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

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Year-Four Overview

of

2007 MURI Topic #12:Science-Based Design of Fuel-flexible Chemical Propulsion/Energy Conversion Systems

MULTI AGENCY COORDINATION COMMITTEE FOR COMBUSTION RESEARCH (MACCCR)

FUELS RESEARCH REVIEW

Argonne National Laboratory

Argonne, Illinois

20-22 September 2011

Improved Representation of Real Jet Fuel Impact on Applications

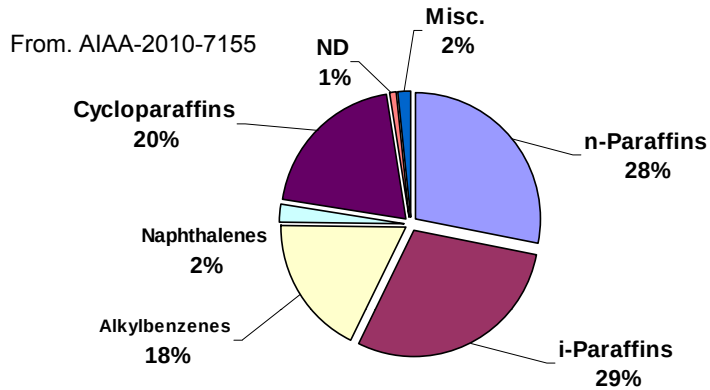
- Enhanced efficacy in evaluating fuel property variations on existing propulsion system performance and emissions.
- Improved design and development for advancing existing and developing new propulsion/combustion concepts.
- Assistance in integrating new non-petroleum-derived alternative fuel resources into the aero-propulsion sector.
- Provide fundamental guidance for developing "Rules and Tools" - type efforts for expediting certification of and integrating new alternative fuels with petroleum-derived products.
  - T. Edwards, C. Moses, and F. Dryer (2010). 'Evaluation of Combustion Performance of Alternative Aviation Fuels', 46th AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit, 25-28 July 2010, Nashville, TN Paper No. AIAA-2010-7155.

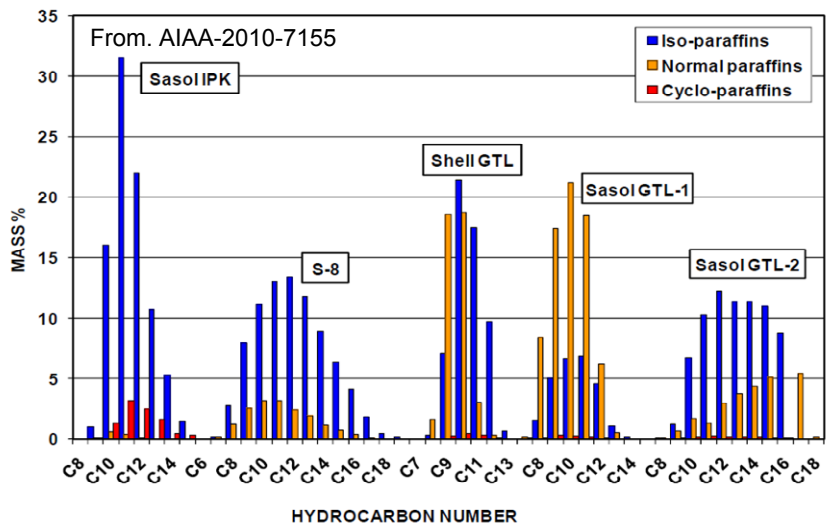
Real Jet Fuels and Alternative Fuel Classes

Two different Jet fuel analyses are shown here to demonstrate that:

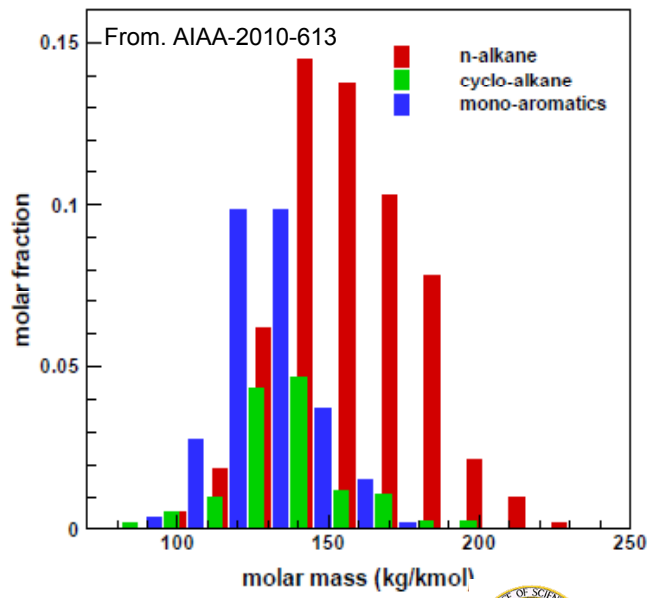
- Jet fuels generally contain n-paraffins, (weakly branched) iso-paraffins, cyclo-alkanes, and alkylated aromatics in varying proportions.
- Each class structure is distributed differently over the distillation curve.
- Different distributions for each alternative fuel stock as well, so blending affects class-content and distillation-distribution.

Hydrocarbon Class Distribution in Jet-A (wt.%)



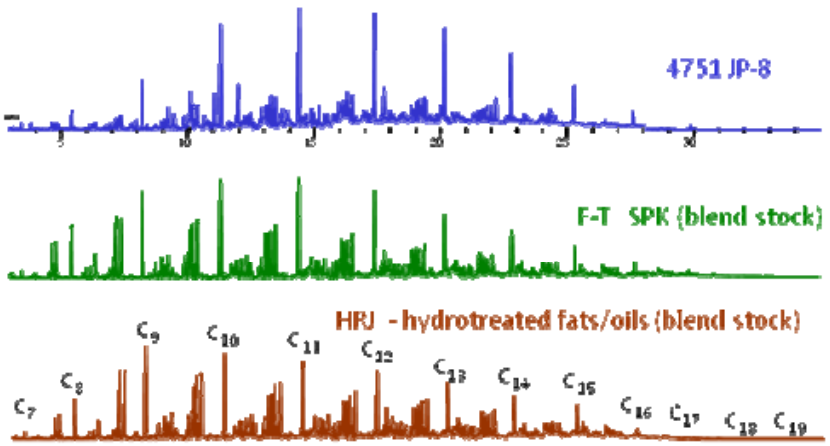


Class Distributions for Various Alternative Liquids



Jet Fuel Composition Variability

- Difficulty increases when fuel-to-fuel supply variability is considered.
- Capability to incorporate emerging alternative fuels is desirable, Synthetic Paraffinic Kerosene (SPK) and Hydrotreated Renewable Jet (HRJ) blended fuels will likely differ in composition from crude oil derived fuels.



Carbon number distributions for a JP-8, Fischer Tropsch Synthetic Paraffinic Kerosene (SPK) and hydrotreated renewable Jet (HRJ) blended fuels.

From AIAA-2010-7155

	JP-8			Jet A		
	Min	Max	Mean	Min	Max	Mean
H_2 Content (mass %)	13.40	14.78	13.81	N/A	N/A	N/A
H/C Ratio	1.844	2.067	1.909	N/A	N/A	N/A
Cetane Index	31.8	56.8	43.9	N/A	N/A	N/A
Smoke Point (mm)	19.0	31.0	22.7	24.0	27.0	26.2
Aromatics (liq. vol %)	0.10	24.60	17.86	15.20	19.40	17.58
TSI	15.72	25.66	21.47	19.71	22.17	20.31
Density (g/ml, 15°C)	0.780	0.832	0.804	0.786	0.799	0.790

http://www.desc.dla.mil/DCM/Files/2006PQISreport.pdf

Physical and Chemical Kinetic Properties

Physical properties of interest: Energy density, distillation curve, phase diagram, Viscosity, surface tension, ….

Physical property modeling, – molecular structure not very important.

- Consensus is that a larger number of components are required to model the distillation curve and phase diagram, particularly including class distributions!

Chemical Kinetic Properties of Interest: autoignition, flame temperature, laminar premixed burning rate, strained diffusive, and premixed extinction, diffusive and premixed sooting, major species emulation, minor species emulation (HC emissions?).

Chemical kinetic modeling – molecular structure very important.

- The type(s) and *number* of components needed to adequately represent real fuel composition strongly impacts dimensional nature of the kinetic model.

- *Required accuracy in reproducing both physical and chemical properties is strongly influenced by need to treat multi-component preferential vaporization.*
  - *Experimental evidence on the relative importance of physical and chemical kinetic effects under multi-phase conditions encompassing those found in real combustors is needed .*

MURI Research Approach

- Encompass both petroleum-derived and alternative fuel physical and chemical property ranges in methodology.
- Understand requirements and experimentally evaluate concepts for describing accurately fully pre-vaporized combustion chemistry of specific gas turbine fuels.
- Expand experimental databases for the selected surrogate components required.
- Advance detailed kinetic modeling capabilities for surrogate components and mixtures.
- Apply methods to simplify dimensional impacts of the detailed kinetic models.
- Integrate in an optimal manner physical and chemical property constraints for emulating multi-phase combustion.

MURI Strategy for Modeling a Specific Jet Fuel

Identify critical fuel property targets that manifest in important practical combustion behavior of each real fuel:

- Adiabatic flame temperature
- Local air-fuel stoichiometry
- Enthalpy of combustion
- Flame velocity
- Overall active radical production
- Premixed sooting

} Ratio of Hydrogen to Carbon (H/C)

- Non-premixed sooting → Threshold Soot Index (TSI), By standardizing smoke point measurement
- Fuel diffusive transport properties → Average Molecular Weight (MW_{avg})
- Autoignition/global kinetics → Derived Cetane Number (DCN), Correlative for macro ignition measure

➢ H/C, TSI, DCN, MW_{avg} can each be determined for the real fuel sample, as well as for the surrogate mixture, using the same, simple experimental procedures.

➢ New experimental method developed to determine MW_{avg}.

No quantitative species classification measurements required for formulating the surrogate mixture.

Surrogate Mixture Procedure and Evaluation

1. ***Characterize the specific real fuel:***

- Determine empirical formula for C_nH_m using CHN analysis (ASTM D5291).
- Determine average molecular weight **(New experimental method developed)**.
- Determine DCN of fuel using Ignition Quality Testing (ASTM D6890).
- Determine TSI from smoke point measurement (ASTM D1322) and average molecular weight.

2. ***Characterize chosen surrogate components and their mixtures***

- Develop experimental self-consistent library of TSI values for surrogate components and mixtures.
- Develop experimental self-consistent DCN database for surrogate component mixtures composed of a base n-alkane to which other components that are added yield 30 <DCN<65 (ASTM D6890).

3. ***Emulate the H/C, DCN, TSI, and average molecular weight of specific fuel by choice of surrogate components and mixture fractions.***

4. ***Compare gas phase experimental observations for specific fuel and the apriori formulated surrogate mixture:***

- Reflected shock tube ignition delay (in collaboration with *RPI*).
- Rapid Compression Machine (RCM) ignition properties (*UCONN*).
- Variable Pressure Flow Reactor (VPFR) reactivity (*PU*).
- Diffusive strained extinction (PU).
- *Premixed laminar burning rate (UCONN, PU).*
- *Premixed strained extinction (UCONN, PU).*
- *Species evolution as extent of reaction (PU, UIC).*
- *Sooting (PSU).*

1st Gen surrogate, Compared in Dooley et al. doi:10.1016/j.combustflame.2010.07.001

1st Gen and 2nd Gen surrogate, Compared in Dooley et al. (2011), Combust Flame, *In review*

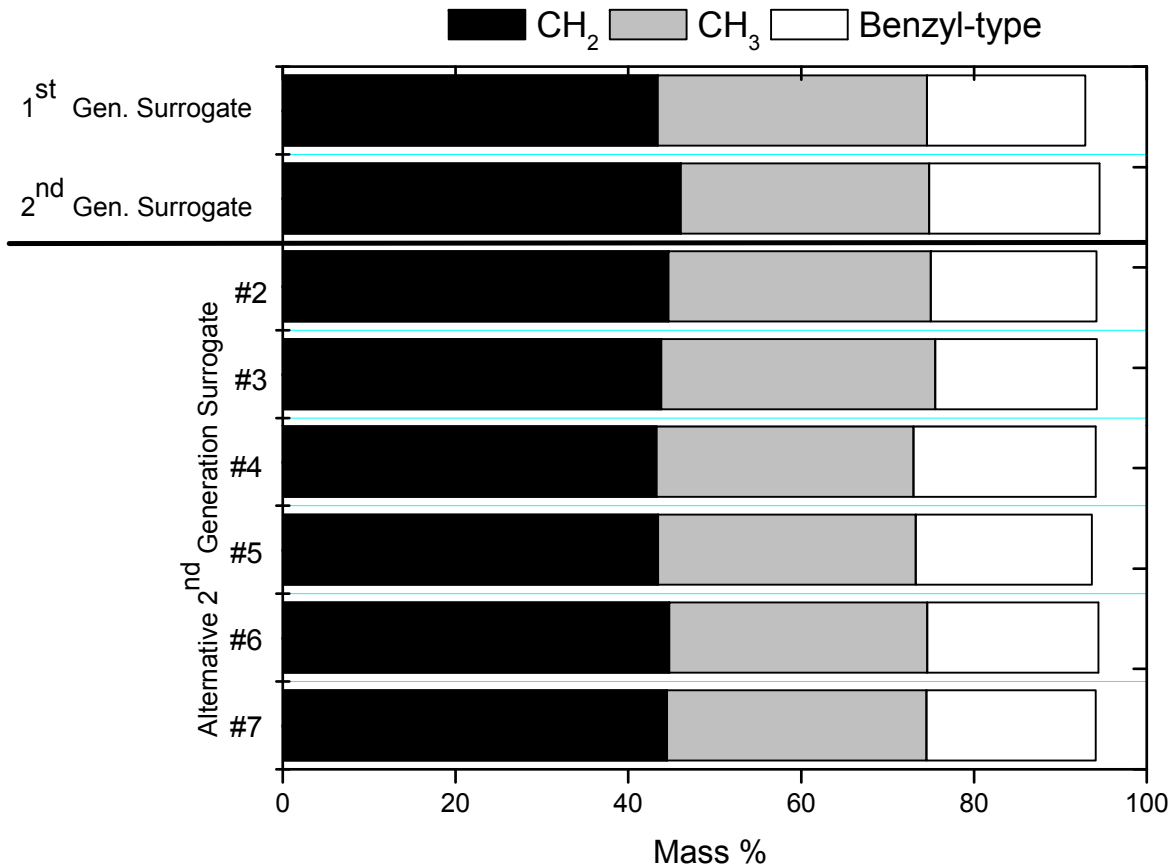
Second Generation Surrogate

Higher molecular weight components permits emulation of all property targets for full range of observed properties for other jet fuel samples.

	Liquid volume fractions			
Component	**A**	**B**	**C**	**D**
n-decane (n-C10) 1st Gen	48.73%		52.47%	
n-dodecane (n-C12) 2nd Gen		41.73%		42.45%
iso-octane (Iso-C8) 1st and 2nd Gen	27.76%	35.43%	18.33%	29.10%
toluene (C_7H_8) 1st Gen	23.51%	22.84%		
n-propylbenzene (n-PB) 2nd Gen			2.20%	14.57%
1,3,5-trimethylbenzene (1,3,5 TmB) 2nd Gen			27.00%	13.88%
H/C	1.909	1.909	1.909	1.909
(Values of a typical JP-8 in blue) **CN**	43.9	43.9	43.9	43.9
TSI	18.55	19.19	21.47	21.47
Aromatics (vol %); avg.=17.86%	23.51%	22.84%	29.20%	28.45%

- Property targets reproduced with variety of class distributions - **no "unique" surrogate blend**.
- *Same approach can be applied to any number of components, provided consistent reference data sets for component TSI, DCN & MW_{avg} are available.*

MURI Strategy to Jet Fuel Modeling



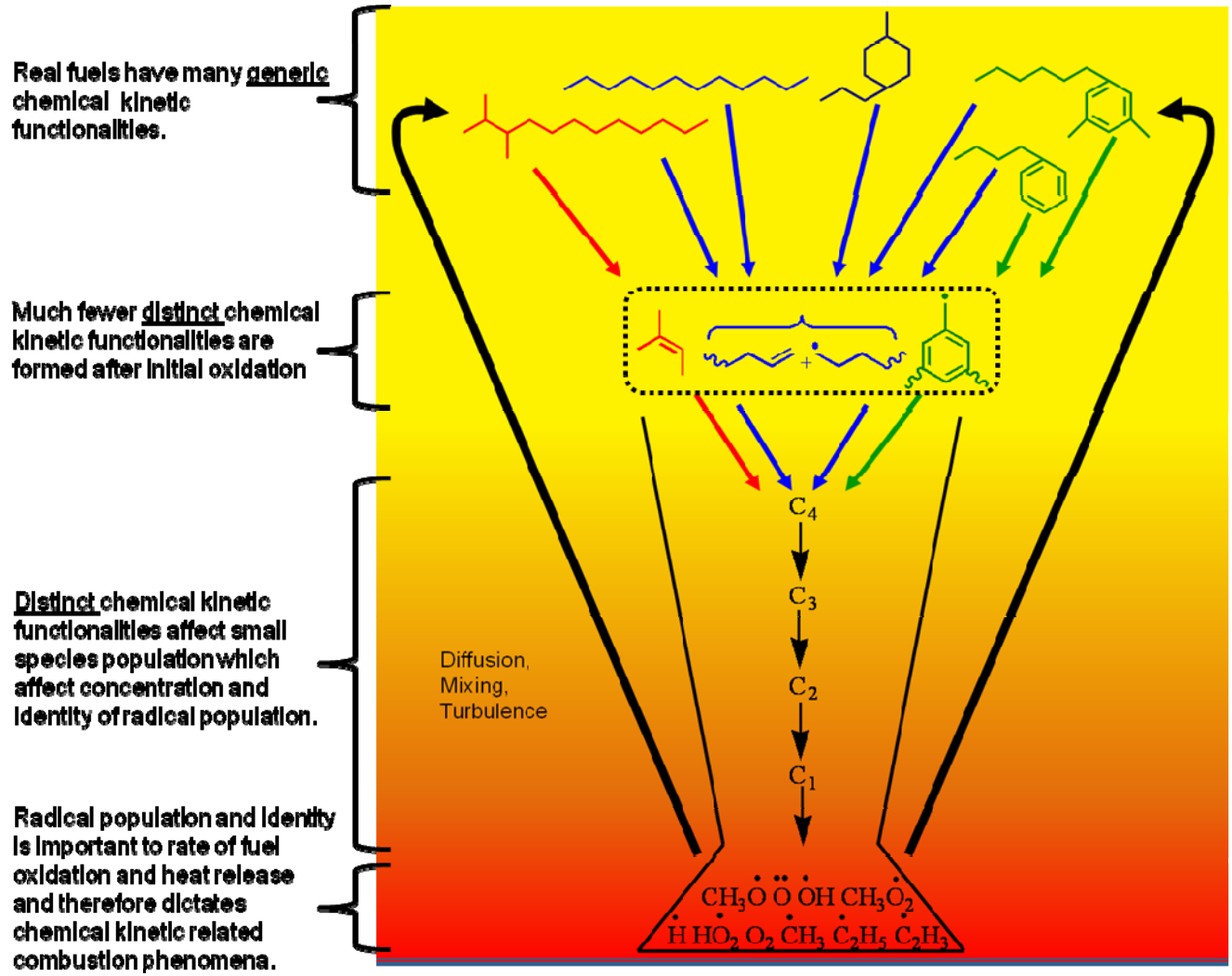
Molecular group mass comparisons for 1st Gen (n-decane/iso-octane/toluene 42.7/33.0/24.3 mole %), 2nd gen (n-dodecane/iso-octane/1,3,5 trimethylbenzene/n-propylbenzene 40.41/29.48/7.28/22.83 mole %) and six ~equally possible *alternative* 2nd gen POSF 4658 surrogate fuel mixtures.

Surrogate mixture compositions that H/C, DCN property targets yield ~same functional group compositions.

Dooley et al. (2011), Combust Flame, *In review*

MURI Strategy to Jet Fuel Modeling

- Molecular structure correlations can yield the chemical functional information for a real fuel if chemical composition is known….
- But, experimental combustion property targets used here provide sufficient constraints with much less effort!
- There is considerable flexibility in choosing appropriate surrogate components.



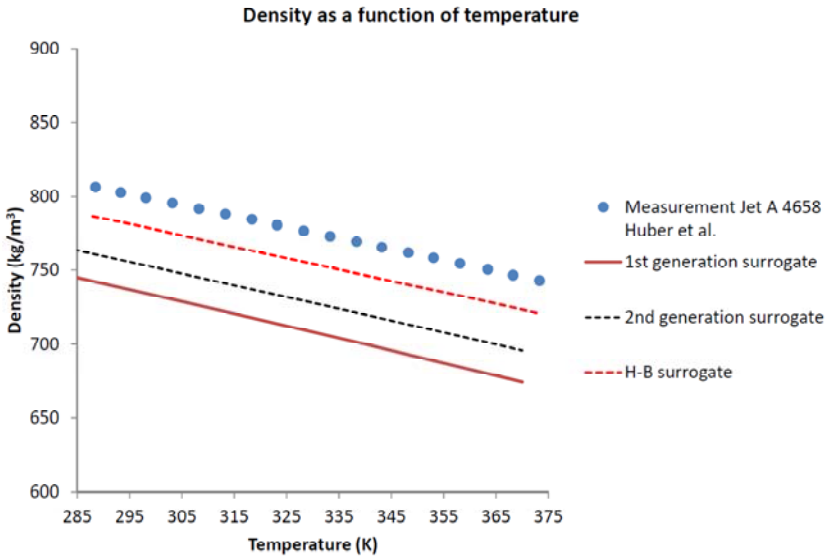
Initial fuel molecular structural issues might become more relevant at low and NTC oxidation conditions (ROOH and QOOH isomerization reactions).

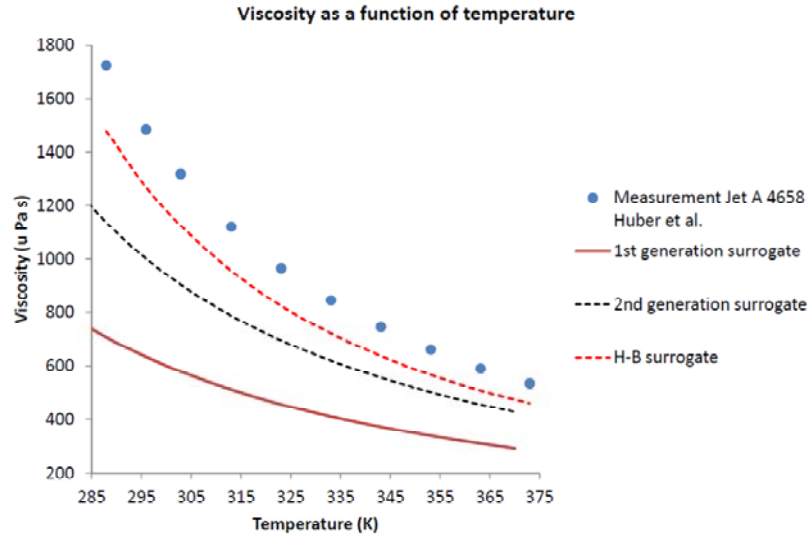
Dooley et al. (2011), Combust Flame, *In review*

Physical Property Considerations

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	1,3,5 TmB	n-PB	48.5	1.95	138.7	20.4
	0.40	0.29	0.07	0.23				
*H-B Surrogate	*n*-dodecane	n-Tetradecane	1,2,4 TmB		60.4	1.89	158.3	28.7
	0.288	0.304	0.408					

*Bruno, and Huber (2010)). Energy Fuels: DOI:10.1021/ef1004978





Physical property emulations (especially distillation/class distributions) require relatively larger numbers of molecular components than needed to model chemical kinetic properties.

Solvent Cut Surrogate Mixtures

- Using pure components to make large volumes of surrogate mixture is expensive!
- MURI surrogate mixture formulation concept should apply even with more complex surrogate component compositions. => *Will it work for formulations using hydrocarbon solvent mixtures or solvent cuts??*

Exxon Narrow Cut Solvent Fractions used for a demonstration:

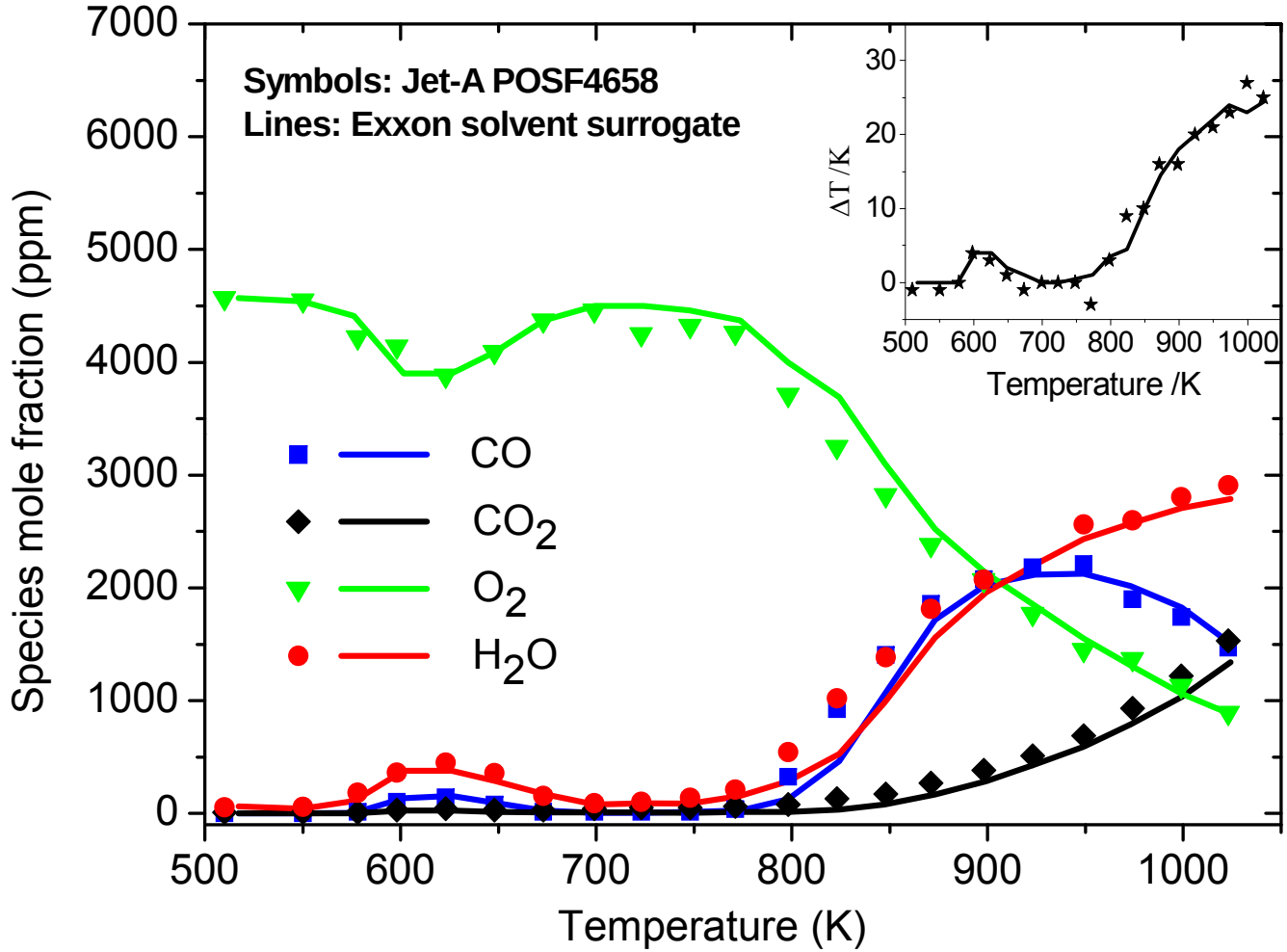
1) Nor-Par 12: a mixture of > 98% (mainly C_{11} - C_{12}) linear alkanes.
2) Iso-Par L: a mixture of > 99% (mainly C_{11} - C_{13}) iso-paraffinic alkanes.
3) Aromatic 150: a mixture of (primarily C_{10}) alkyl-benzenes.

			DCN Predicted	DCN Measured	H/C	MW g mol^{-1}	TSI
Jet-A POSF 4658				47.1	1.957	142.01	21.4
***Nor-Par 12**	***Iso-Par L**	***Aromatic 150**					
42.78	40.62	16.6	47.38	47.27	2.025	162.09	21.4

- ***An enabling result if MURI mixture concept works*:** Produce surrogate fuel compositions in large volumes from carbon-number-classified hydrocarbon solvent fractions.
  - ***~$1.40 per lb vs. ~$100.00 per lb if pure component mixtures are used for surrogates!***

Jahangirian et al. ESSCI (2011)

Jet-A POSF4658 vs Solvent Surrogate Mixture



VPFR reactivity and heat release comparison for Jet-A POSF4658 vs. POSF 4658 Exxon solvent surrogate mixture (nPar 12/isoPar L/Aromatics 150) at 12.5 atm, 1.8 sec, 0.3 % (molar) carbon, φ = 1.0.

Jahangirian et al. ESSCI (2011)

Applied Combustion Research

- Knowledge gained through MURI efforts can impact efficacy of understanding fuel physical and vapor phase kinetic properties on multi-phase combustion.

Methodology:

Specific real fuel property studies => select real fuel of interest

↓

Formulate solvent surrogate mixture for real fuel emulation based on combustion property target emulation

↓

Utilize pure component mixture model (based upon small number of components) for vapor phase chemistry emulation

- Economical applied surrogate through use of molecular class solvent cuts
- Refined vapor phase kinetic/transport models based upon mixture properties of a small number of pure components.

Models based on current 2nd generation component mixtures and combustion target methodologies are adequate for many gas turbine combustion applications.

- *Further refinements possible by addition of a cyclo-alkane and/or weakly-branched isomer species in the future.*

Other Surrogate Formulation Efforts

- 2nd Gen Surrogate Formulation Validation for a Fischer-Tropsch SPK feed stock, S-8 POSF 4734.
- Importance of cycloalkane(s) as additional surrogate component(s).
- Importance of weakly branched isomer(s) as additional surrogate component(s).
- Solvent Surrogate Mixture studies on sooting behavior of a JP-8 sample fuel (POSF 5169).

General directions of continuing experiment to modeling studies:

- Further testing of sufficiency for 2nd generation component mixtures in emulating chemical kinetic behavior for other real jet fuel samples.
- Expand individual component and mixture data base for the 2nd generation components => Further experimental studies at all labs.
- Emphasize model developments for aromatic components:
- Alkane components already heavily emphasized in complementary work of IPT group => strongly influence radical pool production.

Aromatics are key species for modeling real fuel behavior of petroleum derived fuels and their mixtures with alternative components.

MURI Accomplishments in 2010-2011(1)

Major progress on *experimentally confirming* jet fuel surrogate mixture formulation concepts to emulate fully pre-vaporized combustion properties of a specific real fuel

- Collaborative, cross-validated critical experimental data comparisons of a real Jet–A fuel sample (POSF 4658) and surrogate mixture behavior at PU, PSU, UCONN, UIC, RPI (Oehlschlaeger): ignition delay (RST, RCM), VPFR reactivity, diffusive strained extinction, premixed burning rate, premixed strained extinction, high pressure single pulse shock tube speciation, wick flame sooting.
  - 1st generation surrogate (n-C_{10}/iso-C_8/tol) for Jet A-POSF 4658 Dooley et al. Combust Flame (2010).
  - 1st and 2nd generation surrogates (n-C_{12}, iso-C_8/nPB/1,3,5TmB, In review, Combust Flame, Sept. 2011.
- Demonstration of MURI concept using 2nd Gen for a Fisher-Tropsch jet fuel stock, S-8 (POSF 4734).
- Demonstration of MURI concept using *narrow cut solvent mixture* to emulate POSF 4658.
- Testing of additional component classes (weakly branched iso-alkanes, cyclo-alkanes).
- Comparison of sooting of POSF 5699 against *several* surrogate solvent mixtures in a model high pressure dump combustor conditions.
- Property data (H/C, DCN, TSI, MW_{avg}) for other jet fuel samples and suggested 2nd gen surrogate mixtures partially completed.

MURI Accomplishments in 2010-2011(2)

Additional surrogate component experimental database contributions

- High pressure single pulse shock tube (*UIC*): iso C-8, n-C10, n-C12,nPB, 1,3,5 TmB.
- RCM data (*UCONN*): n-C_{10}, n-C_{12}, i-C_8, MCH, Tol, nPB, 1,2,4 TmB, 1,3,5 TmB.
- Laminar flame speeds,1atm (*UCONN*): n-C_7, n-C_{10}, n-C_{12}, MCH, Tol, nPB, 1,2,4 TmB, 1,3,5 TmB.
- Premixed strained extinction (*UCONN*): n-C_7, nC_{10}, n-C_{12}, MCH, Tol, nPB, 1,2,4 TmB, 1,3,5 TmB.
- New premixed bomb flame speed measurements (1,3,5 TmB), others in progress.
- Diffusive strained extinction (*PU*): n-C_{12}, iso-C_8, n-PB, 1,2,4 TmB, 1,3,5 TmB, trimethyl alkane .
- VPFR reactivity and species time history (*PU*): n-C_{10}, n-C_{12}, n-PB, 1,3,5 TmB, 2mH, tri methyl alkane.

Fundamental supporting research

- Model reduction (*UCONN, PU*), Multi-time scale and path analysis integration with adaptive griding (*PU*).
- TSI (*PSU*) and DCN (*PU*) fundamentals, new method for determining MW_{avg} (*PU*).
- Strained diffusive extinction limit correlations that identifies relative effects of MW_{avg}, ΔH_{comb},, kinetics (*PU*).
- Flame speed comparisons - counter flow (*UCONN*) vs spherical flame (*PU*).
- Significant progress on 2nd generation detailed kinetic model development for n-PB and 1,3,5 TmB (*UIC, PU*).
    - Toluene model in press: Energy and Fuels, 2011 (*PU*).
- 2nd Gen component mixture chemical kinetic model in development.
- Physical /chemical property integration concept development (*PU*).

Presentations

MURI Overview
Frederick L. Dryer
Princeton University

Relationship between Threshold Soot Index and Soot Levels for Surrogate Fuels
Robert Santoro
The Pennsylvania State University

Detailed Studies on the Oxidation of Surrogate Fuel Components, Surrogate Mixtures and Real Fuels
Kenneth Brezinsky
University of Illinois, Chicago

Fundamental Combustion Data for Jet-A, Constituent Components, and Surrogate Mixtures
Chih-Jen Sung
University of Connecticut

Kinetic Studies of Flames of Alkanes and Aromatics
Yiguang Ju
Princeton University

Surrogate Mixtures for Real Fuels; Concepts and Associated Kinetic Studies of Surrogate Components
Frederick L. Dryer
Princeton University

Program Summary and Discussion
Frederick L. Dryer
Princeton University

Publications

Archival publications (2010-2011)

- S. Dooley, S.H. Won, J. Heyne, T.I. Farouk, Y. Ju, F.L. Dryer, K. Kumar, X. Hui, C.J. Sung, H. Wang, M. A. Oehlschlaeger, T.A. Litzinger, R.J. Santoro, T. Malewecki, K. Brezinsky. " The Experimental Evaluation of a Methodology to Surrogate Fuel Formulation for the Emulation of Combustion Kinetic Phenomena by a Theory of Real Fuel Oxidation" *Combust Flame*, 2011. *In review*.
- S. Gudiyella and K. Brezinsky, "High Pressure Study of n-Propylbenzene Oxidation", *Combust Flame*, 2011. Submitted.
- W.K. Metcalfe, S. Dooley, F.L. Dryer. "A Comprehensive Detailed Chemical Kinetic Modeling Study of Toluene Oxidation", *Energy Fuels*, 2011. Accepted for Publication.
- S.H. Won, S. Dooley, F.L. Dryer, Y. Ju. "The Chemical Kinetic Contribution to Diffusion Flame Extinction of Large Hydrocarbon Fuels, a Radical Index" *Combust Flame*, 2011. Accepted for Publication.
- S. H. Won, S. Dooley, F. L. Dryer, Y. Ju, A Radical Index for the Determination of the Chemical Kinetic Contribution to Diffusion Flame Extinction of Large Hydrocarbon Fuels, *Combust Flame*, 2011. Accepted for Publication.
- S. Jahangirian, S. Dooley, F.L. Dryer "A Detailed Experimental and Kinetic Modeling Study of n-Decane Oxidation at Elevated Pressures" *Combust Flame*, 2011. In Press. doi:10.1016/j.combustflame.2011.07.002.
- K. Kumar, C. J. Sung, and X. Hui, Laminar Flame Speeds and Extinction Limits of Conventional and Alternative Jet Fuels, *Fuel*, 2011:90,1004-1011.
- S. Dooley, S. H. Won, M. Chaos, J. Heyne, Y. Ju, F. L. Dryer, K. Kamal, C. J. Sung, H. Wang, M. A. Oehlschlaeger, R. J. Santoro, and T. A. Litzinger, A Jet Fuel Surrogate Formulated by Real Fuel Properties, *Combust Flame*, 2010: 157, 2333-2339.
- K. Kumar and C. J. Sung, Flame Propagation and Extinction Characteristics of Neat Surrogate Fuel Components, *Energy and Fuels*, 2010:24, 3840-3849.
- K. Kumar and C. J. Sung, A Comparative Experimental Study of the Autoignition Characteristics of Alternative and Conventional Jet Fuel/Oxidizer Mixtures, *Fuel*, 2010: 89, 2853-2863.
- T. Edwards, C. Moses, and F.L. Dryer, "Evaluation of Combustion Performance of Alternative Aviation Fuels", 46th AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit, Nashville, TN, July 25 – 28, 2010. Paper AIAA 2010-7155.

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