Progress on a Methodology for the Formulation of Jet Aviation Fuel Surrogates

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Introduction

- Availability of high fidelity chemical kinetic models to describe *real fuel* oxidation/combustion at practically relevant conditions is the limiting challenge in the design of advanced engines and fuels to meet energy efficiency and clean combustion demands in a world constrained by fossil fuel depletion.
- Jet fuel composition is prohibitively complex to model as real fuel,
  => jet fuel composition varies markedly with, geographical source, refining method and end use operating condition.
  => must model with a simple mixture of less than approximately six components, a surrogate fuel.
- 1st challenge becomes the identification of a suitable surrogate mixture,
  => must be simple in composition but emulate complex combustion behaviour exhibited by real fuel.
- Difficulty increases when fuel-to-fuel variability is considered, different fuels have different chemical components.
- Capability to incorporate emerging alternative fuels: Synthetic Paraffinic Kerosene (SPK) and Hydrotreated Renewable Jet (HRJ) fuels, bio or fossil derived, can differ in composition considerably from crude oil derived fuels.

Strategy to Jet Fuel Kinetic Modelling and Surrogate Formulation

- For a surrogate to emulate the combustion chemistry of a real fuel, critical fuel properties which manifest in important practical combustion behaviour of the target fuel must be identified and be easily measureable:

- Adiabatic flame temperature
- Local air fuel stoichiometry
- Enthalpy of combustion
- Flame velocity
- Fuel diffusive properties
- Global chemical kinetics/ Overall radical production
- Sooting tendency

→ **Ratio of hydrogen to carbon (H/C)**
→ **Molecular Weight (MW)**
→ **Derived Cetane Number (DCN),** macro ignition measure via Ignition Quality Tester (IQT)
→ **Threshold Sooting Index (TSI),** via smoke point measurement

→ **All Easily Measurable**

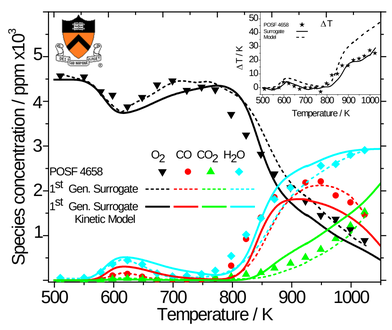
- Surrogate mixture must emulate these parameters, but how?
- **Thesis: Interaction of distinct molecular functionalities in radical generation is manifested in real fuel combustion behaviour.**
- For a surrogate mixture to successfully emulate real fuel behaviour, upon oxidation surrogate components should form the same *distinct* chemical functionalities as the real fuel.
- for petroleum derived fuels => *n*-alkyl, *iso*-alkyl and aromatic.
- Get surrogate *distinct* chemical functionalities and proportions correct, then get real fuel combustion behaviour correct!

1st Generation Surrogate Shows Concept Works[1]

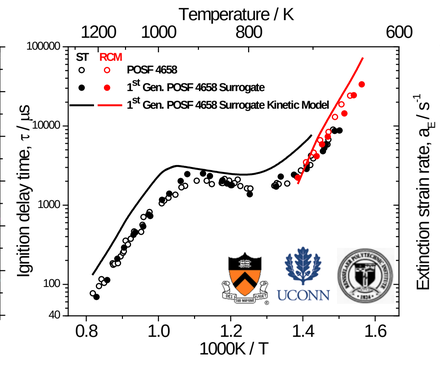
- The variability of real fuels in terms of chemical composition means surrogate formulation must be, at least to some degree, on a fuel-specific basis.
- Experiments conducted on an average Jet-A (POSF 4658) show expected complex combustion character.
- Our 1st generation surrogate[1] is comprised of *n*-decane/*iso*-octane/toluene and matches Jet-A (POSF 4658) H/C and DCN only. Overall, excellent emulation of real Jet-A POSF 4658 chemical kinetic combustion properties is achieved for: ignition delay, heat release rate, diffusion flame extinction.

Table 1: Jet-A POSF 4658 Surrogate Formulations

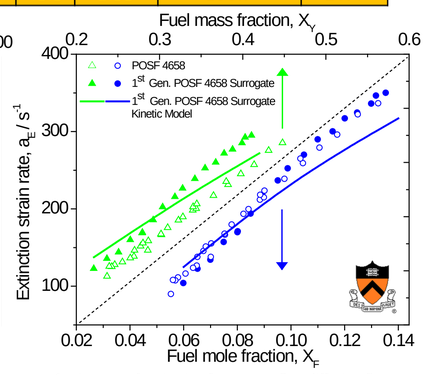
Mole Fraction					DCN	H/C	MW / g mol^{-1}	TSI
Jet-A POSF 4658					47.1	1.957	142.01	21.4
1st Generation surrogate	*n*-decane	*iso*-octane	Toluene		47.1	2.01	120.7	14.1
	0.427	0.33	0.243					
2nd Generation surrogate	*n*-dodecane	*iso*-octane	Mesitylene	n-propyl benzene	48.5	1.95	138.7	20.4
	0.40	029	0.07	0.23				



Flow reactor oxidation data for conditions of 12.5 atm, 0.3% carbon, φ= 1.0 and *t* =1.8s, for POSF-4658, 1st generation POSF-4658 surrogate and model simulation of 1st generation POSF-4658 surrogate, Inset;DT



Ignition delay times, ϕ= 1.0 in air at ~20 atm for POSF-4658, 1st generation POSF-4658 surrogate and 1st generation POSF-4658 surrogate kinetic model simulation



Strain rates of extinction for counter flow diffusion flames at 1 atm, POSF-4658, 1st generation POSF-4658 surrogate and 1st generation POSF-4658 surrogate kinetic model simulation.

Kinetic Models

- Surrogate component palette is assembled with careful consideration to state of kinetic model development, Table 2.
- 1st generation surrogate kinetic model assembled from *n*-decane[6], *iso*-octane[7] and toluene[8] chemistries, on top of a common sub model[2-5], as these are the best characterised and understood required representative chemical functionalities.
- 2nd generation surrogate kinetic model is assembled from *n*-dodecane[6], *iso*-octane[7], 1,3,5 trimethyl benzene (mesitylene)[9] and *n*-propyl benzene[10] chemistries but these components are less well characterised and more poorly understood.
- Effect of cycloalkane chemistries[11,12] on 1st generation surrogate can also be tested.

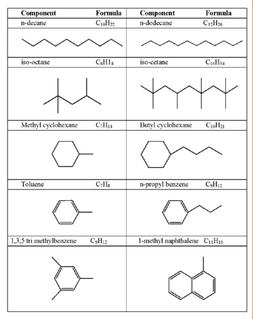
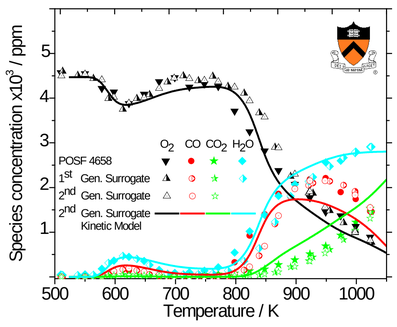


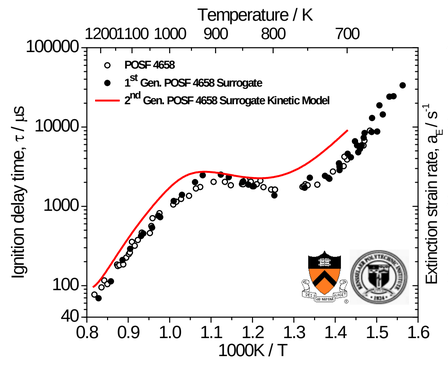
Table 2: Proposed surrogate palette

2nd Generation Surrogate Shows Better Emulation

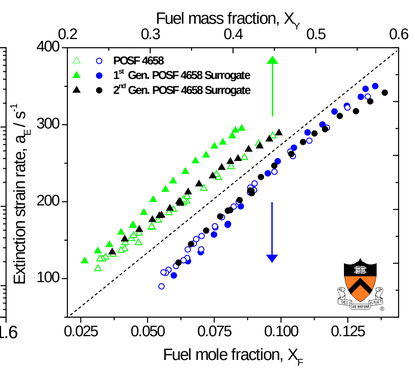
- 1st generation surrogate emulates Jet-A POSF 4658 combustion chemistry vey well but any mixture of *n*-decane/*iso*-octane/toluene can not match Jet-A POSF 4658 threshold sooting index (TSI) and average molecular weight (MW) simultaneously => larger aromatic components are required.
- A 2nd generation surrogate mixture of *n*-dodecane/*iso*-octane/1,3,5 trimethyl benzene/*n*-propyl benzene matches Jet-A POSF 4658 DCN, H/C, MW and TSI.
- Gas phase experiments show that 1st generation surrogate and 2nd generation surrogate share almost identical chemical kinetic combustion behaviour and both are very similar to Jet-A POSF 4658. => conclusively proves concept.



Flow reactor oxidation data for conditions of 12.5 atm, 0.3% carbon, φ= 1.0 and *t* =1.8s, for POSF-4658, 1st generation POSF-4658 surrogate, 2nd generation POSF-4658 surrogate and model simulation of 2nd generation POSF-4658 surrogate.



Shock tube ignition delay times, ϕ= 1.0 in air at ~20 atm for POSF-4658, 1st generation POSF-4658 surrogate, 2nd generation POSF-4658 surrogate and kinetic model simulation of 2nd generation POSF-4658 surrogate.



Strain rates of extinction for counter flow diffusion flames at 1 atm, POSF-4658, 1st generation POSF-4658 surrogate and 2nd generation POSF-4658 surrogate.

- Provisional 2nd generation surrogate kinetic model reproduces experimental data quite well, improved relative to 1st generation surrogate kinetic model.

Remaining Challenges for Surrogate Formulation

- Our philosophy is based on identifying the *distinct* chemical functionalities formed by oxidation of a real fuel, if distinct functionalities vary from fuel to fuel then so must surrogate components.
  => important when considering synthetic fuel where no aromatics are present.
- Cycloalkanes can be present in jet aviation fuels up to approx. 25-30%, analysis[11] of Jet-A POSF 4658 shows approx 25% cycloalkanes, but do cyloalkanes form distinct chemical functionalities?
- With the 1st generation surrogate kinetic model as a base, two additional Jet-A POSF 4658 surrogates are formulated where the *n*-alkane fraction has been replaced with cyclohexane and methyl cyclohexane up to 25 mole% => all mixtures share same DCN, H/C, MW and TSI.

Table 3: Jet-A POSF 4658 Surrogate Formulations to Examine Effect of Cycloalkanes.

Mole Fraction					DCN	H/C	MW / g mol^{-1}	TSI
Jet-A POSF 4658					47.1	1.957	142.01	21.4
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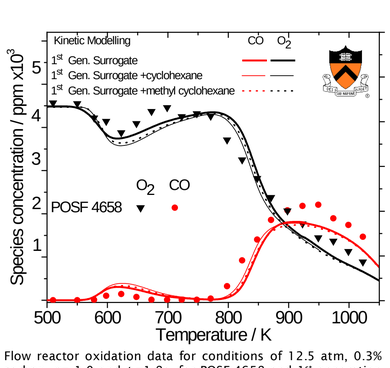
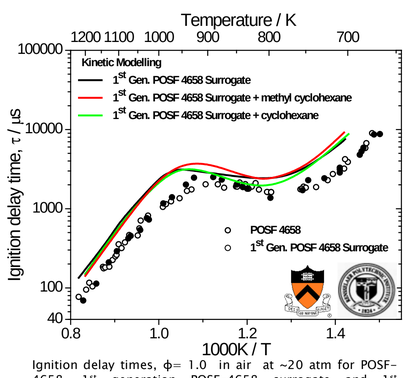
- Test effect of cycloalkane addition to surrogate by adding cyclohexane[12] and methyl cyclohexane[13] chemistries to 1st generation surrogate kinetic model.
- Kinetic model simulations do not show pronounced perturbations due to cycloalkane addition relative to 1st generation surrogate.
  => indicating reduced signifigance of the cycloalkane functionality.



Flow reactor oxidation data for conditions of 12.5 atm, 0.3% carbon, φ= 1.0 and *t* =1.8s, for POSF-4658 and 1st generation POSF-4658 surrogate kinetic model simulations, showing potential effect of cycloalkane addition to 1st generation surrogate as per Table 3.CO_2/H_2O omitted for clarity



Ignition delay times, ϕ= 1.0 in air at ~20 atm for POSF-4658, 1st generation POSF-4658 surrogate and 1st generation POSF-4658 surrogate kinetic model simulations, showing potential effect of cycloalkane addition to 1st generation surrogate as per Table 3.

Conclusions

- A working strategy for the formulation of surrogate fuels to emulate the gas phase combustion chemistry of complex real fuels has been demonstrated.
- Four simply determinable parameters (DCN, H/C, MW and TSI) are used to constrain mixtures of 3-4 components to precisely emulate real fuel behaviour.
- Surrogate formulation strategy and "a priori" kinetic modelling shows that predictive capability of real fuel combustion chemistry is within sight.
- Based on the identification of *distinct* chemical functionalities that when oxidised impact the radical pool, the surrogate formulation strategy is derived from group additivity and may therefore be extended to other fuel classes such as gasolines, diesels and bio-derived oxygenated fuels.

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