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ADVANCED FUEL QUALITY ASSURANCE STANDARDS BASED ON THERMAL TESTING & CHEMOMETRIC MODELING

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- Steve Westbrook, George Wilson (SwRI)
- Joel Moreno, Indresh Mathur (Haltermann Solutions)

Outline

- Motivation/Background
- Approach
- Referee Fuel Set
- Thermal Integrity Test Method and Results
- Model Development and Results
- Future Work

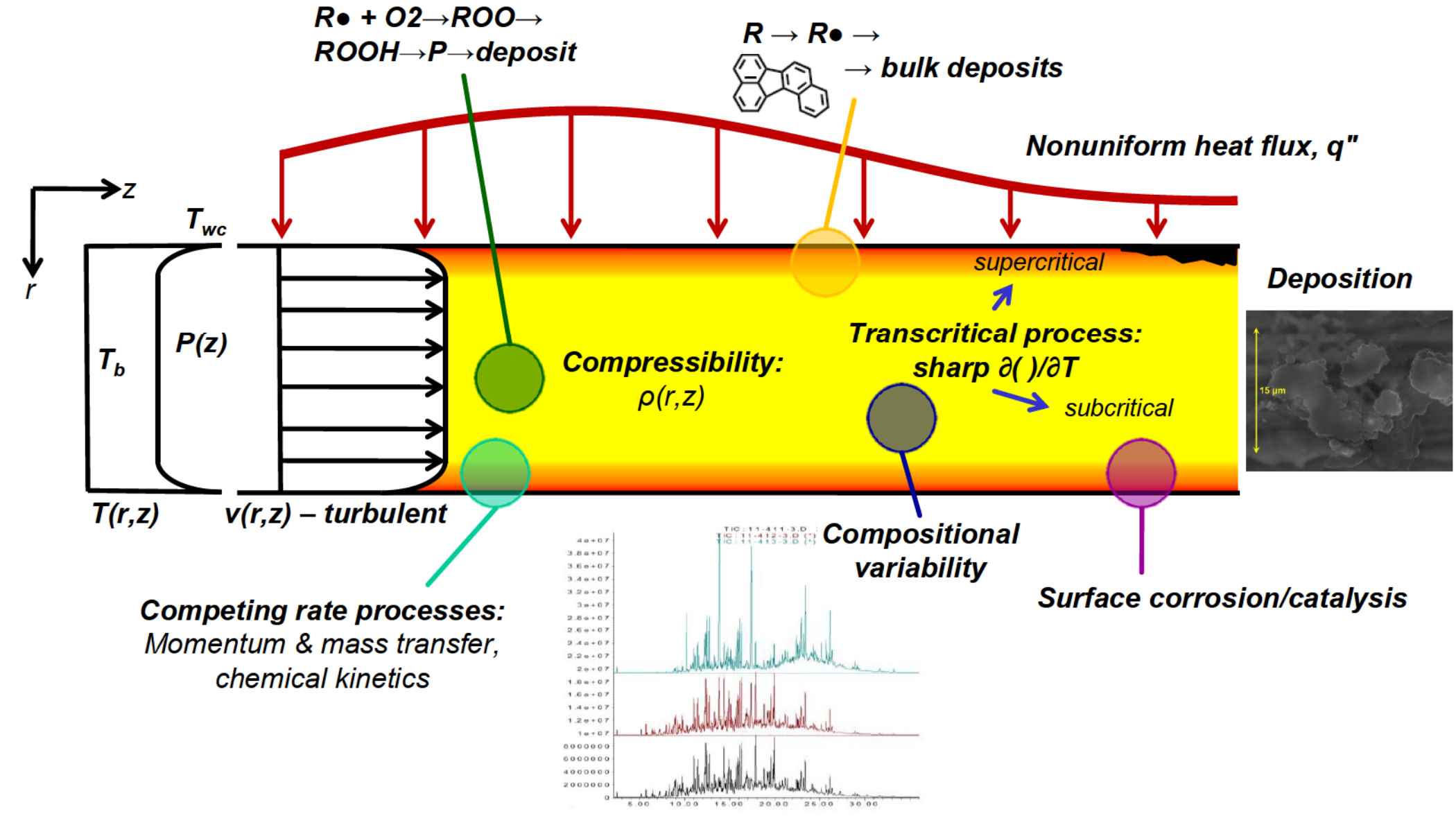
Motivation: Fuel Quality Assurance

- Propulsion fuel performance, quality, and suitability ***must be verified***
- This challenge is faced by:
  - Aerospace propulsion development/demonstration activities
  - Agencies who procure fuels for DoD use
  - Fuel manufacturers and suppliers
- Many requirements to consider:
  - Propellant cost
  - Support operations/infrastructure
  - Product availability & sustainability
  - **Functional performance**: combustion, cooling, lubrication…
    - ***Fuel thermal stability and material compatibility***

Aerospace Cooling System Conditions and Environments

Application	T_{wall} (°F)	$T_{fuel, bulk}$ (°F)	Pressure (psi)	Heat Flux (Btu/in²s)	Material
Rockets	500-900	100-500	700-7000	10-120	Cu alloys
Hypersonics	1200-1500	100-1300	500-1000	0.5-2	Ni alloys
Aircraft	300-400	100-300	500-800	<1	SS alloys

Liquid Rocket Engine (LOX/Kerosene) Regenerative Cooling Environment

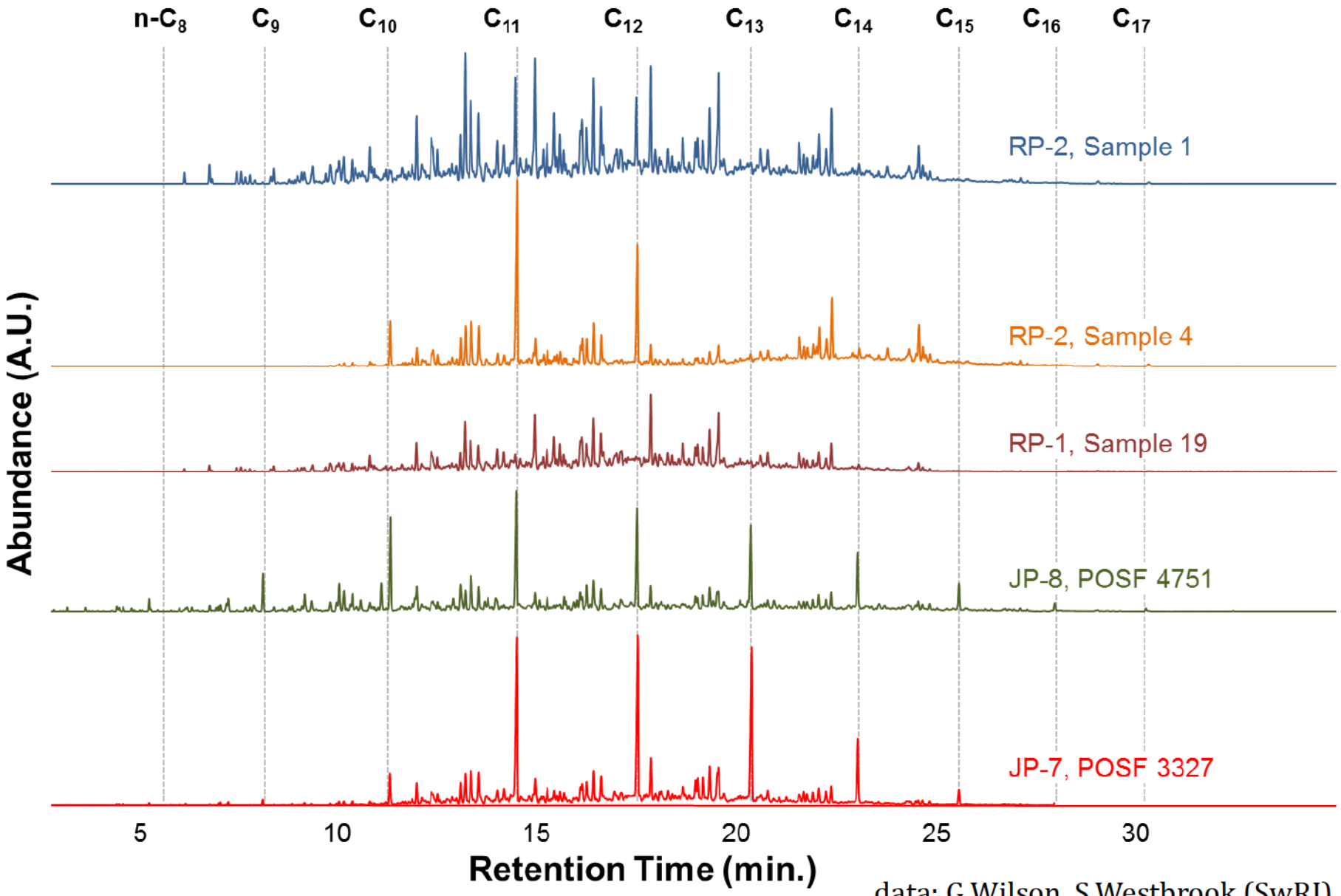


Background
1. Fuel Specification

	ASTM Method	JP-5	Jet A	RP-1	RP-2
Specification		MIL-DTL-5624U	ASTM D1655-15	MIL-DTL-25576E	MIL-DTL-25576E
Requirement, Units					
Distillation, °C					
IBP	D86	report		report	report
10% recovered		<205	<205	(185-210)	(185-210)
20% recovered		report			
50% recovered		report	report	report	report
90% recovered		report	report	report	report
End point		<300	<300	(<274)	(<274)
Density/15°C, kg/L	D1298	0.788-0.845	0.775-0.840	0.799-0.815	0.799-0.815
Viscosity/-20°C, mm^2/s	D445	<8.5	<8.0	<16.5[b]	<16.5[b]
Flash Point, °C	D93[c]	>60	>38	(>60)	(>60)
Freezing Point, °C	D2386[d]	<-46	<-40[e]	(<-51)	(<-51)
Net Heat of Combustion, MJ/kg	varies[f]	>42.6	>42.8	(>43.0)	(>43.0)
Hydrogen, mass %	varies[g]	>13.4	>13.4[h]	>13.8	>13.8
Aromatics, vol %	D1319	<25.0	<25.0	<5	<5
Olefins, vol %	D1319			<2.0	<1.0
Total sulfur, mass%	varies[i]	<0.3	<0.3	<0.003	<0.00001
Mercaptan sulfur, mass%	D3227	<0.002[j]	<0.003[j]	<0.0003	
Thermal Stability: ΔP change, mmHg	D3241[k]	<25	<25		report

- Specification review and development activities are important for fuel qualification
- Physical, chemical spec limits are influenced by operational factors:
  - Performance
  - Handling/storage
  - Cost/Availability
- Neither engine performance *nor* fuel chemical composition are specified *per se*…

Background
2. Compositional Variation



data: G.Wilson, S.Westbrook (SwRI)

Background
3. (Lack of) Thermal Performance Test

ASTM D3241 (JFTOT) Results
(Shaded fuels shown in previous slide)

325°C, 5 hr. ⟷ 355°C, 5 hr.

Fuel Type	JP-7	JP-8	RP-1	RP-2	RP-2	RP-TS-5	RP-2	Fuel Type	RP-1	RP-1
Designation	POSF 3327	POSF 4751	Sample 19	Sample 4	Sample 1	Sample 14	Sample 6	Designation	Sample 18	Sample X
Tube Deposit Rating Code	<2	>4AP[a]	<2	<2	<2	<2	<2	Max ΔTDR, spun	35-38 (17)[b]	5
Maximum ΔP, mmHg	0.1	280.1	0.1	0	0.1	0	0	Maximum ΔP, mmHg	0	0

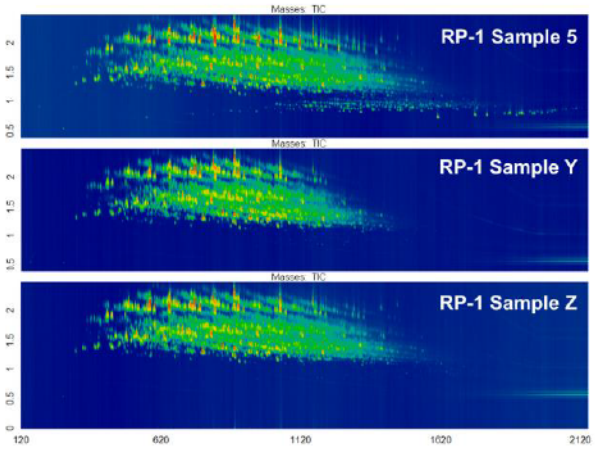
[a] "A" denotes abnormal deposit; "P" denotes peacock deposit.
[b] Filtered

data: G.Wilson, S.Westbrook (SwRI)
R.Cook (AFRL), M.Thiede (AFPET)

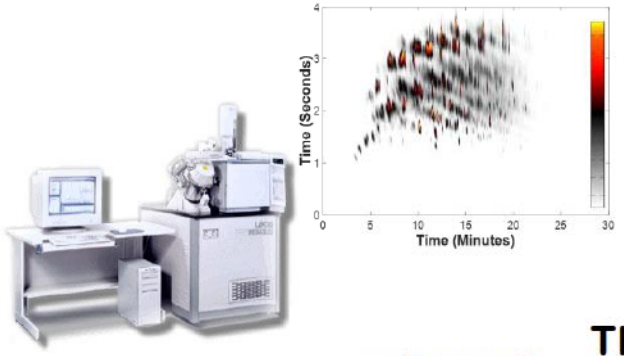
- Rocket kerosene is not quality tested for thermal stability or material compatibility prior to delivery
  - RP-1 is not tested. RP-2 ***is*** tested with ASTM D3241 (JFTOT) but results are "report only"
- JFTOT method ***may be*** valuable for screening very low performing fuels (contamination, alternative sources)…
- ***But the method is inadequate for ensuring fuel quality as increasingly demanding thermal environments arise***

AFQTMoDev Project Structure

Fuel Compositional Variation



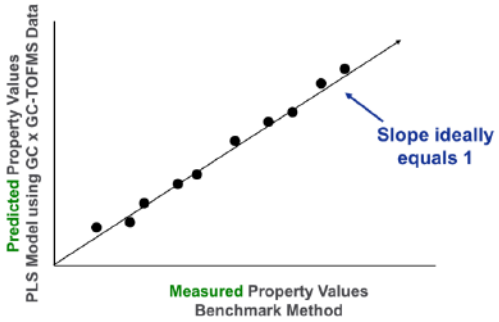
1. Optimize Composition
2. Specification Limits



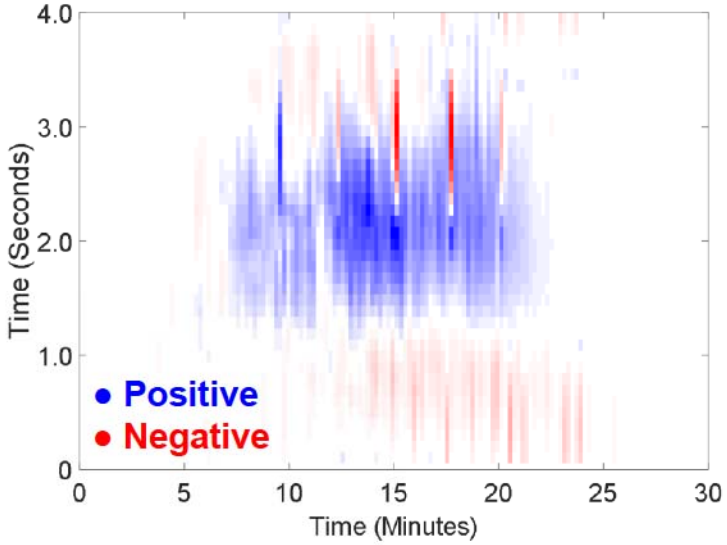
GCxGC-TOFMS
3D Chemical Data

LECO RC612
Test section analysis

CRAFTI
Thermal Integrity Index (TII)



PLS Model Development

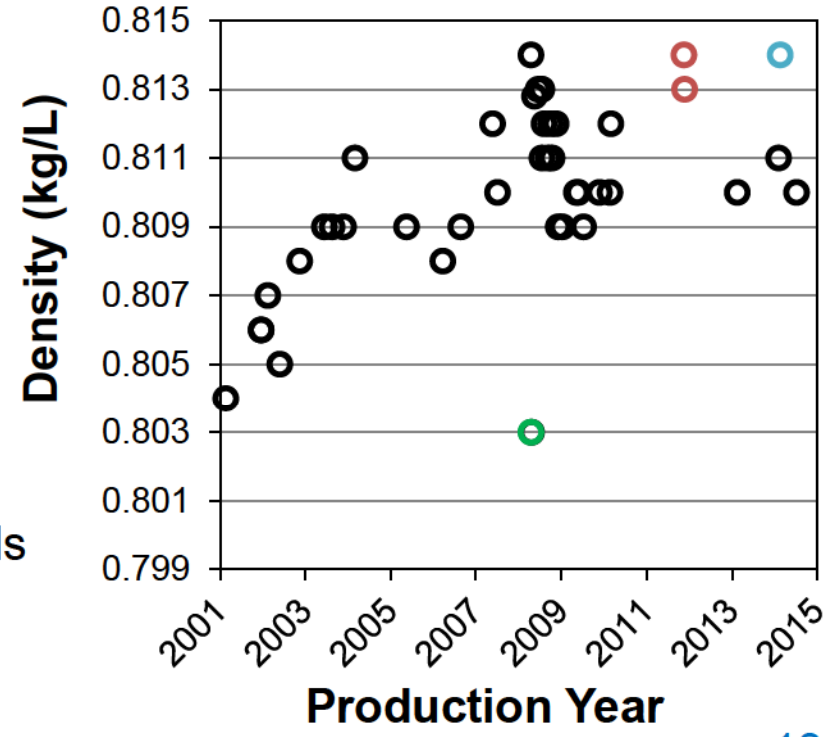


Compound Correlation to TII

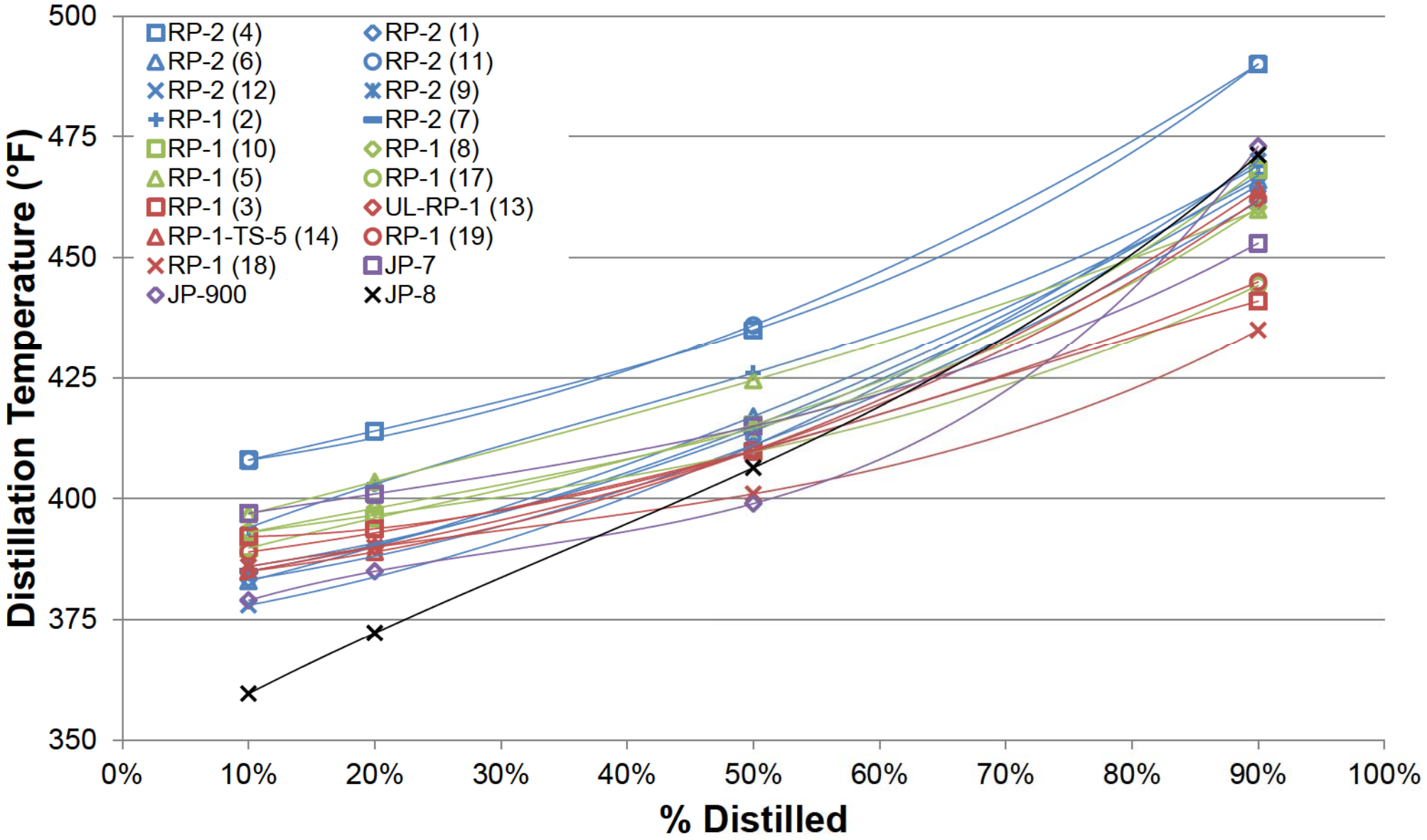
Referee Fuel Set

- Criteria for fuel selection
  - Multicomponent: distribution of hydrocarbon species and/or types
  - Possess heteroatom species diversity
  - Span the compositional range of fuels meeting MIL-DTL-25576E: not necessarily “today’s fuel”
  - Meet aerospace fuel designations for health/flammability/reactivity, etc.

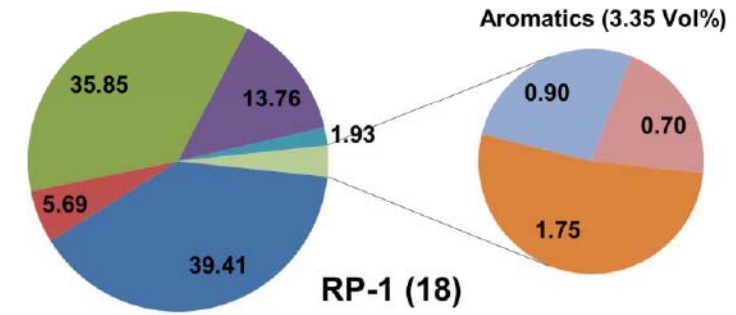
- What we ended up with
  - 51 compositionally unique fuels (or potential blend materials – single/multicomponent)…
  - 19 evaluated for thermal integrity and included in chemometrics/modeling
  - (8) RP-2,(9) RP-1, JP-7, JP-900
  - 3 available from previous SwRI project
  - Less than ideal compositional variation
    - Produced on demand – no repository of historical fuels
    - Relatively consistent production past 20 years
    - Several “interesting” fuels contained common feedstocks

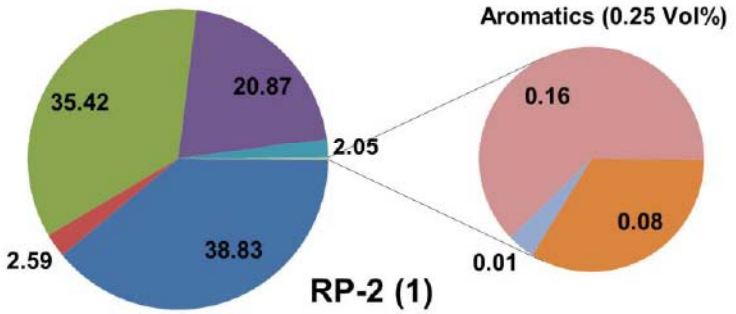


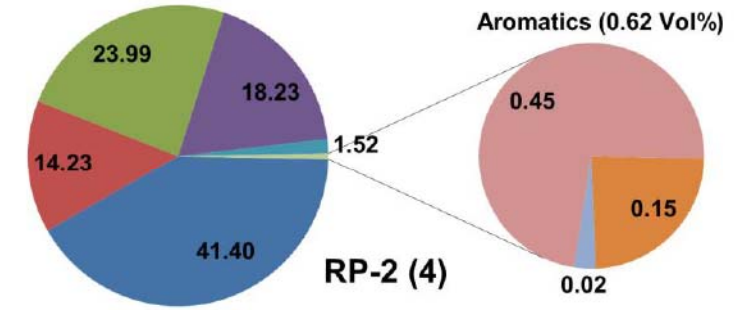
Referee Fuel Set Variation



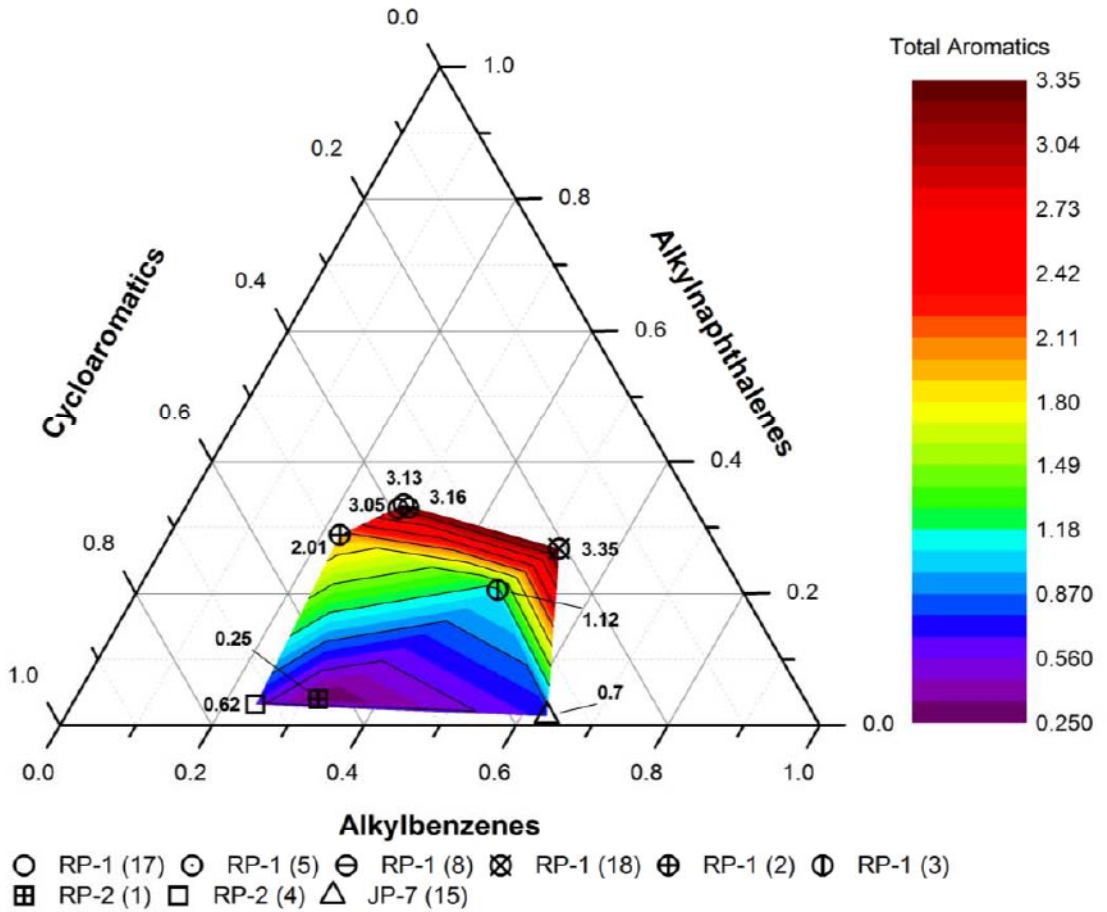
Fuel Set Compositional Variation



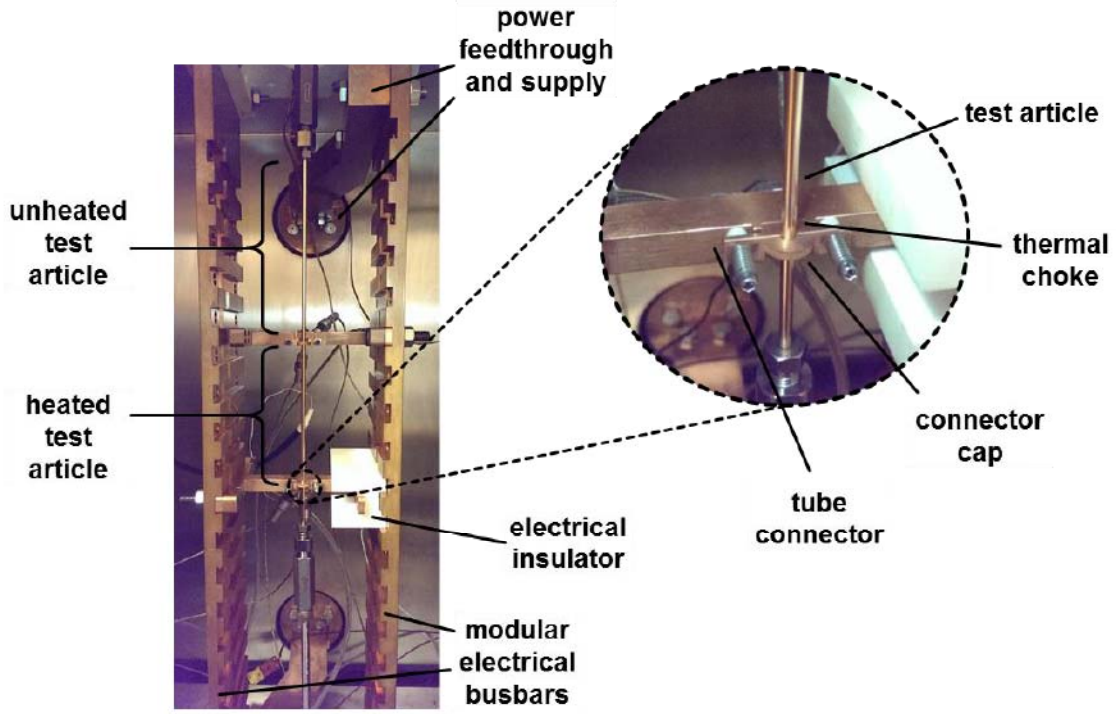




iso-Paraffins
n-Paraffins
Monocycloparaffins
Dicycloparaffins
Tricycloparaffins
Alkylbenzenes
Alkylnaphthalenes
Cycloaromatics



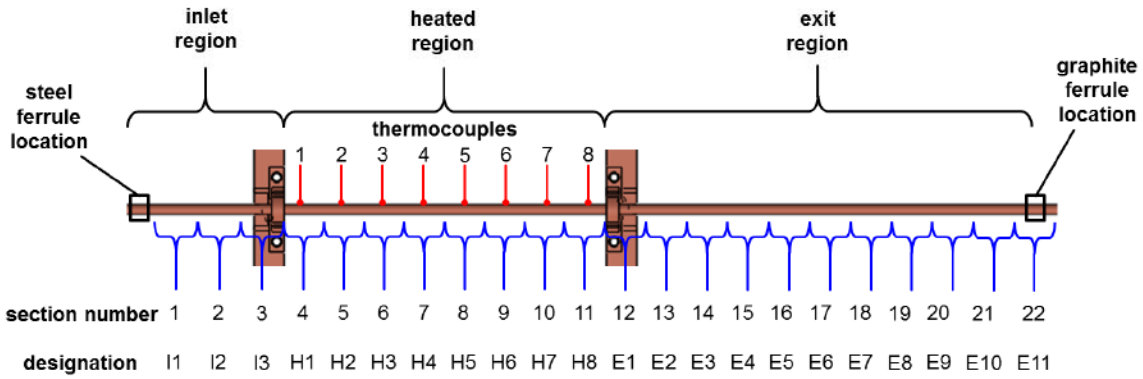
Compact Rapid Assessment of Fuel Thermal Integrity (CRAFTI)



Standard Test Conditions

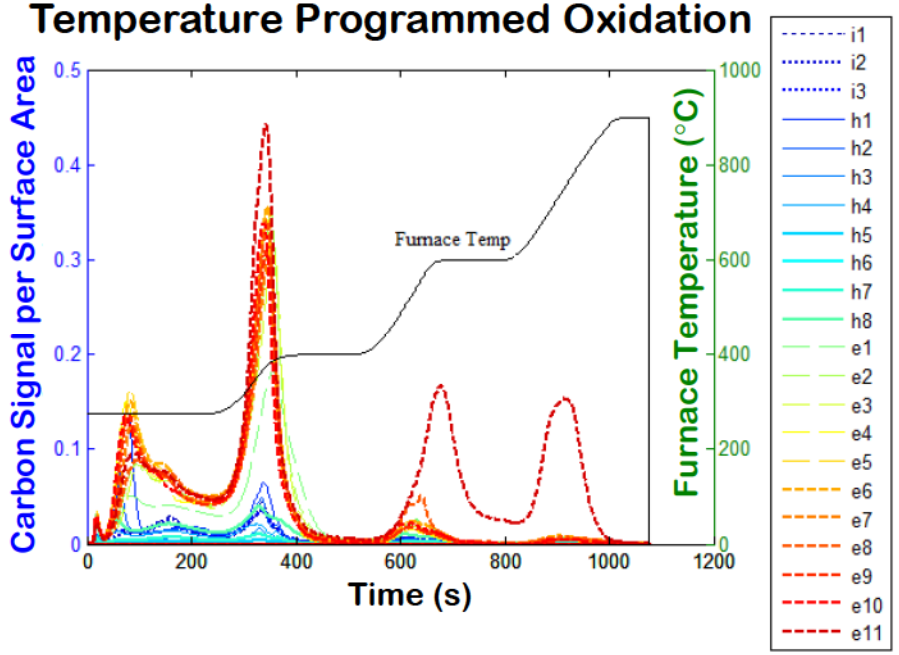
Parameter	Value	Units
Reynolds Number, Re	2000-20,000	-
Test article material	Cu (C10100)	-
Input power	4500	W
Wall temperature (dependent variable)	~1050±250 (560±120)	°F (°C)
Backpressure	1,000 (6.9)	psi (MPa)
Heated length	4 (10.2)	in. (cm)
Test duration	15	min.

Test Article Details & Naming



Test Article Analysis

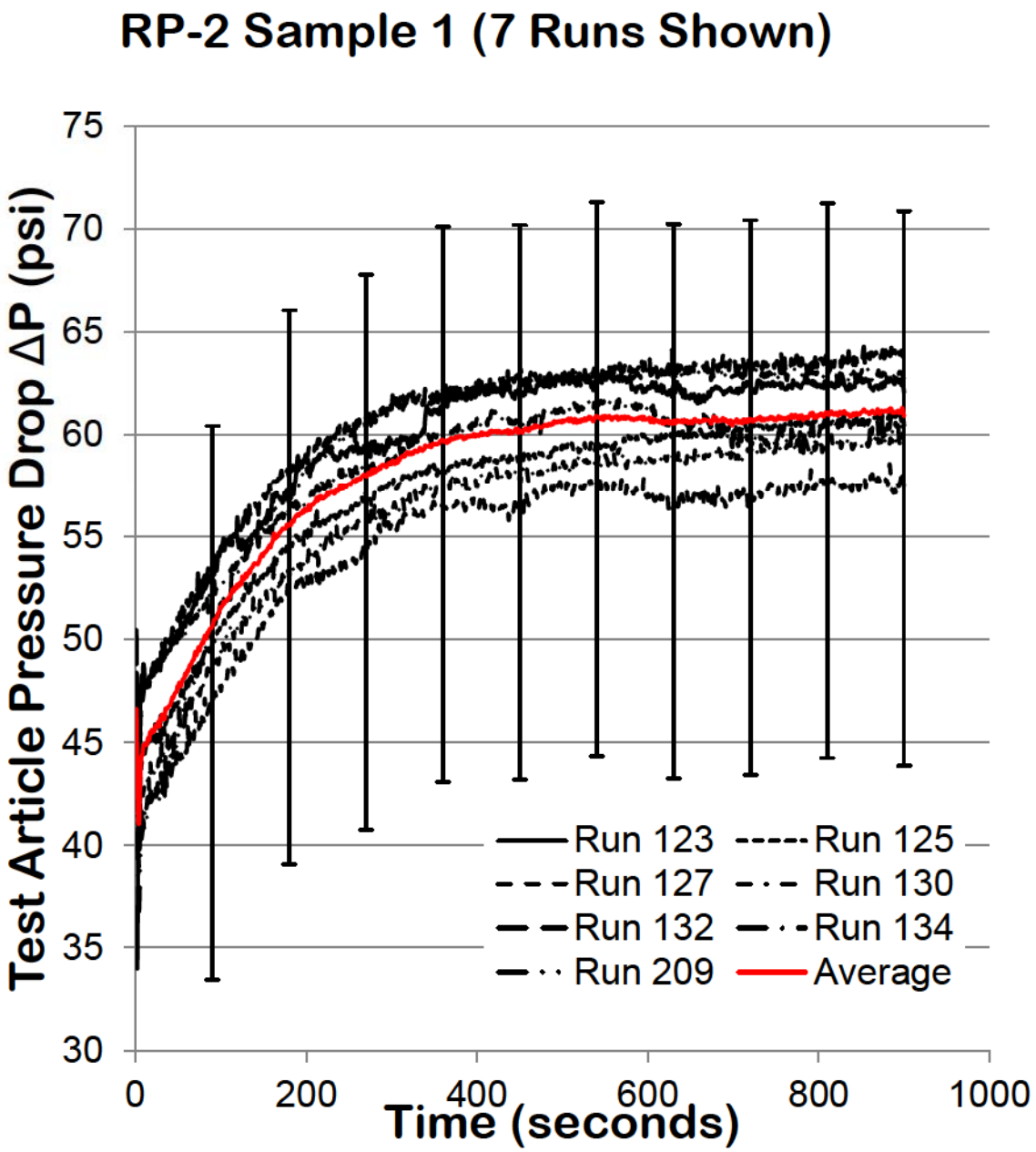
Temperature Programmed Oxidation



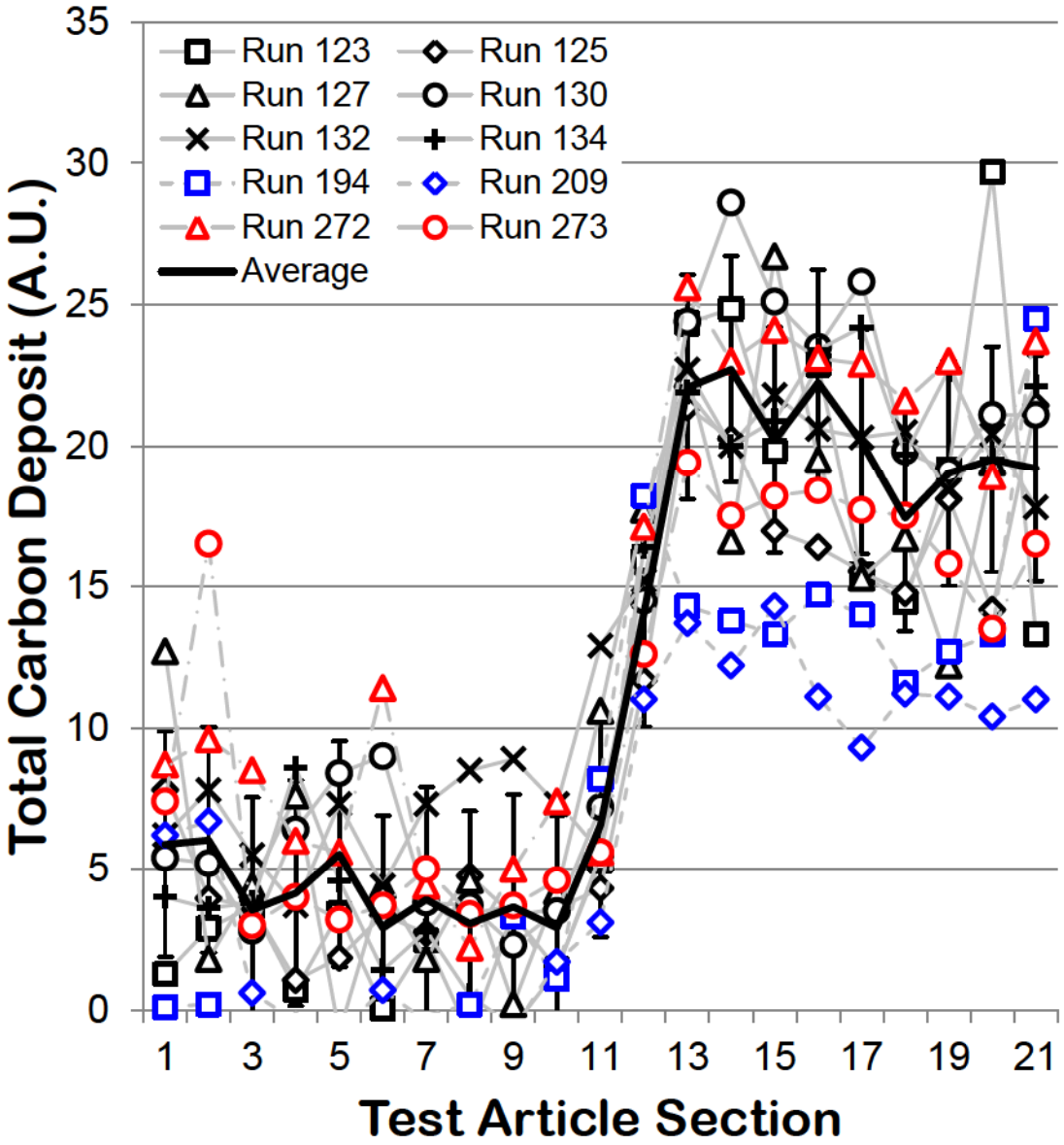
Repeatability: Pressure Drop Increase

- ***Ten runs were performed at standard test conditions using baseline fuel (RP-2 Sample 1)*** :
  - 6 runs – initially
  - 2 runs – 2/3 mo. later
  - 2 runs – 9/10 mo. later
  - Purge/flush/purge protocol between fuels; no disassembly
- Pressure drop *can be* indicative of deposit formation
  - Variation from other sources should be minimized
- Pressure drop variability from test to test was well within measurement uncertainty

$$\delta(\Delta P) \cong \delta(P_{\text{in}}) + \delta(P_{\text{out}})$$



Repeatability: Deposit Formation



- For ten runs with baseline fuel, carbon deposit behavior is similar – and initially somewhat unexpected
- Near detection limits → some noise likely due to instrument response
- These results indicate "end-to-end" variation (fuel, experiment, test article handling, analysis, etc.)
- Will carbon deposit behavior vary with fuel composition?

CRAFTI Results Indicate Method Sensitivity for Thermally Stable Fuels

CRAFTI v1.1 Conditions/Results (15 min., $T_{o,bulk}$ ~ 650°F, T_{wc} ~ 800-1200°F)

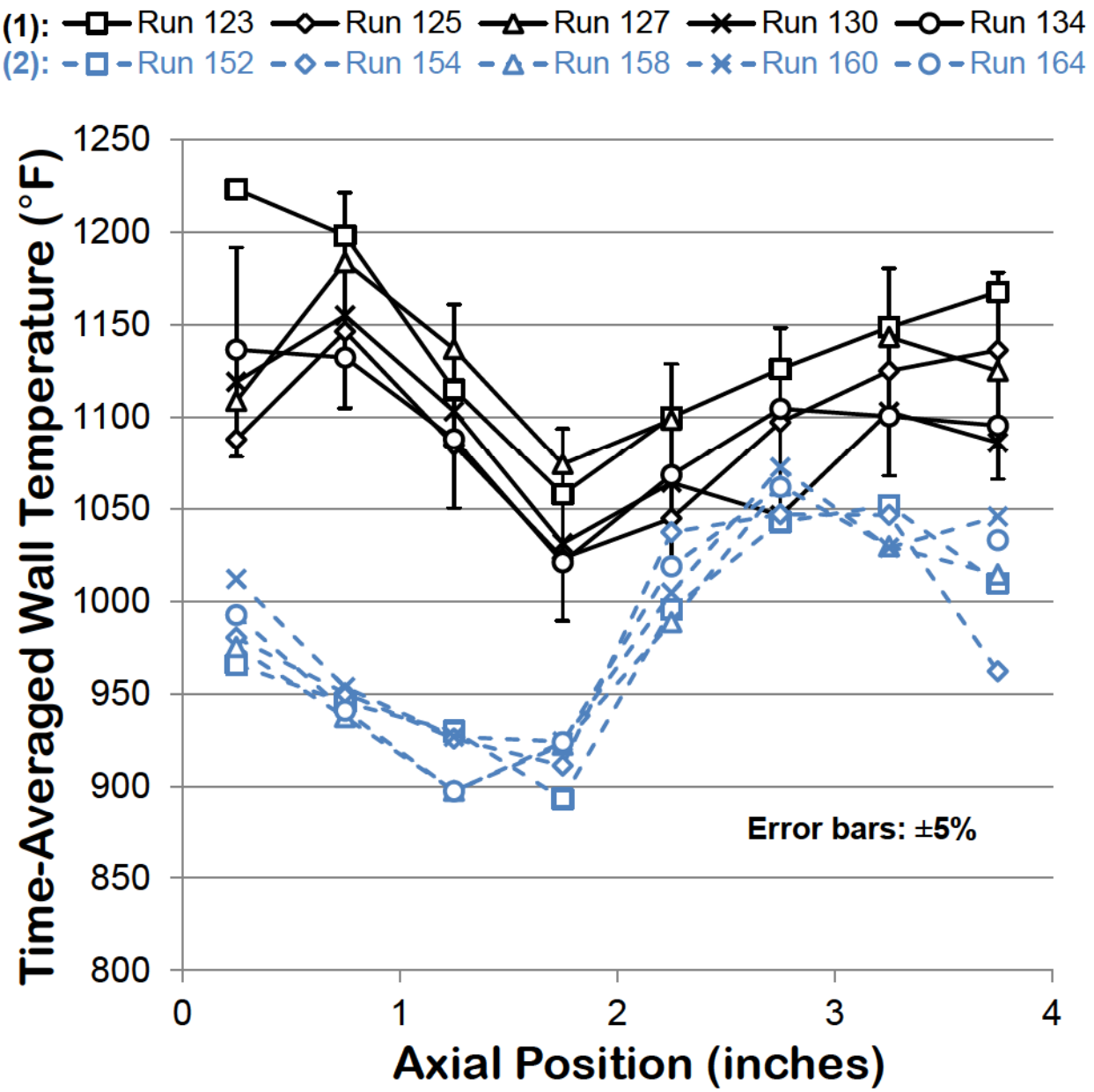
(Shaded fuels: Indistinguishable ΔP with JFTOT)

Fuel	Sample #	# of Runs	Average Wall Temperature °F (°C)	Pressure Drop ΔP, initial psi (kPa)	ΔP Increase during Test psi (kPa)
RP-2	1	10	1158 (626)	44 (306)	16 (113)
RP-2	4	4	1026 (552)	42 (288)	20 (136)
RP-2	7	2	1048 (564)	39 (269)	21 (142)
RP-1	3	7	1112 (600)	46 (320)	21 (146)
UL-RP-1	13	2	1115 (602)	33 (225)	22 (154)
RP-2	9	4	1110 (599)	31 (213)	23 (158)
RP-2	6	2	1145 (618)	47 (326)	23 (158)
RP-1	10	2	1057 (569)	31 (217)	26 (179)
RP-2	12	2	1144 (618)	29 (203)	30 (207)
RP-1	19	2	1074 (579)	26 (180)	30 (210)
RP-2	11	2	1085 (585)	30 (205)	33 (225)
RP-TS-5	14	2	1130 (610)	32 (222)	35 (242)
JP-900	16	2	1015 (546)	31 (217)	45 (313)
JP-7	15	2	950 (510)	30 (205)	50 (343)
RP-1	8	2	964 (518)	35 (241)	79 (545)
RP-1	5	2	985 (529)	41 (281)	82 (563)
RP-1	2	7	1027 (553)	45 (311)	91 (625)
RP-1	17	1	964 (518)	31 (217)	103 (713)
RP-1	18	2	1005 (541)	30 (210)	188 (1293)

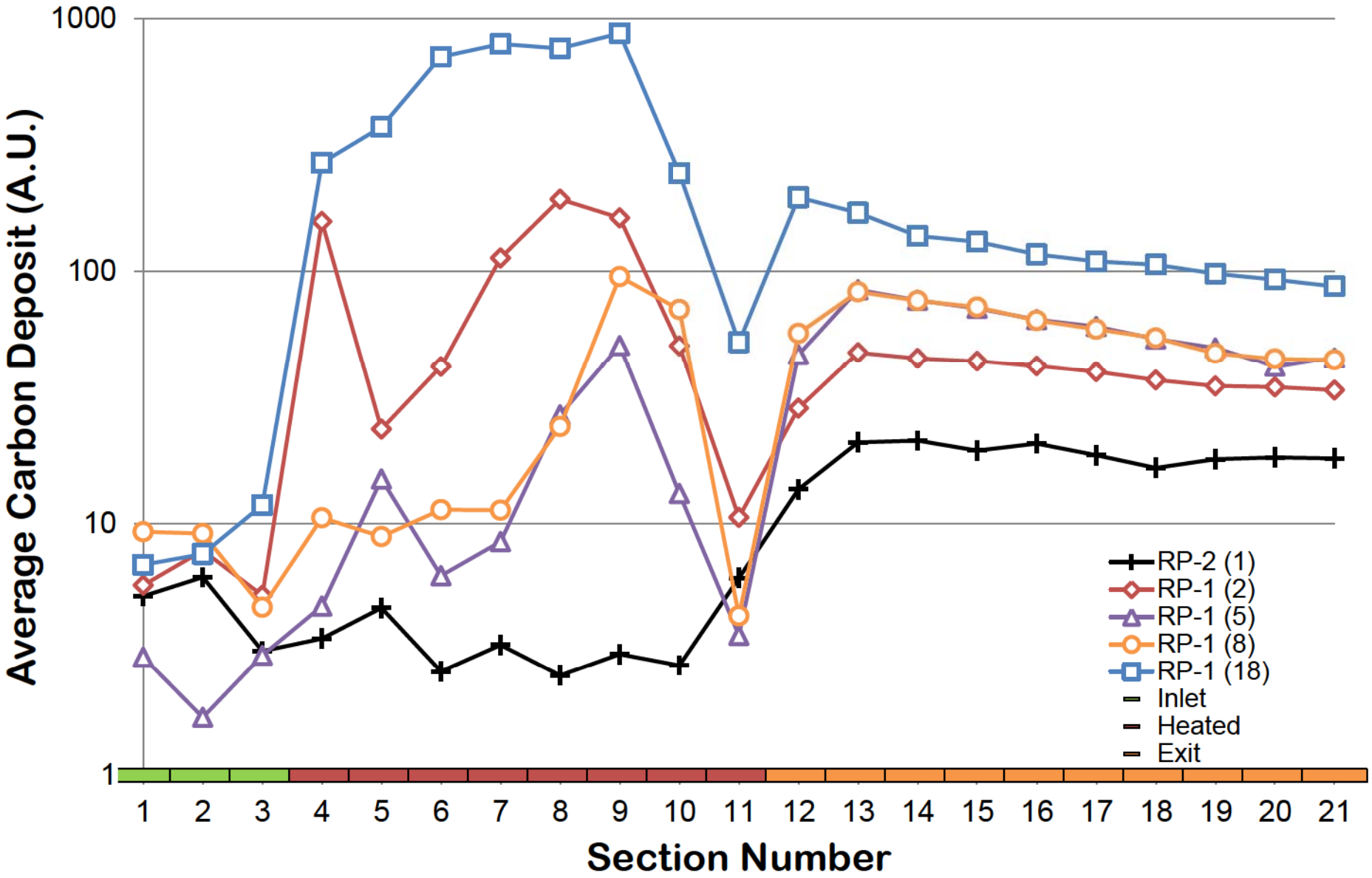
- Standard test conditions produce ***measureable performance differences***
- Pressure drop increase varies from 40-630% of initial value
- Most fuels meet current RP-1/RP-2 limits (MIL-DTL-25576E)
- JFTOT results indicated indistinguishable performance (ΔP increase after 5 hours) for these fuels

Wall Temperature Behavior (Heated Region Only)

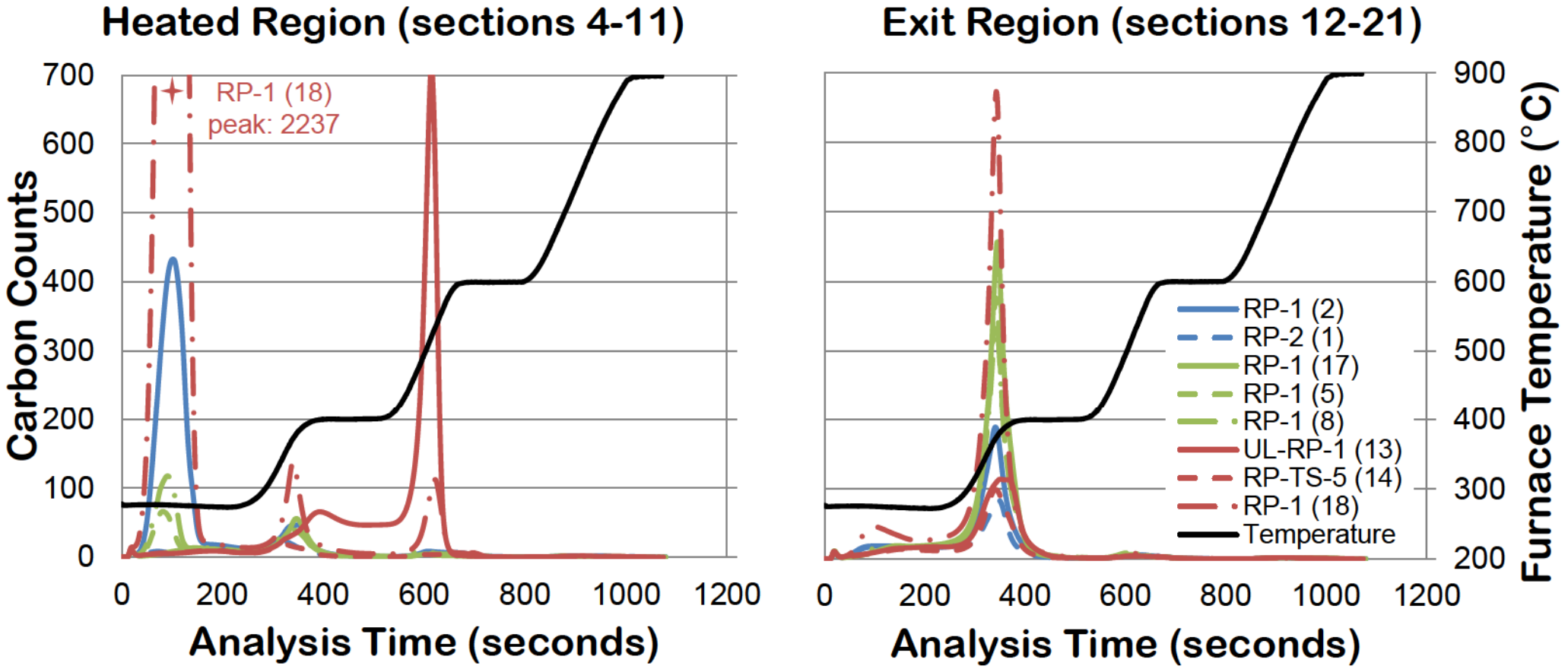
- Wall temperature *can be* indicative of fuel thermal integrity, but is complicated by other factors:
  - Electrical connection → local current flux density
  - Deposit formation → effects on local heat transfer
  - Transcritical flow → property gradients
- Repeatable characteristic profile for fuels of different thermal quality…
- Difficult to explain temperature/ time history variation
- Modeling & simulation underway to characterize fluid/solid thermal environment, flow behavior



Time-Integrated (Total) Carbon Sensitive to Fuel Composition

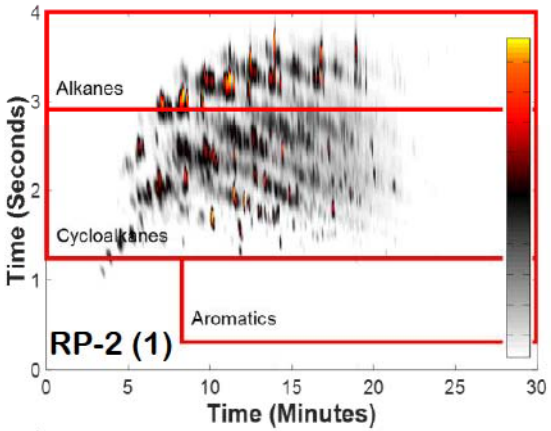


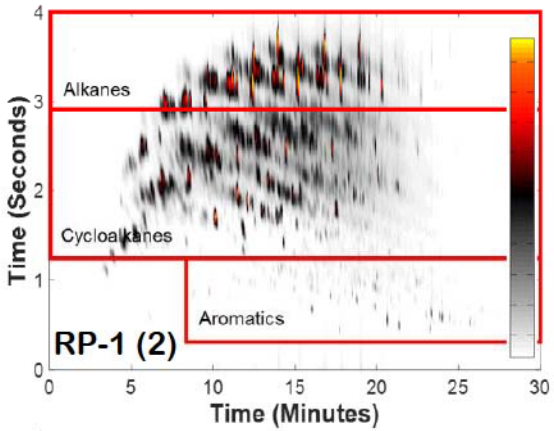
Differentiated Carbon Data Provides Additional Insight

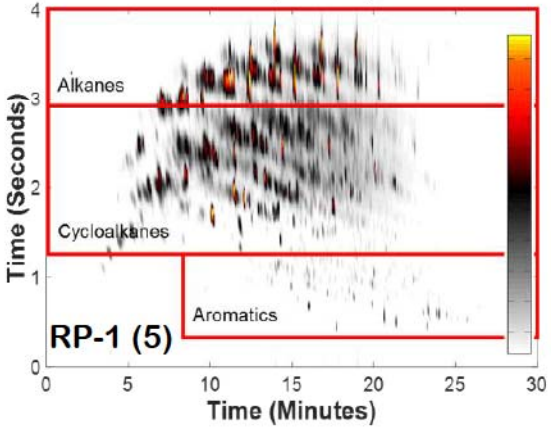


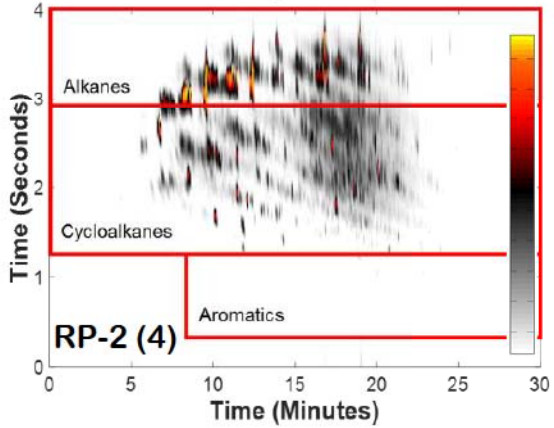
- Highest depositing fuels showed largest pressure drop increase
  - Exception: UL-RP-1 (13): significant deposit but small ΔP increase
- Heated region carbon deposits predominantly chemisorbed (0-200s)
- Amorphous carbon (200-450s) dominates exit region
- Only one fuel with strong filamentous carbon signal (450-800s): UL-RP-1 (13) in heated region
- Pressure drop increase correlated with amorphous deposit in exit region?

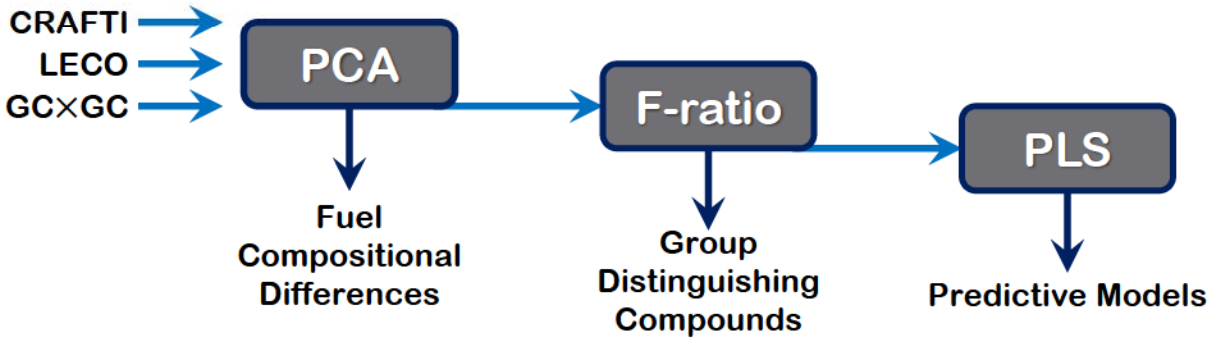
Chemometrics with CRAFTI, Carbon Deposit, & Comprehensive GC×GC-TOFMS Datasets





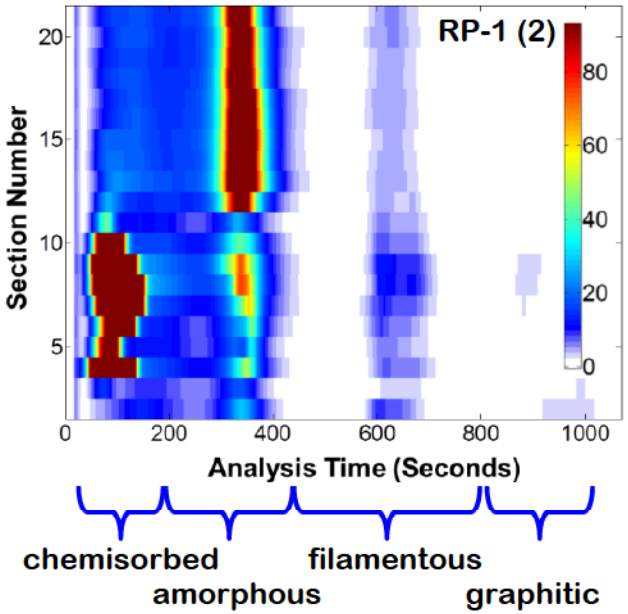




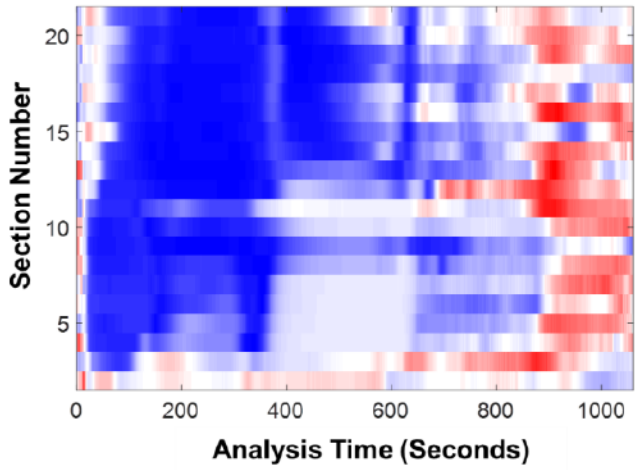


- Purpose of chemometrics: *Clarify role of fuel composition in cooling performance/quality*
  - Guide fuel formulation
  - Advise specification methods/limits
- Implementation:
  - Principal component analysis (PCA)
    - Assign categorical quality
    - Identify important compositional differences
  - Fisher ratio (F-ratio) analysis
    - Refine GC×GC dataset for optimized models
    - Identify distinguishing chemical compounds
  - Partial least squares (PLS) modeling
    - Develop predictive models that relate thermal integrity behavior to fuel composition

PCA Example: Correlate Carbon Deposit Types/Regions with Channel ΔP Increase

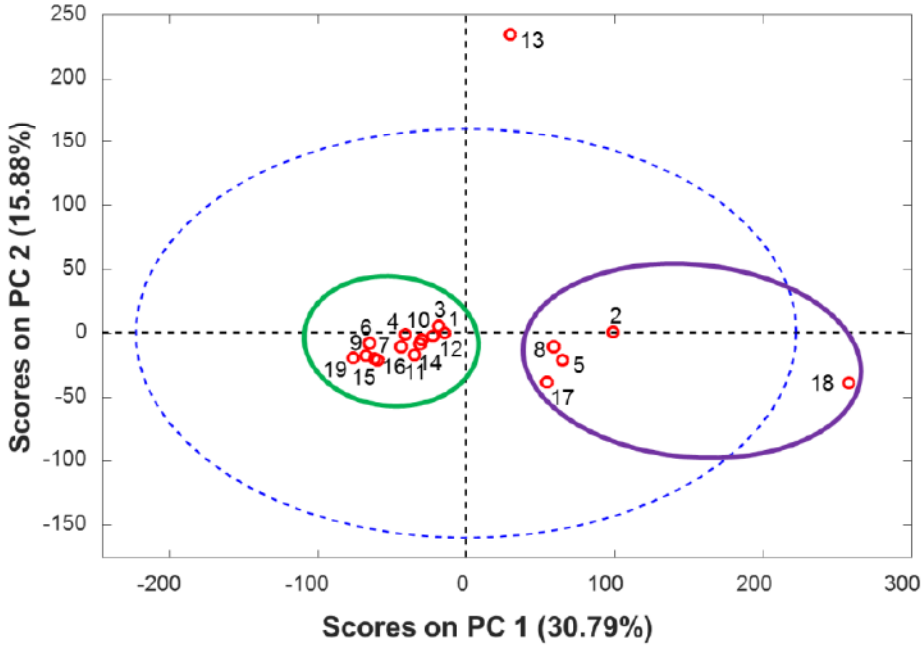


- Map of 3D TPO data
- Available for 19 referee fuels
- Multivariate data: excellent PCA candidate
- How can information be made useful?



- PCA PC1 Loadings Plot
- Associates positive (blue) & negative (red) contributions to PC1 with original data matrices
- Positive contributions to PC1 (blue) correlate with high pressure drop
- ΔP most sensitive to amorphous carbon (200-450s) in exit region (sections 12-21)

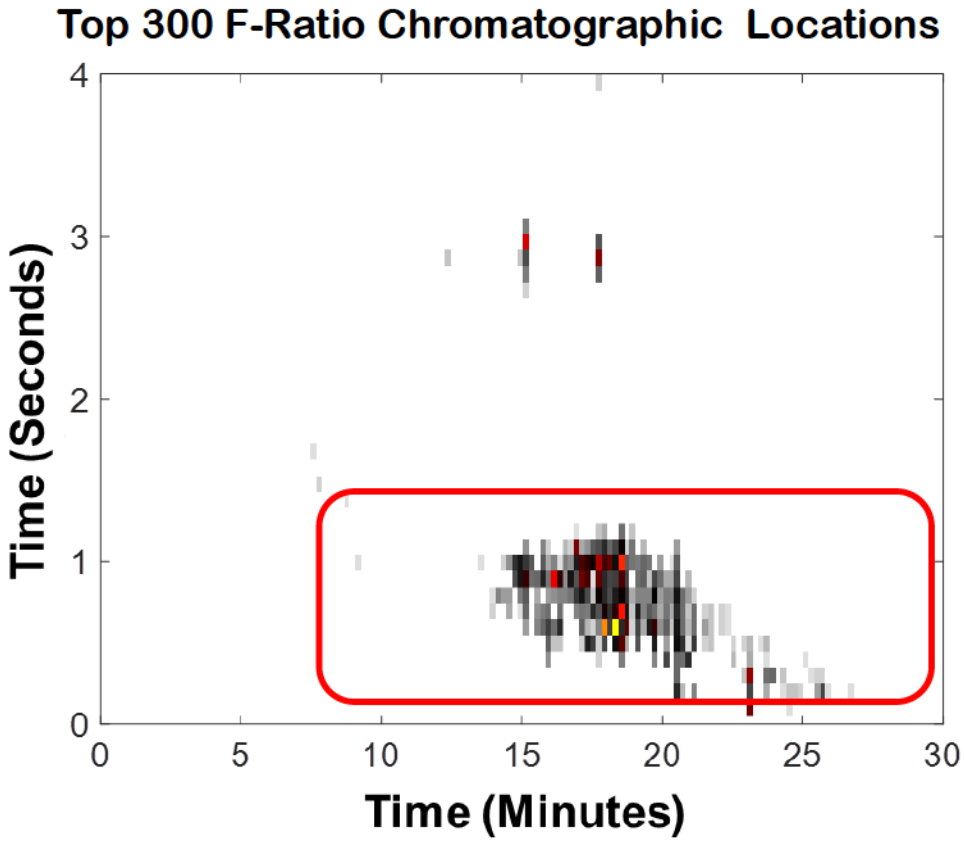
- PCA Scores Plot: PC groupings capture variance in measured data (ideally 100%)
- In this case, high ΔP fuels (purple) and low ΔP fuels (green) group together – primarily along PC1
- A relationship between carbon deposit and pressure drop is confirmed – but what does PC1 represent?



Similar analyses performed for test article pressure drop, wall temperature, GC×GC-TOFMS chromatographic variation

Fisher Ratio Analysis: Identify Compounds Responsible for Group Assignment

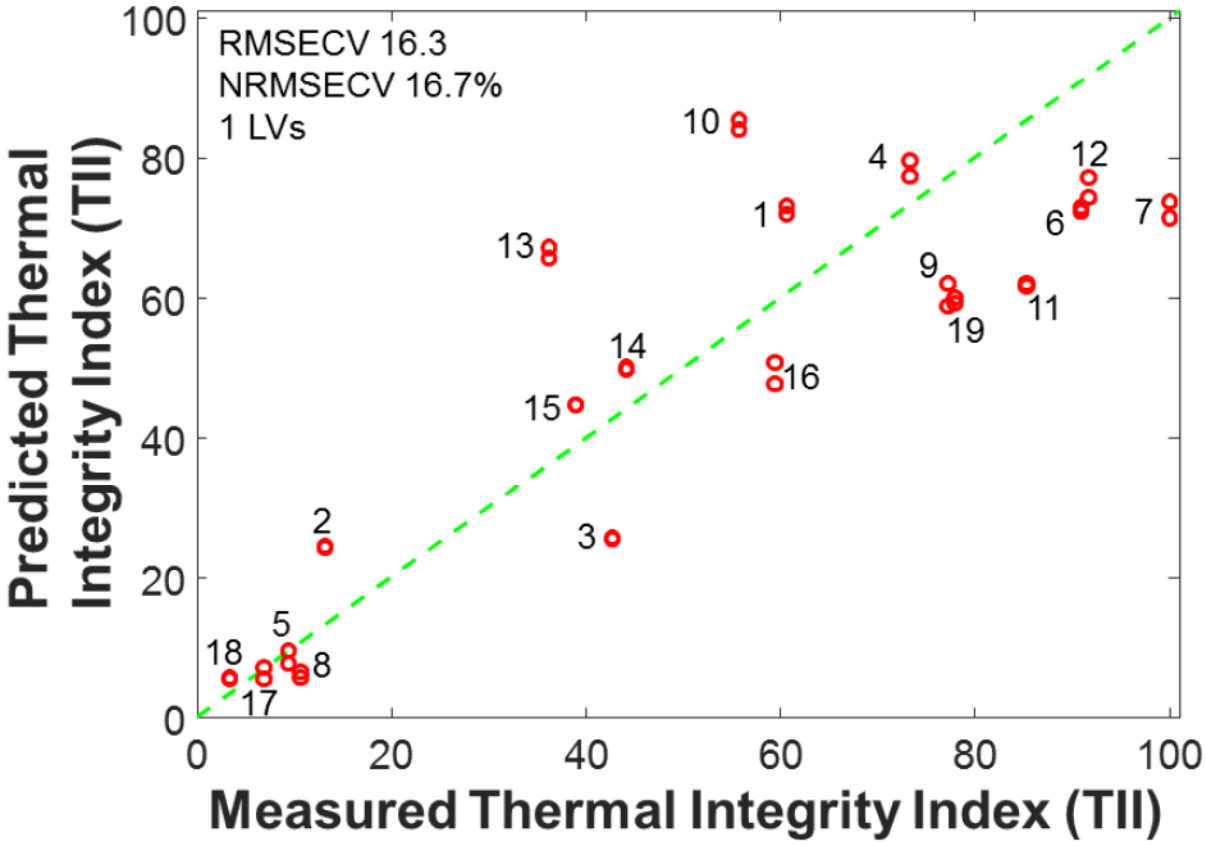
#	F-Ratio	t_r^1 (min.)	t_r^2 (sec)	Compound	Match Value	C-ratio
1	277.1	18.7	0.91	1,1,6-trimethyltetralin	908	13.0
2	254.1	18.3	0.97	5-ethyltetralin	846	15.9
3	233.0	18.7	1.01	(1,4-dimethylpent-2-enyl)benzene	769	16.9
4	231.4	18.8	0.96	1-methyltetralin	751	6.3
5	219.4	16.5	1.20	(1-ethylbutyl) benzene	790	14.5
6	214.0	15.6	1.31	5-methylnonane	840	1.7
7	201.3	18.1	1.31	1,3,5-trimethyl-2-propylbenzene	894	11.9
8	188.5	23.6	0.64	2,6-dimethyl naphthalene	935	68.3
9	188.2	18.2	3.31	2,6-dimethyl heptadecane	900	5.0
10	182.9	17.3	1.43	Adamantane	885	2.4
11	179.4	17.6	1.29	1-ethyl-2,4,5-trimethylbenzene	792	16.0
12	177.6	23.5	0.41	Biphenyl	926	34.8
13	175.9	18.5	1.31	6-propyltetralin	735	9.1
14	172.4	18.9	0.81	6-methyltetralin	955	16.4
15	171.4	19.1	0.91	2,3-dimethyltetralin	711	4.6
16	169.0	17.5	1.31	1,4-dimethyl-2-(2-methylpropyl)-benzene	825	13.3
17	167.9	18.8	1.13	1-heptenylbenzene	794	10.1
18	164.6	17.7	1.19	(5-methyl-1-hexenyl)benzene	764	13.8
19	162.7	18.8	1.33	(1-methylhexyl) benzene	818	18.4
20	161.9	15.4	1.25	p-cymene	814	6.9



- F-Ratio Analysis top hits are primarily aromatic…
- But their relative influence is quantified
- Hits represent class-distinguishing compounds, not necessarily direct influences on fuel thermal integrity
- Reduces superfluous chemical data in PLS model development

PLS Modeling: Predict Thermal Integrity using GC×GC-TOFMS Data

- Leave One Out Cross Validation (LOOCV):
  - *N* models generated, each with *N*-1 datasets
  - Datasets include CRAFTI, TPO, and GC×GC data
  - Each resulting model used to predict behavior for fuel *left out* during model generation
  - Statistical/graphical comparison of predicted vs. measured values
- Top 300 F-Ratio tiles used
- New parameter defined based on PCA, F-Ratio efforts: Thermal Integrity Index (TII):
  - $TII \propto \left(\Delta P_{\max} \times C_{\mathrm{A,exit}}\right)^{-1}$
- Good model agreement
  - Not inclusive of all compositional influences
  - Does not account for ΔP_{init}



Similar predictive models developed for test article pressure drop, wall temperature, carbon deposit

Summary

- A compositionally diverse set of rocket kerosene fuels was acquired and systematically evaluated
- A compact, rapid fuel thermal integrity assessment (CRAFTI apparatus) was developed and used to quantify fuel performance. Qualification criteria:
  - Operates at conditions *relevant* to intended application
  - Produces meaningful data quickly using small fuel quantity
  - Performance data collected with adequate repeatability
  - Discriminate between otherwise indistinguishable fuels
  - Results are *traceable* to existing experiments
  - Possesses characteristics of a *standard test method*
- Chemometric analyses applied to multiparametric datasets
  - Improvements in understanding of physicochemical influences and impacts of deposit formation were made
  - Predictive, composition-based models were developed – these models are *adaptable to additional datasets* and *expandable to diversified fuel sets*:
    - Pressure drop, wall temperature, carbon deposit, etc.

Thank You for Your Attention