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Department of Mechanical and Nuclear Engineering,
and The Propulsion Engineering Research Center

A Study on TSI as a Property Target for Sooting of Jet Fuel Surrogates

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Presentation Outline

- Compare sooting tendencies of pure hydrocarbons through a unified and consistent Threshold Soot Index (TSI).
- Verify functional relationships for predicting TSI's of binary component mixtures.
- TSI studies of surrogate mixtures using surrogate formulation criteria.
- Comparisons with JP-8 using Nonpar13/toluene mixtures
- Fundamental studies of TSI using a wick burner

Smoke point measurement is the basis for the TSI.

Soot Threshold or Smoke Point = maximum height or fuel flow of a smoke free laminar diffusion flame

Calcote and Manos, C&F, (1983) were the first to combine all literature data on smoke point of pure hydrocarbons into a consistent scale from 0-100:

$$TSI = a\left(\frac{MW}{SP}\right) + b \qquad TSI = a\left(\frac{MW}{\dot{m}}\right) + b$$

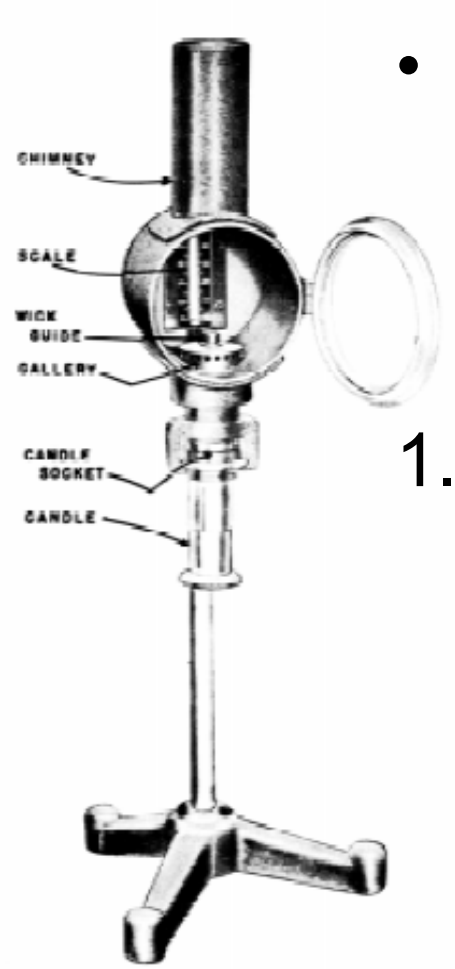
SP = smoke point height

$\dot{m}$ = smoke point mass flow rate

MW = molecular weight

a & *b* = constants dependent on the experiment.

Determination of TSI Values



- We followed the procedure for scaling multiple sets of soot threshold data, outlined by Calcote & Manos (1983).

1. Measured *SP*, to the nearest mm, of 13 pure hydrocarbons in a laminar diffusion flame according to: <u>ASTM D1322, Standard Test Method for Smoke Point of Kerosene and Aviation Turbine Fuel.</u>

Determination of TSI Values

2. Found the constants, a & b, for all TSI's measured at Penn State by assigning the TSI values for the endpoints:

$$TSI_{\text{1-methylnaphthalene}} = 100 = a\left(\frac{142.2\,g/mol}{5.5mm}\right) + b$$

$$TSI_{\text{methylcyclohexane}} = 5 = a\left(\frac{98.19\,g/mol}{40.8mm}\right) + b$$

– Penn State apparatus constants: a = 4.07 mm*(g/mol)$^{-1}$; b = -4.8

Smoke Points and TSI Values

Compound	Formula	MW (g/mol)	SP (mm)	TSI	Uncertainty
cyclohexylbenzene	$C_{12}H_{16}$	160.26	8.9	**69**	**±7%**
1-methylnaphthalene	$C_{11}H_{10}$	142.20	5.5	**100**	**±10%**
decalin	$C_{10}H_{18}$	138.26	22.7	**20**	**±5%**
tetralin	$C_{10}H_{12}$	132.21	7.1	**71**	**±8%**
1,2-dihydronaphthalene	$C_{10}H_{10}$	130.19	5.8	**87**	**±10%**
1,2,4-trimethylbenzene	C_9H_{12}	120.20	7.2	**63**	**±8%**
1,3,5-trimethylbenzene	C_9H_{12}	120.20	7.3	**62**	**±8%**
n-propylbenzene	C_9H_{12}	120.20	8.5	**53**	**±7%**
iso-octane	C_8H_{18}	114.23	40.0	**6.8**	**±10%**
m-xylene	C_8H_{10}	106.17	7.8	**51**	**±8%**
methylcyclohexane	C_7H_{14}	98.19	40.8	**5.0**	**±10%**
toluene	C_7H_8	92.14	8.4	**40**	**±8%**
benzene	C_6H_6	78.12	9.1	**31**	**±8%**

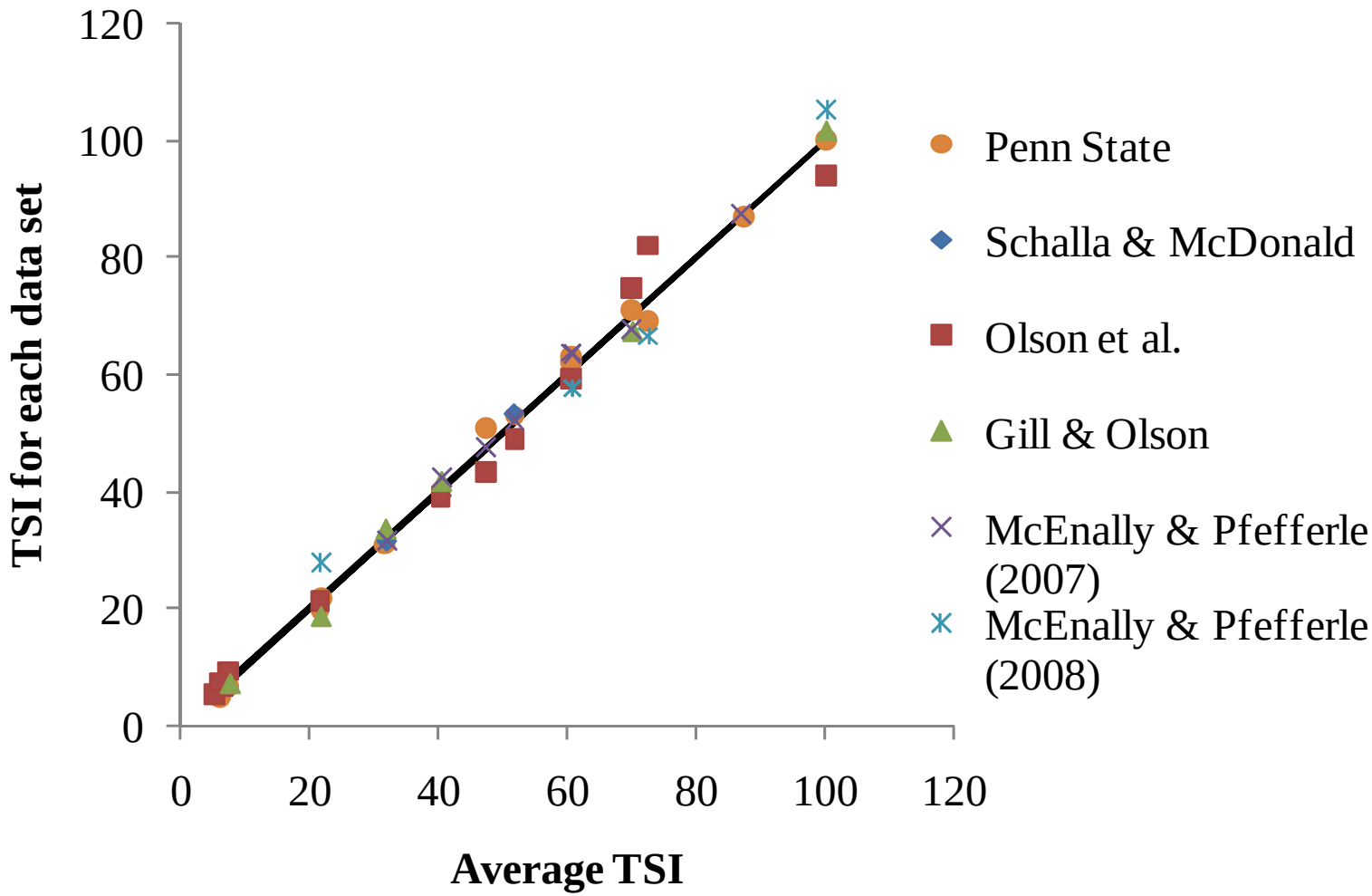
Incorporating YSI Values

- McEnally & Pfefferle, C&F (2007) and Comb. Symp. (2008), offered an alternative to the TSI, the **Yield Soot Index (YSI)**, which could measure the sooting tendency of aromatics with more precision than the smoke point method.

$$\mathbf{YSI} = \boldsymbol{a}\,(\boldsymbol{f}_{\boldsymbol{v,max}}) + \boldsymbol{b}$$

  - $\boldsymbol{f}_{\boldsymbol{v,max}}$ is the maximum soot volume fraction measured in a co-flow methane diffusion flame doped with the hydrocarbon being tested.
  - Reported a total uncertainty of ±3-10%.

$$\text{Overall standard deviation} = \left[\frac{\sum_{i=1}^{n} \left(TSI_i - TSI_{ave} \right)^2}{(n-1)} \right]^{1/2} = 2.6$$



Binary Mixtures

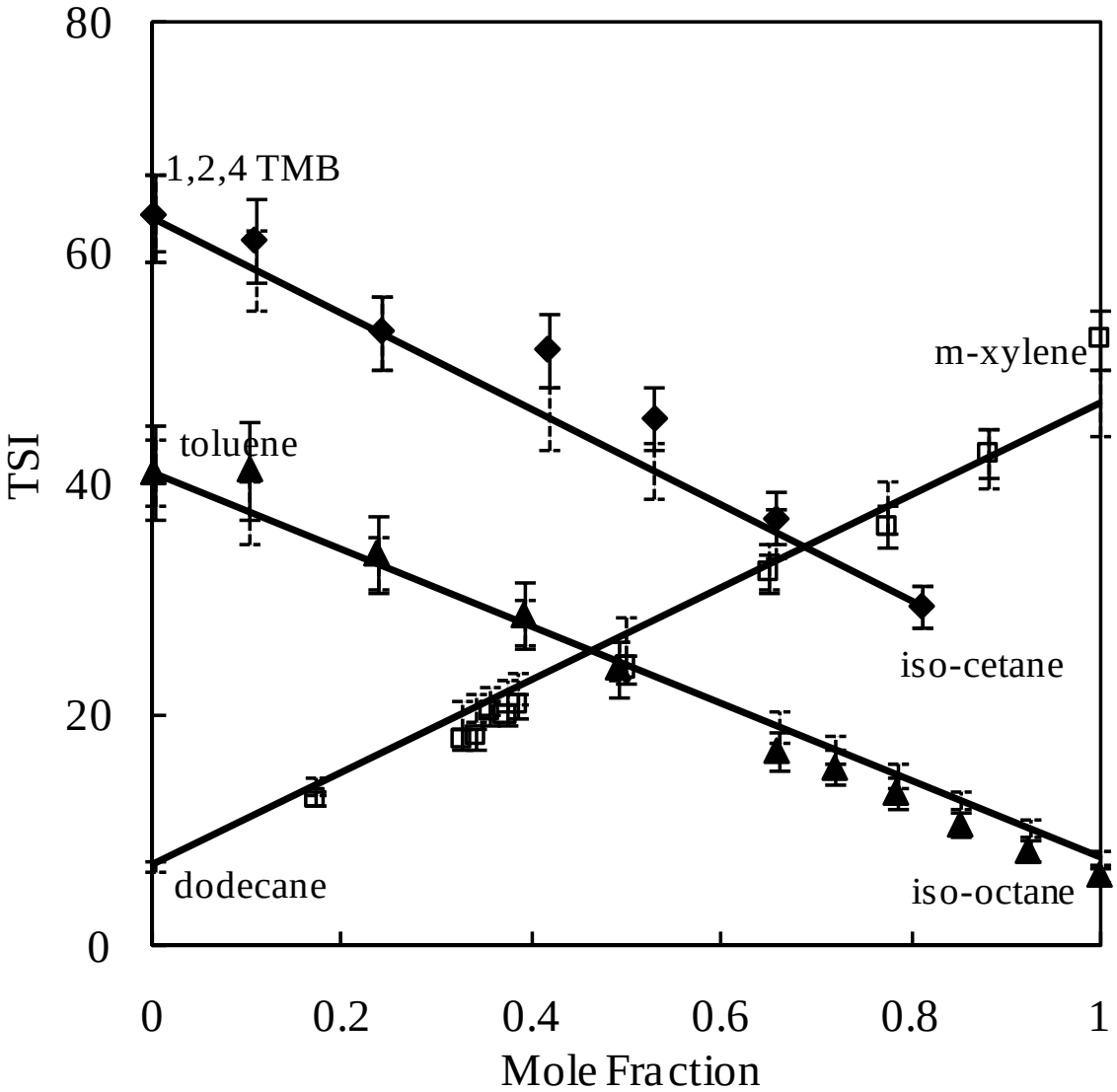
- Binary mixtures were tested to see if they followed the mixture rule proposed by Gill and Olson, CST, (1984).

$$TSI_{mix} = \Sigma(x_i TSI_i)$$

  - x_i is the component mole fraction

- 20mL samples were mixed by measuring volumes with pipettes (resolution 0.1mL)
- Volume fractions of components were also verified by measuring component masses with a balance (resolution 1mg).
- For all cases, mole fraction accuracy was 1%.
- Mixtures were let stand for at least 4 hours before smoke point measurements.

Results from binary mixtures followed the linear mixture rule.

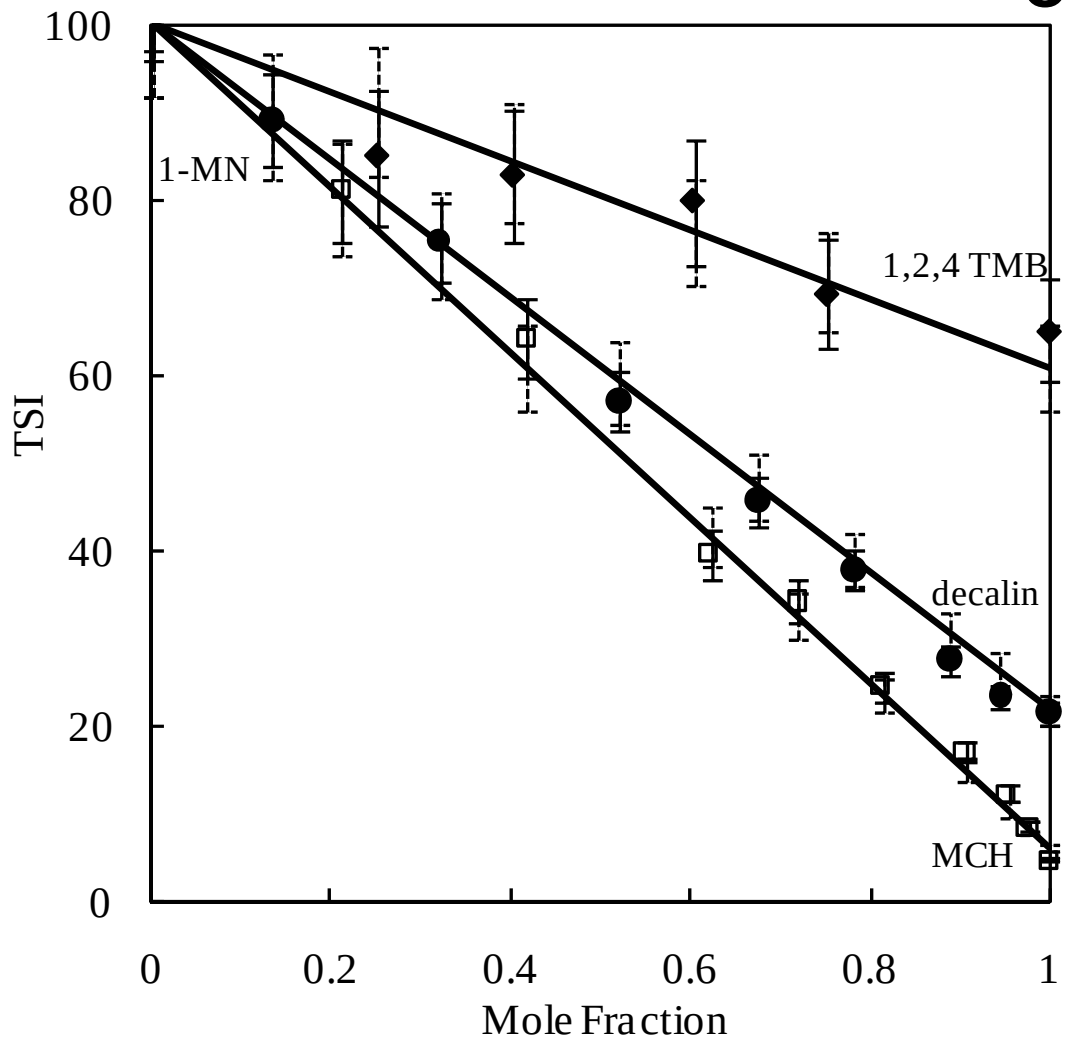


Uncertainties ranged from 6-10%

TSI of iso-cetane was calculated to be 22.

GC Analysis of mixtures before and after test showed no change in mixture composition.

Three binary mixtures were tested to verify the TSI of 1-methylnaphthalene.



TSI's calculated from mixtures: 96, 101, 103

Surrogate Mixture Results (with iso-cetane)

- 1-Methylnaphthalene does not currently have a verified chemical kinetic model.
- We showed that it is possible to achieve the same TSI with 1,3,5-trimethylbenzene instead (3A and 3B).

Surrogate	Molar Composition	MW (g/mol)	H/C ratio	SP (mm)	Measured TSI =4.07*(MW/SP) – 4.8	Predicted TSI = $\Sigma(x_i\ TSI_i)$
3A	52% iso-cetane 23% n-dodecane 25% 1,3,5-trimethylbenzene	186.8	1.998	22.5	**29.0**	**28**
3B	64% iso-cetane 23% n-dodecane 13% 1-methylnaphthalene	202.5	2.011	24.2	**29.3**	**29**

JP-8 TSI

	MW (g/mol)	SP (mm)	Measured TSI = 4.07*(MW/SP) – 4.8
JP-8	153.3*	22.8	22.6
JP-8	153.3	22.2	23.3
JP-8	153.3	23.8	21.4
JP-8 average	**153.3**	**23.0**	**22**

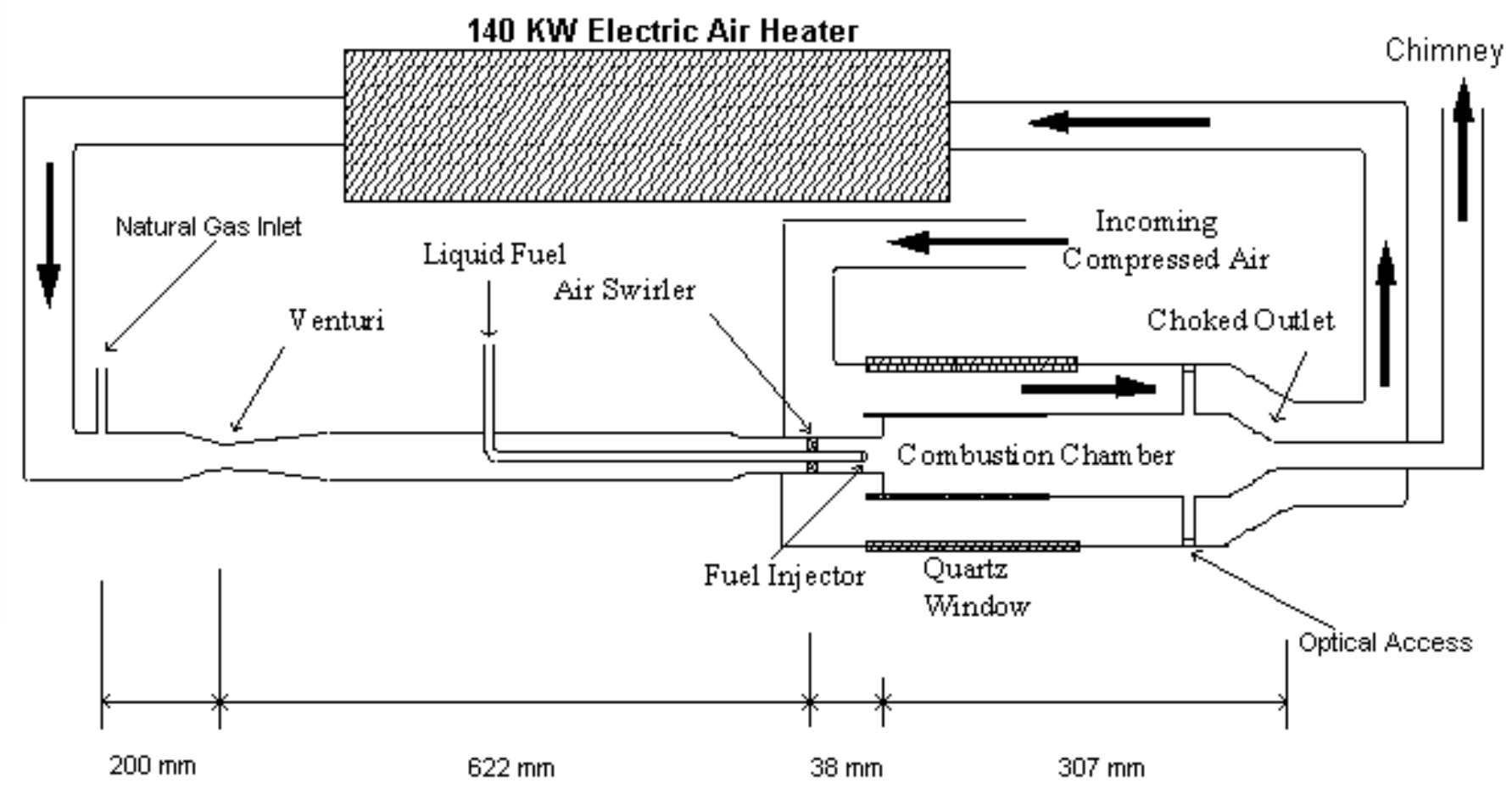
*MW of JP-8 estimated from $C_{11}H_{21}$ (H/C ratio = 1.909)

This surrogate mixture with iso-octane more closely matches the TSI of JP-8, but *MW* is much lower.

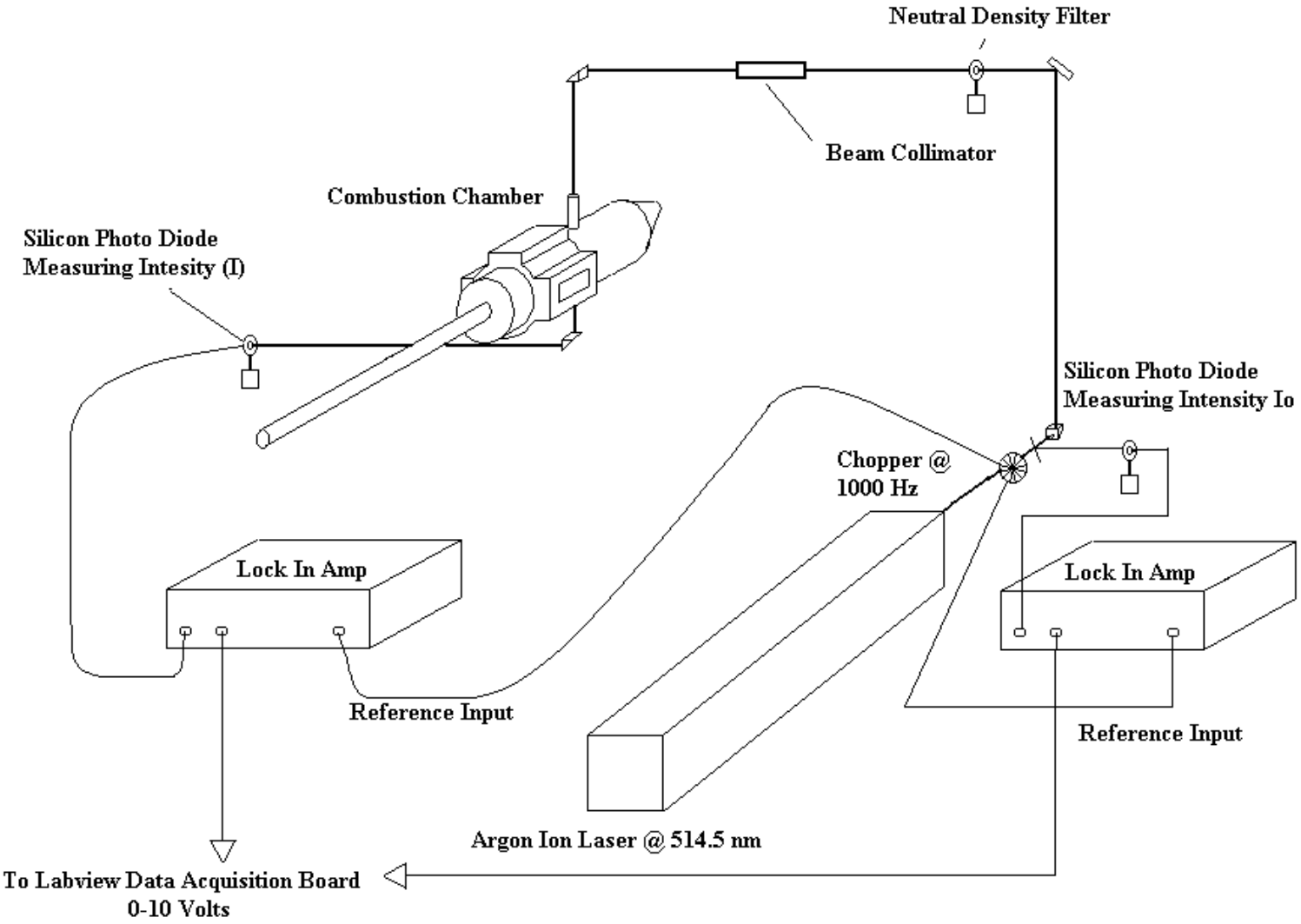
Surrogate	Molar Composition	MW (g/mol)	H/C ratio	SP (mm)	Predicted TSI = $\Sigma(x_i\ TSI_i)$	Measured TSI = 4.07*(MW/SP) – 4.8
JP-8 (22)	54% iso-octane 18% n-dodecane 28% 1,3,5-trimethylbenzene	125.9	1.975	17.8	**22.5**	**24.0**

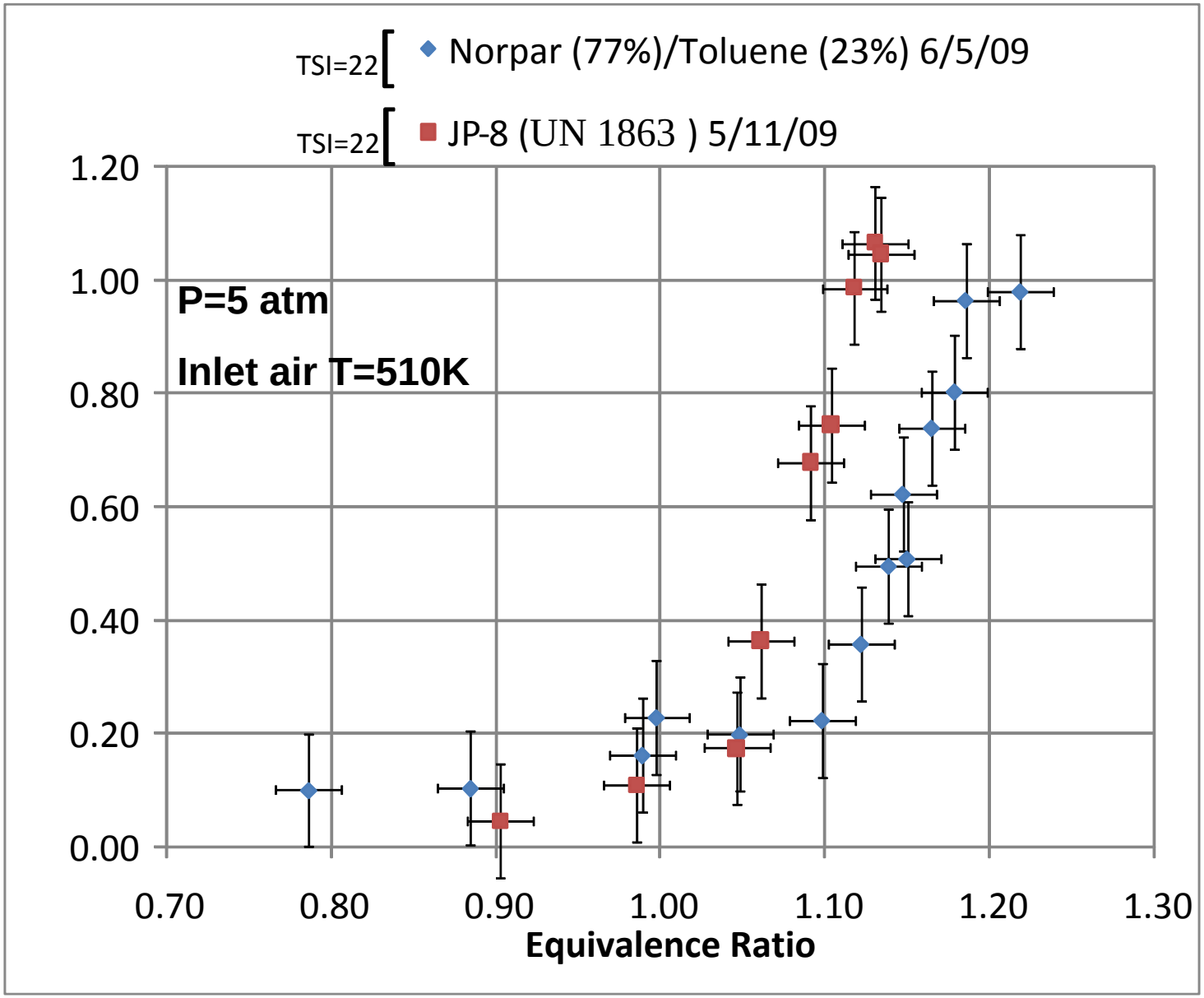
- **Dump Combustor Studies of JP-8 and Norpar 13/Toluene mixture**

Dump Combustor



Schematic of Laser Extinction Optical Setup.




TSI=22
Norpar (77%)/Toluene (23%) 6/5/09
TSI=22
JP-8 (UN 1863) 5/11/09
P=5 atm
Inlet air T=510K
1.20
1.00
0.80
0.60
0.40
0.20
0.00
0.70
0.80
0.90
1.00
1.10
1.20
1.30
Equivalence Ratio

Issues

- Agreement between JP-8 and Norpar13/toluene mixtures were modest (a factor of 2)
- Peanut spray nozzles used in these studies had a very limited lifetime in the combustor and introduced some run to run differences in the soot volume fraction measurements
- We have designed an alternate nozzle that should solve the problem
- Since we were using a two component mixture, we could not match TSI and C/H ratio as we did with the surrogate mixtures.

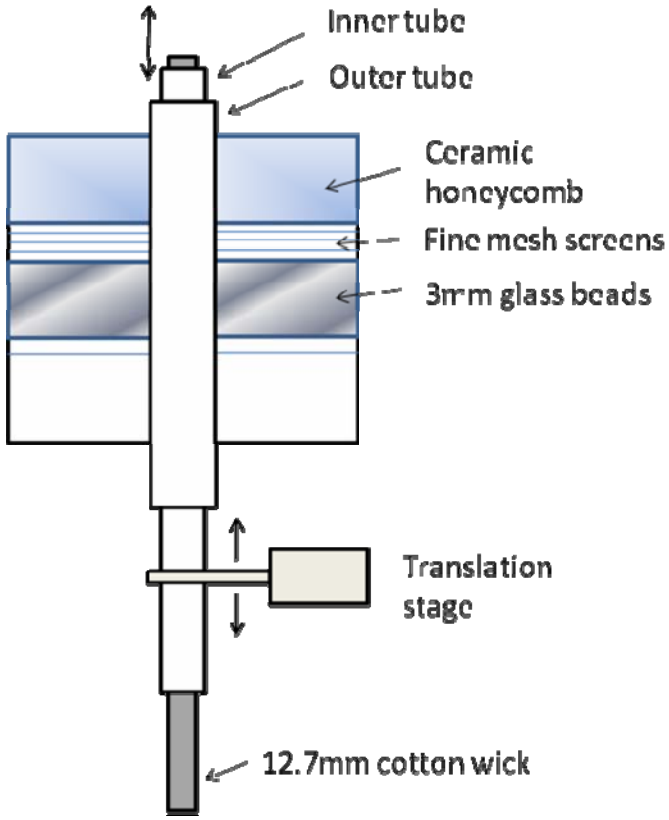
Development of a Wick-fed Diffusion Flame Burner for Surrogate Fuel Studies

Motivation

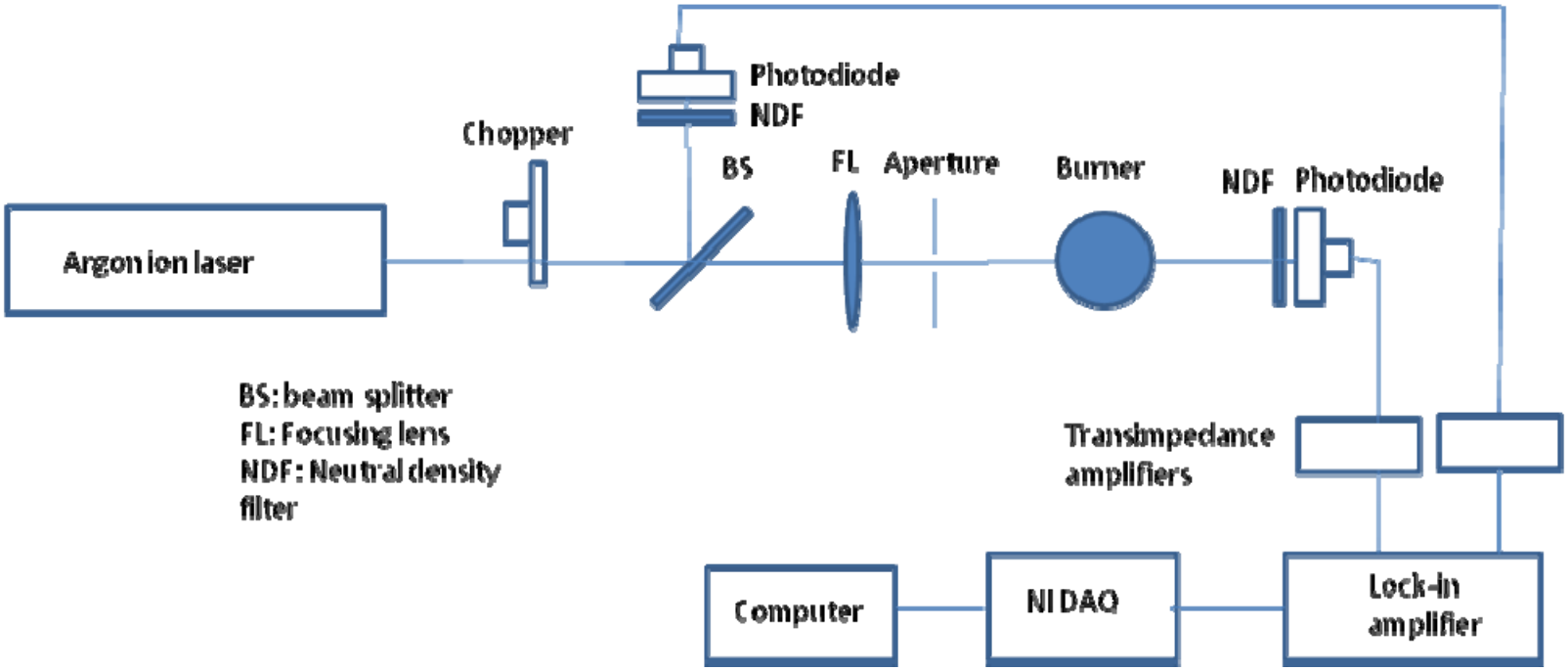
- Gain deeper understanding of effects of fuel composition on smoke point
  - Why does TSI work so well?
- Use of wick flame provides a simple fuel delivery system and closely replicates the ASTM test used to qualify JP-8
- Determine whether surrogates with same TSI as JP8 reproduce the soot field of JP8
  - As opposed to reproducing soot distribution along the centerline of the flame.
  - Provides a second test environment that complements the dump combustor studies.

Experimental set-up

- Burner combines design of co-flow gaseous fuel burner and ASTM smoke point lamp
- 12.7mm wick (~2.5x ASTM wick diameter)
- Thermocouple embedded in wick for surface temp.

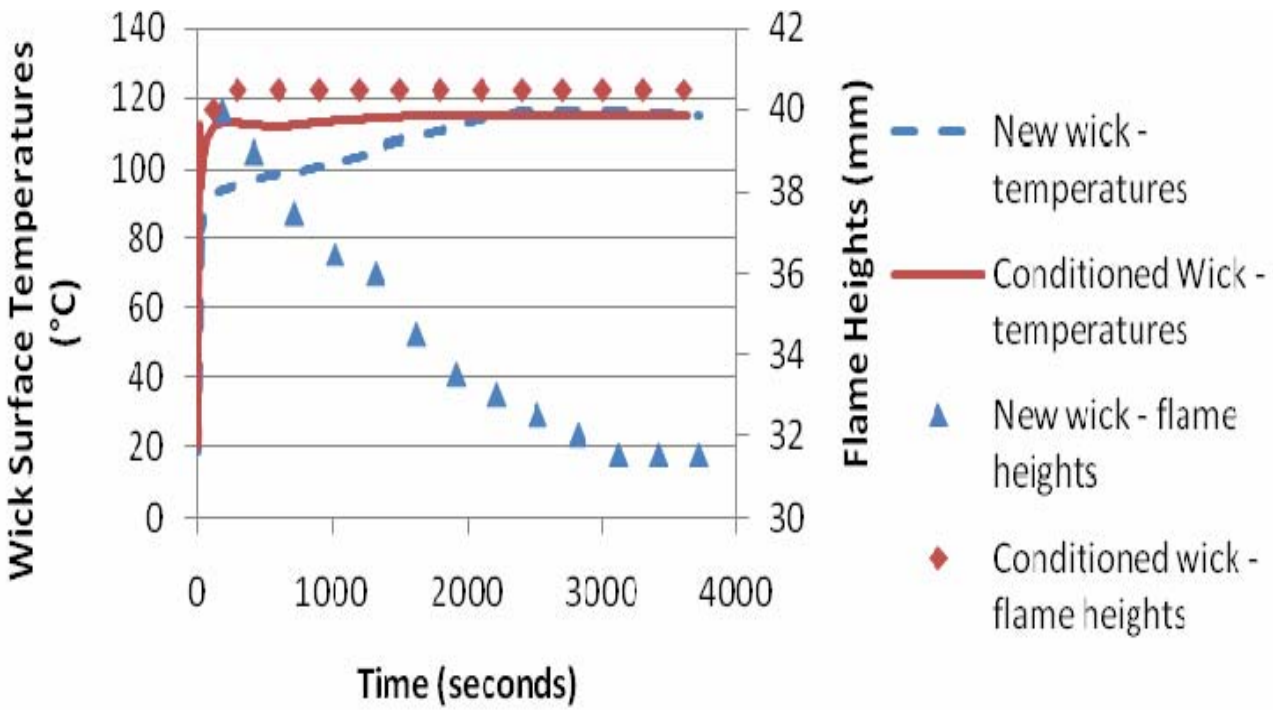


Light Extinction for Soot Volume Fraction



- Abel inversion procedure used to obtain spatially resolved soot profile from line-of-sight measurements
- m = 1.57 - 0.56i used to be consistent with earlier work

Wick conditioning procedure



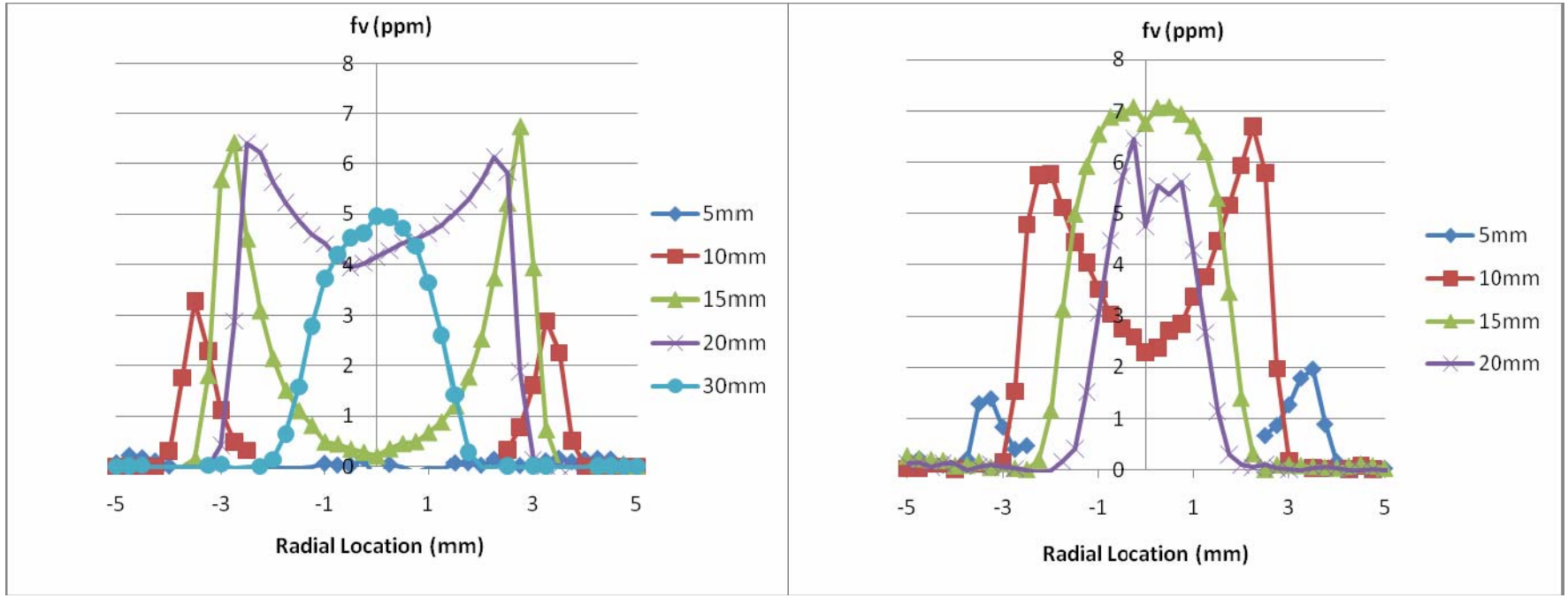
- New wicks produce flames that decrease continuously in height
- Conditioning procedure developed to overcome this difficulty

Images of Flames Studied

Isooctane flame
Smoke point: 41mm
Smoke Point ASTM lamp: 40mm
Olson et al. 38mm

90% i-C8H18/ 10% 1,3,5-trimethylbenzene
Smoke point: 25mm
Smoke point from TSI mixture rule: 25.9mm

Effect of 1,3,5-trimethylbenzene on soot



Isooctane

90% Isooctane –
10% 1,3,5-trimethylbenzene

Summary/Accomplishments

- Completed TSI/YSI studies to develop a consistent, unified set of TSI values.
- Used TSI methodology to evaluate sooting threshold of several mixtures to confirm utility of the TSI approach for screening component mixtures.
- Obtained initial results comparing soot volume fraction between JP-8 and a surrogate fuel with the same TSI
- Wick-fed diffusion flame burner appears to be viable for comparing soot fields of JP8 and surrogates

Future Work

- Continue to evaluate TSI of proposed surrogate fuel mixtures
- Conduct comparisons of soot volume fraction in the dump combustor using JP-8 and surrogate mixtures where both the TSI and C/H ratio are matched
- Future work with JP8 and surrogates:
  - Planar LII measurements for soot
  - Particle size measurements via light scattering
  - Qualitative PAH distributions
- Begin high pressure autoignition studies of surrogate mixtures

Acknowledgments

Dr. Julian Tishkoff, Air Force Office of Scientific Research (AFOSR)

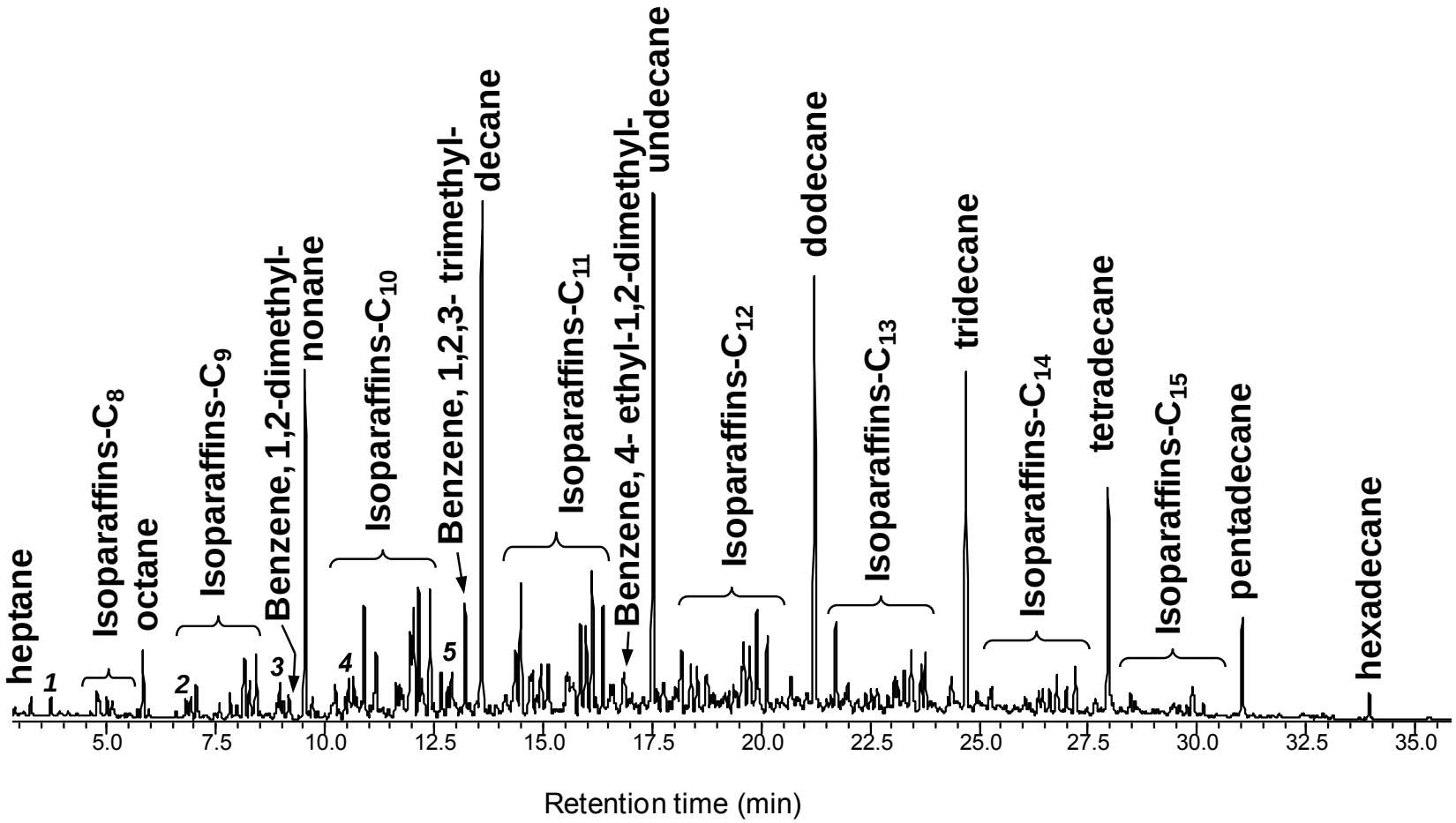
MURI - Generation of Comprehensive Surrogate Kinetic Models and Validation Databases for Simulating Large Molecular Weight Hydrocarbon Fuels

Dr. Dryer, Princeton University

Dr. Colket, United Technologies Research Center

Questions?

JP-8 (UN 1863)


heptane
1
Isoparaffins-C8
octane
Isoparaffins-C9
2
Benzene, 1,2-dimethyl-
nonane
3
Isoparaffins-C10
4
Benzene, 1,2,3- trimethyl-
decane
5
Isoparaffins-C11
Benzene, 4- ethyl-1,2-dimethyl-
undecane
Isoparaffins-C12
dodecane
Isoparaffins-C13
tridecane
Isoparaffins-C14
tetradecane
Isoparaffins-C15
pentadecane
hexadecane
5.0
7.5
10.0
12.5
15.0
17.5
20.0
22.5
25.0
27.5
30.0
32.5
35.0
Retention time (min)