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AFRL Efforts in RP Thermal Stability Characterization and Improvement

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Agenda

- Introduction/Background
- Motivation
- Experimental Approach
- Experimental Results
- Implications
- Direction for Future Work

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Overview: Advanced Hydrocarbon Activities

Characterize Baseline; Identify Improvement Needs	Improve Baseline Performance (e.g. Thermal Stability)	Develop/Transition New Materials (e.g. Synthetics)
RP-1/RP-2 properties measurement/database *NIST*	**Development of engine design tools** *REFPROP*	**Improved Synthesis Routes** **Scale-up** **Testing** *Thermal Stability* *Hot Fire (EC-1)* **Functional Changes, Scale-up, …**
RP-2 thermal stability testing *RZSA HHFF* *NASA-GRC* *RZPF*	**RP-2 MIL-spec mods** **Model Validation** *CFD++ deposition model*	
Stressed RP-2 hot-fire testing *EC-1* *RZSE 1-14 hot-fire*	**Additives & Formulations** *NIST* *Stanford*	**New Candidate Fuels/ Compositional Changes/**

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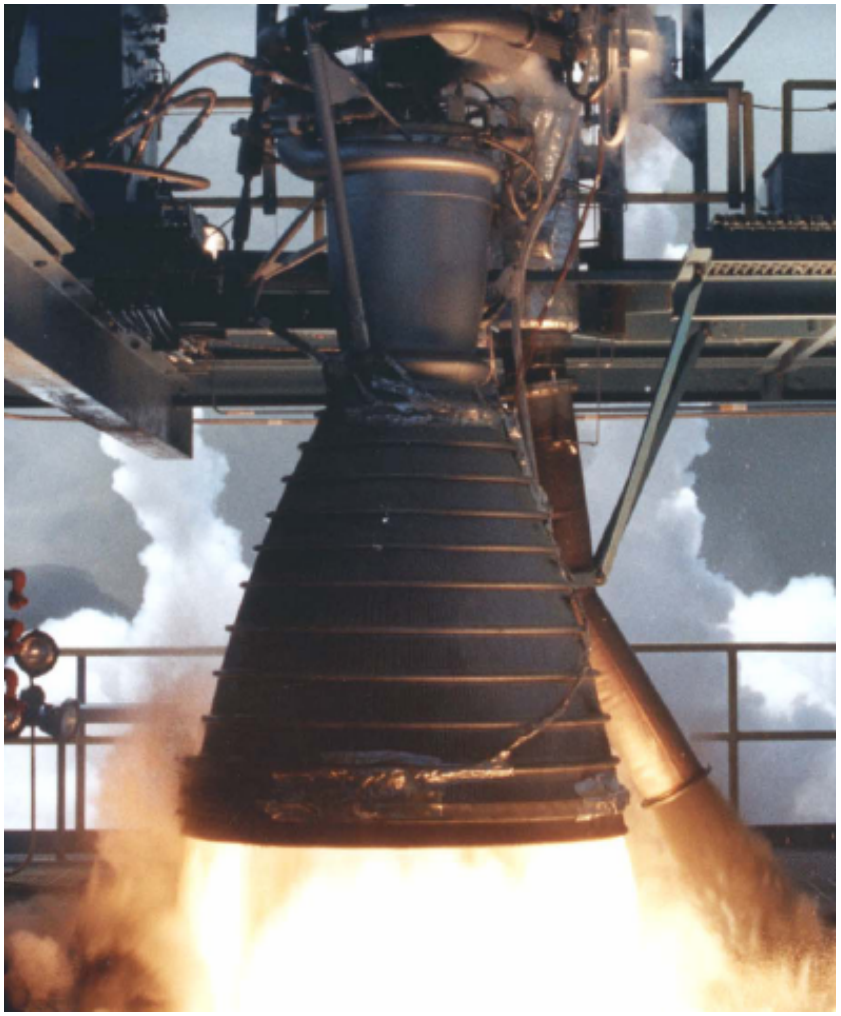
Regeneratively-cooled LREs place tremendous heat load on fuel/coolant

Regen channel environment:

- 3000 psi (270 atm)
- 200 ft/s (60 m/s)
- 900°F Twc (750 K)
- q″: 20-100 Btu/in^{2}s (30-160 MW/m^2)
- Property gradients near critical point
- Variable fuel composition
- Turbulent, developing flow
- Material compatibility
- Reacting flow – thermal/oxidative and pyrolytic decomposition



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Engine-level design criteria drive fuel thermal stability research efforts

Engine-level Goal:	Reusability/ Operability	High Performance (Isp, T/W)	Reduced Risk
Limiting Obstacles:	• Deposit formation • Surface corrosion	• Wall heat flux limit → Pc limit • Regen Pressure Demands (pump) • Film/Transpiration Cooling: "Degen?"	• Complicated Cooling Concepts • Hot Spots Requirements • Structural Limits
Root Problem:	Fuel Thermal Instability		

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Engine-level design criteria drive fuel thermal stability research efforts

Engine-level Goal:	Reusability/ Operability	High Performance (Isp, T/W)	Reduced Risk

Current LRE goals, along with changing cycle (RBCC/TBCC) requirements, present need for better understanding of rocket fuel thermal stability

Root Problem: **Fuel Thermal Instability**

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Questions to answer in considering hydrocarbon thermal stability

System Level:

- How are engine operability/reusability affected?
- Will temperatures remain below structural limits?
- Mission/lifetime impact on cooling system ΔP, etc.?

Engineering/ Design:

- Deposition: pressure drop/heat transfer tradeoff?
- How does thermal stressing affect fuel properties?
- Coking/corrosion interaction under rocket conditions?
- Roles of T, t, v, P, S, etc. on deposition/heat transfer?

Chemical Processes:

- Can insoluble-forming reactions be delayed/avoided?
- Active decomposition mechanisms? Endothermicity?
- Primary deposit growth pathways? Sulfur effects?
- Measurement/modeling of decomposition rates: predict products, deposit growth rate, set res. time

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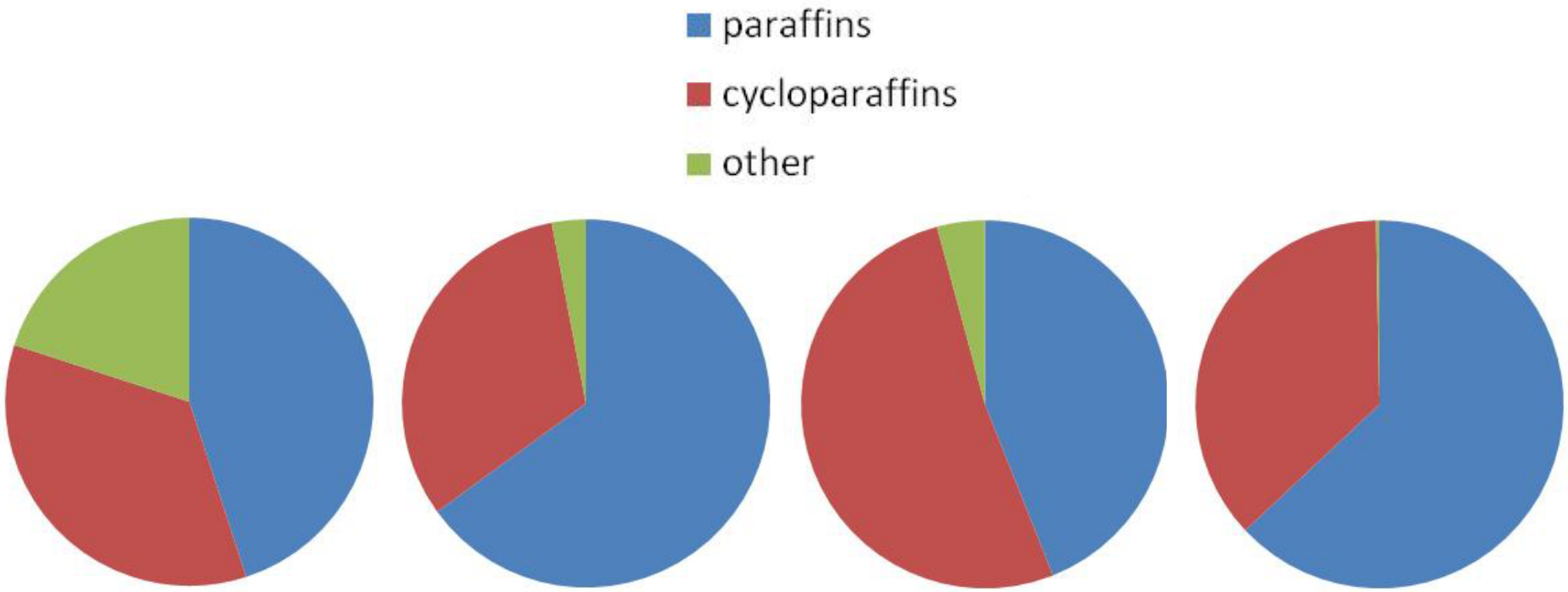
Composition of Various Aviation Fuels



JP-8

- **"other" is aromatics/olefins (18/2 vol%)**
- **500 ppm total sulfur**

JP-7

- **"other" is aromatics**
- **60 ppm total sulfur**

RP-1

- **"other" is aromatics**
- **30 ppm total sulfur (max)**

RP-2

- **"other" is mostly aromatics**
- **0.1 ppm total sulfur (max)**

Different composition means different chemistry

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Experimental indicators of a fuel's performance as an effective coolant

How is thermal performance gauged?

- Measured heat transfer – heat transfer rate, usually non-D
- Coking temperature – measure carbon deposit formed (or rate) and relate this to wall temperature, test duration, etc.
- Visual inspection of cooling channel surfaces – morphology, elemental composition
- Increased pressure drop across test section
- Localized temperature rise indicating thermal resistance
- Visual appearance changes (particulates, color change)
- Compositional changes in bulk fuel (e.g., GC)

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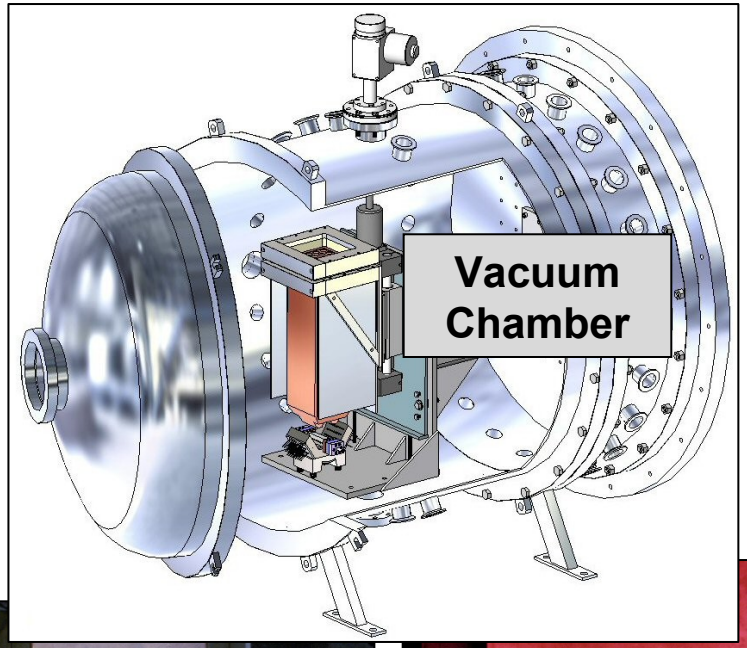
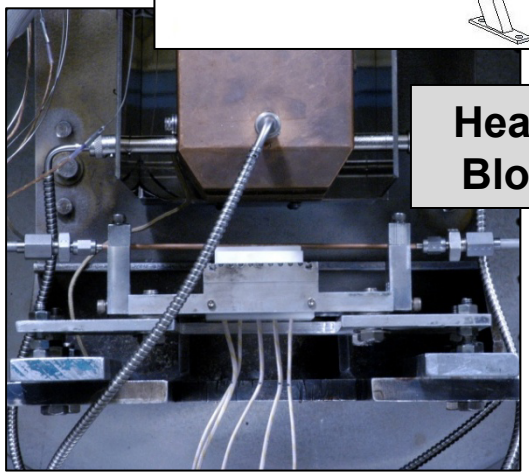
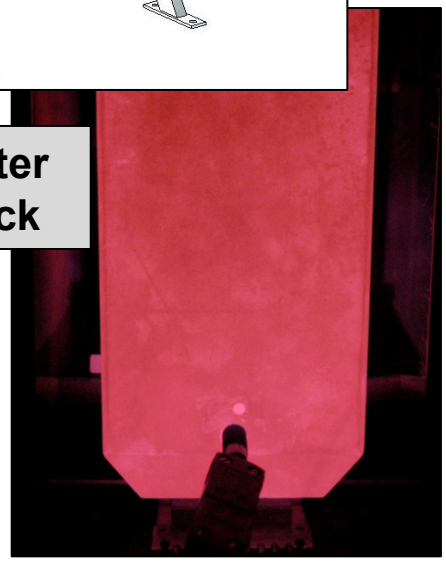
HHFF simulates cooling channel conditions in subscale environment

- 4500 psi (31 MPa) channel pressure
- 400F (480K) bulk T_{in}
- >10 lb_m/min (0.075 kg/s) flow rate
- >1100F (870K) T_{wc}
- 25 PID-controlled heaters maintain block temperature
- O_2 sparging capability
- Vacuum environment
- Long test durations at high heat fluxes
- Complements existing HTFs
- *Flexibility* in test section geometry







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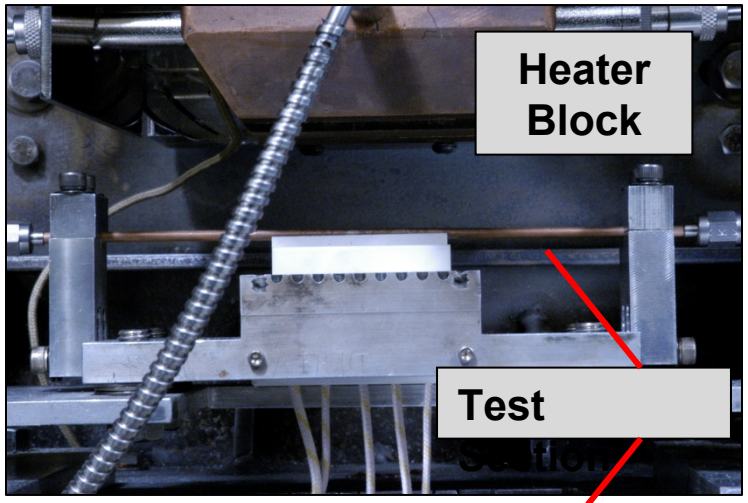
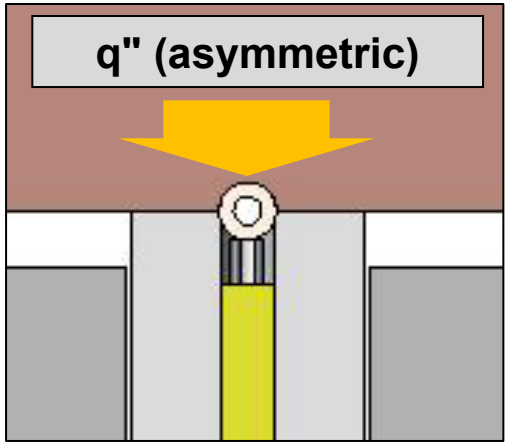
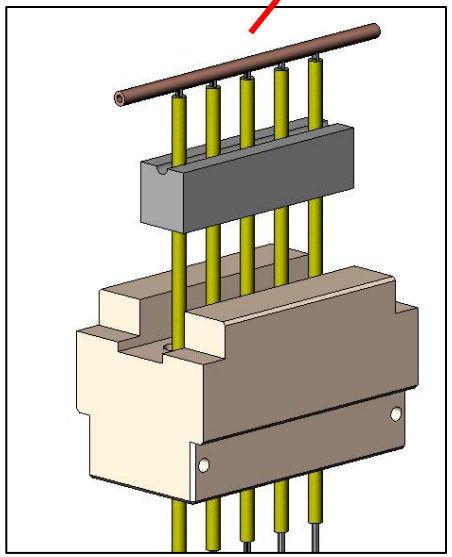
Simplified geometry allows parametric fuel study

- **This work is primarily a fuel study – future efforts to include realistic geometry (D_h, v, AR, alloys)**
- **Inexpensive, readily available, easy to analyze post-test**
- **Also allows facility shakedown**
- **Test section: 1/8-in. (0.32-cm) o.d.; 0.061-in. (0.16-cm) i.d; OFE Cu; 2.5-in. (6.4-cm) heated length**
- **Current test conditions:**
  - 1000 psi (7 MPa) test section
  - 600-1200F (590-920K) T_{wc}
  - 50-80 ft/s (15-24 m/s) V_{ts}
  - 90-320F (300-430K) $T_{m,i}$
  - 15000-70000 Re
  - 2 “types” of tests







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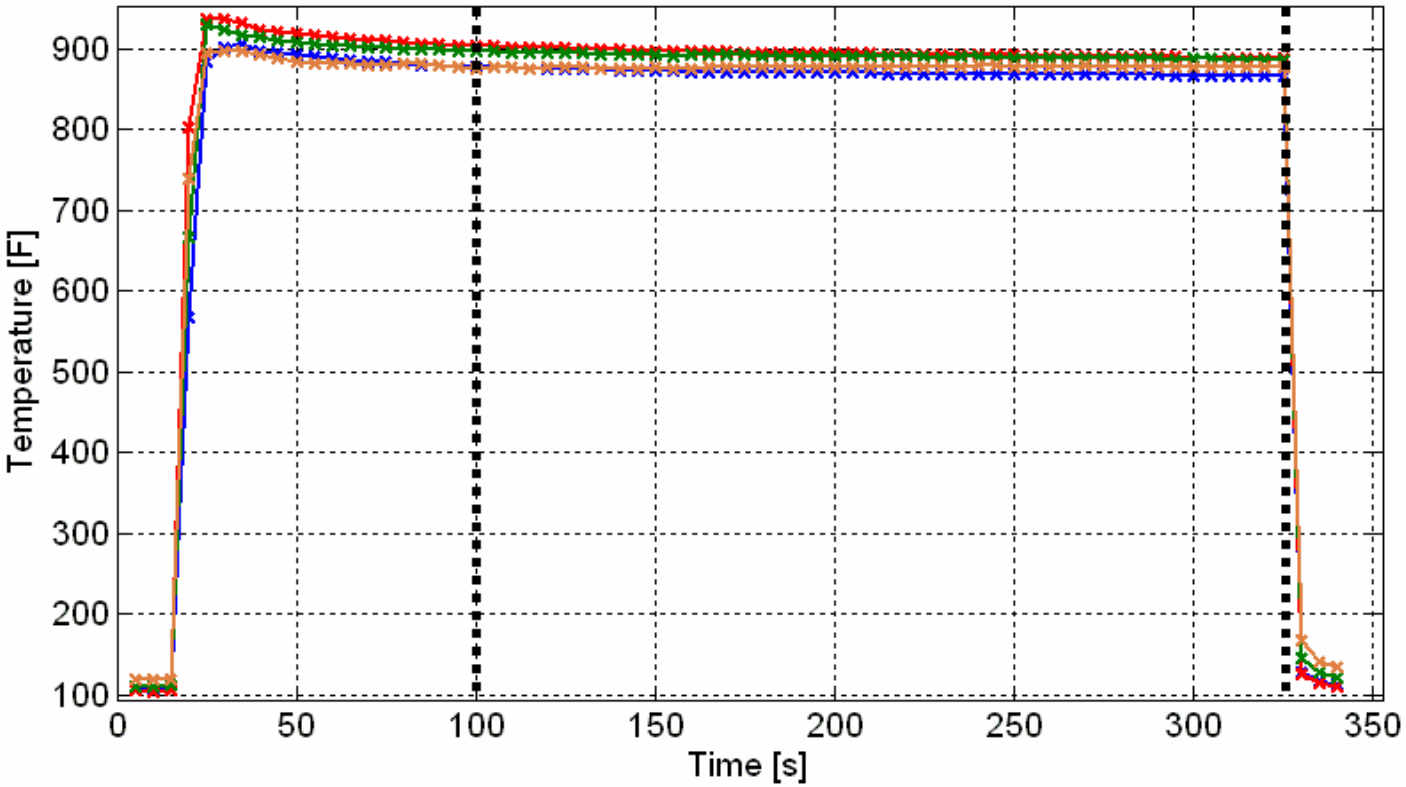
Typical surface temperature trace for short-duration heat transfer test



- **Uniform: All T/Cs within 2% of average wall temperature**
- **Instantaneous: 800F (440K) temperature increase in ~10s (heat-up transient ~3% total run time for *short* duration tests)**
- **High wall temperatures achievable**

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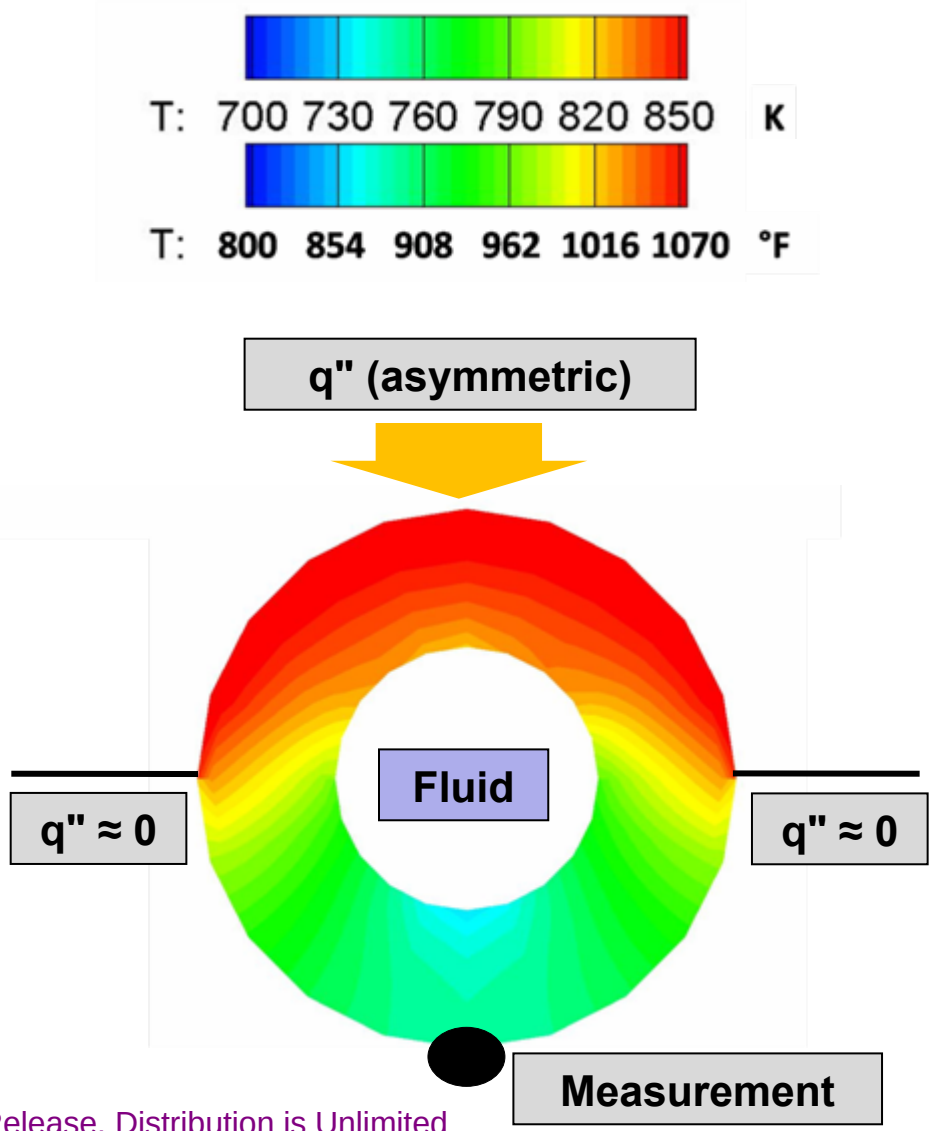
Conjugate heat transfer calculations show circumferential variation

- **Metacomp's CFD++ predicts higher *average* inner wall temperature for given measured outer wall temperature**
- **Characteristic of conduction-heated rig**
- **Small gradient between measurement and lower T_{wc}**
- **Asymmetry simulates real engine environment**
- **Must be noted when reporting temperatures**



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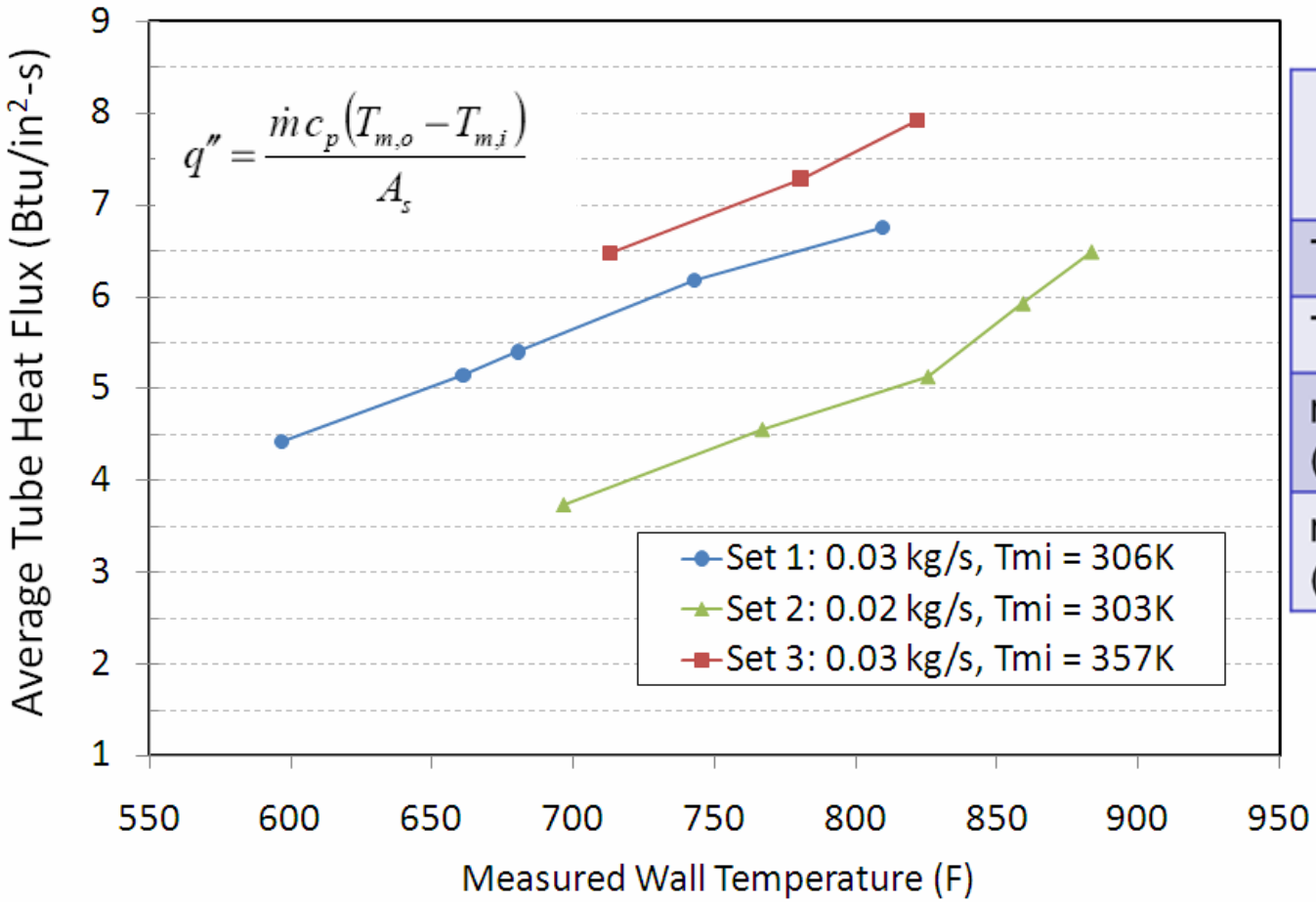
Expected heat transfer trends observed for short duration tests



	Set 1	Set 2	Set 3
$T_{m,i}$ (F)	91	86	183
$T_{m,i}$ (K)	306	303	357
mdot (lbm/hr)	270	180	260
mdot (kg/s)	0.03	0.02	0.03

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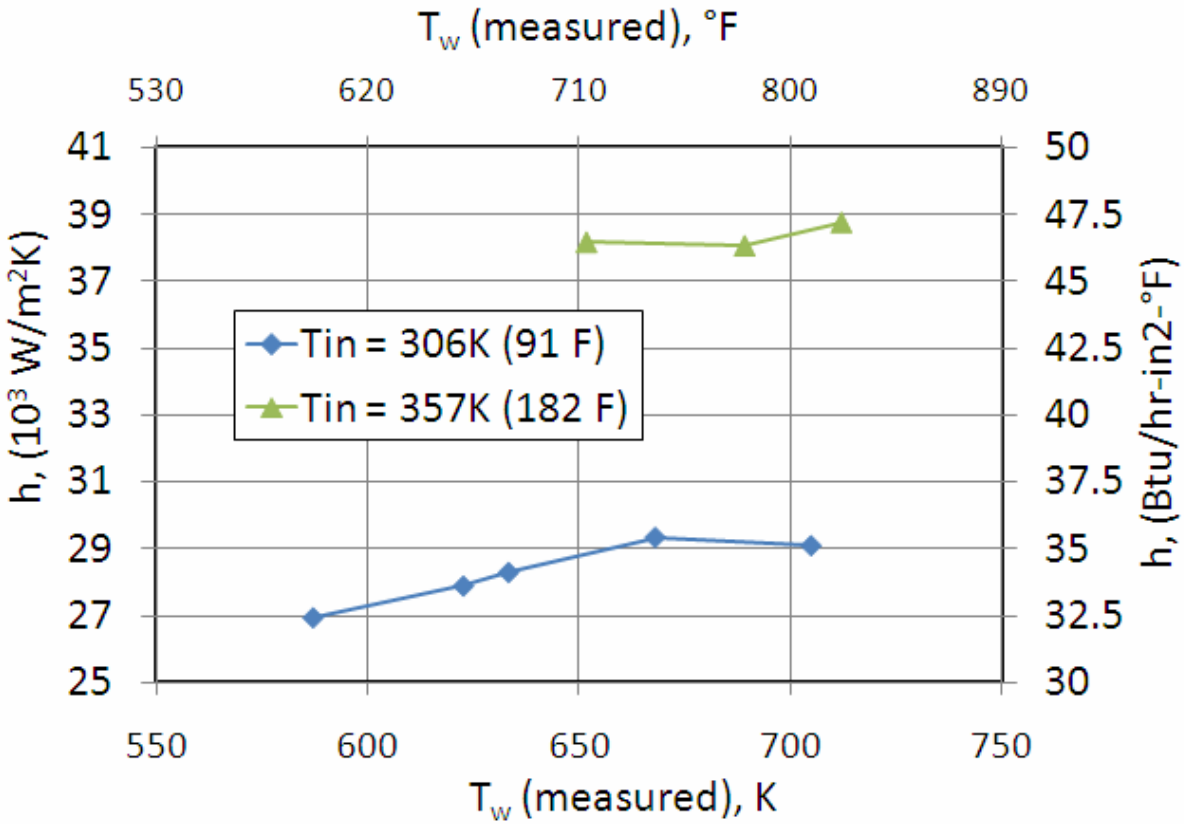
Expected heat transfer trends observed for short duration tests



$$\bar{h} = \frac{\dot{m}c_p}{A_w} ln \frac{T_w - T_{m,i}}{T_w - T_{m,o}}$$

$$\frac{\bar{h}_2}{\bar{h}_1} \propto \left[\frac{Re_2}{Re_1}\right]^c \propto \left[\frac{\mu_1}{\mu_2}\right]^c$$

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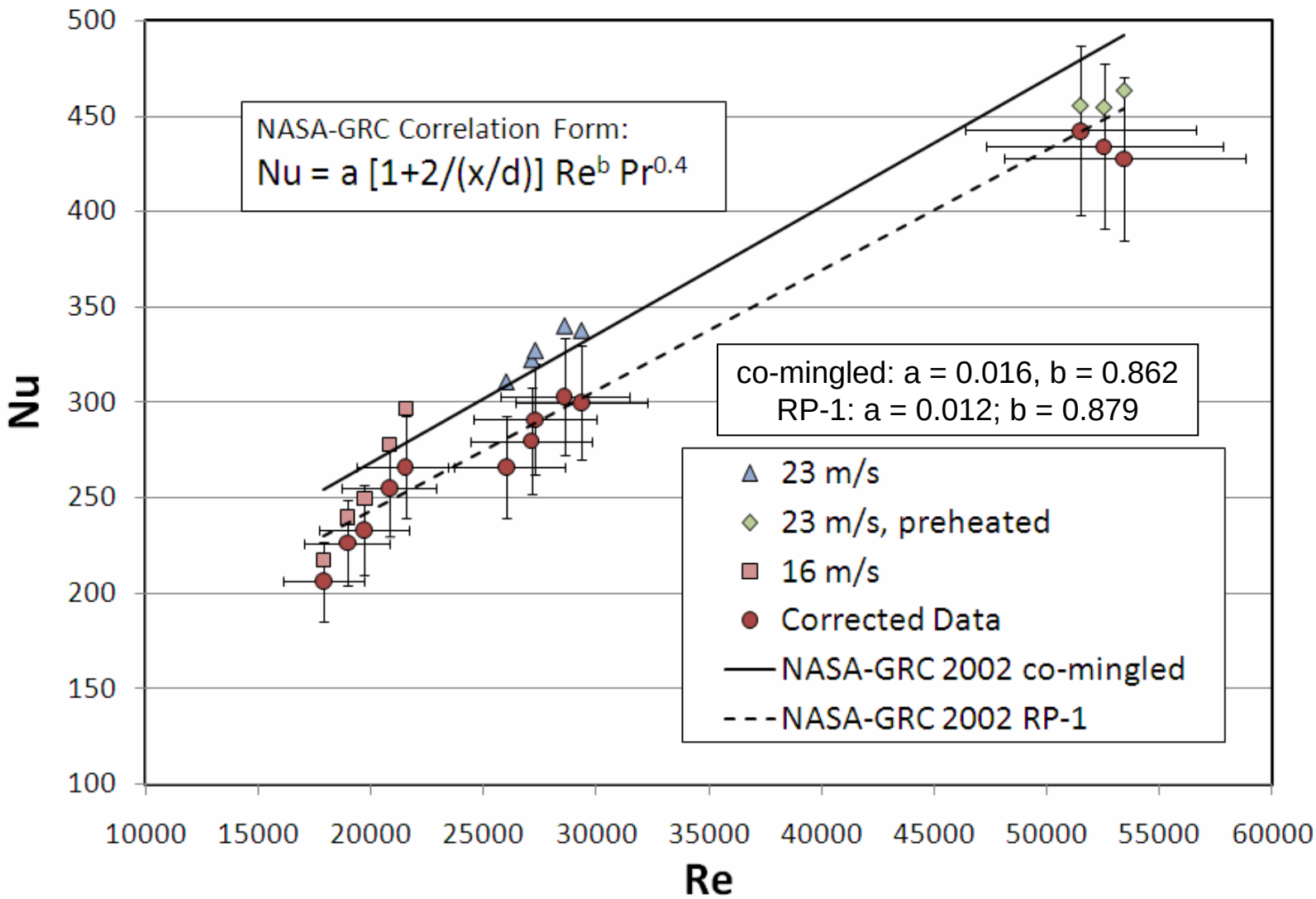
Corrected data correlates well with existing RP-1 heated tube results



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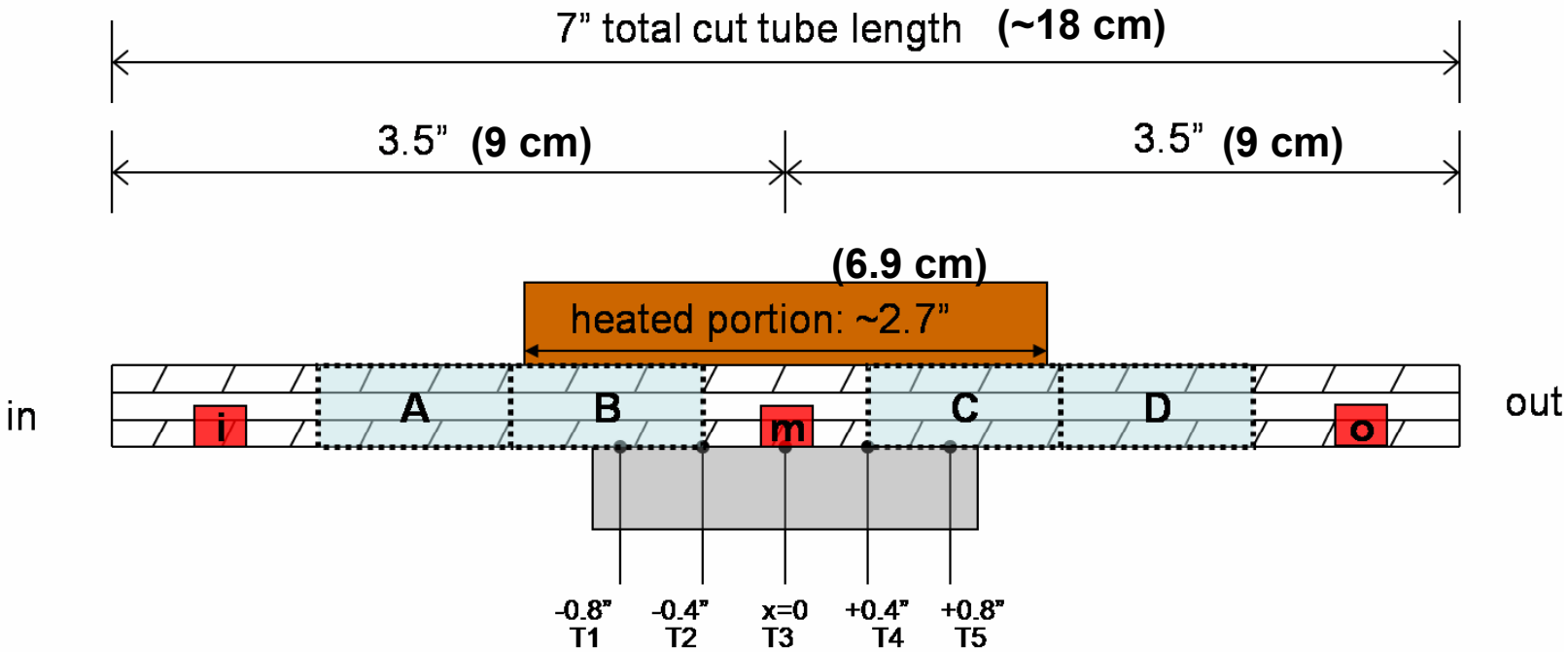
Schematic for post-test segmenting and analysis of test section tubes



mill cut, ~0.2" wide, ~1/16" deep, exposing upper wetted wall of tube for SEM

~1" cut sections for LECO deposition measurements

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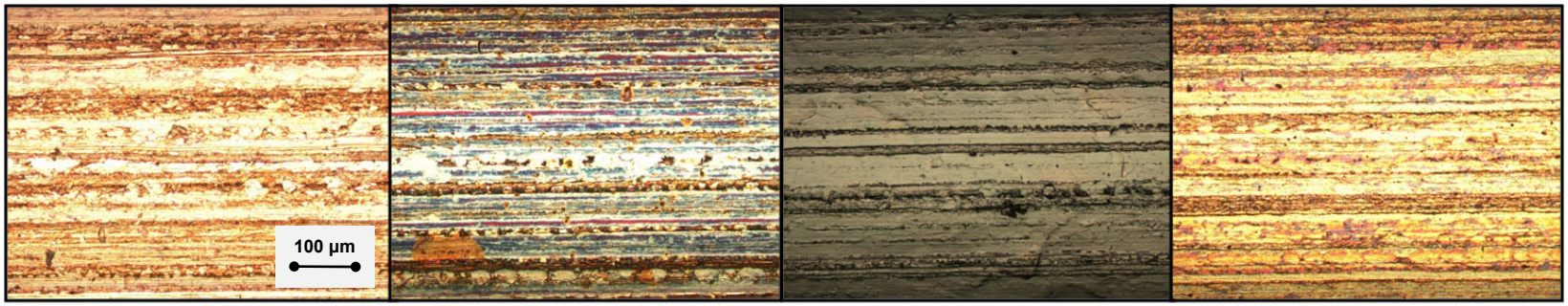
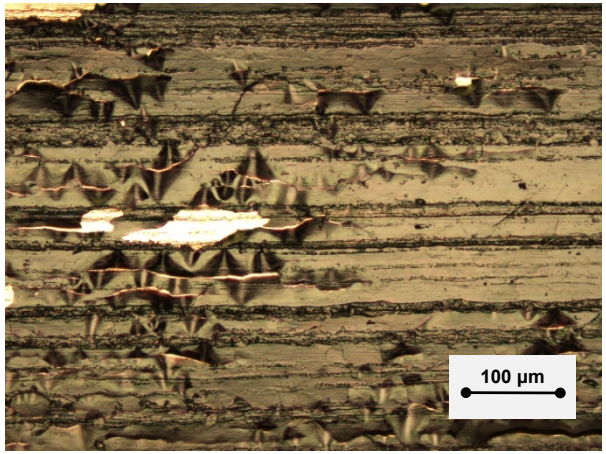
Optical microscope images show coke deposit layer on middle segment

200x



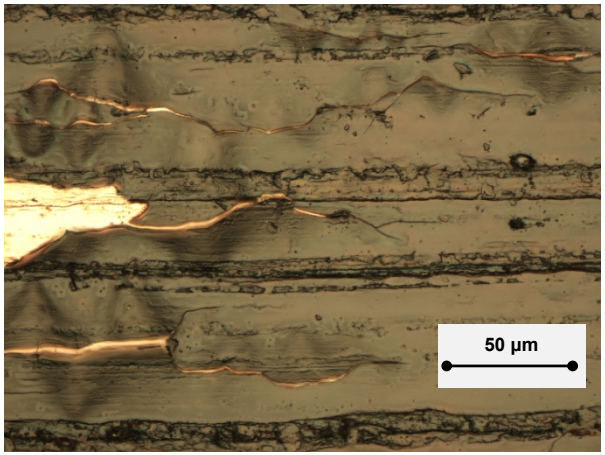
(blank) (inlet) (middle) (outlet)

200x



(middle, slight handling)

500x



(middle, slight handling)

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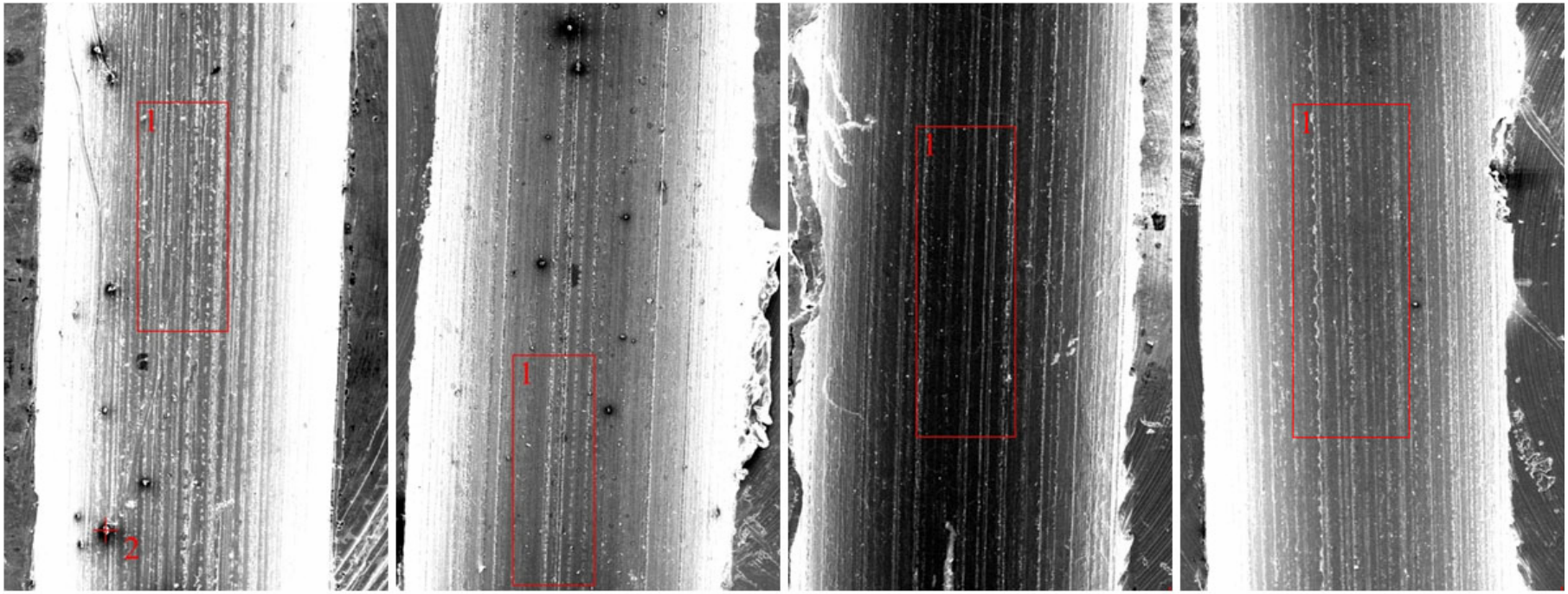
SEM images were taken to examine deposit structure



(blank) (inlet) (middle) (outlet)

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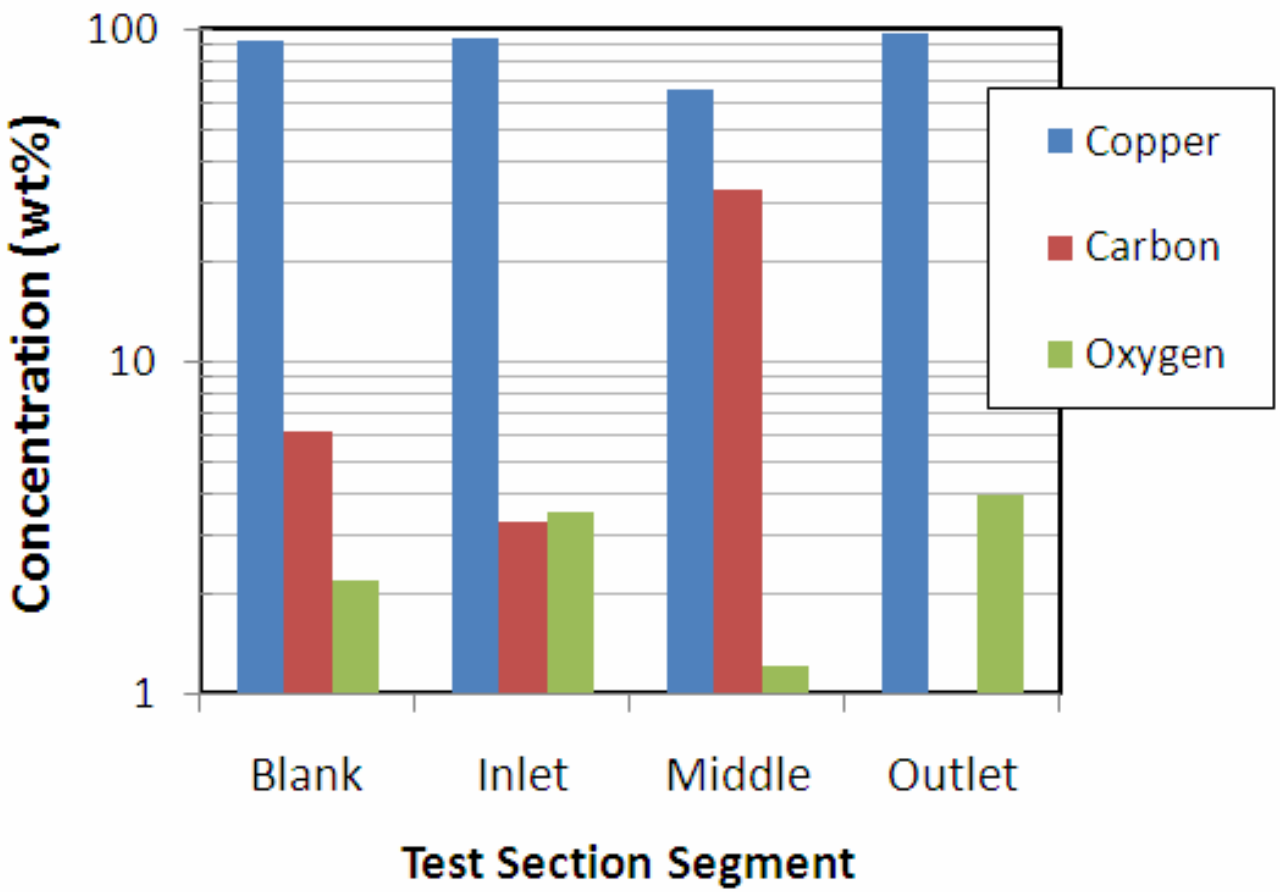
SEM/EDX analysis confirms carbon content of deposit formation



- Axial variation in carbon content
- Presence of oxygen: autoxidation-related deposits?
- Careful sample prep needed to avoid contaminants

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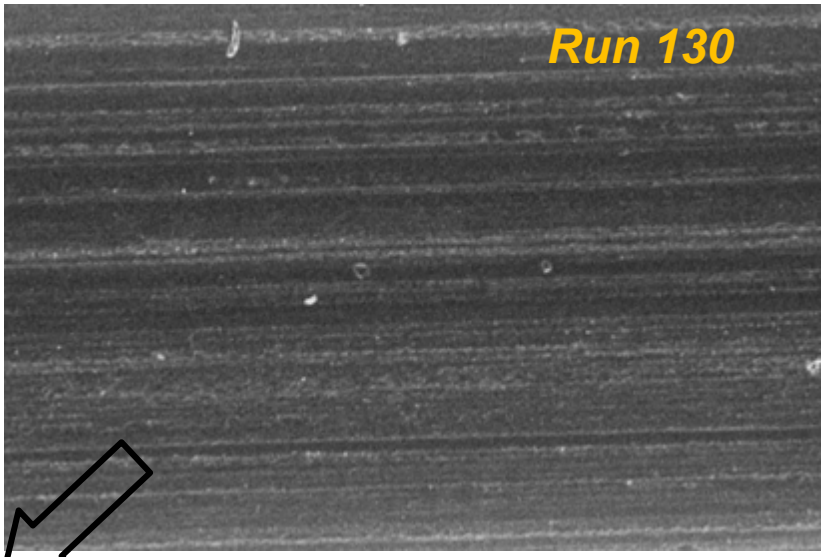
SEM comparison with standard-grade RP-1 thermal stress tests

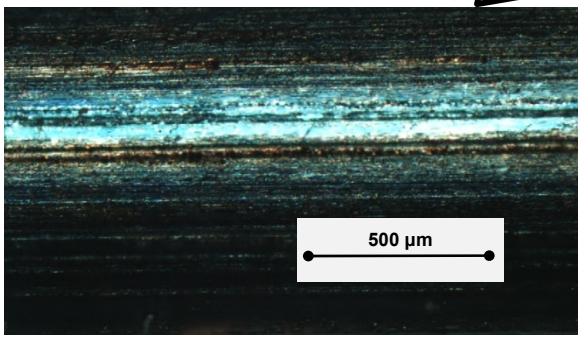
RP-1 (30 ppm total sulfur)

20 min. duration; 750F (670K) T_{wc}; 75 ft/s (23 m/s)

RP-2 (100 ppb total sulfur)

35+ min. duration; >1000F (810K) T_{wc}; 53 ft/s (16 m/s)





- **No obvious deposit shedding**
- **Surface not clean**
- **Very high wall temperature**
- **Different velocity**

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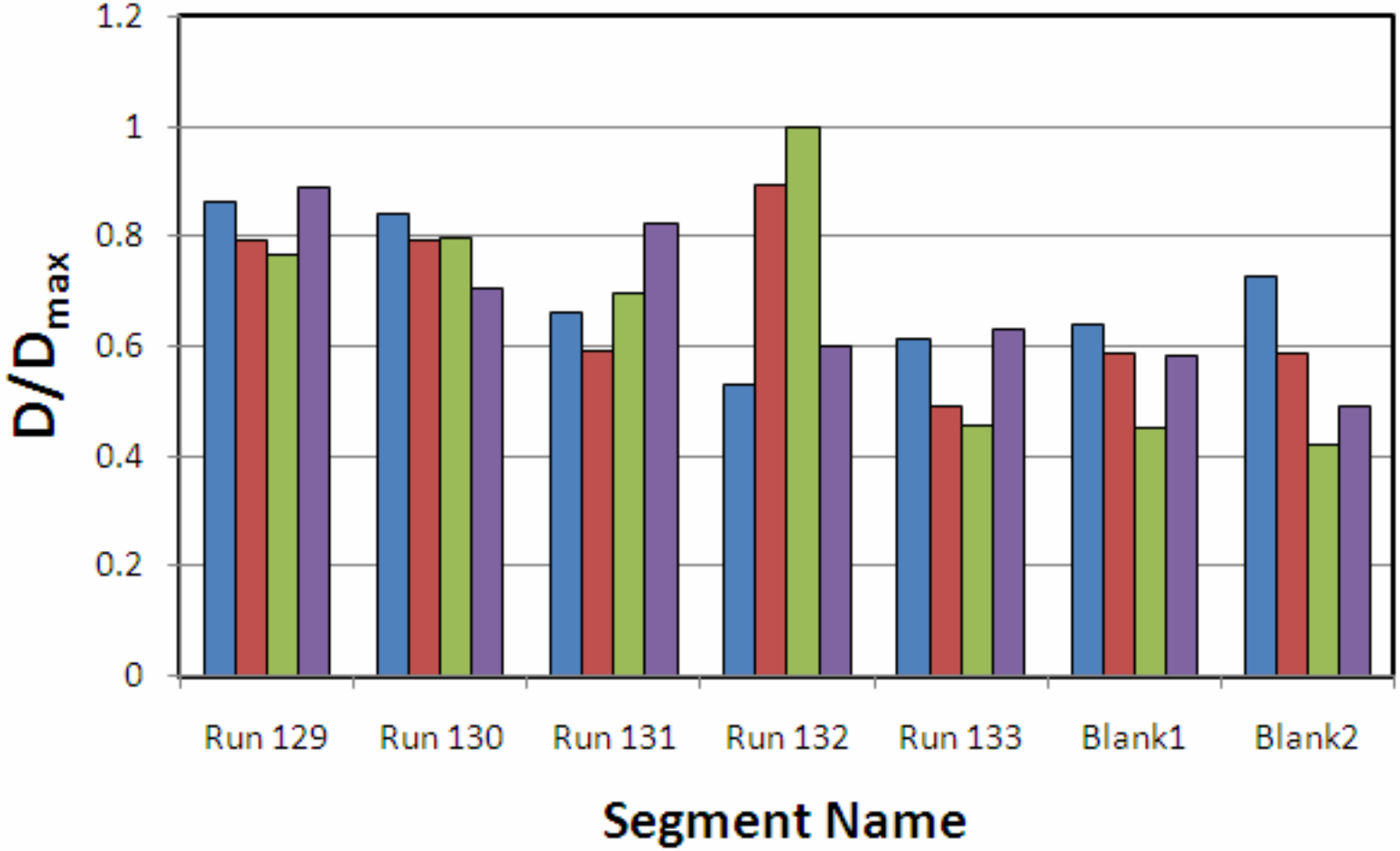
LECO carbon deposition results for individual test segments



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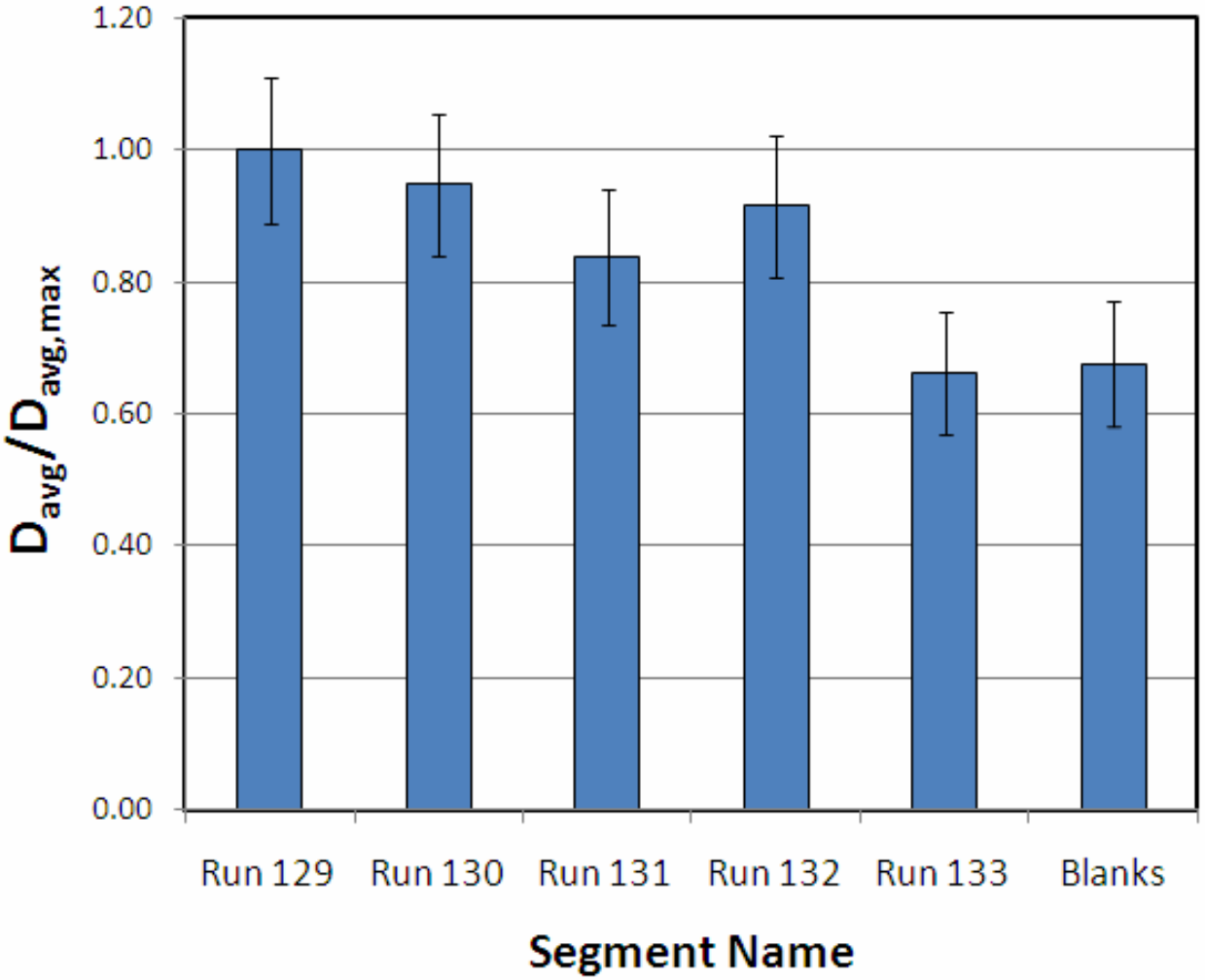
Average LECO carbon deposition results averaged over four segments



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Summary & Conclusions

- The need for understanding and improving hydrocarbon thermal stability is motivated by current LRE engine program goals and future cycle requirements
- A complicated problem with many scientific questions provides wide-ranging opportunities for research
- HTFs can provide valuable insight – AFRL's High Heat Flux Facility is capable – realistic regen conditions approached with RP-2
- Expected trends in heat transfer shown – improved thermophysical property information forthcoming
- Visual and SEM/EDX analysis shows carbon coverage (but also O) – need to look at S content for Cu_xS products
- Carbon deposit formation was measured with a LECO carbon determinator, but *repeated testing* at modified conditions is necessary to make definite conclusions on *coking rates at maximum allowable wall temperature*
- RP-2 appears more thermally stable than RP-1 at similar test conditions…

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Acknowledgments

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- Dr. Simon Lyu (Advatech Pacific)
- Marietta Fernandez and Wesley Alleman (AFRL/RZSM)
- Dave Brooks (AFRL/RZPF)

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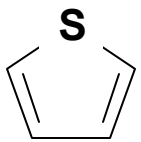
Backup Slides

All Sulfur is Not Created Equal

- Three major types of sulfur in distillate fuels
  - Thiols (mercaptans): -C-SH (<50 ppm in RP-1 spec)
  - Sulfides/Disulfides: -C-S-C- , -C-S-S-C-
  - Thiophenes:



- Recent JP-8 analyses indicate sulfur is roughly evenly divided between sulfides and thiophenes (few thiols)
- Data indicates that mercaptans are the ringleaders, sulfides are accomplices, and thiophenes are bystanders in deposition
- Experience indicates that most sulfur in RP-1 is thiophene, and very hard to measure

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MIL-DTL-25576E reflects necessity for lower sulfur content

Property	Limits		ASTM Test Method
	RP-1	RP-2	
Distillation			D86
Initial Boiling Point, °F	\1	\1	
Fuel Evaporated, 10%, °F	365-410	365-410	
Fuel Evaporated, 50%, °F	\1	\1	
Fuel Evaporated, 90%, °F	\1	\1	
End Point, °F	525 max	525 max	
Residue, % Vol	1.5 max	1.5 max	
Distillation Loss % Vol	1.5 max	1.5 max	
Specific Gravity, 60/60°F	0.799 – 0.815	0.799 – 0.815	D 1298\2
Existent Gum, mg/100mL	1 max	1 max	D 381
Sulfur, Total, mg/Kg	30 max	0.1 max	D 5623\3
Mercaptan-sulfur, mg/Kg	3 max	\4	D 3227
Freezing Point, °F	- 60 max	- 60 max	D 2386

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MIL-DTL-25576E, Cont.

Thermal Value: Net Heat of Combustion, BTU/lb	18500 min	18500 min	D 240
Viscosity at - 30°F, cSt	16.5 max	16.5 max	D 445
Aromatics, % Vol	5.0 max	5.0 max	D 1319
Olefins, % Vol	2.0 max	1.0 max	D 1319
Hydrogen Content, % mass	13.8 min	13.8 min	D 3343
Copper Strip Corrosion	1 max	1 max	D 130\5
Water Reaction Interface	\6	\6	D 1094
Flash Point, °F	140 min	140 min	D 93
Thermal Stability (JFTOT)			D 3241\7
JFTOT, change in pressure drop (ΔP) in 5 hours, mm Hg	\4	\1	
JFTOT, delta TDR Spun	\4	\1	
Particulate, mg/L	1.0 max	1.0 max	D 5452

NOTE:

\1 – Report only
\2 – ASTM D 4052 may be used. In case of a dispute, ASTM D 1298 shall be the referee.
\3 – ASTM D 4045 may be used for RP-2 grade. ASTM D 5453 may be used for RP-1 grade. In case of a dispute, ASTM D 5623 shall be the referee.
\4 – Not required
\5 – Follow the procedures specific to kerosene.
\6– See 3.2.1 for requirements and 4.3.2.1 for exceptions to ASTM D 1094.
\7 – For specific test conditions see 4.3.2.2.

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RP-1 Composition (WPAFB)

- GC-FIMS analysis not in total agreement with other methods, but gives overview of composition

	Isoparaffins	n-Paraffins	1-ring cycloparaffins	2-ring cycloparaffins	3-ring cycloparaffins	Alkylbenzenes	Benzo-cycloalkanes	Benzo-dicycloalkanes	Naphthalenes
c7	0.000	0.000	0.004	0.000	0.000	0.021	0.000	0.000	0.000
c8	0.000	0.011	0.030	0.002	0.002	0.350	0.000	0.000	0.000
c9	0.044	0.063	0.697	0.135	0.013	1.149	0.009	0.000	0.000
c10	0.590	0.244	4.154	2.372	0.113	1.848	0.132	0.000	0.003
c11	4.810	0.817	11.525	7.590	0.607	1.807	0.372	0.005	0.327
c12	8.058	0.687	10.637	6.514	1.167	1.205	0.496	0.014	0.041
c13	7.902	0.052	5.855	3.427	1.117	0.372	0.180	0.006	0.011
c14	4.465	0.136	2.580	1.585	0.608	0.048	0.018	0.000	0.000
c15	1.099	0.039	0.736	0.651	0.150	0.005	0.003	0.000	0.000
c16	0.158	0.016	0.056	0.041	0.002	0.000	0.000	0.000	0.000
sum	27.127	2.064	36.274	22.316	3.778	6.806	1.210	0.025	0.384

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RP-1/RP-2 Comparison (ASTM D2425)

	RP-1/5235	RP-2/5433
Summarized D2425 (vol%)		
Paraffins	44	63
Cycloparaffins	33	18
Dicycloparaffins	16	14
Tricycloparaffins	2.8	4.7
Alkylbenzenes	<0.5	<0.5
Indan and Tetralins	<0.5	<0.5
Indenes CnH2n-10	<0.5	<0.5
Naphthalene	<0.5	<0.5
Acenaphthenes	<0.5	<0.5
Acenaphthylenes	<0.5	<0.5
Tricyclic Aromatics	<0.5	<0.5
Total	100	100

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RP-1/RP-2 Aromatic Comparison (ASTM D6379)

	RP-1/5235	RP-2/5433
Monoaromatics (vol%)	<0.2	0.2
Diaromatics (vol%)	<0.2	<0.2
Total Aromatics (vol%)	<0.2	0.2
Total Saturates (vol%)	>99.8	99.8

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RP-2 Composition (NIST 2008, GC-MS)

peak #	R. T. (min)	% of total	name	CAS	% match	confidence
1	5.528	1.388%	2,6-dimethyl nonane	17302-28-2	27.4	M/H
2	5.855	1.018%	3,7-dimethyl nonane	17302-32-8	18.1	M
3	6.279	2.846%	trans-decalin	493-02-7	15.2	H
4	6.37	1.886%	2-methyl decane	6975-98-0	31.5	H
5	7.425	1.705%	2-methyl decalin	n/a	29.7	H
6	7.48	1.463%	2,6-dimethyl decane	13150-81-7	22.7	M
7	7.771	1.822%	1-methyl decalin	2958-75-0	23.3	H
8	7.892	1.108%	pentylcyclohexane	4292-92-6	45.6	H
9	8.292	2.196%	5-methyl undecane	1632-70-8	11.4	M/H
10	8.389	1.487%	4-methyl undecane	2980-69-0	35.2	H
11	8.48	2.104%	2-methyl undecane	7045-71-8	28.6	H
12	8.62	2.396%	3-methyl undecane	1002-43-3	18.3	H
13	9.087	1.283%	1-methyl 2-pentyl cyclohexane	54411-01-7	8.0	M
14	9.25	2.480%	cannot identify			
15	9.547	2.285%	x,y-dimethyl undecane			
16	9.857	1.015%	2-ethyl decalin	66660-42-2	21.6	H
17	10.087	1.086%	hexylcyclohexane	4292-75-5	23.9	H
18	10.384	1.408%	x,y-dimethyl undecane			
19	10.481	1.103%	4-methyl dodecane	6117-97-1	38.1	H
20	10.584	2.307%	2-methyl dodecane	1560-97-0	13.6	H
21	10.718	1.128%	3-methyl dodecane	17312-57-1	24.4	H
22	10.772	2.332%	4,6-dimethyl dodecane	61141-72-8	6.7	M
23	11.688	1.328%	6-methyl tridecane	13287-21-3	9.6	M
24	12.009	0.995%	3-methyl tridecane	6418-41-3	23.3	M/H
25	12.221	1.231%	heptylcyclohexane	5617-41-4	37.6	H
26	12.506	1.172%	4-methyl tridecane	26730-12-1	29.3	M/H
27	12.603	1.571%	2-methyl tridecane	1560-96-9	15.2	M/H
28	12.737	1.092%	3-methyl tridecane	6418-41-3	27.3	M/H
29	12.864	2.104%	2,6,10-trimethyl dodecane	3891-98-3	25.2	H
30	14.501	1.087%	hexadecane	544-76-3	6.0	M/H

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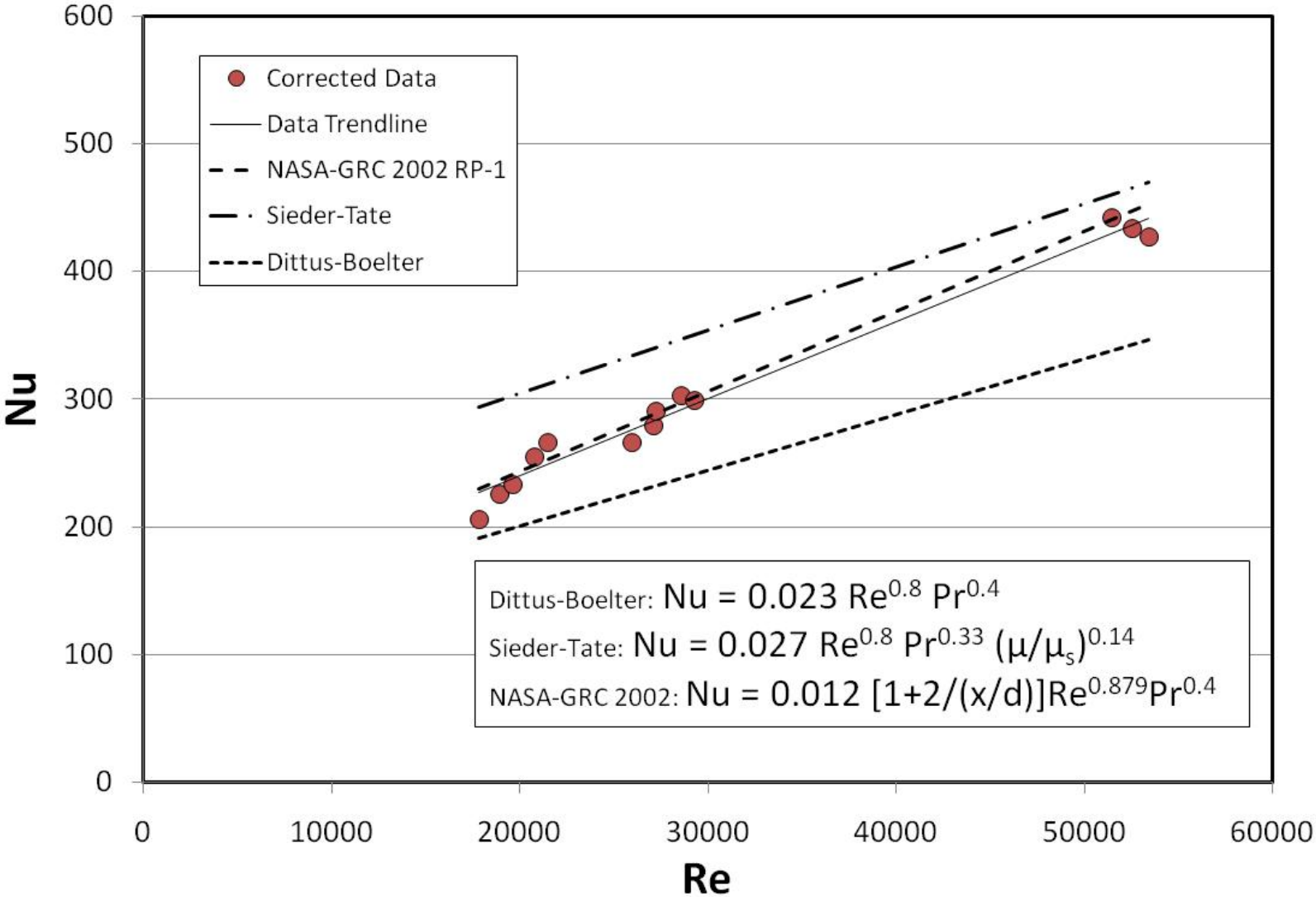
Realistic Heat Transfer Correlations are Important to Engine Design



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