iso-octane/1,3,5 trimethyl benzene/n-propyl benzene 40.41/29.48/7.28/22.83 mole %) Jet-A POSF 4658 surrogate laminar burning velocities at 1 atm and 400 K¹³ (symbols) and computations with reduced models of this study (lines), where “2Gen_425” refers to a reduced model produced for the 1st generation composition containing 425 species, and so forth¹⁴. Burning velocities are obtained by the non-linear extrapolation technique as appearing in Hui & Sung Fuel 109 (2012) 191–200¹⁵, [personal communication C. J. Sung 2012 University of Connecticut].

Building on this work, the present study aims to further extend and demonstrate the performance of a fundamentally constructed chemical kinetic model to numerically reproduce the combustion characteristics of proposed alternative aviation fuels, their surrogates and surrogate components. As before, we select global combustion phenomena of ignition delay and laminar burning velocity (both of which are important initial performance targets for aviation gas turbine applications) as reference criteria for homogeneous and simple flame geometry reaction conditions respectively.

The detailed chemical kinetic model is first tested against available homogeneous mixture measurements of each pure component not reported in ¹⁴. Subsequently, reduced models for each of these are produced from the parent detailed model and tested against the available laminar burning velocity data. The same procedures are then employed to test model performance against the further ignition delay and burning velocity data of the surrogate fuel mixtures for Jet-A POSF 4658, as well as surrogate formulations for alternative jet fuels derived from coal and gas by synthetic means.

Complimentary to this model development, the model fidelity-model size limitations for exemplar synthetic aviation fuels is established by the production of a range of reduced kinetic models for the surrogate compositions that are elaborated from the detailed combined model. These reduced models range in content, from very many species (to retain fidelity over a generalized set of combustion conditions), to extremely few species (suitable for computational reacting flow applications, albeit with less general fidelity).

For this purpose, three such alternative fuels are chosen as jet fuel targets; “S-8”, a Fischer-Tropsch fuel produced from natural gas by Syntroleum; “Iso-paraffinic kerosene, IPK”, a Fischer-Tropsch fuel produced from coal by Sasol, and “Synthetic-paraffinic kerosene, SPK”, a Fischer-Tropsch fuel produced from natural gas by Shell. Toward the objective stated above and as applied before ¹⁴, a five step procedure is followed;

- 1) Combustion Property Target Measurement of Target Fuel.
- 2) Surrogate Fuel Formulation.
- 3) Chemical Kinetic Model Construction.
- 4) Chemical Kinetic Model Reduction.
- 5) Chemical Kinetic Model Calculation.

It is emphasized that it is not the objective of the present study to optimize any component of the above sequence to achieve improved performance against any particular data set. Rather, we seek to establish confidence limits and an understanding of the potential of this overall procedure to deliver actual “predictions” of quantitative accuracy for presently unknown liquid fuel identities. In so studying this procedure, we aim to provide guidance on its potential to allow such predictive utilities for the gas phase combustion behavior of any selected real liquid transportation fuel of interest. These goals are advised by strictly following the prevailing scientific state-of-art established for each item #1-5 of the strategy above.

II. Experimental

Combustion Property Target Measurement of Target Fuels

We have previously elaborated and tested a Combustion Property Target (CPT) methodology to identify and regulate the gas phase combustion behaviors of complex multi component mixtures that are real liquid transportation fuels. The motivations and assumptions describing its appropriateness are outlined in ¹²⁻¹³. In brief summary, this approach is based on matching select physical and chemical properties of a targeted aviation fuel to be used as constraining parameters of fundamental significance, such that the reactivity of one fuel may be constrained to that of another. These studies have utilized the Derived Cetane Number (DCN), molar hydrogen to carbon (H/C) ratio, average molecular weight (MW), and the Threshold Sooting Index (TSI) as fundamental metrics to define properties of aviation fuels that are important for a large variety of combustion phenomena. From this methodology, two surrogate mixtures have been formulated targeting a specific real-life jet fuel, Jet-A POSF 4658. A battery of

detailed laboratory combustion measurements show that this procedure successfully regulates the reactivity of simple (2-4 component) surrogate mixtures to share the detailed combustion behaviors of a conventional Jet-A and those of a target synthetic fuel of this study, S-8¹⁶. The combustion property targets for these fuels, and those of their previously formulated surrogates is presented in Table 1. Also presented in Table 1 are the combustion property targets, and formulated surrogate fuels, for Shell SPK and Sasol IPK, following the experimental procedures below:

A. Derived Cetane Number, DCN

DCN measurements are performed on the synthetic aviation fuels, Sasol IPK and Shell SPK, in an identical fashion to Dooley et al.¹²⁻¹³ using an Ignition Quality Tester (IQT) apparatus. The ASTM D 6890¹⁷ procedure for determination of autoignition characteristics of diesel fuels is followed. The IQT determines an experimental ignition delay of a fuel spray in a pressurized (22.1 atm) and heated (~833 K) constant volume chamber of air. The DCN is produced through a correlation of the IQT measured ignition delay time to the cetane scale that is provided for in ASTM D 6890. The main purpose in using DCN is as a relative comparative parameter to compare the overall chemical kinetic reactivity of a particular fuel to that of multi-component mixtures of defined surrogate fuel components. The resulting standard deviation in the reported DCN is less than ± 0.6 .

B. Mixture Averaged Molecular Weight, MW

ASTM methods presently found in the literature for determining the average molecular weight of hydrocarbon mixtures estimate this quantity by empirical correlations of more easily measurable parameters such as mixture boiling point and density. These methods have typical uncertainties of ~ 20 g/mol for the average molecular weight of jet fuels. We have developed an improved method to determine the average molecular weight of fuel samples, based upon application of the ideal gas law¹⁸. The repeatability of these measurements is less than ± 2.5 g/mol for the data reported here. The absolute uncertainty of the new measurement method is conservatively estimated to be less than 3% (< 6 g/mol, one sigma). The average molecular weights of each of the jet fuels were determined using this new method and are reported in Table 1. Some of the values differ from those reported in our earlier publications with the earlier value uncertainties encompassing the present data.

C. Threshold Sooting Index, TSI

The Threshold Sooting Index (TSI) is defined by Calcote and Manos¹⁹ as,

$$TSI = a \left(\frac{\text{Molecular weight}}{\text{Smoke point}} \right) + b$$

where the smoke point is the maximum smoke free laminar diffusion flame height (*mm*), molecular weight is in $g\ mol^{-1}$ and a ($mol\ mm\ g^{-1}$) and b (dimensionless) are experimental constants. The TSI values utilized in this work were obtained by the smoke point technique as described in^{20, 21}. The TSI values quoted in this study for the synthetic fuels were calculated from the experimentally determined smoke point measurements using the ASTM D 1322²¹ methodology and the average molecular weights determined by the method above, or in combination with the smoke points that have been originally reported by the same methods for the Jet-A¹². In the case of S-8 and SPK, the flames are very weakly or entirely non-sooting, showing no discernible smoke point within the ~50 mm test range of ASTM D 1322. Thus, for these fuels no TSI may be determined. While this is the case, the absence of a strong sooting tendency is constraining to surrogate formulation, therefore such fuels are assumed to have a TSI of < 5 in order that the TSI parameter may act as constraint rather than a degree of freedom to the formulation. Note that as the molecular weight determination of a particular fuel varies, so does the threshold sooting index. The pure surrogate fuel component TSI values utilised are those measured by Mensch et al.²¹. As the TSI of a mixture has a linear dependence on the TSI of its constituent

components, the TSI values quoted in this study for mixtures are *calculated* assuming this relation. The estimated upper uncertainty limit is less than two TSI units.

D. Hydrogen to Carbon Molar Ratio (H/C)

The H/C molar ratio of each of the jet fuel samples is determined experimentally using CHN (carbon, hydrogen, nitrogen) analysis following the methodology of ASTM D 5291²². The estimated uncertainties are less than 0.03 of the reported value.

Surrogate Fuel Formulations

The 2nd Generation combustion property target surrogate formulator reported previously¹³, considers n-dodecane, iso-octane, n-propyl benzene and 1,3,5, trimethyl benzene as surrogate fuel components. These are sufficient components with which to compose surrogate mixtures of S-8¹⁶ and Shell SPK by the combustion property target matching technique. The 2nd generation surrogate fuel formulator returns mixtures of n-dodecane/iso-octane of 51.9/48.1 mole %¹⁶ and 61.0/39.0 mole % when supplied the S-8 and Shell SPK combustion property targets respectively. These mixtures are considered as surrogates for the respective fuels, where the viability of this S-8 surrogate has been demonstrated experimentally in¹⁶ to share very similar reflected shock measured ignition delay, flow reactor reactivity and diffusion flame extinction limits, each across broad domains of temperature.

From Table 1, the combustion property targets of Sasol IPK, are significantly different to those of the other alternative fuels, and also to those of the conventional Jet-A, in that it exhibits a very low DCN of 31.3, while also having a high molecular weight of 148.5, relative to the components of the 2nd generation surrogate formulator. There, iso-octane occupies the low-DCN high-H/C ratio parameter space. Thus reproducing a DCN of ~30 with a H/C of ~2, carries with it a lower molecular weight than desired in this case, due to the required large fraction of the 114.2 g/mol iso-octane. Therefore the combustion property target combination offered by Sasol IPK is outside of the viable range provided by the 2nd generation component palette.

In order for a surrogate mixture to simultaneously reproduce this set of parameters, a low-DCN/high-molecular weight surrogate component is required. For this purpose iso-cetane, 2,2,4,4,6,8,8-heptamethylnonane is selected as it is of DCN ~14.8 and of 226.4 g/mol. Note, that the cetane number-to-derived cetane number correlation provided by ASTM D 6890 is strictly valid only within the range of 30-65 DCNs. Consequently, many pure components are at or beyond the limits of its applicability. The values quoted are intended as reference values presented only for the purposes of discussion.

The IPK surrogate fuel is formulated by linearly interpolating between the separate empirical relations previously reported which relate the mass fraction of n-dodecane/iso-octane to DCN and a separate relation that relates the mass fraction of n-hexadecane/iso-cetane to DCN. Both equations are reported in²³. This procedure suggests a 30.1/3.5/60.7/5.7 mole % mixture of iso-cetane/n-hexadecane/iso-octane/n-dodecane to share the ~31 measured DCN of the IPK, while also closely sharing the remaining combustion property targets, see Table 1.

Kinetic Modeling

A growing body of data on the gas phase combustion behaviors of the reference synthetic fuels of this study, and indeed others, is appearing in the literature. We have selected homogenous ignition delay and laminar burning velocity as initial prototypical combustion behaviors with which to test the capability of burgeoning reduced numerical models for conventional and alternative fuels, produced by the five step procedure outlined in introduction. Toward this purpose, Table 2 summarizes the data sets used as reference for this study.

A. Motivations and Objectives

The technical objectives of the modeling aspect of this study is to;

- 1) Establish the limits in state of art numerical reproduction of the combustion behaviors of synthetic aviation fuels.
- 2) Provide analysis of the nature of any model shortcomings.
- 3) Provide further suggestions in achieving additional gains in the model accuracy/model size vector.

Fuel	DCN	H/C	MW / g mol ⁻¹	TSI
Toluene	~17 ^{Ψ F}	1.14	98.2	40.0*
<i>iso</i> -octane	<10 ^{Ψ F}	2.25	114.2	6.8*
1,3,5, trimethyl benzene	21.8 ^F	1.33	120.2	62.0*
<i>n</i> -propylbenzene	28.2 ^F	1.33	120.2	53.0*
<i>n</i> -decane	~65 ^{Ψ F}	2.20	142.3	4.5*
<i>n</i> -dodecane	~78 ^{Ψ F}	2.16	170.3	7.0*
<i>iso</i> -cetane	~14.8 ^{Ψ m}	2.13	226.4	22.0*
<i>n</i> -hexadecane	~110.0 ^{Ψ m}	2.13	226.4	9.0*
Jet-A POSF 4658 (Conventional)	47.1 ^F	1.95 ^F	157.5±2 ^{#‡}	24.2 [#]
S-8 POSF 4734 (Natural Gas to Liquid)	58.7 ^I	2.14	154.5±1.4 [‡]	n/a [‡]
SPK POSF 5172 (5729) (Coal to Liquid)	58.4	2.24	138.3±2.4 [‡]	n/a [‡]
IPK POSF 7629 (5642) (Natural Gas to Liquid)	31.3	2.195	148.5±1.8 [‡]	10
Jet-A POSF 4658 1 st Generation Surrogate (mole %)	47.4 ^F	2.01	120.7	14.1 ^F
<i>n</i> -decane				
<i>iso</i> -octane				
Toluene				
42.7				
33.0				
24.3				
Jet-A POSF 4658 2 nd Generation Surrogate (mole %)	48.6 ^F	1.96	138.7	20.4 ^F
<i>n</i> -dodecane				
<i>iso</i> -octane				
1,3,5, trimethyl benzene				
<i>n</i> -propylbenzene				
40.4				
29.5				
7.3				
22.8				
S-8 POSF 4734 Surrogate (mole %)	58.7 ^I	2.14	143.4	6.8
<i>n</i> -dodecane				
<i>iso</i> -octane				
51.9				
48.1				
SPK POSF 5172 Surrogate (mole %)	62.1	2.19	147.9	6.9
<i>n</i> -dodecane				
<i>iso</i> -octane				
61.0				
39.0				
IPK POSF 5642 Surrogate (mole %)	31.7 [†]	2.22	155.1	11.1
<i>n</i> -dodecane				
<i>iso</i> -octane				
<i>n</i> -hexadecane				
<i>iso</i> -cetane				
5.7				
60.7				
3.5				
30.1				

Table 1, Combustion Property Targets of selected alternative aviation fuels, conventional jet-A, and their suggested surrogates. * Measured by Mensch et al.²⁰. ^Ψ The cetane number to derived cetane number correlation provided by ASTM D 6890 is strictly valid only within the range of 30-65 DCNs. [#] Originally reported in¹²⁻¹³ as 142±20 g/mol and 21.4 (TSI) based upon less accurate molecular weight determination methodology, correction discussed in²⁴. [‡] Measured molecular weight by procedure discussed in¹⁸. All parameters are measured in this study, unless ; [‡] Smoke points greater than 50 mm, not measurable within the ASTM D 1322 methodology, thus TSI is not determinable. ^F Dooley et al.¹². ^F Dooley et al.¹³. ^m Won et al.²³. ^I Dooley et al.¹⁶. [†] estimated, see text.

This is achieved by;

- a) Demonstrating the performance of the detailed model in reproducing the shock tube ignition delay and laminar burning velocity data available for the newly considered surrogate fuel components of n-hexadecane, iso-cetane and their mixtures. In this manner, the model may then be tested against data from more complex mixtures with an identified level of confidence.

- b) Demonstrating the performance of the detailed model in reproducing the available shock tube ignition delay and laminar burning velocity data available for alternative aviation fuels, and if available, also for their surrogates.

- c) Ascertaining the effectiveness of kinetic model reduction techniques in minimizing the model size that will allow for reasonable reproduction of the shock tube ignition delay and laminar burning velocity data available for an exemplar synthetic fuel in S-8.

B. Detailed Chemical Kinetic Model Construction

A single municipal detailed chemical kinetic model comprising the surrogate components of both the 1st generation and 2nd generation Jet-A POSF 4658 surrogate fuel components has been assembled and reported previously¹⁴. Here, the surrogate fuel chemistry is described by using the recent aromatic chemistry sets of Metcalfe et al.²⁵, Won et al.²⁶ and Diévarit et al.²⁷ for toluene, n-propyl benzene and 1,3,5-trimethyl benzene respectively. These assemblies are extensions of one another, entirely self-consistent in construction. Thus, the performance demonstrated in each supporting work is expected to be implicitly valid in the surrogate model performance.

The higher *n*-alkane chemistry of Westbrook et al.²⁸ has been adopted for *n*-alkanes from *n*-pentane up to and inclusive of *n*-dodecane. The *iso*-alkane chemistry of Mehl and co-workers²⁹ is adopted to describe the oxidation of *iso*-octane and related *iso*-alkenyl species of carbon numbers greater than four. So called *cross-reactions* involving the interaction of high molecular weight fuel radicals or intermediates from the different generic functional classes are not considered in the kinetic model, which only allows fuel components to interact through their respective influence on the small species population (C₄-C₅ chemistry level).

Following careful considerations of the observations discussed above in composing surrogate fuels for typical synthetic paraffinic alternative fuels, this model has been expanded for the capacity of larger normal alkanes up to *n*-hexadecane through further adoption of the work of Westbrook et al.²⁸ and also to describe *iso*-cetane low and high temperature chemistry through adoption of the *iso*-cetane submodel proposed by Oehlschlaeger et al.³⁰. In the case where there has been a conflict or duplication of nomenclature, chemistry or thermodynamic parameters between the individual component sub-models, chemical reaction, rate constant and thermodynamic parameters have been chosen in the following order of preference; Metcalfe et al. (Won et al., Diévarit et al.) > Mehl et al. > Westbrook et al. > Oehlschlaeger et al. Careful attention has been taken to ensure that each submodel is properly compatible at the interface C₄-C₅ chemistry level. A Lennard-Jones model is utilized to estimate binary diffusion coefficients. Wherever possible the input parameters are retained from the parent models. Otherwise collisional diameter and energy well depth parameters have been estimated largely based on those recommended in a review conducted by Mourits et al.³¹, and correlated to molecular weight in a similar manner to Wang and Frenklach³² by Dooley et al.³³. The detailed model construction is composed of 3147 species and more than 10,000 reactions. The eventual performance previously documented for the target scenario of Jet-A combustion properties is summarized in Figures 1-4 for reference conditions of ignition delay and laminar burning velocity. The legend refers to calculations with the detailed model and also those of reduced models produced by the Path Flux Analysis technique³⁴. The reduced models for the 1st generation *n*-decane/*iso*-octane/toluene and the 2nd generation *n*-dodecane/*iso*-octane/1,3,5-trimethyl benzene/*n*-propyl benzene surrogate fuels are labeled as “1Gen_species#” and “2Gen_species#”

respectively, indicating the surrogate composition and the size of the reduced models produced by incremental adjustment of the path flux analysis reduction fidelity threshold^{14, 34}.

The important conclusion from these figures, pertains to the absolute accuracy of the detailed model calculations, and also to the model size required to retain this accuracy. Specifically, in order to numerically reproduce real fuel ignition delay within a factor-of-two of experiment, current minimal model sizes are 144 species for temperatures > 1100 K at 20 atm, and 233 species > 500 K at 20 atm, where both limits allow atmospheric pressure laminar burning velocity to be reproduced to within ~5 cm/s, which is ~8%. Note that the complexity of the surrogate selection also imparts a species cost, with 384 species being required by the four component surrogate to reproduce low and high temperature ignition delay, compared to only 233 species for the three component option.

Shock Tube Ignition Delay	Conditions	Reference
iso-cetane	953-1394 K, 8-47 atm, phi 0.5, 1.0, 1.5, in air	Oehlschlaeger et al. ³⁰
iso-cetane/n-hexadecane	645-1250 K, 20 atm, phi 1.0 in air	Won (Oehlschlaeger) et al. ²³
Jet-A	650-1300 K, 20 atm, phi 1.0 in air	Dooley, (Oehlschlaeger, Wang) et al. ¹²
Jet-A	650-1400 K, 8,12, 20, 40 atm, phi 1.0 in air	Wang and Oehlschlaeger ³⁶
Jet-A surrogates S-8		
S-8 surrogate	650-1300 K, 20 atm, phi 1.0 in air	Dooley, (Oehlschlaeger, Wang) et al. ^{12,13,16}
IPK, SPK		Wang and Oehlschlaeger ³⁶
Laminar Burning Velocity	Conditions	Reference
n-hexadecane	443 K, 1 atm,	Li et al. ³⁷
iso-cetane	phi 0.8-1.4	Li et al. ³⁸
Jet-A		Dooley, (Hui, Sung) et al. ¹⁴
2 nd generation Jet-A surrogate	400 K, 1 atm, phi 0.7-1.4	Dooley, (Hui, Sung) et al. ¹⁴
S-8		Ji et al. ⁴⁰
		Hui et al. ³⁹
IPK		Hui et al. ³⁹

Table 2. Homogeneous shock tube ignition delay and laminar burning velocity data sets utilized in this study.

C. Chemical Kinetic Model Reduction

Even for the idealized one dimensional flame geometries considered for parametric kinetic model testing, as here, a certain level of model reduction from the highly detailed parent model is a prerequisite. Model reduction techniques are essential, not just to reduce computational costs but also to reduce the numerical stiffness associated with such a large number of conservation equations for broad classes of independent fuel chemistries and reaction pathways. When performing model reduction to ascertain detailed model performance, great care has been taken to ensure that the reduced model computations retain fidelity to those of the detailed parent model.

The Path Flux Analysis (PFA) kinetic model reduction scheme³⁴ has been utilized in this study. The procedure to produce reduced models first involves obtaining a numerical database of time dependent detailed chemical species profiles computed by the detailed model under homogenous constant volume

ignition delay conditions (as described below). Subsequently, a second speciation database is constructed under steady-state perfectly stirred reactor conditions.

For the objective of ascertaining the performance of the detailed model under flame conditions for surrogate fuel components, after inspection of the target datasets, both databases are populated by considering conditions of: fuel/air mixtures of equivalence ratio of 0.6, 1.0 and 1.5, at 1 atm and temperatures of 1000 K, 1200 K, 1500 K, and 1800 K. It is important to note that the choice of target conditions that define the reduction process, is a decision (an assumption) made by the user. Thus it should be regarded as a source of uncertainty in the reduced model. The limitations of these approaches in terms of how smaller reduced models can be produced without losing the “true” fidelity of the parent model has not been fully addressed. In order to discuss this issue, as before, a range of reduced models for each fuel component have been generated by exercising the PFA “fidelity threshold” value incrementally from 0.05 to 0.35.

This procedure is followed specifying each “fuel” individually (n-hexadecane, iso-cetane, and each of the multicomponent mixtures suggested as surrogate fuels) to produce the range of reduced models presented in Table 3, models #1-16. By testing the entire range of reduced models for each individual surrogate fuel component, the minimum model size to deviate in performance is identified, thus indicating an invalid reduction.

D. Chemical Kinetic Model Simulations

All modelling simulations are conducted with a modified CHEMKIN II solver. Shock tube simulations are zero-dimensional and begin at the onset of the reflected shock period. Constant volume and homogeneous adiabatic conditions are assumed behind the reflected shock wave, consistent with the experimentally observed pressure profiles in e.g. ^{30, 36}. The reflected shock pressure and temperature are input as the initial pressure and temperature respectively. The simulated ignition delay time is defined consistent with the diagnostic utilised in each particular set of experiments.

Laminar burning velocities are calculated by simulating freely propagating flames using the PREMIX module with the mixture averaged transport model. Simulations were performed over a constant domain size. The use of at least 900-1300 grid points for each computation of each model assured that increments of at least 0.04 for both CURV and GRAD are met and that the reported solutions are sufficiently resolved to be practically independent of grid size. In addition, the computation of a valid solution is verified by confirming that the computed peak flame temperature is equivalent to the adiabatic flame temperature of each respective flame. For the pure component reduced models presented below, peak flame temperatures are always within at most +/- 14 K of the adiabatic flame temperature at constant pressure. The laminar burning velocity computations reported are estimated to be within +/- 0.5 cm/s of the true (grid independent) solution.

At the outset of this study it is recognized that numerical calculations of the combustion process in practical combustor geometries under flowing conditions requires significant large memory allocations. Considering this intended application, a mixture averaged transport model is more desirable than the alternative multicomponent description as it is computationally much less expensive. Thus we have chosen to evaluate model performance against experiment with this transport description even though it is less fundamentally accurate than alternatives. It is also recognised that calculations with a multicomponent transport approach and treatment of thermal diffusive effects will result in burning velocities generally 1-2 cm/s lower than those reported here.

Model #	Fuel	Species #	Short Name
1	iso-cetane	221	ic16_221
2	iso-cetane	213	ic16_213
3	n-hexadecane	145	nc16_145
4	n-hexadecane	110	nc16_110
5	n-hexadecane	100	nc16_100
6	n-hexadecane	85	nc16_85
7	S-8 surrogate, n-dodecane/iso-octane, 0.519/0.481	1164	S-8_1164
8	S-8 surrogate, n-dodecane/iso-octane, 0.519/0.481	698	S-8_698
9	S-8 surrogate, n-dodecane/iso-octane, 0.519/0.481	589	S-8_589
10	S-8 surrogate, n-dodecane/iso-octane, 0.519/0.481	473	S-8_473
11	S-8 surrogate, n-dodecane/iso-octane, 0.519/0.481	305	S-8_305
12	S-8 surrogate, n-dodecane/iso-octane, 0.519/0.481	193	S-8_193
13	S-8 surrogate, n-dodecane/iso-octane, 0.519/0.481	157	S-8_157
15	IPK surrogate, n-dodecane/iso-octane/ iso- cetane/n-hexadecane, 0.057/0.6-7/0.301/0.035	361	IPK_361
16	IPK surrogate, n-dodecane/iso-octane/ iso- cetane/n-hexadecane, 0.057/0.6-7/0.301/0.035	221	IPK_221
17	S-8 surrogate, n-dodecane/iso-octane, 0.519/0.481	36	S-8_c_36

Table 3. List of reduced and compact (“c”) kinetic models generated in this study.

III. Results and Discussions

At the outset, it is emphasized that the calculations presented below are the results of the hierarchical model strategy exactly as described above, which we consider to fairly approximate the state of the art. At this time, absolutely no adjustments have been made to any parameters of the adopted submodels in order to produce improved performance. The calculations are the result of the careful incorporation of the work of others into the aromatic submodel that serves as the base H₂/O₂ and C₁/C₄ chemistry set. As such, the comparisons presented below may be viewed as genuine tests of “predictability”.

Detailed Model Performance in a Homogeneous System: Ignition Delay Time

Firstly, the performance of the fully detailed model (3147 species) against high pressure shock tube ignition delay measurements available for the additional surrogate fuel components, iso-cetane and n-hexadecane, is ascertained.

A.iso-cetane and n-hexadecane/iso-cetane Shock Tube Ignition Delay

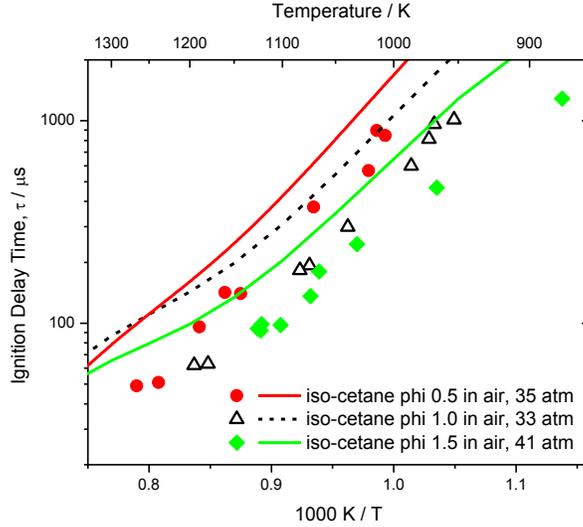


Figure 5. Oehlschlaeger et al. [30] shock tube ignition delay times for fuel in air mixtures of iso-cetane at 33-41 atm (symbols) and model calculations with the detailed model of this study (lines).

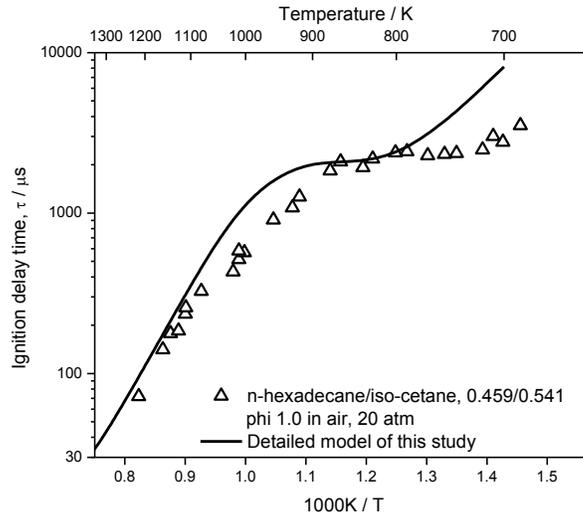


Figure 6. Won (Oehlschlaeger) et al. ²³ shock tube ignition delay times for stoichiometric fuel in air mixture of n-hexadecane/iso-cetane, 0.459/0.541 at 20 atm (symbols) and model calculations with the detailed model of this study (lines).

Figure 5 presents comparison of the high pressure iso-cetane reflected shock ignition delay data of Oehlschlaeger et al. ³⁰ to the computations of the detailed model between 875-1270 K. The model tracks the equivalence ratio dependence observed by experiment, but the computed ignition delays are approximately twice as long as measured in this Arrhenius-like regime. Comparisons to n-hexadecane ignition delay are not presented here, but we highlight that this general over estimation of alkane ignition

delay is a feature of the modeling construct, as noted previously for n-decane and n-dodecane data sets. This behavior is also observed when testing the model against the measurements of the 0.459/0.541 n-hexadecane/iso-cetane mixture reported by Won et al.²³. While the model is capable of reproducing the data to a reasonable degree, the calculations are marginally longer than experimental measurement, Figure 6.

B. Jet-A POSF 4658 Shock Tube Ignition Delay

Having previously established the performance of the detailed model against surrogate component¹⁴ ignition delay data, Figure 7 presents the ignition delays measured by Wang and Oehlschlaeger³⁰ for Jet-A POSF 4658 at pressures close to 8, 12, 20 and 40 atm with calculations of the detailed model assuming the 2nd generation surrogate composition (n-dodecane/iso-octane/1,3,5 trimethyl benzene/n-propyl benzene 40.41/29.48/7.28/22.83 mole %). We have previously demonstrated this comparison for ϕ 1.0 in air at 20 atm conditions¹³, but this is the first test of the end-to-end modeling strategy at variable pressures. Wang and Oehlschlaeger³⁰ have used our earlier modelling construct¹² to simulate this data with the 1st generation n-decane/iso-octane/toluene composition. Figure 7 reports a similar level of agreement, where the modeling methodology traces the pressure dependence to near quantitative accuracy at the highest temperatures, degrading to a more qualitative agreement at the lower temperatures where the complex intermediate temperature chemistry dominates the reacting flux. While the calculated and measured reactivities always trend in the same direction of, highest pressure fastest, lowest pressure slowest, the quantitative mismatch approaches a worse case factor-of-two over-estimation for the 40 atm condition at ~900 K. Overall, while the agreement is encouraging in terms of the applicability of the overall approach, it is to be noted that the model calculations generally show a reactivity somewhat slower than experiment, as exhibited by marginally longer ignition delays than measured.

Figure 7 presents more of the measurements of Wang and Oehlschlaeger, showing the effect of equivalence ratio (in air) on the ignition delay of Jet-A POSF 4658 at 20 atm. As before, the data is simulated assuming the 2nd generation surrogate composition. The simulations generally reproduce the quantitative temperature dependence of the ignition delay, again more accurately at high temperatures than low, with the trends in the equivalence ratio captured in the correct order but quantitatively offset to longer ignition delays at temperatures lower than ~1100 K.

C. Syntroleum S-8, Shell SPK and Sasol IPK Shock Tube Ignition Delay

Wang and Oehlschlaeger further report ignition delay measurements of stoichiometric fuel-in-air mixtures of the specific synthetic fuels referred to in the formulation section; S-8, iso-paraffinic kerosene, IPK and Synthetic-paraffinic kerosene, SPK, at 20 atm. In the previous dedicated work¹⁶, we have experimentally verified the appropriateness of a 51.9/48.1 mole % mixture of n-dodecane/iso-octane as a valid surrogate fuel for this S-8. Thus, this composition is confidently used to test the ability of the modeling strategy to at least differentiate between the reactivity exhibited by each fuel. The IPK and SPK fuels are simulated under the assumption that the surrogate fuel compositions provided in Table 1 properly emulate the respective target fuels. The comparison is thus quite a genuine test of the end-to-end predictability of the modeling strategy to indicate the reactivity of prototypical alternative liquid fuels. These data are compared to calculations with the detailed model in Figure 9.

Firstly, it is encouraging that both model and experiment indicate that each fuel should converge in reactivity at high temperature (> 1100 K) conditions, where the alkyl radical beta-scission mechanism can be expected to dominate the large radical consumption. Consistent in feature with the previously discussed comparisons of Jet-A at variable pressure and variable equivalence ratio, and also with the iso-

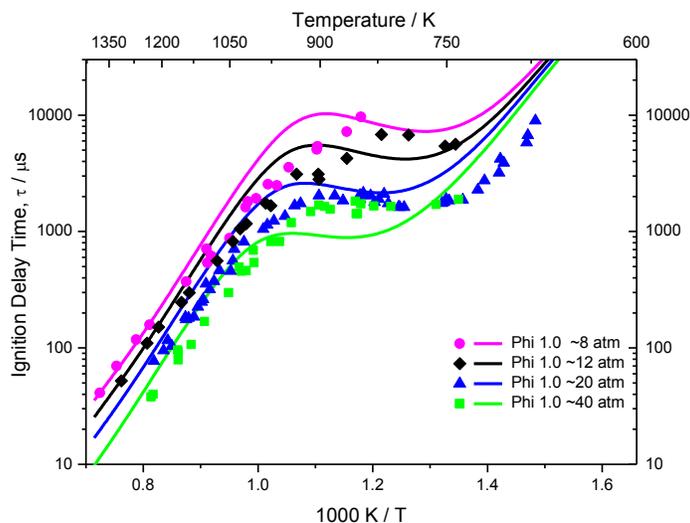


Figure 7. Wang et al.³⁰ shock tube ignition delay times for stoichiometric fuel in air mixtures of Jet-A POSF 4658 showing effect of pressure (symbols) and model calculations with 2nd generation (n-dodecane/iso-octane/1,3,5 trimethyl benzene/n-propyl benzene 40.41/29.48/7.28/22.83 mole %) Jet-A POSF 4658 surrogate. Lines are simulations with the detailed kinetic model of this study.

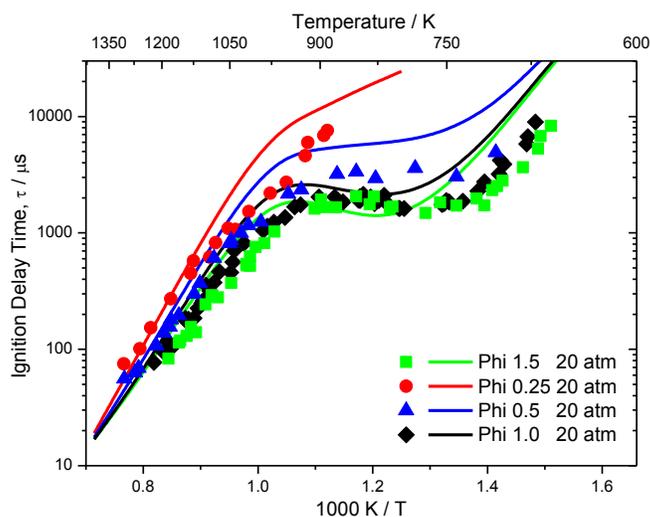


Figure 8. Wang et al.³⁰ shock tube ignition delay times for fuel in air mixtures of Jet-A POSF 4658 showing effect of equivalence ratio (symbols) and model calculations with 2nd generation (n-dodecane/iso-octane/1,3,5 trimethyl benzene/n-propyl benzene 40.41/29.48/7.28/22.83 mole %) Jet-A POSF 4658 surrogate. Lines are simulations with the detailed kinetic model of this study.

cetane, and indeed n-alkane comparisons remarked previously¹⁴, the model suggests ignition delays that are somewhat longer than actually measured. The magnitude of the quantitative offset varies with temperature and from fuel to fuel, but is approximately a factor-of-two at higher temperatures, and somewhat less than this in the negative temperature coefficient regime, with the case of the IPK being an exception. Here, it is impressive that the model would indicate this fuel to be of notably different

reactivity in the low temperature regime only, as also observed by experiment. However, the model calculated ignition delays are approximately twice as long as measured.

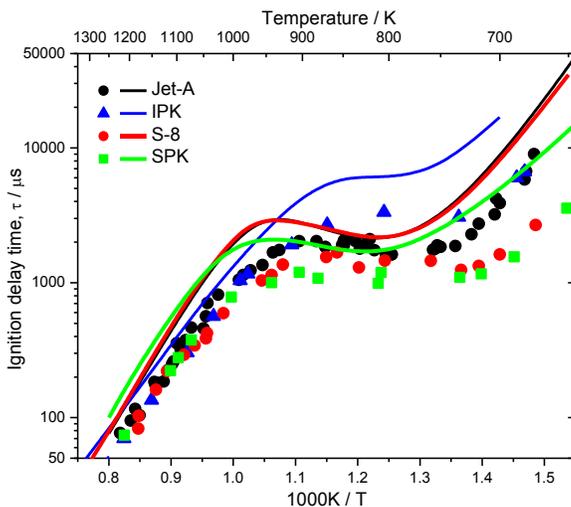


Figure 9. Wang et al.³⁰ shock tube ignition delay times for fuel in air mixtures of Jet-A POSF 4658, iso-paraffinic kerosene (IPK) POSF 5642, S-8 POSF 4734 and synthetic paraffinic kerosene (SPK) POSF 5729 at 20 atm, and model calculations with surrogate fuels of Table 1 and the detailed kinetic model of this study. Lines are simulations, symbols are experiment.

Reduced Model Performance in a Flame Geometry: Laminar Burning Velocity

Several reduced models are produced to test flame performance as detailed by Table 1. The motivation to produce several models for the same purpose but of varying dimension is to provide some confidence that the model computations are fundamental in nature, predictive, and not adversely effected by over reduction.

A. iso-cetane and n-hexadecane Laminar Burning Velocity

The laminar burning velocities of iso-cetane/air mixtures and n-hexadecane/air mixtures at equivalence ratios of 0.7-1.5 at 1 atm and an unburned gas temperature of 443 K are computed at various levels of detail and compared in Figure 10 to the measurements of Li et al.^{37, 38}. Firstly, in two separate counter flow flame studies, Li et al. determine the laminar flame behavior of these isomers to be quite different, with the highly methylated cetane isomer retarded in reactivity by approximately 10% relative to the normal-alkane. As the flame temperatures and Lewis numbers of the isomers are equivalent at comparable conditions, this would indicate an important difference in the chemical kinetic character of each molecule. It can be seen that each of the reduced models reproduce the main body of experimental data reasonably well, accurately deciphering the difference in reactivity of each fuel. More specifically, the model marginally under represents the burning velocity of iso-cetane by ~2-3 cm/s (in ~65 cm/s), whereas in the case of n-cetane, the model over estimates the peak burning velocity by ~5 cm/s at rich equivalence ratios. While not regarded as definitive proof of the values to be indicated by the parent detailed model, the close similarity in burning velocities calculated by several reduced models ranging from 85 to 145 species and 213 to 221 species for each fuel is assuring.

These tests, in addition to those we report previously¹⁴ on model reproduction of the laminar burning velocity are important. The model is shown to reproduce the peak laminar burning velocity of all eight surrogate components of Table 1 to within a maximum deviation of ~10% and does not show a consistent

bias to lower or higher burning velocities to the reference experimental determinations. This is shown to be the case for heavily reduced models, even for large molecular weight fuels. For example, Figure 10 shows that a model comprised of just 86 species can accurately reproduce n-hexadecane burning velocities. This is an important confidence lending feature when reducing models for multicomponent surrogates, as apparent in the following section.

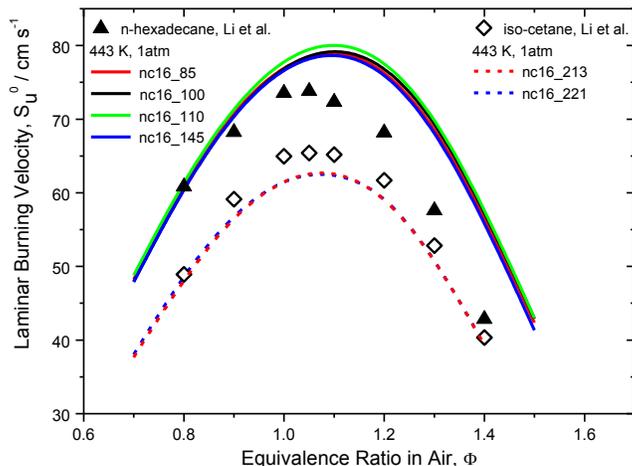


Figure 10. Laminar burning velocities of n-hexadecane (solid triangles, Li et al.³⁷) and iso-cetane (hollow diamonds, Li et al.³⁸) at 443 K and 1 atm, experiment (symbols) and model calculations with the reduced models of this study (lines).

B. Jet-A, Syntroleum S-8 and Sasol IPK Laminar Burning Velocity

Amongst the various determinations of the laminar burning velocity for conventional and alternative aviation fuels, are the data sets of Hui et al.³⁹ and Ji et al.⁴⁰ which have both been obtained with the counterflow flame method. These data sets for equivalence-ratio-in-air mixtures are presented in Figure 11 for the candidate reference fuels that are the subject of this study, Jet-A POSF 4658 and S-8 POSF 4734, where experimentally verified surrogates have been formulated, and for IPK POSF 5642, where the surrogate composition has not been verified by experiment.

Hui et al.³⁹ contend that the laminar burning velocities of these fuels ought to show no discernible difference, whereas Ji et al.⁴⁰ report that jet propulsion type fuels exhibit a lower rate of flame propagation than various alternative aviation fuels on account of the presence of an aromatic fraction. Ji et al. do not study the particular Jet-A or IPK that are the reference fuels of our work, however they do report data for S-8 POSF 4734. Thus to enable direct comparisons, only this S-8 data set is included in Figure 11. Note that the Hui et al. and Ji et al. experimental data sets of S-8 (both 1 atm counterflow flames, at 400 and 403 K) are inconsistent, particularly at rich equivalence ratios, where the difference approaches ~10 cm/s. The true laminar burning velocity of these fuels may consequently be regarded as uncertain to some extent.

It is viewed as important to test if the overall modeling strategy, through the described five-step procedure, possesses sufficient accuracy to inform this discrepancy. Model calculations, employing reduced models, are also included in Figure 11 resulting from initial conditions of 1 atm and 400 K. First, for S-8, it is apparent that these calculations better approximate the measurements of Ji et al. than those of Hui et al. The calculations of three reduced models, of various degrees, for the S-8 surrogate composition

are quantitatively accurate to the data of Ji et al. at all but the richest equivalence ratio. Conversely, comparison of the model calculations are consistently 3-7 cm/s lower than the data of Hui et al.

Hui et al. also determined the burning velocity for the iso-paraffinic kerosene sample studied by Wang and Oehlschlaeger and discussed in this paper. The model calculations for this synthetic fuel are also consistently lower than the recommendations of Hui et al.³⁹. Here, the lack of experimental verification of the viability of the suggested IPK surrogate to the IPK target fuel is a recognized source of uncertainty. More generally, by the inclusion of previously reported analysis of the petroleum derive aviation fuel, Jet-A POSF 4658, the model informs the debate above, by suggesting that the burning velocities of these fuel ought to lie in the order of IPK<Jet-A<S-8, in apparent consistency with the recommendations of Ji et al. who state that premixed laminar flames of conventional jet propulsion type fuels should propagate at velocities lower the non-aromatic alternative fuels. However, these differences suggested by the model are small, the peak laminar burning velocities are calculated to differ by at most 7 cm/s (in 60 cm/s).

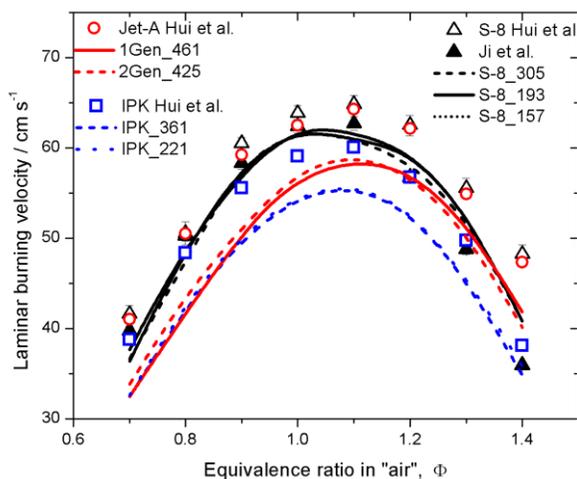


Figure 11. Laminar burning velocities at 1 atm and 400 K for S-8 (Hui et al.³⁹, hollow triangles) and 403 K (Ji et al.⁴⁰, solid triangles), for Jet-A (Hui et al.³⁹, hollow circles) and for IPK (Hui et al.³⁹ hollow squares). Model computations are performed with reduced models of this study and those of¹⁴ (lines), with the S-8 surrogate composition (n-dodecane/iso-octane 51.89/48.11 mole %), the 1st generation (“1Gen_461”¹⁴, n-decane/iso-octane/toluene 42.7/33.0/24.3 mole %) and 2nd generation (“2Gen_425”¹⁴, n-dodecane/iso-octane/1,3,5-trimethyl benzene/n-propyl benzene 40.41/29.48/7.28/22.83 mole %) Jet-A surrogate compositions, and the IPK surrogate composition (30.1/3.5/60.7/5.7 mole % mixture of iso-cetane/n-hexadecane/iso-octane/n-dodecane) .

Compact (CFD-appropriate) Model Performance for S-8 as a Prototypical Alternative Aviation Fuel

In addition to high fidelity combustion chemistry models, there is also a practical need for low-dimensional kinetic models for simulation of real fuel combustion chemistry, particularly for the aviation turbine applications we address here. To be useful for parametric computational combustor design and analysis, such models must be sufficiently compact to be used in multi-dimensional, multi-physics, reacting computational fluid dynamics (CFD) simulations. However, they must also retain sufficient complexity to be able to predict combustor temperature distributions; non-equilibrium emissions; and transient combustion behaviors such as lean blow-out, high altitude relight, and flashback [42]. Global and few-step models involving only a handful of species [42, 43] or models involving quasi-steady assumptions [44,45] typically lack the feedback coupling of radical/small molecule chemistry with the

decomposition of the parent fuel species [41-46]. Even the most severely reduced (e.g., by PFA) models – such as those discussed above with ~100 species – incur prohibitive computational costs when used for complex model-based combustor design and analysis. Compact CFD-appropriate kinetic schemes of the order of 2-3 dozen species (or even fewer) can therefore provide a compromise between predictive fidelity in global combustion behavior and computational costs. By sacrificing (often) unimportant species as well as strict adherence to best-available chemical kinetic constraints, these compact models remain sufficiently detailed to capture the global reacting flow feedback dynamics among fuel, intermediates, pollutant species, and radicals without the excessive computational costs associated with larger models.

As a generalizable example of a framework for generation of CFD-appropriate kinetic models, this section describes preliminary efforts towards the formulation of a compact model for the alternative (natural gas-to-liquid, POSF 4734) S-8 fuel. The compact model is benchmarked against predictions of a more detailed 437 species kinetic model developed for the S-8 surrogate (Model 10 in Table 3). In principle, this basis provides for predictions of the compact model to exhibit *fuel-specific* global combustion behaviors of the real S-8 fuel since the benchmark model is itself based on an experimentally-validated surrogate formulation, as discussed above. Predictions of the compact model therefore reflect the joint fidelity of the surrogate fuel formulation as well as the detailed kinetic model. Examples of fuel-specific combustion behavior variations for real fuels are demonstrated in Figures 9 and 11.

A. Formulation of CFD-compact model

In broad terms, the provisional 36 species S-8 surrogate compact model, labeled as “S-8_c_36” (model #17 in Table 3), is developed as follows. First, the identified surrogate formulation is imposed on a conservative model reduction (by PFA), which removes unnecessary fuel and intermediate species from the total 3147 species count of the detailed municipal model. The resulting S-8_473 reduced model is then used to generate transient, zero-dimensional, fuel-air model predictions over a wide, user-specified range of (ϕ , T, p), similar to the PFA reduction approach discussed above. These benchmark calculations serve as a target database for compact model optimization. Specific targets for optimization are user-specified; for the present example, the compact model seeks to emulate CO, CO₂, and H₂O mole fraction histories computed from S-8_473 simulations. At fuel-air conditions relevant to aviation combustor applications, these particular species tightly constrain heat release rate (and therefore, temperature evolution), as well as indicate ignition delay time and the radical pool responsible for flame propagation rate and CO/NO_x emissions. In other words, these targets are regarded as excellent minimal constraints for global combustion behaviors.

The compact model to-be-optimized (“seed” model) begins as an assumed assembly that includes the previously validated, hierarchically constructed H₂/CO core chemistry of the 3147 species detailed model. This core chemistry is not subject to optimization. In this way, the “frozen” core chemistry respects the previous hierarchical construction and validation, as well as reduces the number of degrees of freedom for compact model optimization. Chemistry for intermediate C₁-C₃ species is added to the frozen core. This chemistry is also in common with the municipal model, but is subject to optimization. Several intermediate species identified as unimportant by PFA reduction of the full detailed model (e.g., HOOCH) are removed from the seed model as an initial step toward reducing the overall species count and optimization computational costs for the compact model. Finally, skeletal and lumped chemistry relevant to the parent fuel components is added to the seed chemistry. The corresponding reaction rate coefficients of this fuel chemistry subset are also subject to optimization.

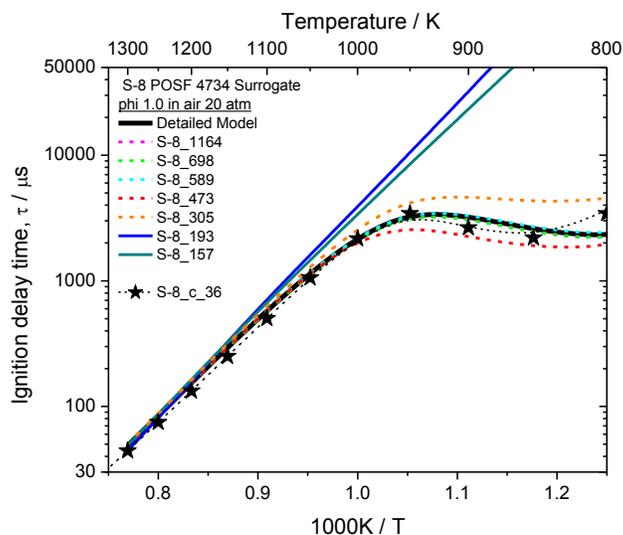


Figure 12. Predicted homogeneous, constant volume/internal energy ignition delay times for stoichiometric fuel-in air-mixtures of the S-8 surrogate (n-dodecane/iso-octane 51.89/48.11 mole %) at ~20 atm. Lines are models simulations using the S-8 surrogate composition and the detailed and reduced kinetic models of this study, symbols are calculations with the 36 species compact S-8 surrogate model.

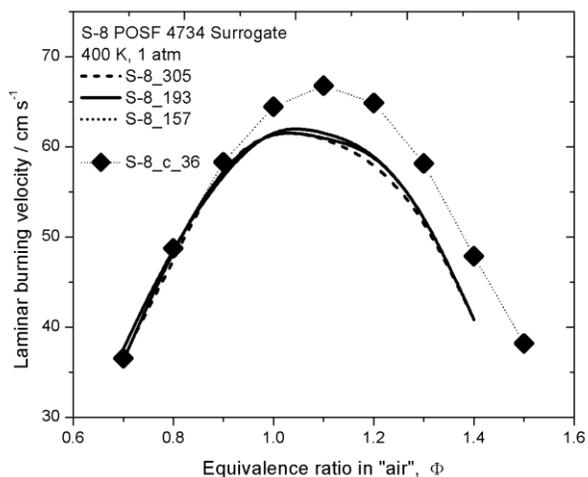


Figure 13. Predicted laminar burning velocities at 1 atm and 400 K for the S-8 surrogate (n-dodecane/iso-octane 51.89/48.11 mole %). Lines are model calculations with PFA-reduced models of this study, symbols are calculations with the 36 species compact S-8 surrogate model

The complete seed model discussed here involves 36 species describing S-8 combustion, and its inputs are optimized to reproduce the benchmark predictions of the S-8_473 reduced model. To efficiently sample the rate coefficient space that is to-be-optimized, rate coefficients for reactions of the fuel components and intermediates are initially populated using Latin hypercube sampling and user-defined rate coefficient bounds. An evolutionary algorithm applied to these rate coefficients to-be-optimized seeks an optimal solution over the whole discretized (ϕ , T, P) space previously identified.

B. Compact Model Performance

Exemplar results of the present S-8_c_36 optimization against PFA-reduced models appear in Figures 12 and 13. For ignition delay, Figure 12, the compact model essentially performs as well as the 473 species reduced model over the ≥ 800 K temperature range targeted by the compact model optimization. Also worth noting are the predictions of the (PFA-reduced) S-8_193 and S-8_157 models. Despite a significantly higher species count than the compact model, these models are unable to predict intermediate and low temperature ignition delay times, even qualitatively. This suggests that the mechanistic content of the present compact model seed may be of higher fidelity than that of models produced by aggressive application of PFA or other non-optimization-based methods.

Particularly at fuel rich conditions, the S-8 compact model predictions of laminar burning velocity, Figure 13, appear to deviate from the predictions of larger PFA-reduced models. The maximum deviation from consensus of the more detailed models is ~ 5 -6 cm/s, which is similar to the consistency in burning velocity data sets from independent laboratory determinations as discussed previously and shown in Figure 11. These fuel-rich burning velocity deviations are a target of future investigation and improvement as the CFD-compact model approach continues to develop.

The present demonstration of compact model generation is provisional, and we anticipate significant room for improvement, particularly in the reduction of species from the compact model example discussed here. Initial computations suggest that several species appearing in the compact model (e.g., CH_2 , C_3H_3) are unnecessary to achieve the present (or better) agreement with more complex model predictions and optimization targets. Nevertheless, the present preliminary level of *fuel-specific* model reduction is significant. Using the number of species cubed as a computational figure-of-merit (the cost of simple Jacobian inversion), computations with the present 36 species model may be accelerated by a factor of ~ 100 compared to those of the S-8_157 reduced model, which has been demonstrated here to fail in predicting ignition below ~ 1000 K. Relative to the benchmark S-8_473 reduced model, compact model computational times may improve by a factor of ~ 2000 . Future improvements to the compact model generation approach will further improve computation time and predictive accuracy.

Acknowledgments

Work at University of Limerick is supported by Science Foundation Ireland under the Charles Parsons Energy initiative. Research performed at Princeton University was supported by an AFOSR MURI under grant number FA9550-07-1-0515; by a NASA Phase I SBIR subcontract from Spectral Energies, LLC, Dayton OH, Sivaram Gogineni (PI); and by discretionary resources available to the senior author (FLD). Work at University of South Carolina was supported by the College of Engineering and Computing. The assistance of Dr. Timothy James Edwards of the United States Air Force in procuring fuel samples is gratefully acknowledged. The careful technical assistance of Mr. Timothy K. Bennett and Mr. Allen Qin in performing experimental measurements is acknowledged.

References

1. Edwards, T., Maurice, L. Q., J. Prop. Power. 17 (2001) 461–466.
2. Wood, C. P., McDonell, V. G., Smith, R. A., Samuelsen, G. S., J. Prop. Power 5 (1989) 399–405.
3. Schulz, W. D., American Chemical Society 37 (1992) 383–392.
4. Violi, A., Yan S., Eddings, E. G., Sarofim, A. F., Granata, S., Faravelli, T., Ranzi, E., Combust. Sci. Technol. 174 (2002) 399–417.
5. Ranzi, E., Dente, M., Bozzano, G., Goldaniga, A., Faravelli, T., Prog. Energy Combust. Sci. 27 (2001) 99–139.
6. Guéret, C., Cathonnet, M., Boettner, J.-C., Gaillard, F., Proc. Combust. Inst. 23 (1990) 211–216.
7. Agosta, A., Miller, D. L., Cernansky, N. P., Favarelli, T., Ranzi E., Exp. Therm. Fluid Sci. 28 (2004) 701–708.

8. Cooke, J. A., Bellucci, M., Smooke, M. D., Gomez, A., Violi, A., Faravelli, T., Ranzi, E., *Proc. Combust. Inst.* 30 (2005) 439–446.
9. Eddings, E. G., Yan, S., Ciro, W., Sarofim, A. F., *Combust. Sci. Tech.* 177 (2005) 715–739.
10. Dagaut, P., El Bakali, A., *Fuel* 85 (2006) 944–956.
11. Gokulakrishnan, P., Gaines, G., Klassen, M. S., Roby, R. J., Currano, J., *J. Eng. Gas Turb. Power* 129 (2007) 655–664.
12. Dooley, S., Won, S. H., Chaos, M., Heyne, J., Ju, Y., Dryer, F. L., Kumar, K., Sung, C.-J., Wang, H., Oehlschlaeger, M. A., Santoro, R. J., Litzinger, T. A., *Combust. Flame* 157 (2010) 2333–2339.
13. Dooley, S., Won, S. H., Heyne, J., Farouk, T. I., Ju, Y., Dryer, F. L., Kumar, K., Hui, X., Sung, C.-J., Wang, H., Oehlschlaeger, M. A., Iyer, V., Iyer, S., Litzinger, T. A., Santoro, R. J., Malewicki, T., Brezinsky, K., *Combust. Flame* 159 (2012) 1444–1466.
14. Dooley, S., Won, S. H., Farouk, T. I., Ju, Y., Dryer, F. L., 51st American Institute for Aeronautics and Astronautics, Aerospace Sciences Meeting, Grapevine Texas, 7-10 January 2013.
15. Hui, X., Sung, C. J., *Fuel* 109 (2012) 191–200.
16. Dooley, S., Won, S. H., Jahangirian, S., Ju, Y., Dryer, F. L., Wang, H., Oehlschlaeger, M. A., *Combust. Flame*, 159 (2012) 3014-3020.
17. ASTM D 6890, ASTM International, West Conshohocken, PA, 2007.
18. Dryer, F. L., Won, S. H., Dooley, S., A Measurement Process for the Determination of the Mixture Averaged Molecular Weight of Complex Mixtures, Provisional Patent Disclosure, Princeton University, Princeton NJ 08544. February 17, 2012.
19. Calcote, H. F., Manos, D. M., *Combust. Flame* 49 (1983), 289-304.
20. Mensch, A., Santoro, R. J., Litzinger, T. A., Lee, S. Y., *Combust. Flame* 157 (2010) 1097-1105.
21. ASTM D1322, Standard Test Method for Smoke Point of Kerosine and Aviation Turbine Fuel. ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States, 2008.
22. ASTM D5291-10, Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Petroleum Products and Lubricants. ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. 2010.
23. Won, S. H., Dooley, S., Veloo, P. S., Wang, H., Oehlschlaeger, M. A., Dryer, F. L., Ju, Y., *Combust. Flame*. 161 (2014) 826-834.
24. Dryer, F.L. , Jahangirian, S., Dooley, S., Won, S.H., Heyne, J., Iyer, V., Litzinger, T., Santoro, R.J., *Energy and Fuels*, 28 (2014) 3474-3485.
25. Metcalfe, W. K., Dooley, S., Dryer, F. L., *Energy & Fuels* 25 (2011) 4915–4936.
26. Won, S. H., Dooley, S., Dryer, F. L., Ju, Y., *Proc. Combust. Inst.* 33 (2011) 1163–1170.
27. Diévar, P., Won, S. H., Kim, H. H., Ju, Y., Dooley, S., Dryer, F. L., Wang, W., Oehlschlaeger, M. A., *Fuel*. 109 (2013) 125-136.
28. Westbrook, C. K., Pitz, W. J., Herbinet, O., Curran, H. J., Silke, E. J., *Combust. Flame*, 156 (2009) 181–199.
29. Mehl, M., Pitz, W. J., Westbrook, C. K., Curran, H. J., *Proc. Combust. Inst.* 33 (2011) 193–200.
30. Oehlschlaeger, M. A., Steinberg, J., Westbrook, C. K., Pitz, W. J., 156 (2009) 2165-2172.
31. Mourits, F. M., Rummens, F. H. A., *Can. J. Chem.* 55 (1977) 3007–3020.
32. Wang, H., Frenklach, M., *Combust. Flame* 96 (1994) 163–170.
33. Dooley, S., Uddi, M., Won, S. H., Dryer, F. L., Ju, Y., *Combust. Flame* 159 (2012) 1371–1384.
34. Sun, W., Chen, Z., Gou, X., Ju, Y., *Combust. Flame* 157 (2010) 1298–1307.
35. Lu, T., Law, C. K., *Proc. Combust. Inst.* 30 (2005) 1333–1341.
36. Wang, H., Oehlschlaeger, M. A., *Fuel* 98 (2012) 249-258.

37. Li, B., Liu, N., Zhao, R., Zhang, H., Egolfopoulos, F. N., Proc. Combust. Inst. 34 (2013) 727-733.
38. Li, B., Zhang, H., Egolfopoulos, F. N., Combust. Flame 161 (2014) 154-161.
39. Hui, X., Sung, C.-J., Fuel 109 (2012) 191-200.
40. Ji, C., Wang, Y. L., Egolfopoulos, F. N., J. Prop. Power. 27 (2011) 856-863.
41. Ajmani, K., Mongia, H. C., and Lee P. *49th AIAA/ASME/SAE/ASEE Joint Propulsion Conference, San Jose CA, 14-17 July*. 2013.
42. Iannetti A. C., and Moder J. P., NASA Glenn Research Center, 2010.
43. Westbrook, C. K., Dryer, F. L., Combust. Sci. Tech. 27 (1981) 31-43.
44. Montgomery, C. J., Cannon, S., Mawid, M., Sekar, B., 40th AIAA Aerospace Sciences Meeting and Exhibit, 2002.
45. Montgomery, C. J., Cremer, M. A., Chen, J.-Y., Berkeley, B., Westbrook, C. K., Maurice, L. Q., J. Prop. Power 18 (2002) 192-198.
46. Westbrook, C. K., Dryer, F. L., Symposium (International) on Combustion 18 (1981) 749-767.