Formulation and Some Applications of Jet Fuel Surrogates

Shihong Yan, Eric G. Eddings, Ronald J. Pugmire, and Adel F. Sarofim

Center for the Simulation of Accidental Fires & Explosions (C-SAFE)

Department of Chemical & Fuels Engineering

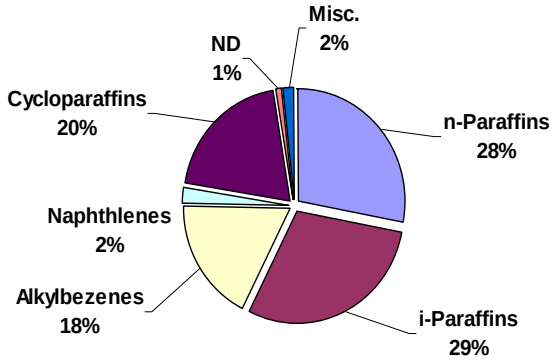
University of Utah

Outline

- Introduction
  - Jet Fuel Description
  - Reasons for Surrogates
- Formulation of Surrogates
  - Criteria
  - Approaches
  - Some Examples
  - Validation
- Case Study: Open Pool Fire
- Case Study: Droplet Combustion
- Summary

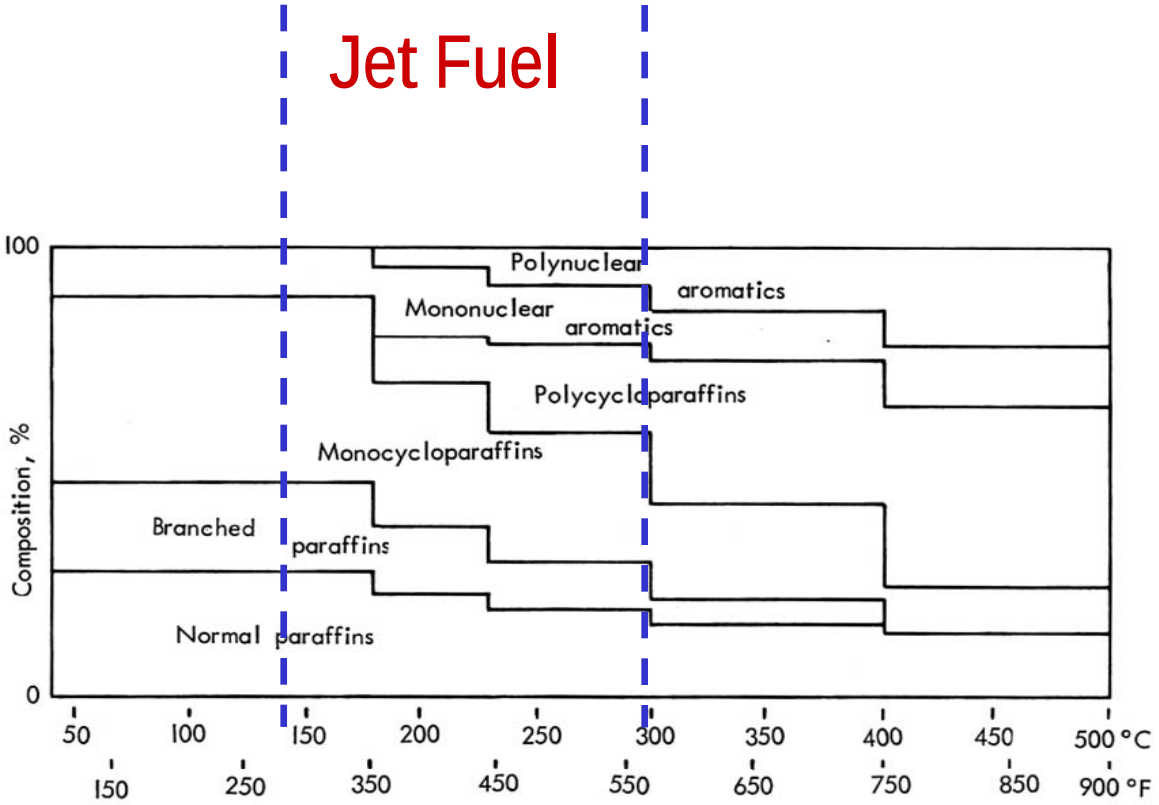
JP-8 Description

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



Top Three Compounds

- *n*-C_{11}, 4.43 wt.%
- *n*-C_{10}, 4.10 wt.%
- *n*-C_{13}, 3.85 wt.%



Reasons for Surrogate Development

- Chemical complexity in JP-8
  - More than 300 hydrocarbons exist
  - Few of these compounds are greater than 1% wt.
  - Detailed chemical kinetics are currently available for only a limited number of compounds
- Computational limitations
  - Tracking a large number of species in a CFD code is not yet feasible
  - the feed specification must be simplified to be tractable
- Experimental Uncertainties
  - Jet fuels manufactured to meet ASTM specification may have large compositional differences from each other, *e.g.*, aromatic content, density, cetane index, and etc.

Formulation Methodology

- Key to surrogate formulation
  - Clear definition of properties to be matched
    - Stability? Vapor Pressure? Surface Tension? Density? Boiling point? Auto-ignition Temp.? Soot? Unburned HCs ? NOx? …
  - Understanding of physical and chemical processes that relate surrogate composition to desired properties

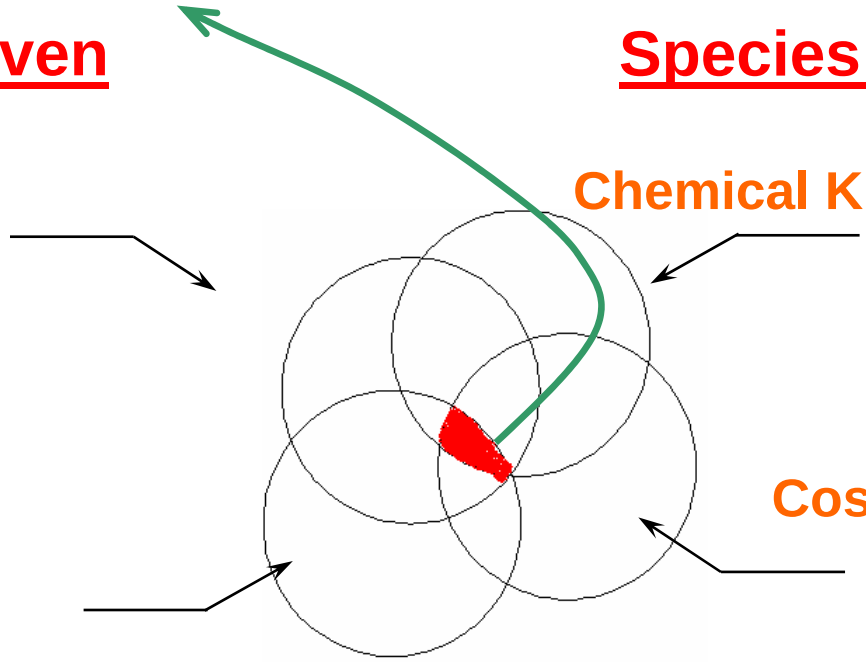
- Criteria for Surrogate Formulation

Application Driven

Species Driven

Relevant Physical Properties

Chemical Kinetics Availability



Flame Properties

Cost

Formulation Methodology

Empirical Approach: Past

- Select compounds from parent fuel composition profile, estimate mixture properties with available correlations.
- Has been used most widely.
- Trial and error based; the selection of compounds may not represent fuel well.

Structural Group Contribution Approach: Future

- Fuel structure determines its properties.
- Many properties could be estimated with structural group contribution theory.
- Currently, a lack of model integrating physical properties estimation and kinetics simulation.

Hybrid Semi-empirical approach: Current

- Combination/compromise of the above two approaches
- Set up a pool of candidates; filter the pool with constraints; study the effect of species change on mixture properties
- Has provided a preliminary working surrogate

C-SAFE
UNIVERSITY OF UTAH

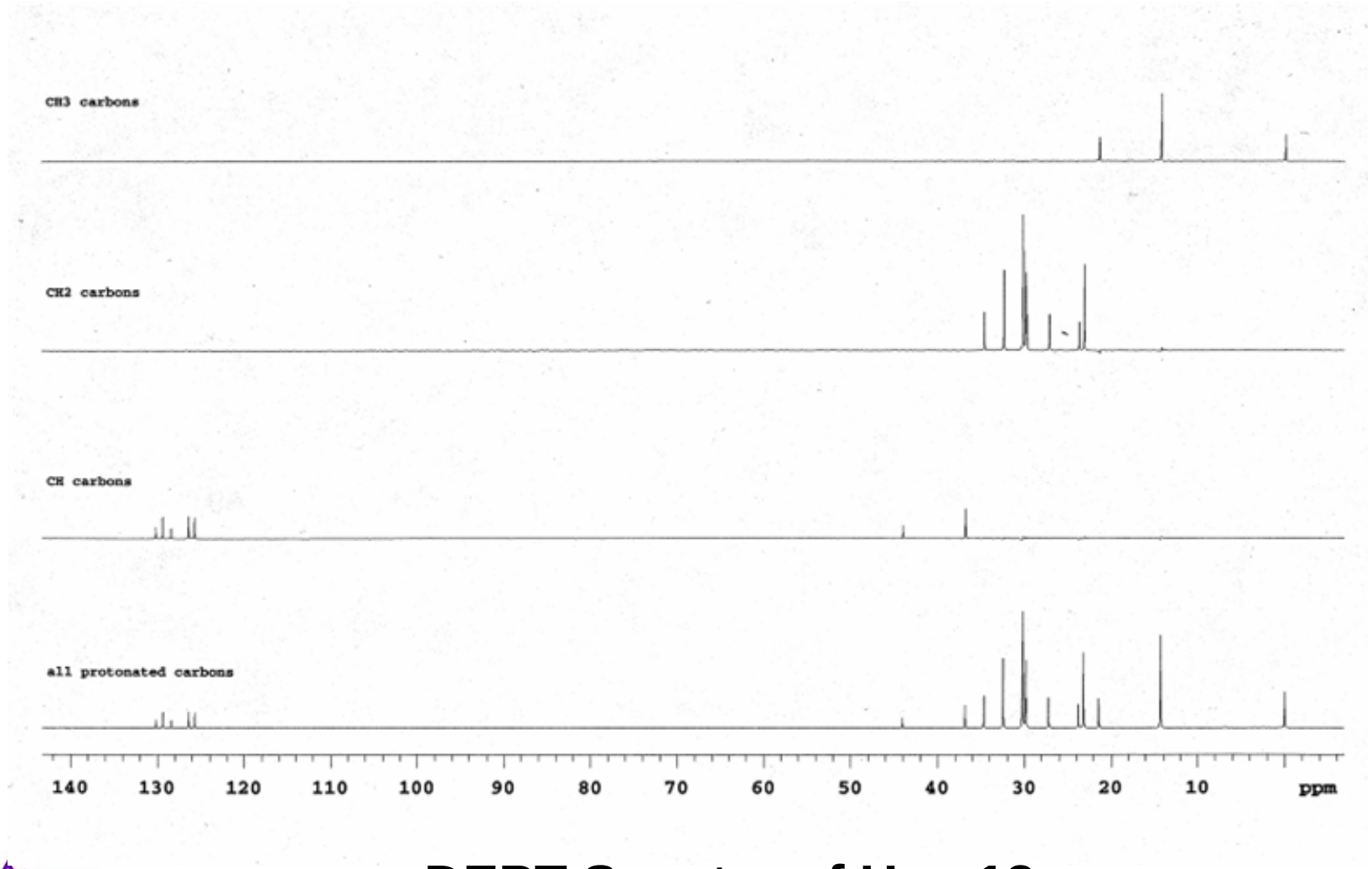
Selected Known Surrogates for Transportation Fuels --- Based on Empirical Approach

Author	Parent Fuel	Paraffins		Cyclo Paraffins	Aromatics	Objective
		Normal	*Iso-*			
Westbrook et al., '61-'99	*Gasoline Diesel*	*n-C_7 (+ additives)*	*i-C_8*[b]			*Unburned HCs, Stratified Charge, autoignition, soot*
Prabhu, '97	*Gasoline*[a]	*n-C_7*	*i-C_8*		*Toluene*	*Engine Ignition*
Hallet, '92	*Diesel*	*n-$C_{7\sim10,16,20}$*			*Toluene, Na., 1-me-Na.*[c]	*Auto Ignition*
Woods, '89	*JP-4*	*n-$C_{6\sim10,12,14}$*		*Cyclo-$C_{6,8}$ MCH, Decalin*	*Toluene, 1-me-Na.*	*Atomization, swirl stabilized lab. Combustor*
Schulz, '91	*JP-8*	*n-$C_{10,12,14,16}$*	*i-C_8*	*MCH*[d]*, Cyclo-C_8*	*M-Xylene,Na., Butylbenzene, durene*[e] *, Di-me-Na.*	*Oxidation, Deposition, Stability*
Maurice,'00	*JP-8*	*n-C_{10}*			*Benzene, Toluene, ETB*[f]*, Na.*	*Kinetics, NOx, CO,…*
Agosta,'02	*JP-8*	*n-C_{10}*	*HMN*[g]	*MCH, Decalin*	*1-me-Na.*	*Kinetics*

Note: a, 1-pentene is not listed for gasoline surrogate; b, i-C_8,2,2,4-trime-pentane, c; 1-me-Na., 1-methyl-naphthalene; d, MCH, me-cyclohexane,; e, durene, 1,2,4,5 tetramethylbenzene; f, ETB, ethylbenzene; g, HMN, 2,2,4,4,6,8,8-heptame-nonane.

C-SAFE UNIVERSITY OF UTAH

Example of Structural Group Analysis



DEPT Spectra of Hex-12

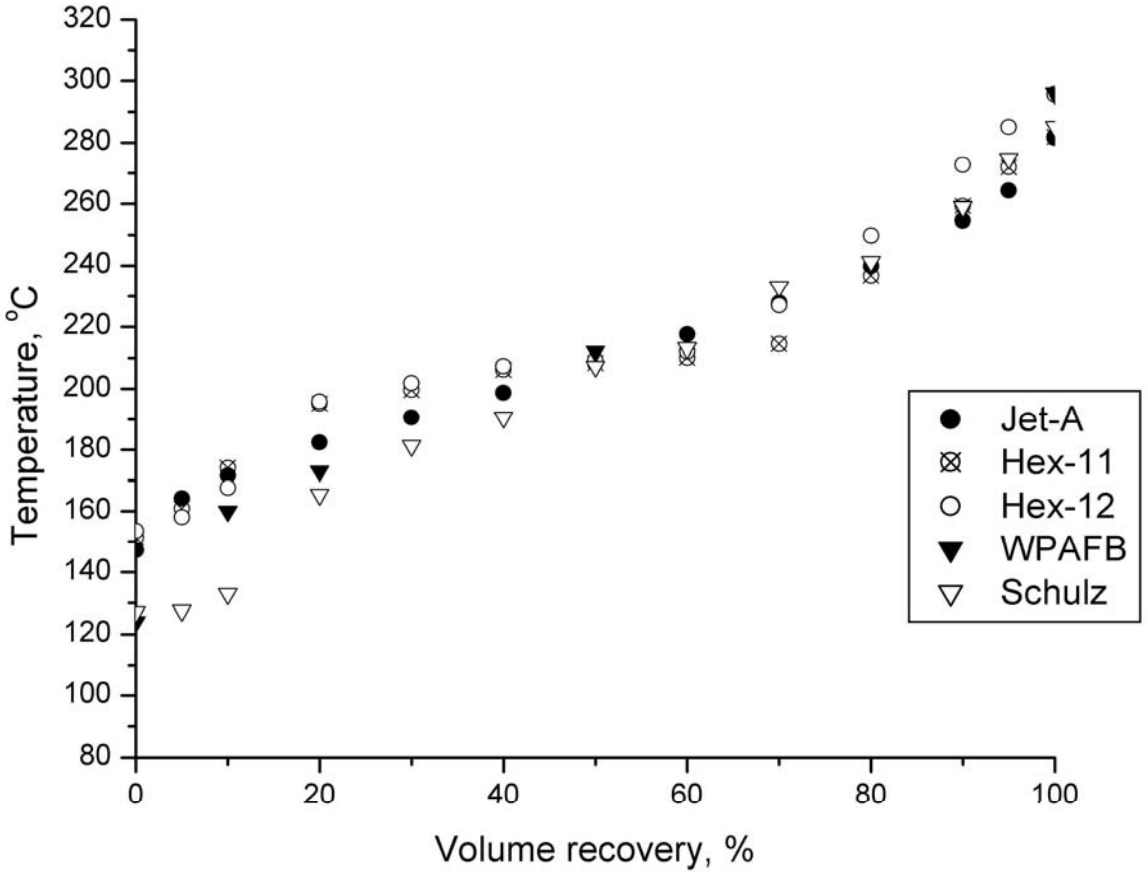
Suggested JP-8 Surrogates

# of Species	Components	Objective
1	*n-C_{12}*	*Thermal conductivity, heat capacity, density etc.*
1*	*decalin*	*Smoke Point, PAH and soot formation*
2	*n-C_{12} , PMB*	*Smoke point, average volatility, flame properties*
3	*n-$C_{12,}$, decalin, PMB*	*Same*
6	*n-$C_{8,12,16}$, xylene, tetralin, decalin*	*Volatility, soot formation, pool fire, kinetics*
7	*i-C_8, n-$C_{10,12,15}$, Decalin, PMB, Na.,*	*same*

Hex-12, based on hybrid approach

C-SAFE UNIVERSITY OF UTAH

Boiling Range for Jet A and Selected Surrogates



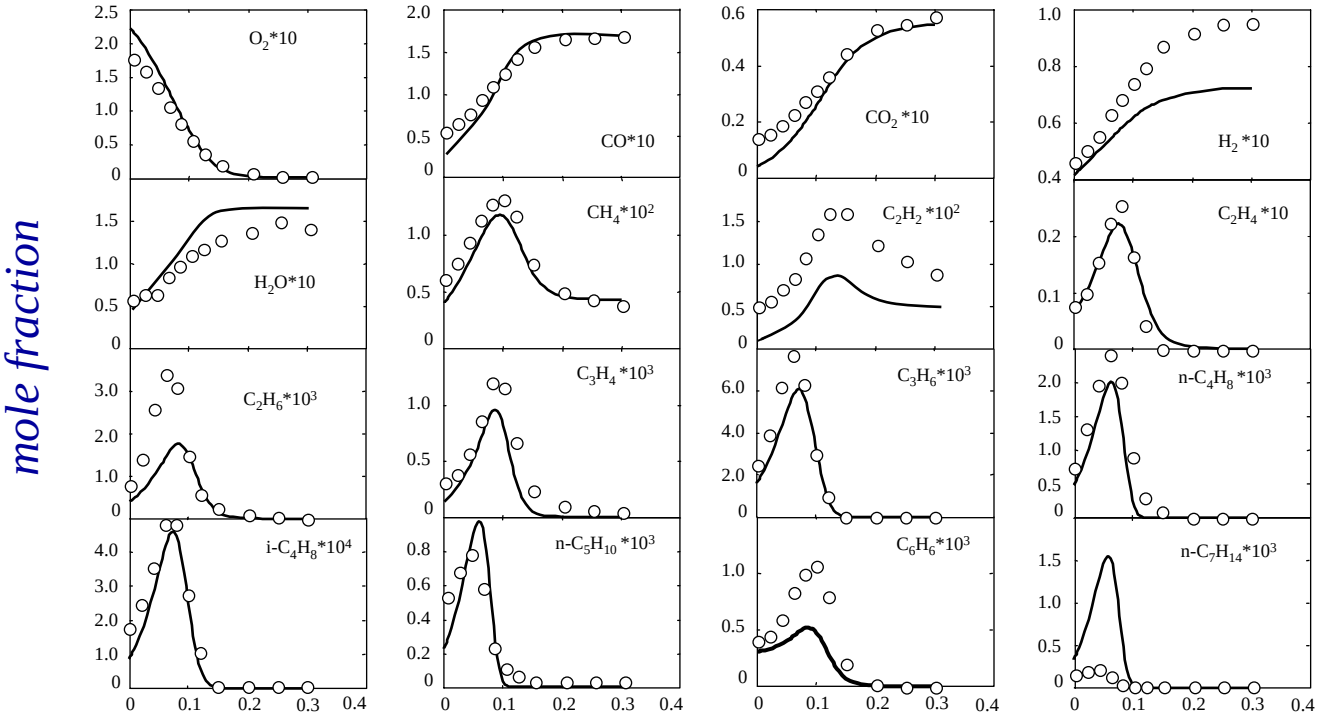
"Hex-12" Composition

n-Octane, 3.0%
Xylene, 15.0%
Decalin, 27%
Tetralin, 13%
Dodecane, 30%
Cetane, 12%

** Distillation created in accordance with ASTM D86.*

Validation of Gas-Phase Kinetics for Surrogate Mixture

Kerosene surrogate Composition: 73.5 mol% n-dodecane,
5.5 mol% i-octane,
10 mol% MCH
11 mol% aromatic



Case Study: Jet Fuel Pool Fires

Surrogate formulated to match

- Physical properties
  - Flash point
  - Boiling point distribution
- Chemical properties
  - Hydrocarbon classes distribution
  - Sooting index

• Validation

- Pool burning rate, transient and steady state
- Radiative heat flux

• Application

- Coupled gas phase chemistry to HACA & CFD in simulation of pool fire

C-SAFE
UNIVERSITY OF UTAH

Experimental Setup

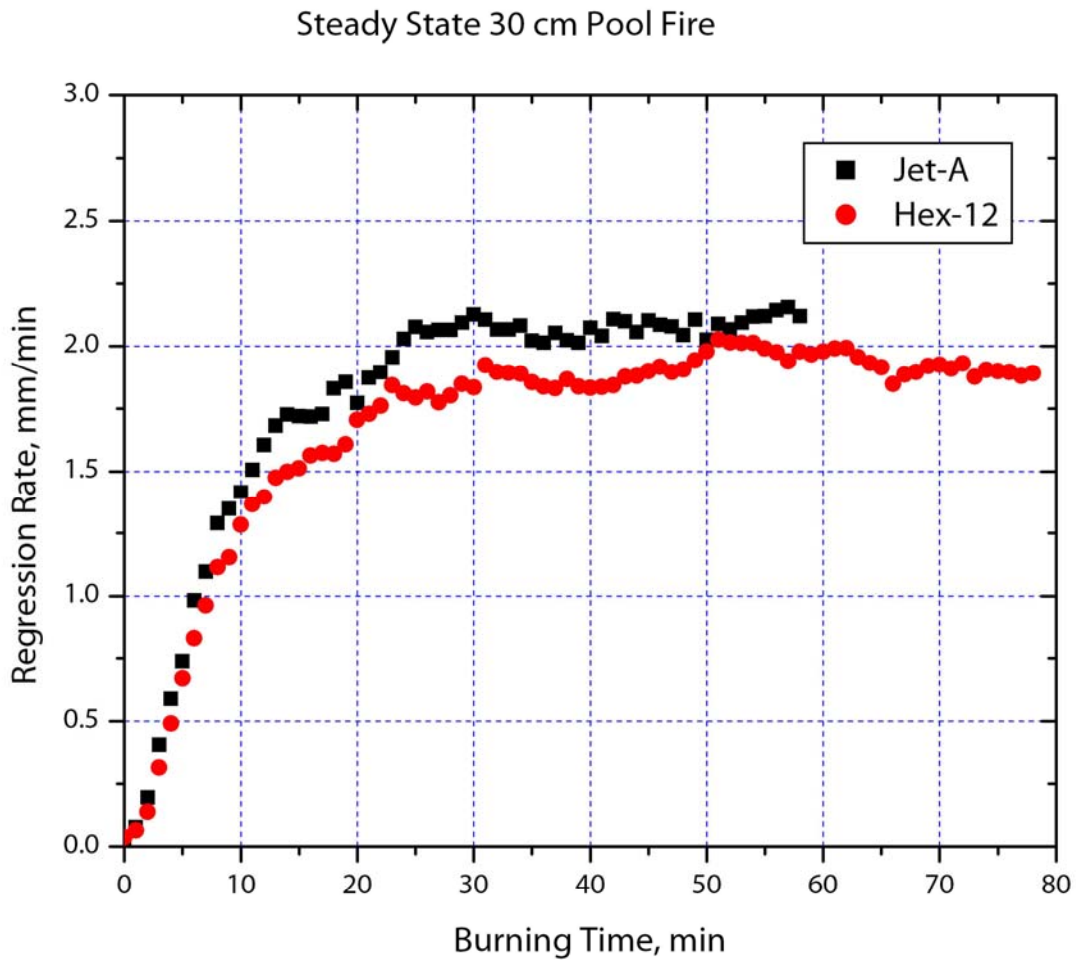
C-SAFE Pool Fire Facility

- **0.30 m diameter pool (up to 1 m)**
- **Fully closed 4.5 x 4.5 m chamber with floor-mounted dampers for flow control.**
- **Steady-state and transient pool fires**
- **Flame shape and height using still and high-speed digital photography**

- Compositional Analysis
  - **GC/GC-MS**
  - **^{1}H and ^{13}C NMR**
- Fuel Property Measurements
  - **Volatility/Boiling Curve**
  - **Smoke point**
- Fire Measurements
  - **Burning rate**
  - **Total and radiant heat flux**
  - **Temperature profile**
  - **Real-time and high-speed video**

Experimental Results – Steady State

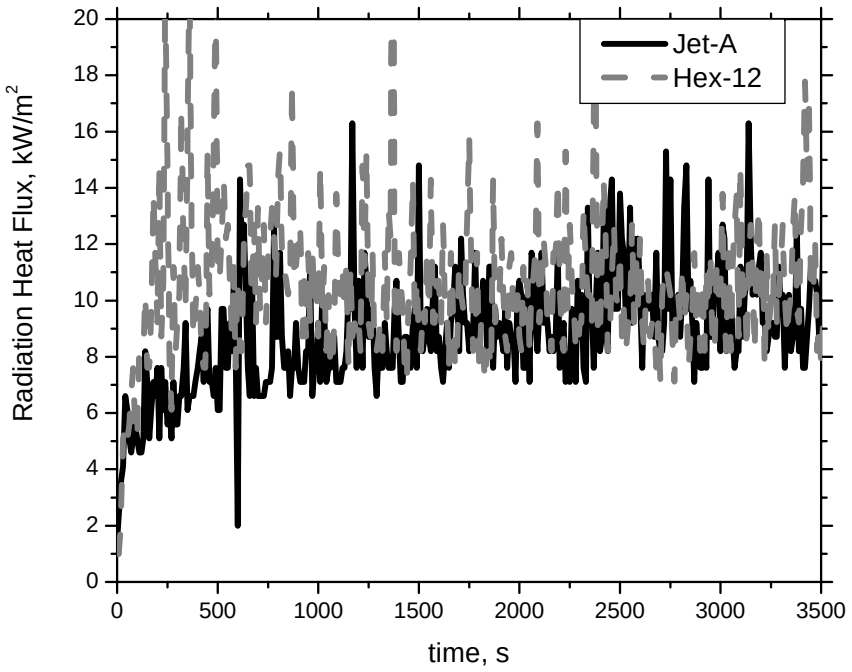
Comparison of Burning Rates

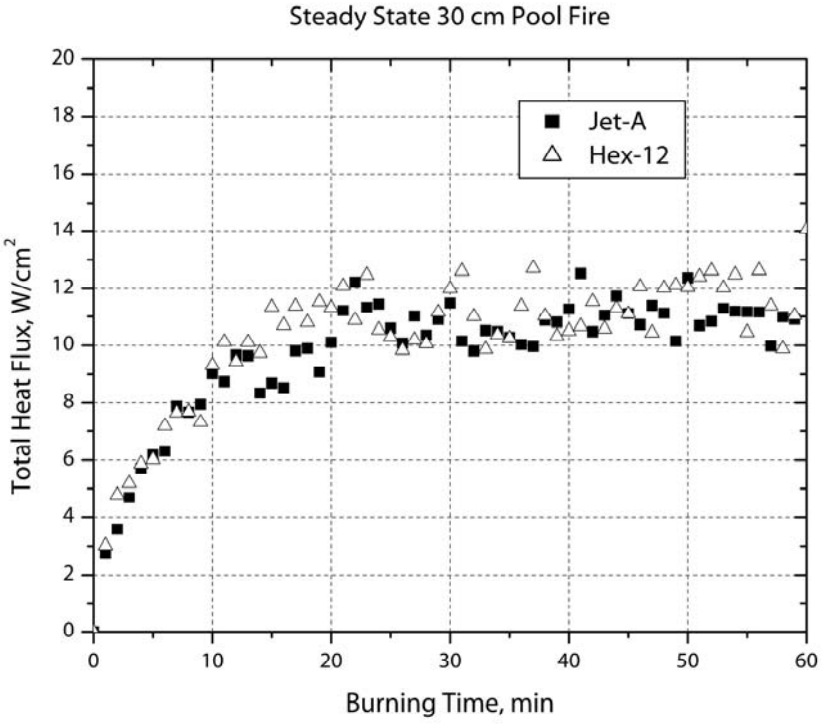


Note: Literature values and correlations for jet fuel/kerosene range from 1.9 – 2.1 mm/min

Experimental Results – Steady State

Comparison of Heat Flux Measurements



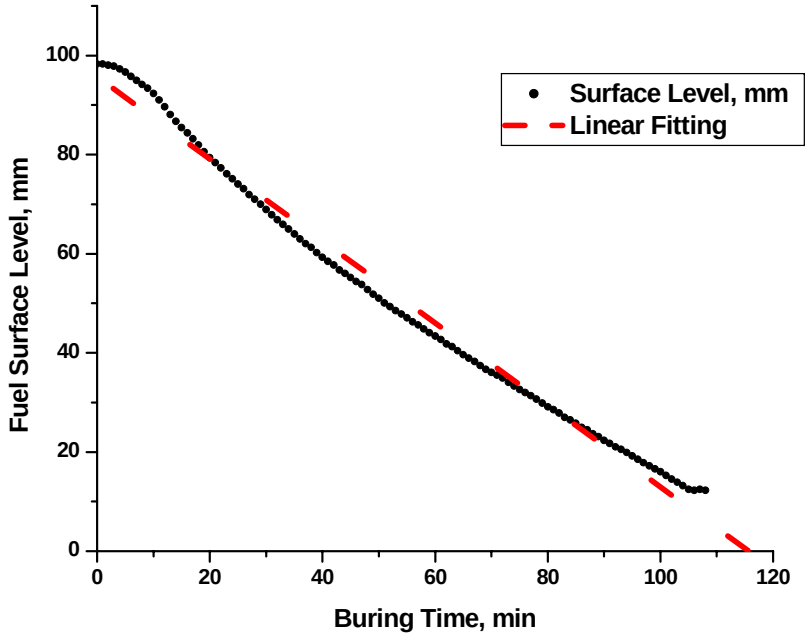


Real-Time Measurements

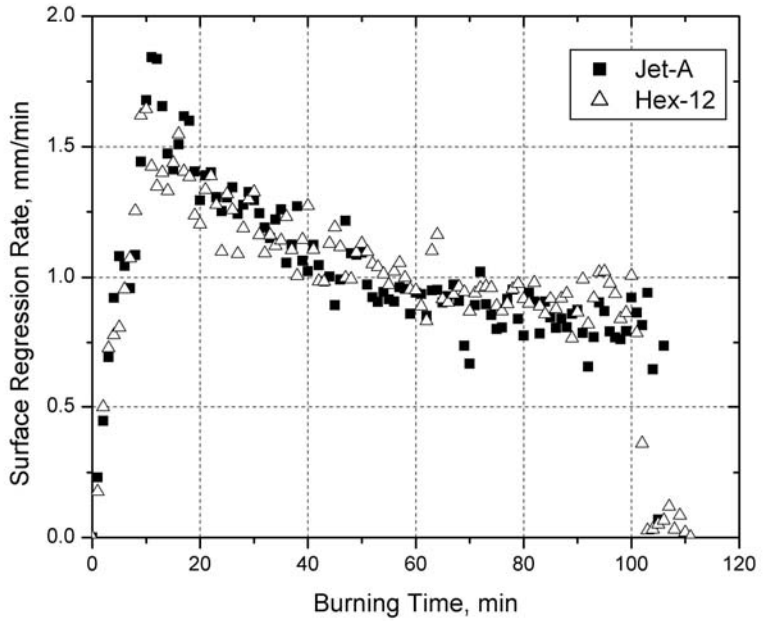
Minute-Averaged Measurements

Experimental Results – Transient

Surrogate matches burning rate in transient pool fire



Level vs. time – slope yields average rate



Derivative of level vs. time - yields instantaneous rate

C-SAFE
UNIVERSITY OF UTAH

Case Study: Droptube Combustion

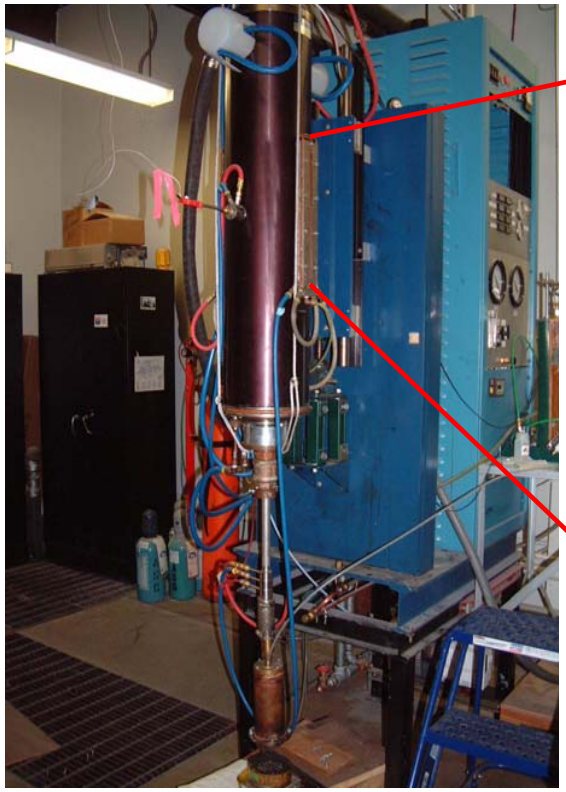
Surrogate formulated to match

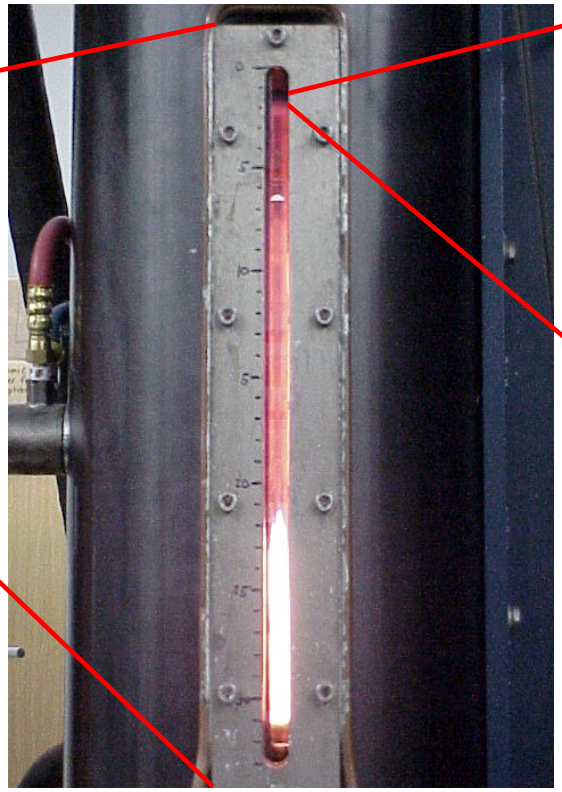
- Physical properties
  - Ignition Point
  - Similar list as before
- Chemical properties
  - Gross soot yield, sooting index
  - Tar (Soluble Organic Fraction) speciation

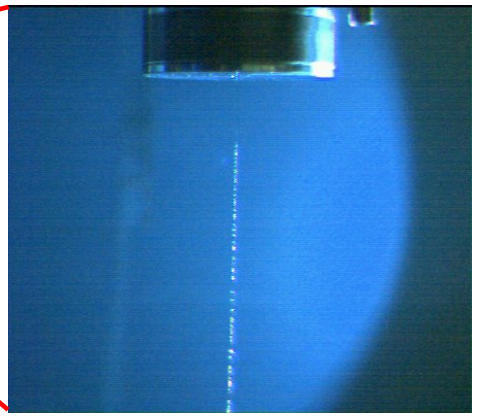
- **Validation**
  - Soot mass
  - Tar characterization
- **Application**
  - Soot/tar formation & evolution
  - Evaluate soot suppressing additives in turbines.

C-SAFE
UNIVERSITY OF UTAH

Experimental Set-up







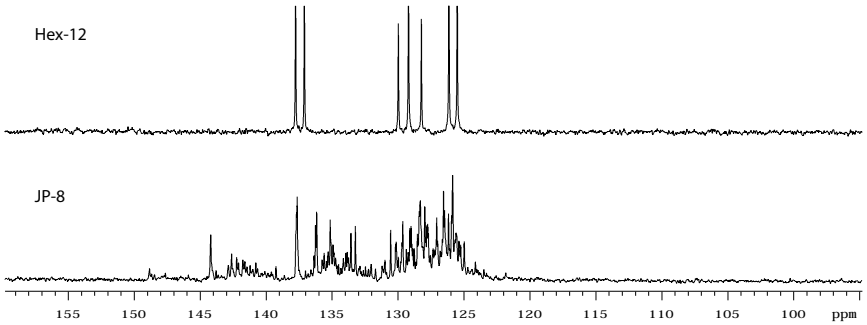
A monodisperse droplet stream is injected into a hot, co-flow air stream, producing a laminar diffusion flame.

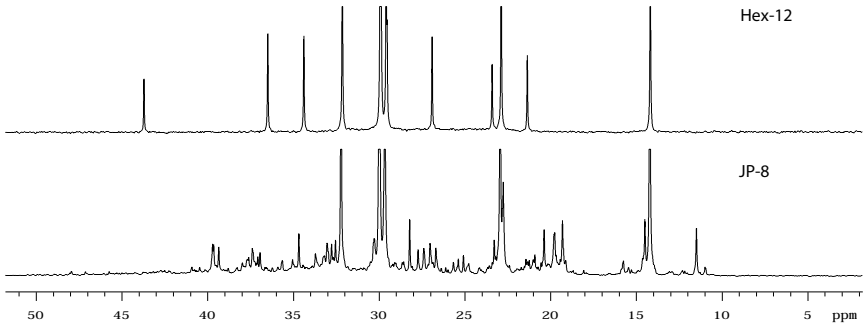
At the reactor exit, the flame is quenched and the soot is collected for further analysis.

C-SAFE
UNIVERSITY OF UTAH

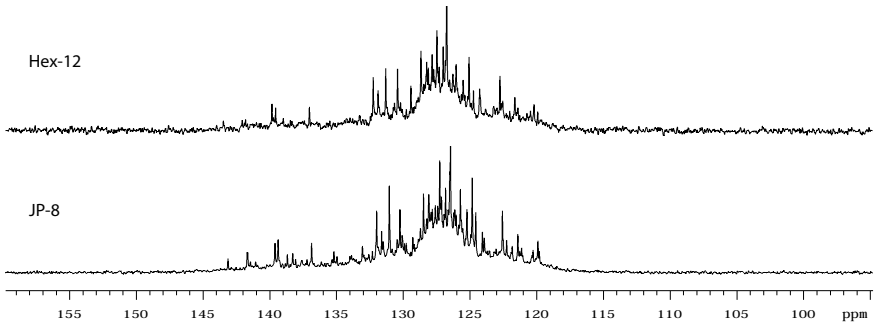
NMR Spectrum of Soot Extracts from JP8 & Surrogate

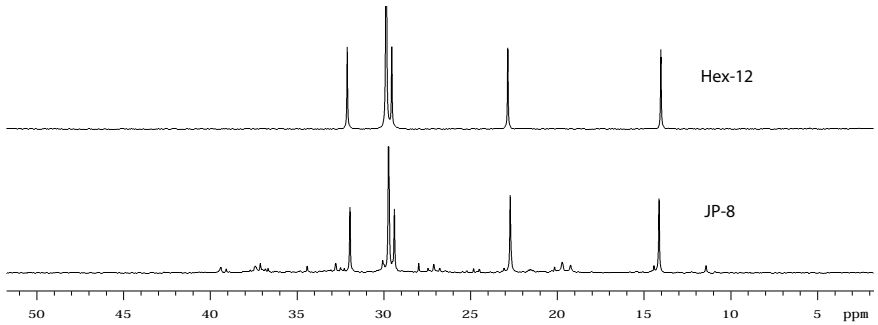
Un-combusted Oil



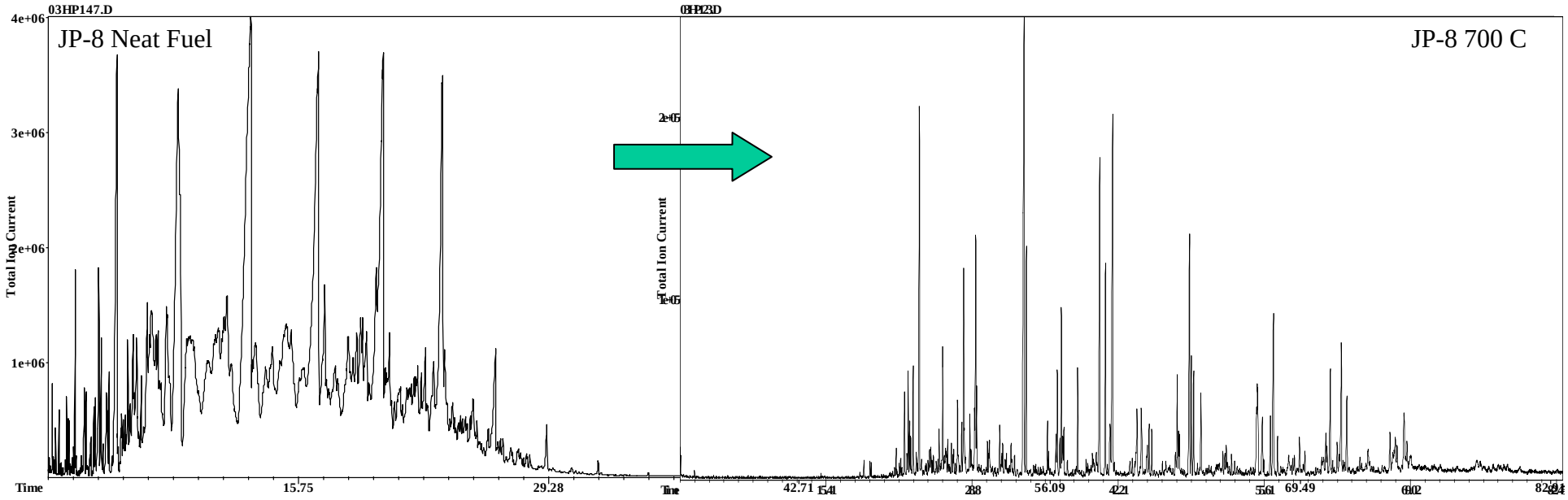


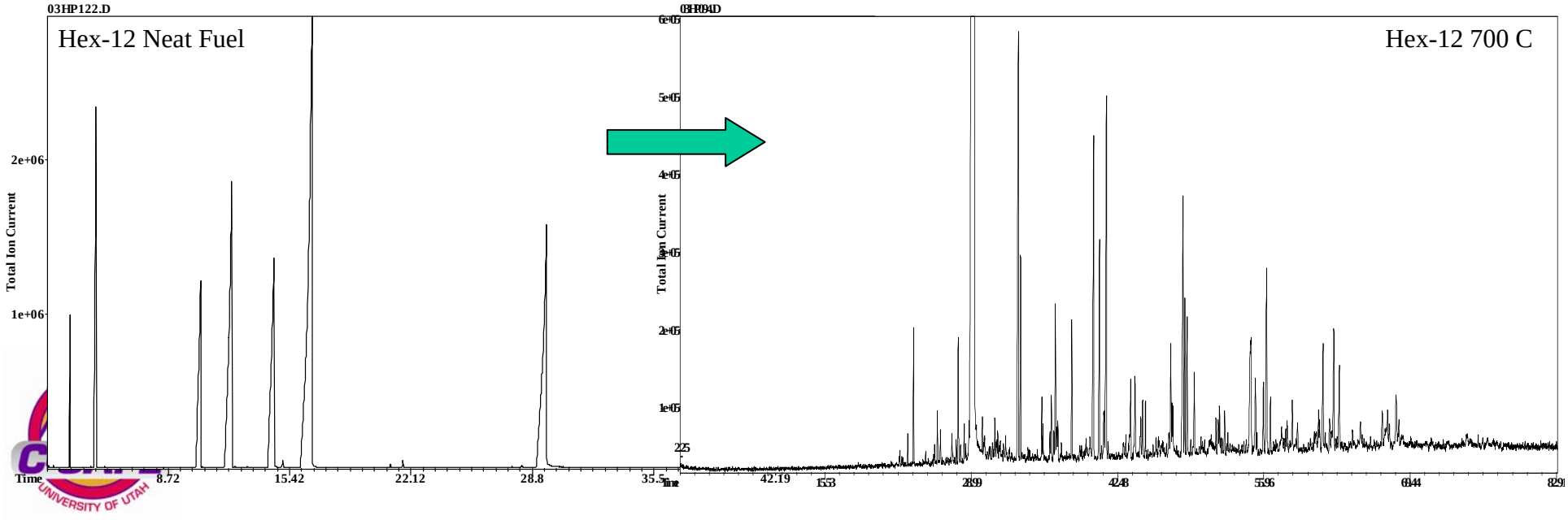
Collected Soot Extracts





Comparison of GC Spectrum of Soot Extracts From Surrogate and JP8





Properties of Soot Aerosols Collected in Droplet Combustion

Fuel	Ignition Point	Gross Soot Yield,	Tar yield,	Tar Aromatic carbon ratio	Graphite Factor
	cm	Wt.%	wt. %	mol.%	%
JP-8	10.5	8.2	30.0	73.9	44.10
Hex-12	11.5	8.9	19.5	55.4	34.10
Decalin	9.0	8.9	13.2	95.5	72.37
i-C8/Tol.	5.5	8.8	8.3	78.3	53.55
n-C12	13.0	4.5	42.0	98.0	72.51

C-SAFE
UNIVERSITY OF UTAH

Conclusion

- A series of JP-8 surrogates have been formulated under semi-empirical approach.
  - Results show that the surrogates can match properties such as boiling range, flash point, smoke point etc.
- Preliminary kinetics modeling on surrogate is encouraging.
- JP-8 surrogate and parent fuel were tested under pool fire tests.
  - Results show that surrogate capture most global flame characteristics, such as flame height, puffing frequency, etc.
  - Surrogate also showed to match burning rate and time average heat flux of parent fuel under both steady state and transient tests.
- Under droplet combustion, surrogate showed similar ignition point and gross soot yield.
  - Analysis of collected soot samples suggest a convergence of intermediate products from surrogate and parent fuel.

C-SAFE
UNIVERSITY OF UTAH

Future Work

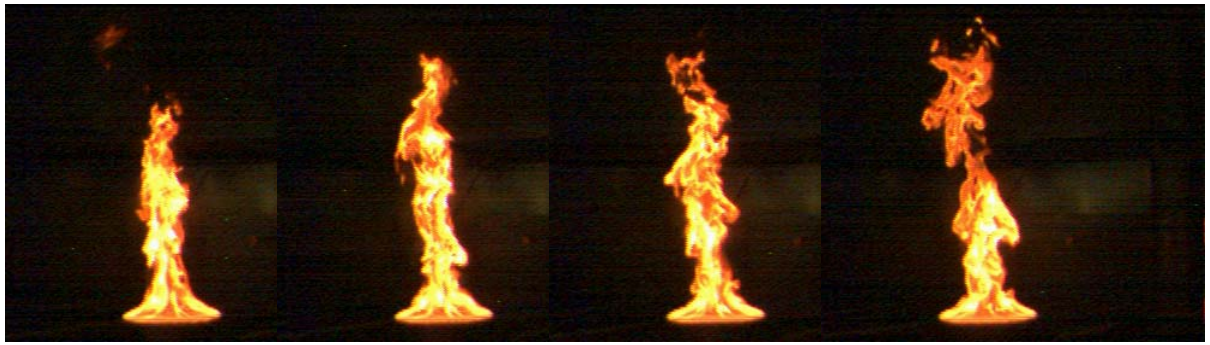
- **Future efforts on surrogate formulation will focus on formalizing the structural group contribution method.**
- **Current surrogates neglect the effect of branching and side chain substitution.**
  - **Suitable candidates to represent branched paraffin are needed.**
- **New correlations between physical properties of interest and models to incorporate kinetics are required.**

Acknowlegements

- support of C-SAFE through the ASCI program under DOE
- guidance from Prof. Eddings, Prof. Pugmire and Prof. Sarofim
- help from Mr. Overacker, Dr. Marsh, Dr. Violi, Mr. Ciro, Mr. Preciado and the combustion research group
- help from Dr. Jiang, Dr. Solum, Dr. Ma from the NMR research group

The jet fuel and surrogate pool fires were found to have similar height: 1.0m for Jet-A and 1.1m for Hex-12.

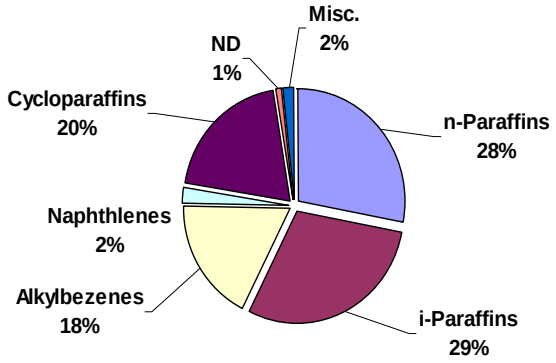
Both fire has a puffing frequency ~ 3Hz.



C-SAFE
UNIVERSITY OF UTAH

JP-8 Composition

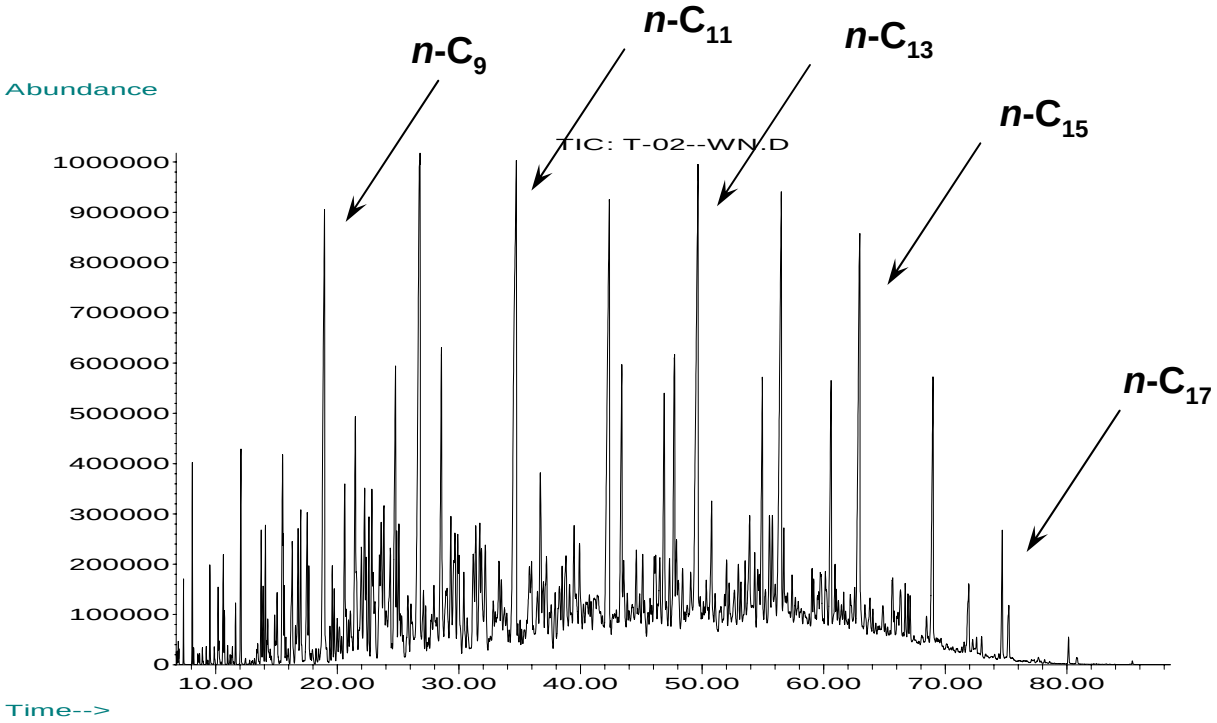
Hydrocarbon Class Distribution in Jet-A (wt.%)



Top Three Compounds

- *n*-C_{11}, 4.43 wt.%
- *n*-C_{10}, 4.10 wt.%
- *n*-C_{13}, 3.85 wt.%

GC Chromatography of JP-8



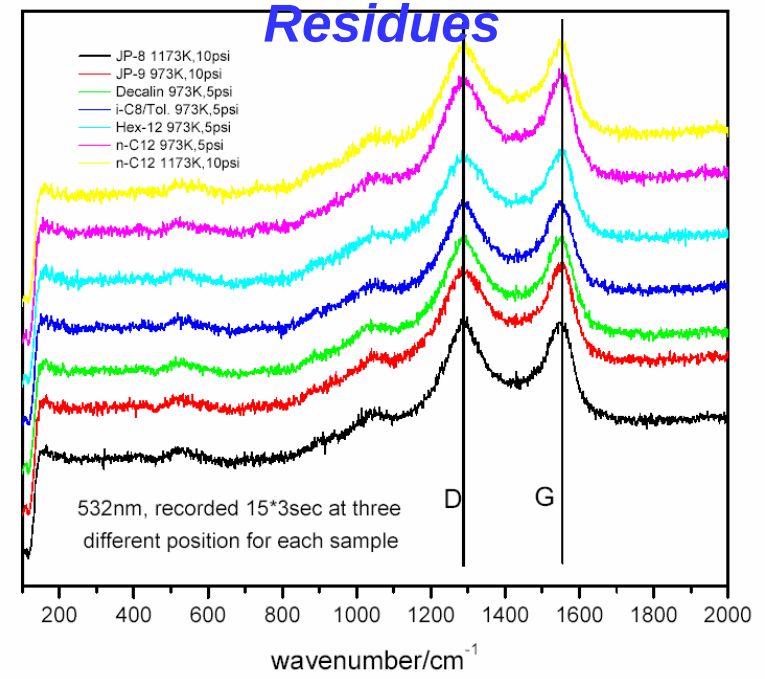
Properties of Jet Fuels

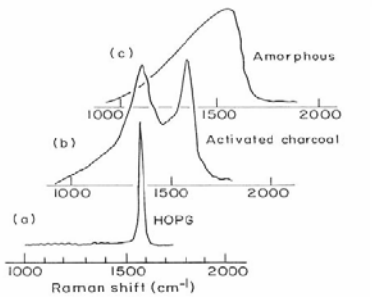
Name	JP-4	JP-5	JP-7	JP-8
Avg. Formula	C_9H_{20}	$C_{12}H_{22}$	$C_{12}H_{25}$	$C_{12}H_{24}$
Density, Kg/L	0.76	0.81	0.79	0.81
Flash Point, °C	-20	60	60	38
Freezing Point, °C	-60	-50	-38	-47
Net Comb. Heat, MJ/Kg	42.9	42.7	43.9	42.8
Boiling Range, °C	60-230	180-260	180-250	140-260

C-SAFE
UNIVERSITY OF UTAH

Soot Residue Analysis Results

Raman Spectra of Soot Residues



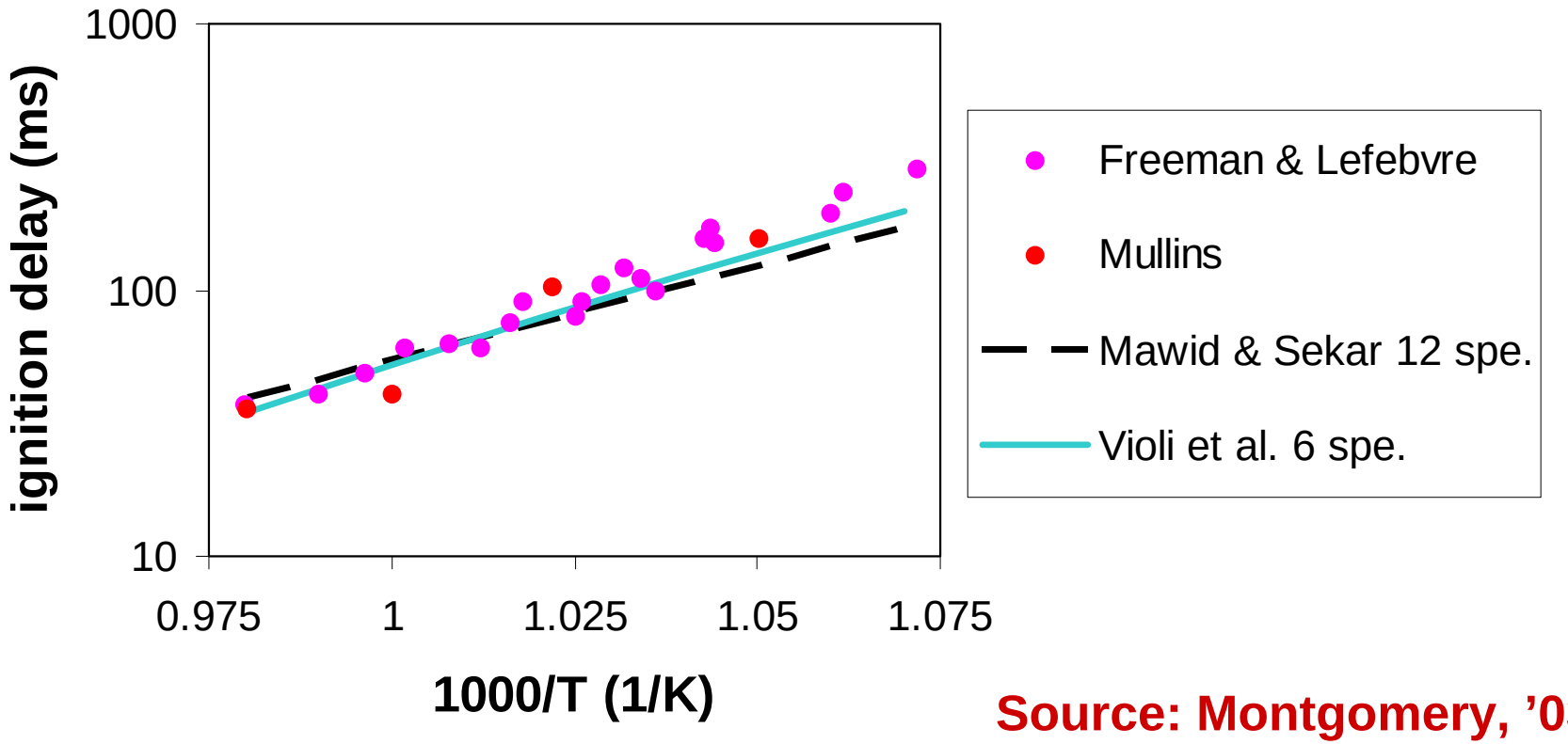


The Raman spectra of soot residues are in agreement with results from Solid State NMR, ESR and Graphite Factor tests:

1. All spectra of soot residues feature both “D-band” and “G-band” as in graphite and other graphene materials.
2. The amount of disorder-induced D-band (ω_D = 1200 ~ 1400 cm^{-1}) is ~ the same as the G-band (ω_G = 1580 cm^{-1}) derived from in plane displacement in graphite.
3. The spectra indicate that these residues are highly disordered pre-graphitic materials.
4. Under current test conditions, no significant structure differences are noted.

Ignition Delay Predictions for Jet Fuels

Equivalence ratio = 0.5, P = 1.0 atm.

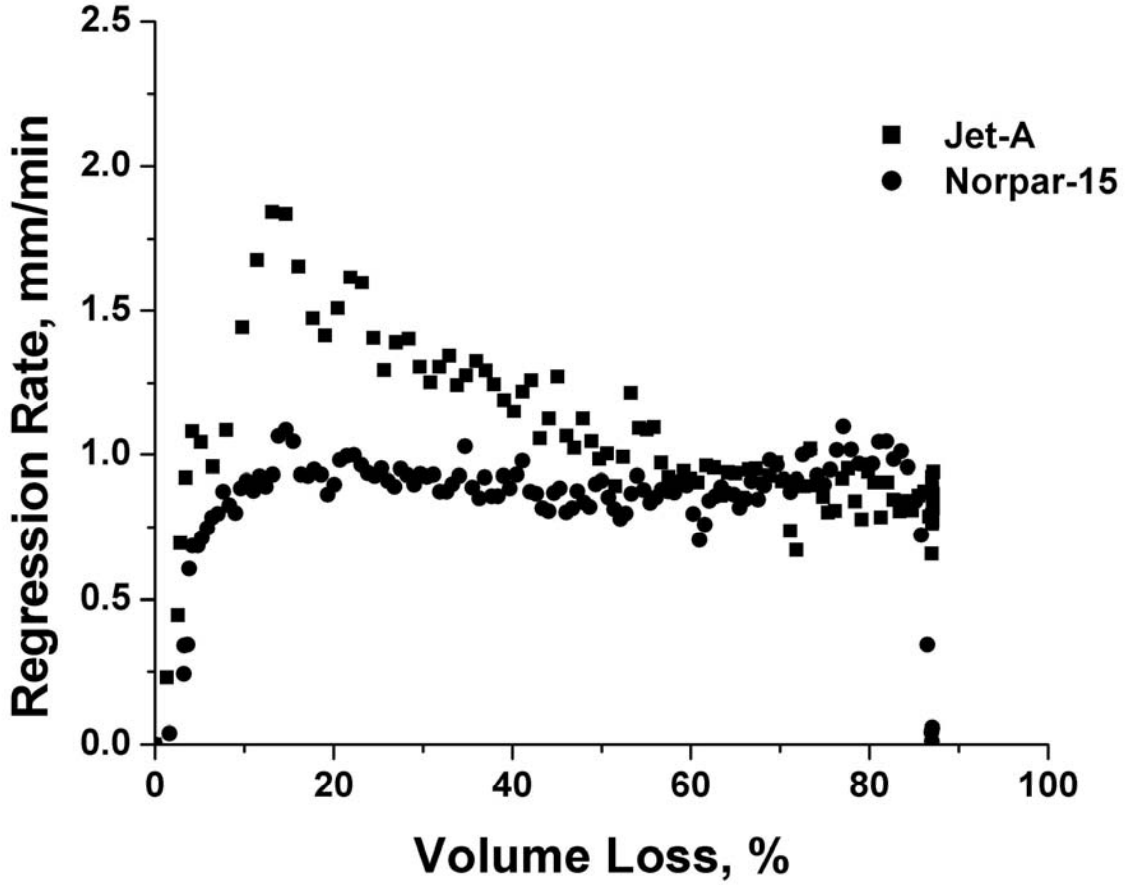


Source: Montgomery, '03

Note: The Violi et al. mechanism has not been tuned to match this data.

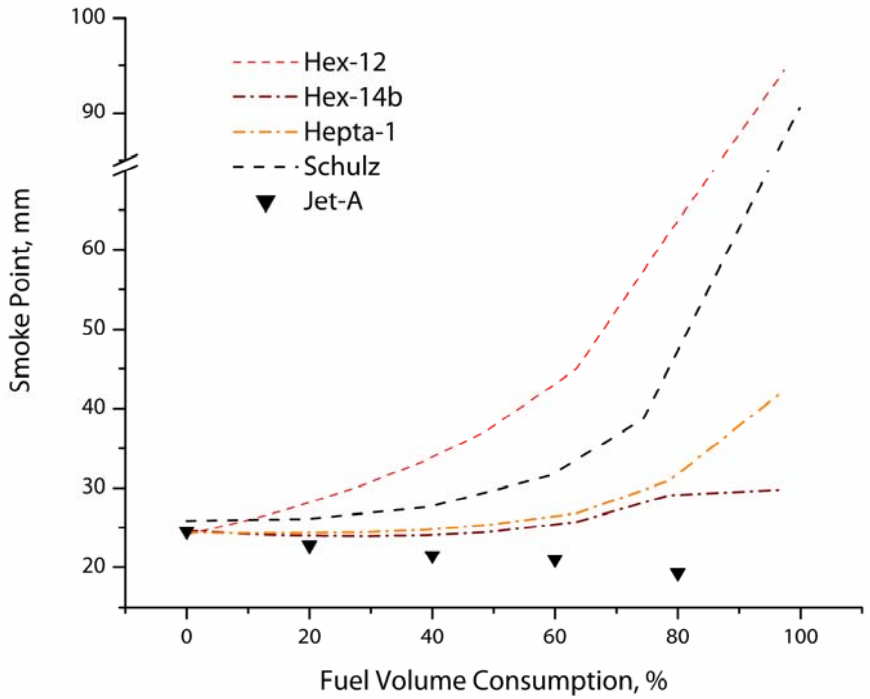
Experimental Results – Transient

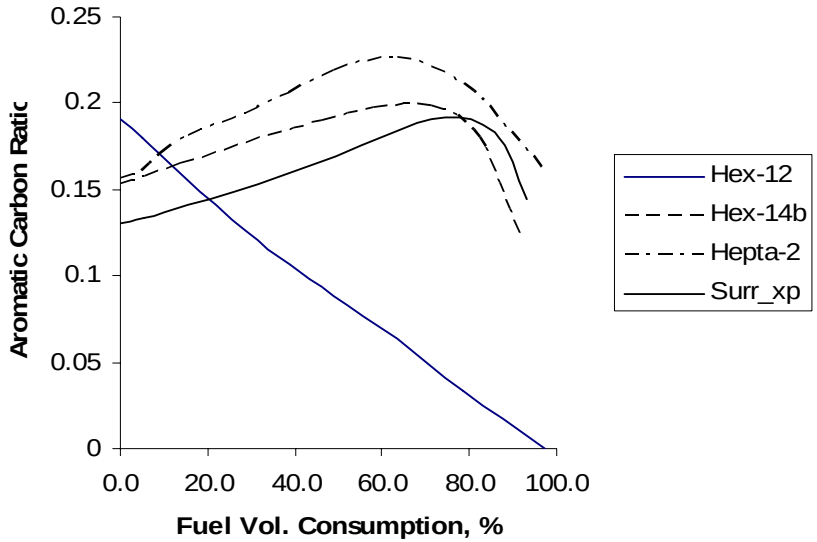
Heat Transfer versus Compositional Effects



Tailored Surrogates for Transient Tests

Smoke Point (SP) Variation in Batch Distillation Tests



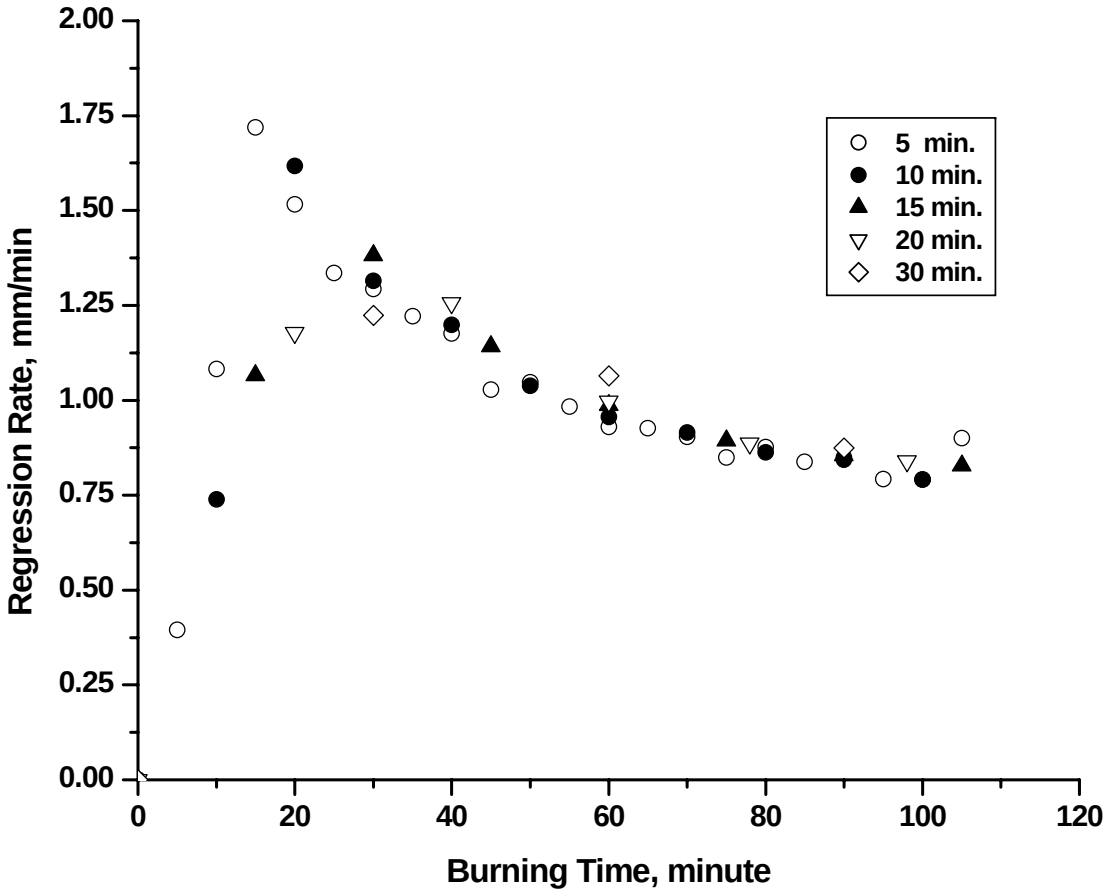


New surrogates are designed to address the composition change during a typical batch pool fire test.

- **The rapid decrease of aromatic carbon ratio with fuel consumption in Hex-12 explain the dramatic increase of smoke point during the batch test**
- **SP of Hex-14b could be contained in the range of 23.5 ~ 30 mm during most of the process.**

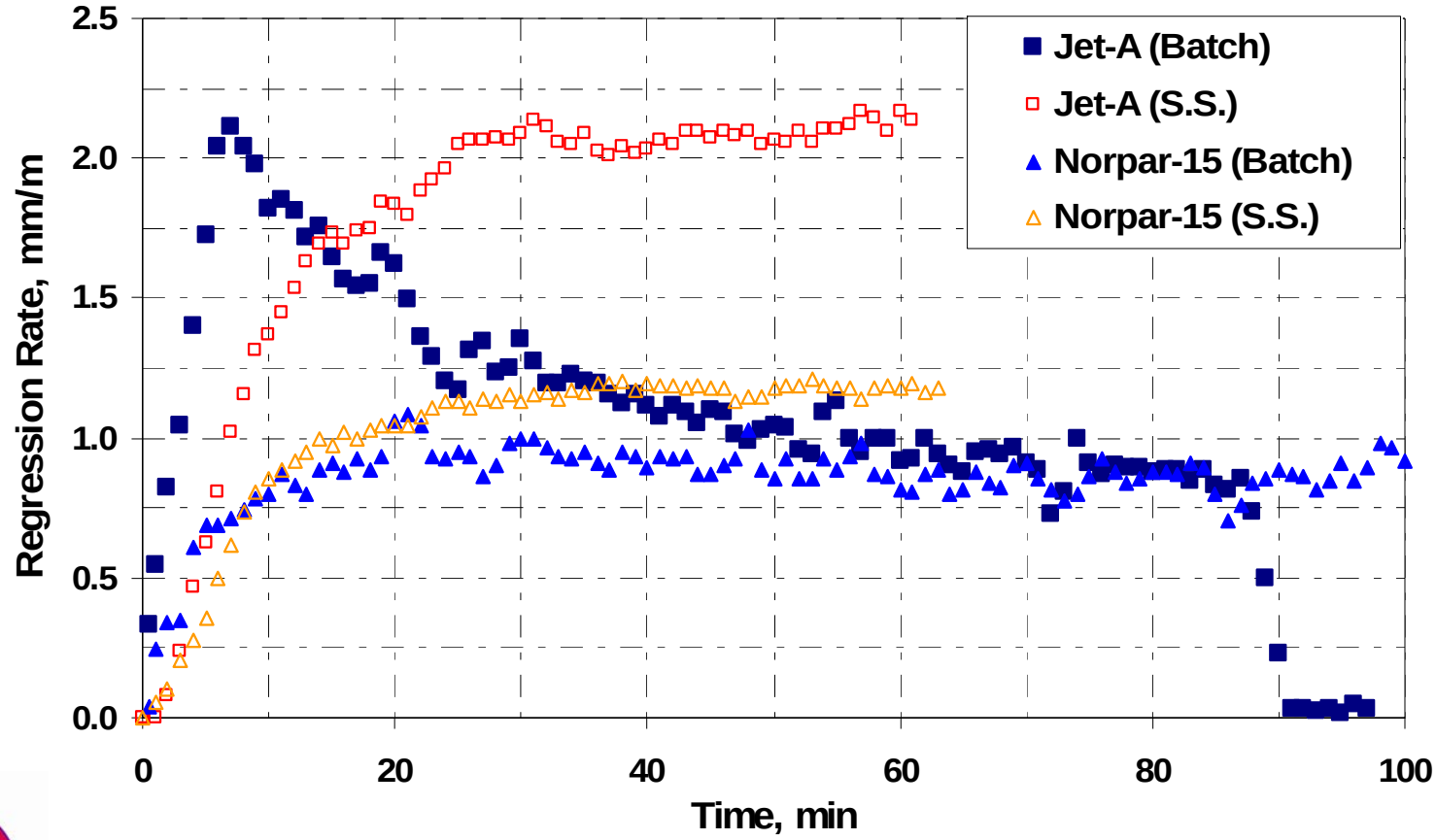
Experimental Results – Transient

Effect of Data Sampling Rate



Experimental Results – Transient

Narrow versus Wide Boiling Range Mixtures for Transient and Steady State Pool Fires



C-SAFE
UNIVERSITY OF UTAH

Multiple Solutions for the Surrogates

Properties	Jet-A	Hex-12	Hex-12a	Hex-12b
Smoke Point, mm	24.5	25.1	25.8	26.4
MW, g/mol	167.0 [a]	152.2	154.3	153.9
Density, g/mL	0.805	0.818	0.814	0.814
VABP [b], °C	210.7	215.7	214.6	213.7
Flash Point, °C	37.8	41.3	40.7	40.6
Latent Heat [c], kJ/kg	254.6	281.8	277.4	279.5
Combustion Heat, MJ/kg	44.9	44.6	44.6	44.6

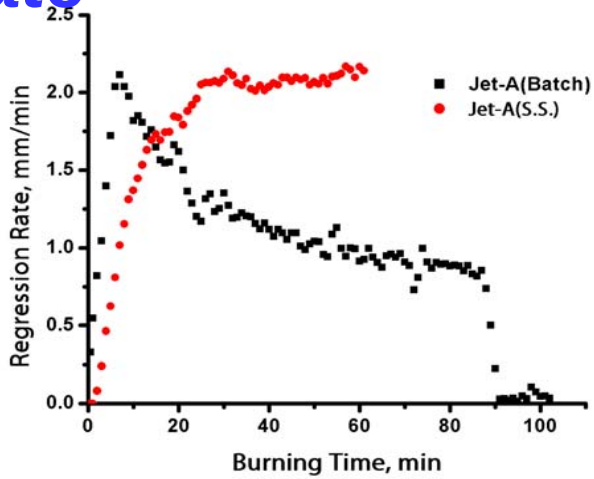
Fuel Properties

Compound	Hex-12	Hex-12a	Hex-12b
n-Octane	3	3	3
m-xylene	15	15	15
Tetralin	13		
Decalin	27	27	31
PMB		13	
2-Me-Na			7
n-dodecane	30	30	32
n-cetane	12	12	12

Surrogate Compositions (mol%)

Fuel Burning Rate Study

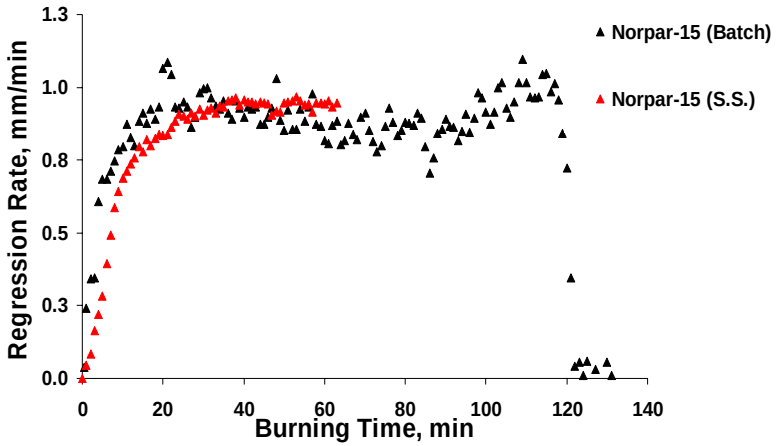
JET-A: Batch vs. Steady-State



- The steady-state burning rate of Jet-A, 2.07mm/min is close to the prediction value, the literature value and the peak burning rate in transient tests
- Both steady-state & transient tests with Norpar-15 show relative constant rate of burning

Batch Pool Fires

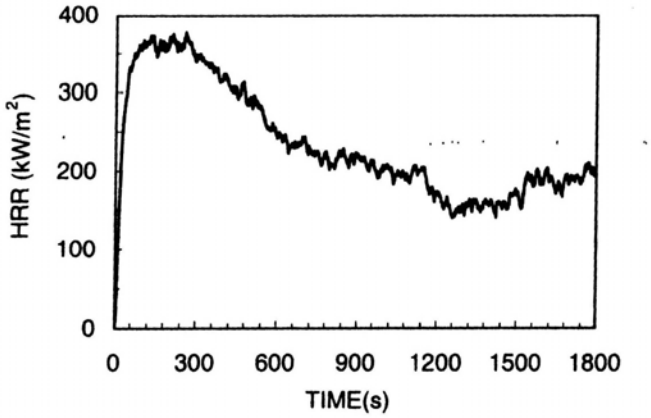
- With JET-A, burning rate changes rapidly in batch tests, peak rate is twice as high as average rate
- With Norpar-15, burning rate is constant as expected

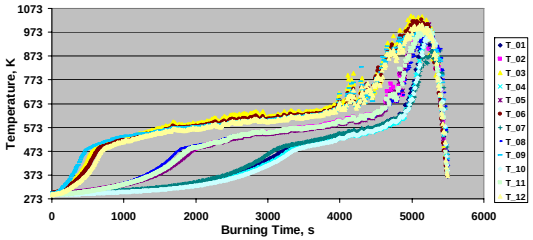


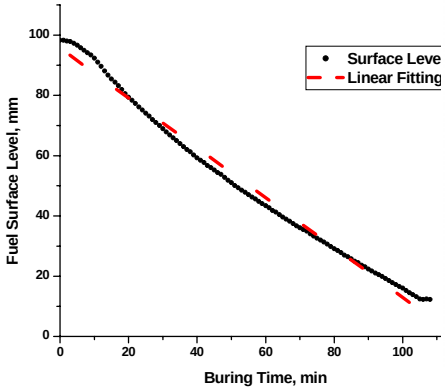
Fuel Burning Rate Study

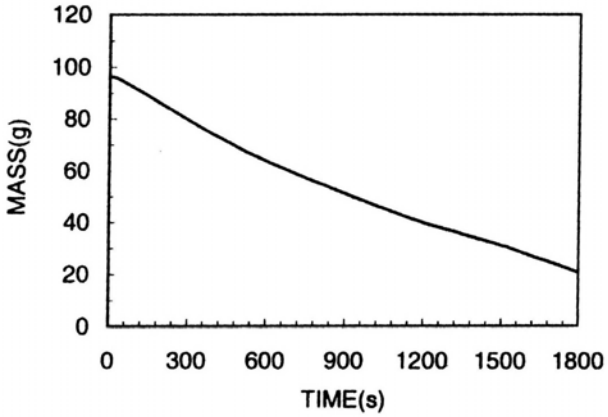
Postulation of burning rate variation in transient JET-A pool fire

- Thermal equilibrium and possible composition change in the induction period are often used to explain the higher burning rate in this period and constant rate in the rest
- Norpar-15 tests don't support thermal equilibrium idea
- 'Quasi steady-state' may not exist in transient pool fire
- Measurement resolution is important



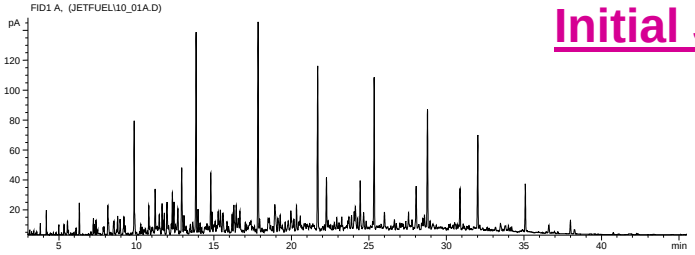




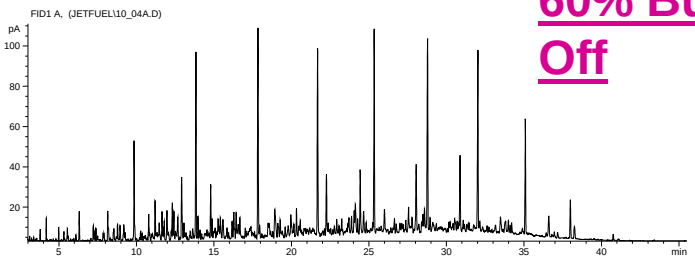


Iwata et al, *Fire & Materials*, 2001

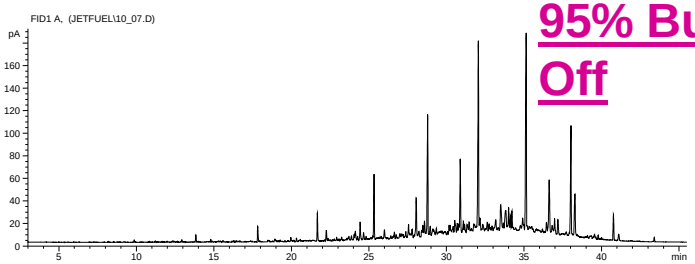
Change of Fuel Composition in Transient Pool Fire



Initial JET-A



60% Burn Off



95% Burn Off

GC/MS Analyses of Liquid Fuel in a Batch Experiment

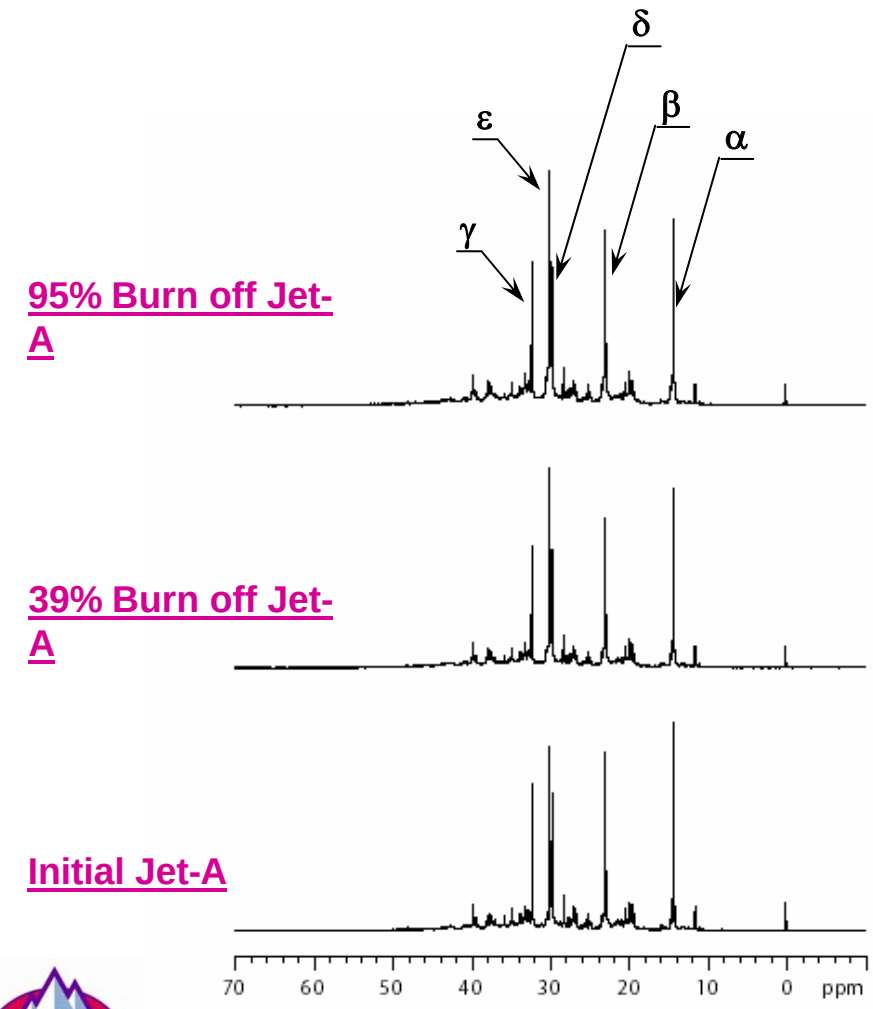
- **Light components are preferentially destroyed**
  - **compounds with boiling points below *n*-C12 are depleted as the burn progresses**
  - **naphthalenes might be enriched though light aromatics are destroyed**

Sample	Toluene /Na.[i]	Na./*Me*-Na.[iii]	n-C_{12}/n-C_{17}
Jet-A_B-0	1.5	0.4	7.7
Jet-A_B_95	0.0[ii]	0.2	1.0

Note: i- Na. is Naphthalene; ii- Toluene peak is non-detectable in this sample; iii- *Me*-Na. is mixture of 1-*Me*-naphtahlene, 2-*Me*-naphthalene and isomers of dimethyl naphthalene

C-SAFE UNIVERSITY OF UTAH

Change in Paraffins ?



^{13}C NMR Spectrum of Liquid Fuel in Batch Experiment

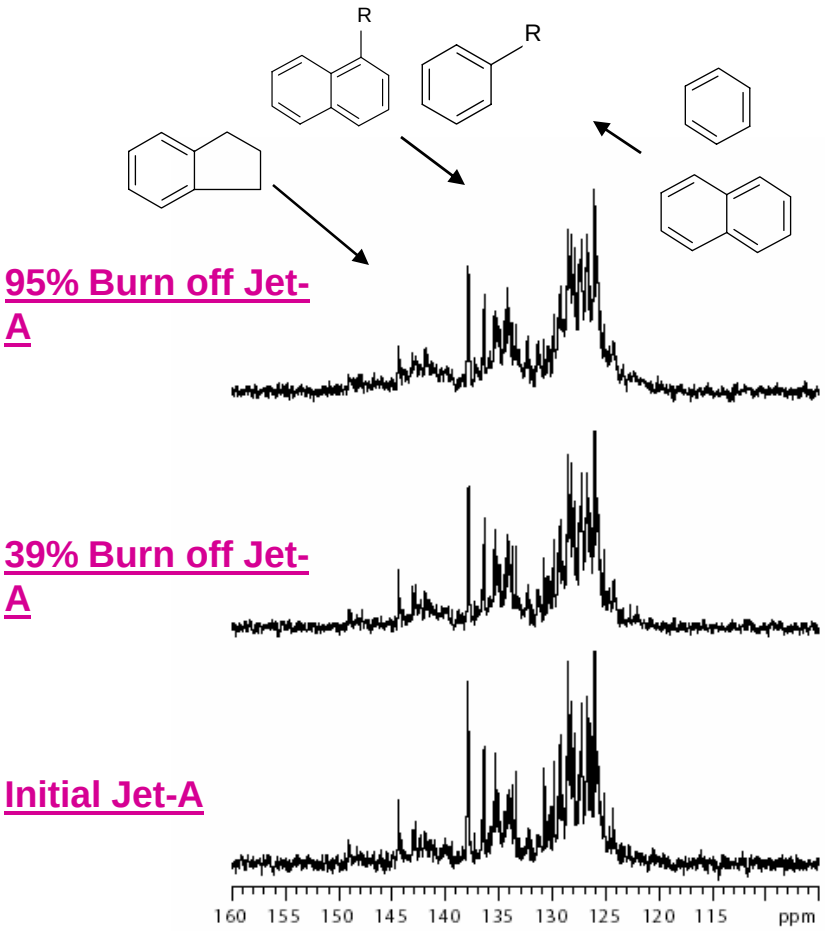
…. C_ε-C_ε-C_δ-C_γ-C_β-C_α

(Assignment scheme for *n*-C12)

α_C/ε_C decreases with burning implying that the aliphatic chain length increases as observed in GC-MS data.

Less cyclic aliphatics are found in burned oil samples, same trend is found in ^{1}H NMR spectra.

Change in Aromatics ?



^{13}C NMR Spectrum of Liquid Fuel in a Batch Experiment

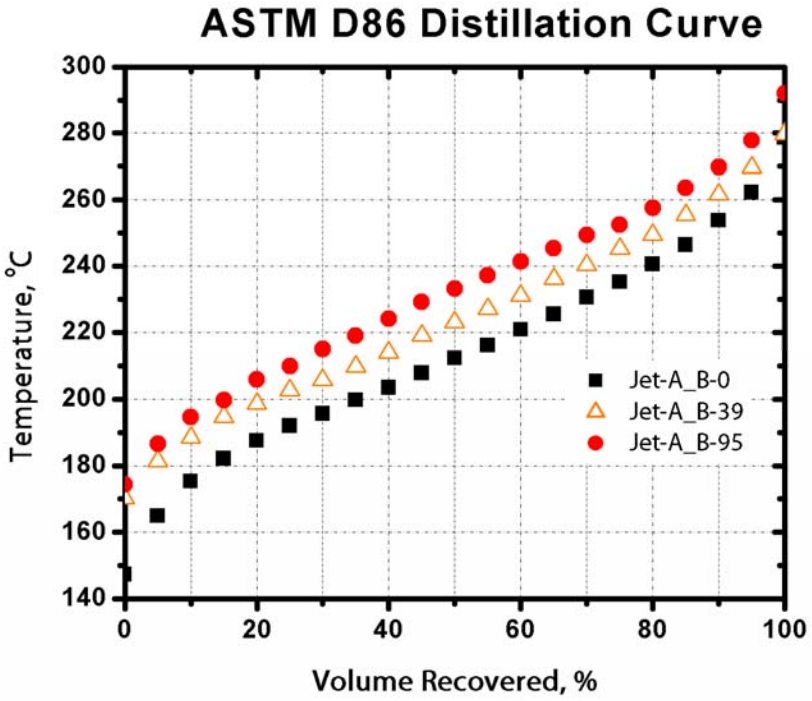
No major difference is found

- **Aromatics content increases slightly with burning**
- **Indan like compounds increase as much as 60%**

Sample	Aro. C, %[i]	Aro. H, %
Jet-A_B-0	10.6	3.3
Jet-A_B-39	11.4	3.3
Jet-A_B-95	12.2	3.2

Note: i- Aro. C % is the ratio of aromatic carbon atoms to total carbon atoms; ii-Aro. H % is the ratio of aromatic hydrogen atoms to total hydrogen atoms

Change in Selected Fuel Properties

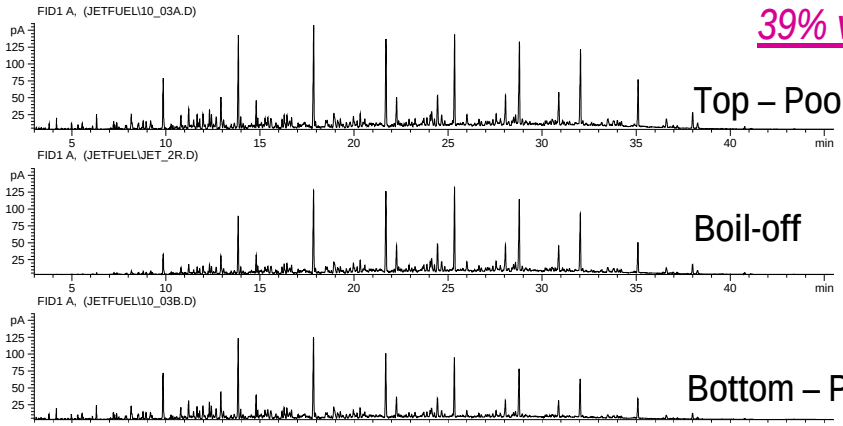


- **D86 distillation tests agree with GC-MS analysis**
- **Volatility of burned-off oil is lower than initial JET-A**

Sample	API, °	MW[i],g/mol	Flash Point[ii], °C
Jet-A_B-0	43.3	164.2	38.2
Jet-A_B-39	42.2	171.8	52.0
Jet-A_B-95	41.3	177.9	54.9

Note: i- Molecular weight (MW) is estimated; ii- Flash point is estimated.

Prediction of Composition Change as Distillation?

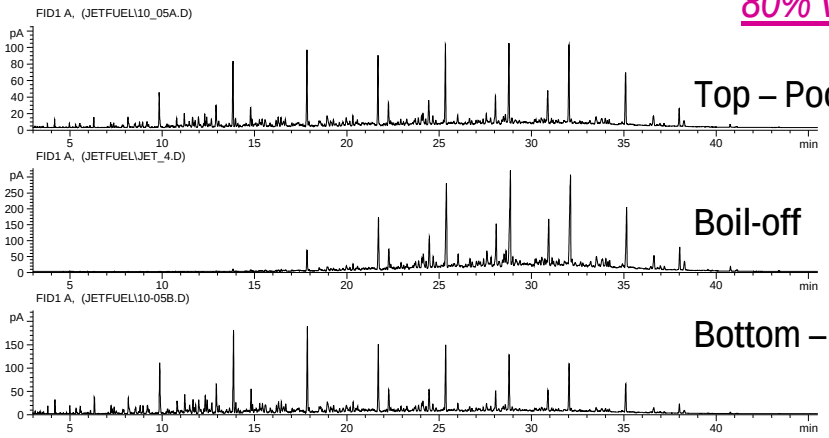


39% v. off

Top – Pool Fire Pan

Boil-off

Bottom – Pool Fire Pan



80% v. off

Top – Pool Fire Pan

Boil-off

Bottom – Pool Fire Pan

GC Analyses of Liquids

Batch Pool Fire vs. Boil-off Experiments

- Composition changes in both tests show similar trends
- Large conc. & temp. gradients exist in fire tests: well-mixed condition exists in distillation
- Fuel at bottom of pan changes more slowly than at the top: molecular diffusion & convection are important factors in fire tests

Batch pool fire tests appear more complicated than distillation process

C-SAFE
UNIVERSITY OF UTAH

Cost of chemicals for bench scale experiments

Only **three** *n*-paraffins under $50/L;

Only **one** branched paraffins under $100/L

Normal Paraffins	Cost /Liter	Branched Paraffins	Cost /Liter	Cyclo Paraffins	Cost /Liter	Aromatics	Cost /Liter
n-C_7	$24	*i*-C_7	$11k	*MCH*	$69	*Benzene*	$18
n-C_{10}	$118	*i*-C_8	$12	*Cyclo*-C_8	$135	*m-cymene* *p-cymene*	>$100k $29
n-C_{11}	$300	*i*-C_9	$25k	*Decalin*	$52	*1-phenyldecane*	$2k
n-C_{12}	$143	*i*-C_{12}	$12k	*Cyclo*-C_{10}	$25k	*Naphthalene* *Di-me-Na.*	$21 $3k
n-C_{16}	$143	*HMN*	$411	*Cyclo*-C_{12}	$100	*Anthracene* *Phenanthrene*	$240 $340

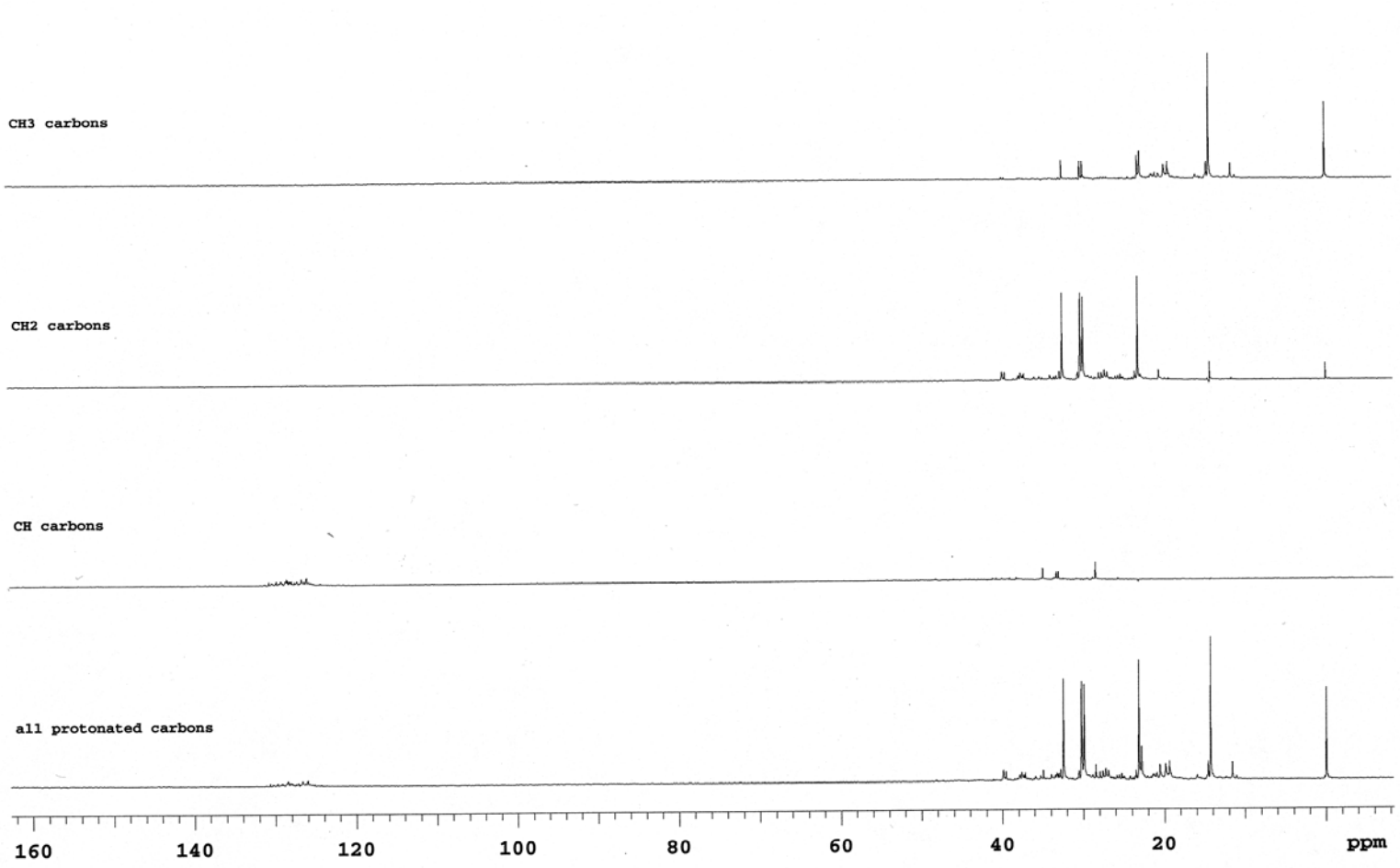
C-SAFE
UNIVERSITY OF UTAH

Fuel components available for reproducible pilot-scale testing

Parent Fuel	Characteristics/Description	Applications	Cost
Gasoline	*Known octane # gasoline blends w/o additive or oxygenates* *PRF's or toluene standardized fuel*	Engine Test Octane #	Very low high
Diesel	*U-15, cetane # 18.7, ~75% paraffin and ~25% aromatics, from 154~271 ^{o}C* *T-22, cetane # 74.8, ~50% paraffin, ~40% kerosene and ~10% aromatics, from 172 ~ 278^{o}C*	Engine Test	low
Jet Fuel	*Norpar series, for normal paraffins from C11 to C16* *Isopar series, for branched paraffins from 98 ~ 329^{o}C (C_{11}~C_{18} ?)* *Aromatic series for alkylbenzenes within 154 ~ 293^{o}C*	Pool Fire, Ignition delay, Engine test, Flame properties, Stability	~$300 (55 gal.)

Norpar-15 = 34.4% n-C_{14} + 49% n-C_{15} + 13.5% n-C_{17} + 3.1% n-C_{17+}

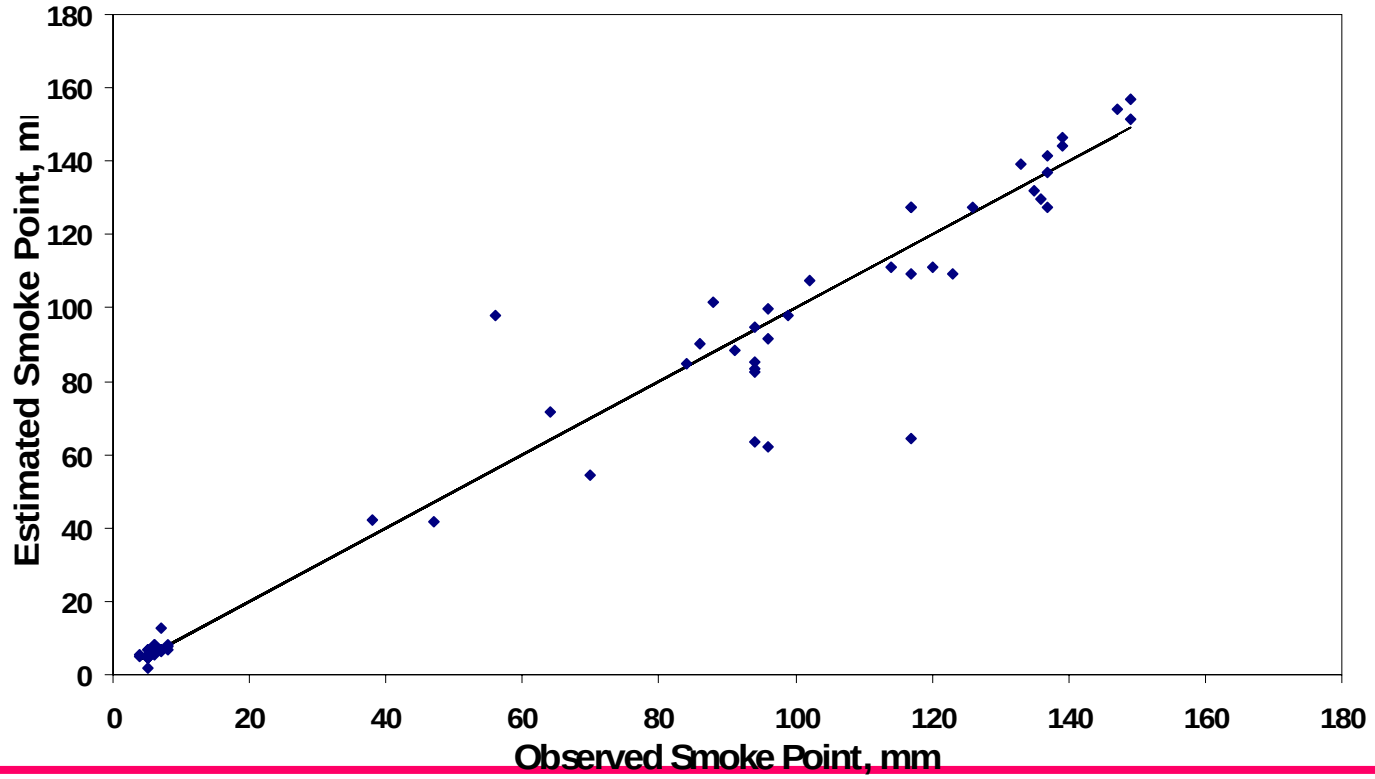
Group Analysis of JP-8



DEPT Spectra of JP-8

Smoke Point Projection w/ SOL Approach

Compound	A6	A4	A2	N6	N5	N4	N3	N2	N1	R	Br	Me	IH	AA	SP	SP*
2,4-dimepentane	0	0	0	0	0	0	0	0	0	7	2	0	1	0	109	**117**
isooctane	0	0	0	0	0	0	0	0	0	8	3	0	1	0	90	**86**
n-propylbenzene	1	0	0	0	0	0	0	0	0	3	0	0	0	0	7.8	**8**
Decalin	0	0	0	1	0	1	0	0	0	0	0	0	0	0	42	**38**



Formulation Methodology

Empirical Approach

- The basis is species concentration profile of parent fuel. The Selection of candidate compounds is often arbitrary.
- Mixture properties are estimated with empirical correlations.
- Example of surrogates: a 12 compounds surrogate for JP-8, by Schulz et al, 1991.
- Example of estimation equation: Closed cup flash point, API

  $T_{FP} = 0.68 * T_{10\%} - 109.6,$

  where $T_{10\%}$ is the temp. at 10 v.% recovery in ASTM D86 test

Pros & Cons

- Easy to apply
- Available empirical correlations
- Has most available references
- Trial and error based
- Often inaccurate representation of HC's in parent fuel
- Not suitable for use in multiple applications

Formulation Methodology

Structural Group Contribution Approach

- Fuel properties are determined by its structure.
  - •Surrogates could be proposed by analyzing the existing functional groups in parent fuel and their correlations with fuel properties.
- The *i* th properties (P_i) of surrogate may be predicted as
  - •$P_i = |A_{ij}| * |f(Y_j)|$

  Where, A_{ij} is the contribution on P_i from the j th group in the surrogate, and Y_j is the mole fraction of group j in the surrogate.
- Example of group classifications: Quann et al, 1992 proposed Structural Orientation Lumping method to describe compounds found in crude oil with 22 structural increments.
- Example of estimation equation: boiling point, Joback, 1987

  $T_b = 198 + \Sigma N_k * T_{bk}$

Pros & Cons

- Accurate representation of real fuel structure
- Systematically study the effect of each group on various properties
- Easily adapt to change in parent fuel composition
- Lack of model to integrate physical property estimation and chemical kinetics simulation

C-SAFE
UNIVERSITY OF UTAH

Formulation Methodology

Hybrid: Semi-empirical Approach

- The basis is still the species concentration profile of the parent fuel.
  - Set up a surrogate candidates pool from the basis;
  - filter candidates with quantitative constraints from prior formulation criteria;
  - propose surrogate formula and estimate properties from both empirical correlation and group contribution theory;
  - tailor the surrogate fuel composition towards specific application.
- Candidate compounds
  - n-paraffins
    - decane, dodecane, cetane,..
  - i-paraffins
    - Iso-octane, iso-cetane (2,2,4,4,6,8,8 heptamethyl nonane),…
  - Napthenes (cycloaliphatic, alicyclic)
    - Methyl cyclohexane, decalin, tetralin,…
  - Aromatics
    - Benzene, alkylated benzenes, napthalenes,…
- Constraints
  - boiling range, flash point, $T_{10\%}$, T_{FBP}, smoke point, density, latent heat, etc.
- Example of surrogate: Hex-12

C-SAFE
UNIVERSITY OF UTAH