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and The Propulsion Engineering Research Center

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

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Outline

- Compare sooting tendencies of pure components through a unified and consistent Threshold Soot Index (TSI).
- Verify functional relationships for predicting TSI's of binary component mixtures.
- Attempt to replicate TSI of real fuels using surrogate mixtures.

Background on TSI

- Soot Threshold or Smoke Point = maximum height or fuel flow of a smoke free laminar 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* is the height of the flame at the smoke point.
  - $\dot{m}$ is the mass flow rate of the fuel at the smoke point.
  - *MW* is the molecular weight of the fuel.
  - *a* & *b* are constants dependent on the experiment.

Determination of TSI Values

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

1. Measured *SP*, to the nearest mm, of 12 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:

$$\mathrm{TSI}_{1-\mathrm{methylnaphthalene}} = 100 = a\left(\frac{142.2\,\mathrm{g/mol}}{5.3\mathrm{mm}}\right) + b$$

$$\mathrm{TSI}_{\mathrm{methylcyclohexane}} = 5 = a\left(\frac{98.19\,\mathrm{g/mol}}{41.1\mathrm{mm}}\right) + b$$

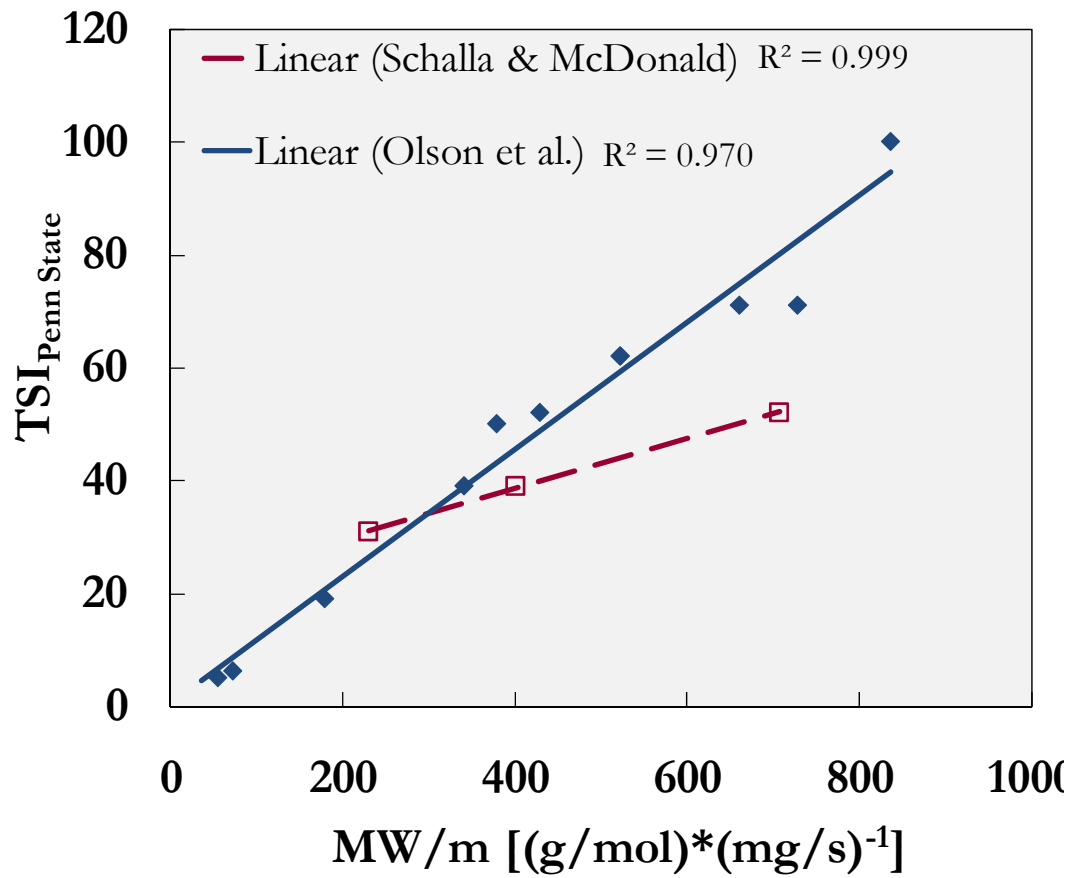
   – Penn State apparatus constants: a = 3.9; b = -4.3

Smoke Points and TSI Values

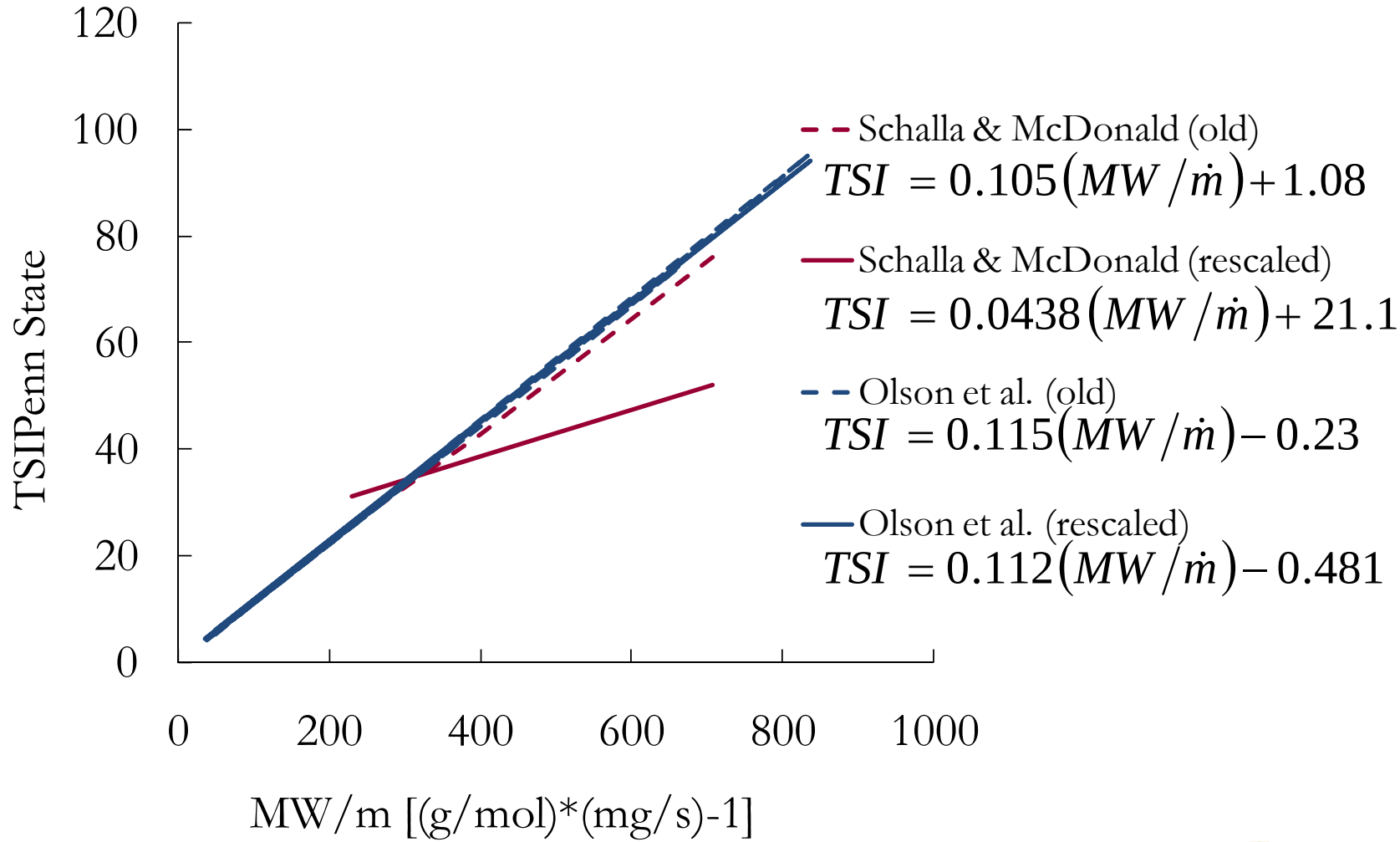
Compound	Formula	MW (g/mol)	SP	TSI	Uncertainty
1-methylnaphthalene	$C_{11}H_{10}$	142.20	5	**100**	**±11%**
methylcyclohexane	C_7H_{14}	98.19	41	**5.0**	**±2%**
cyclohexylbenzene	$C_{12}H_{16}$	160.26	8	**71**	**±7%**
decalin	$C_{10}H_{18}$	138.26	23	**19**	**±6%**
tetralin	$C_{10}H_{12}$	132.21	7	**71**	**±9%**
1,2,4-trimethylbenzene	C_9H_{12}	120.20	7	**62**	**±9%**
1,3,5-trimethylbenzene	C_9H_{12}	120.20	7	**62**	**±9%**
n-propylbenzene	C_9H_{12}	120.20	8	**52**	**±8%**
iso-octane	C_8H_{18}	114.23	42	**6.2**	**±13%**
m-xylene	C_8H_{10}	106.17	8	**50**	**±8%**
toluene	C_7H_8	92.14	8	**39**	**±8%**
benzene	C_6H_6	78.12	9	**31**	**±8%**

Example of Incorporating Other TSI Values

3. We rescaled the TSI's of past smoke point studies to minimize the absolute differences from our data.
   - Plot our TSI's vs. *MW/SP* or $MW/\dot{m}$ for the other sooting tendency studies.
4. Solve a linear regression, which defines the constants, a & b, and a correlation coefficient, R^2.



Example - Comparison of Rescaled TSI's



Incorporating YSI Values

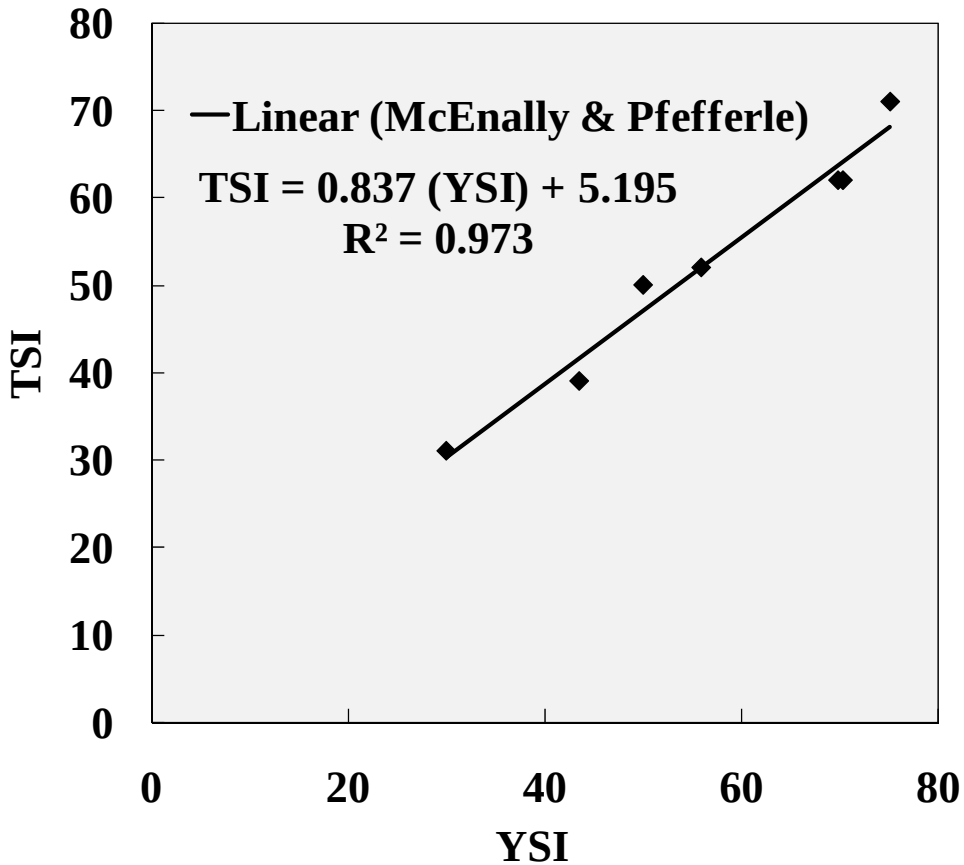
- McEnally & Pfefferle, C&F, (2007) offered an alternative to the TSI, the **Yield Soot Index (YSI)**, which could measure the sooting tendency of aromatics with more precision than the smoke point method.

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

  - $\boldsymbol{f}_{\boldsymbol{v,max}}$ is the maximum soot volume fraction measured in a co-flow methane diffusion flame doped with 400 ppm of the hydrocarbon being tested.
  - Reported a total uncertainty of ±3%.

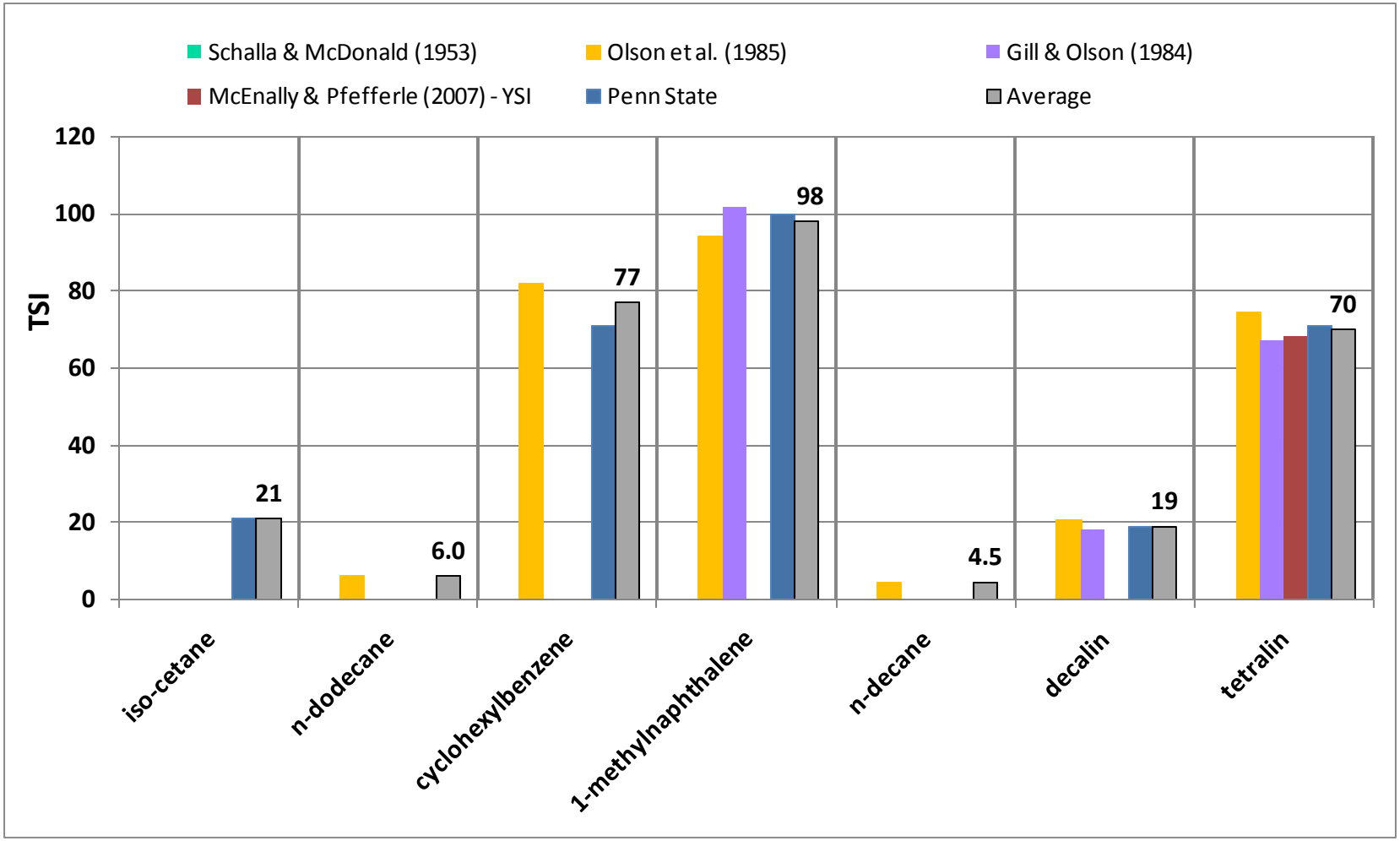
Incorporating YSI Values

- In order to incorporate the YSI data into this data set, YSI was also rescaled.
  - The correlation coefficient is greater than the minimum acceptable value of 0.95.

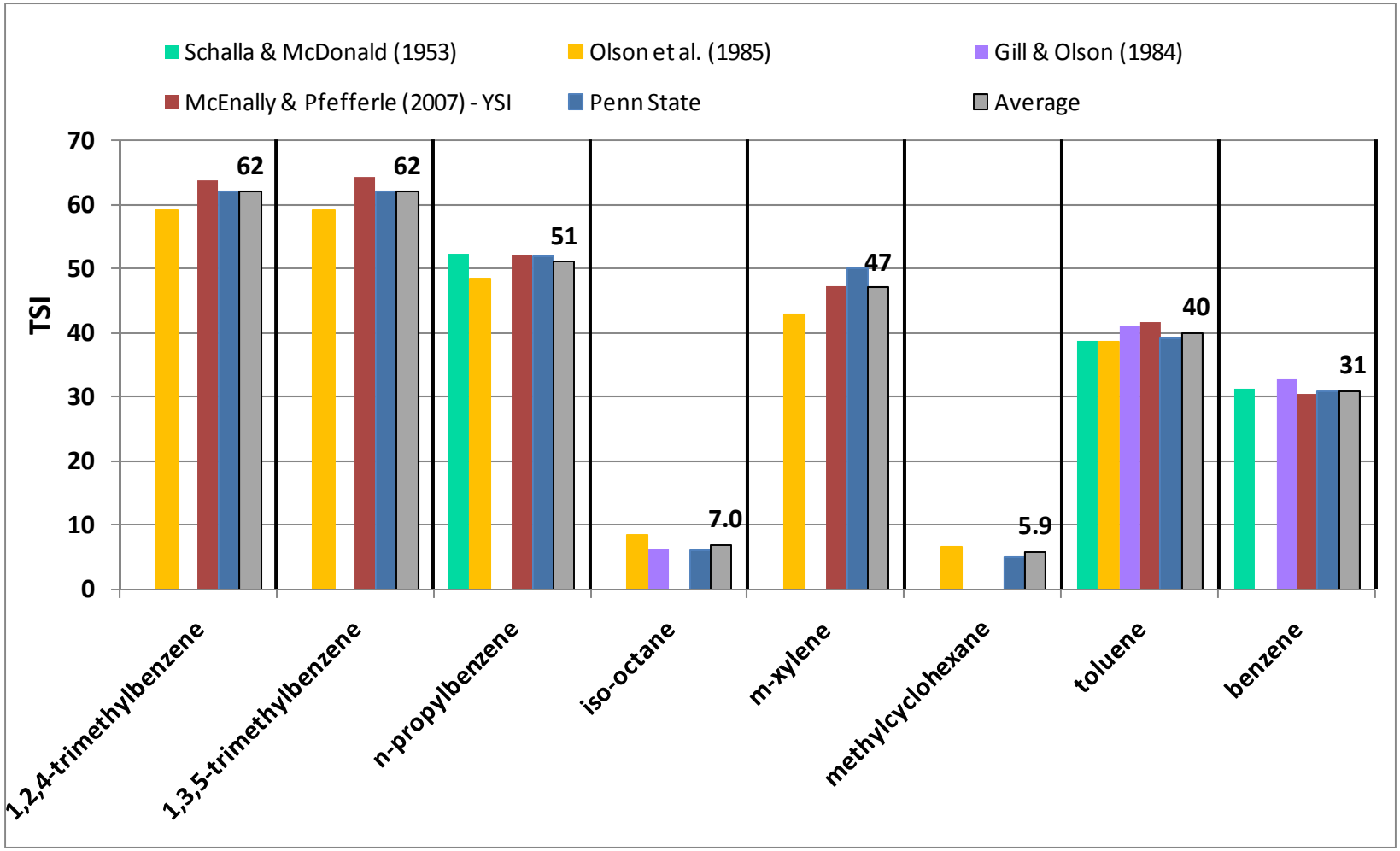


Scaled TSI's and Average Values

Data sets with good correlation, $R^2 > 0.95$, were included in the final average.



Scaled TSI's and Average Values



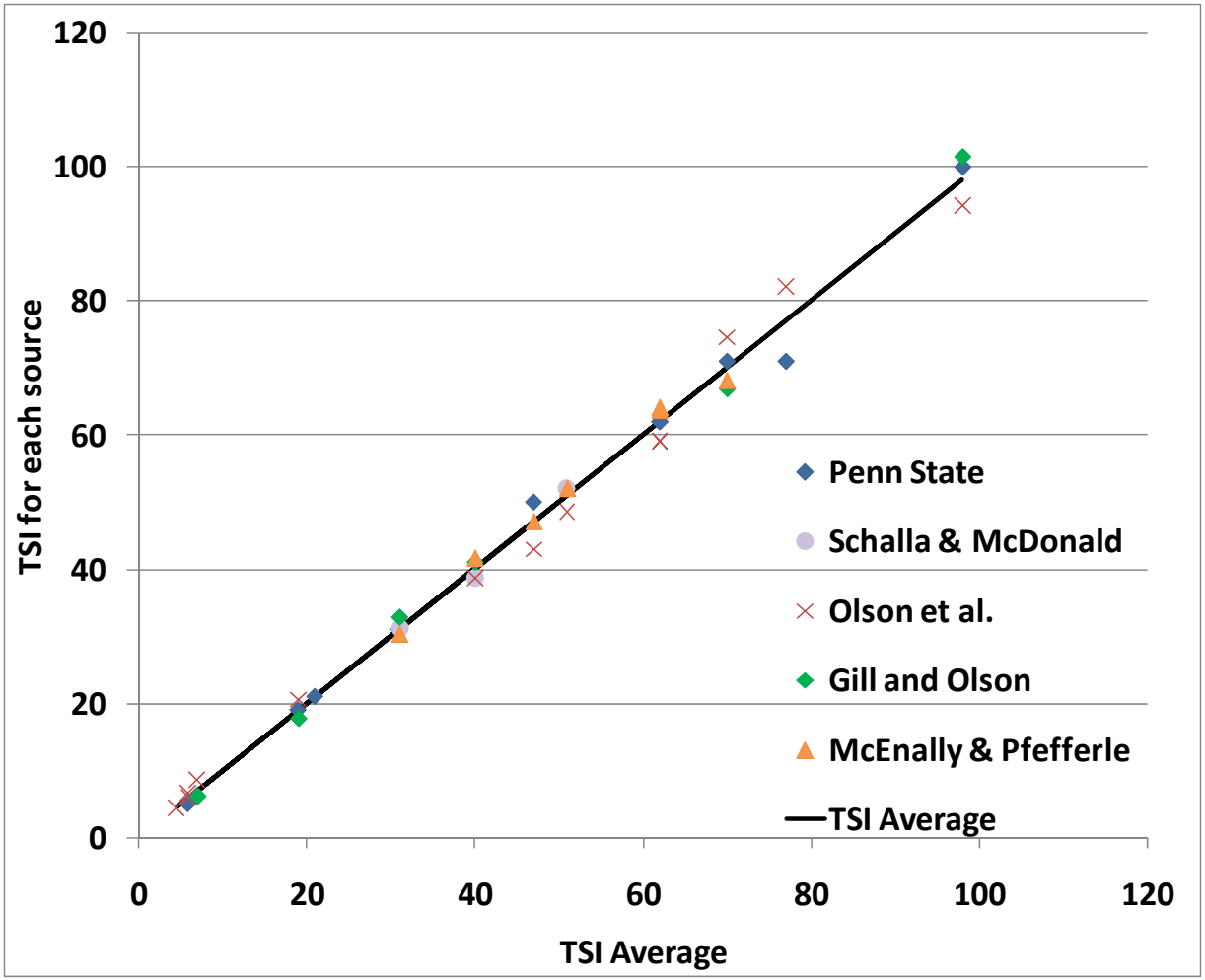
Largest Deviation of TSI Values

By excluding some of the earlier data sets, which did not correlate well:

- The largest deviation, or the maximum value of [any TSI – TSI_{ave}], is much improved from the earlier studies that reported multiple sources of TSI values.

Study reporting TSI's from multiple sources	**Worst Deviation of TSI for tetralin ($C_{10}H_{12}$)**
Calcote & Manos (1983)	15
Olson et al. (1985)	20
Penn State	4.5

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



Binary Mixtures

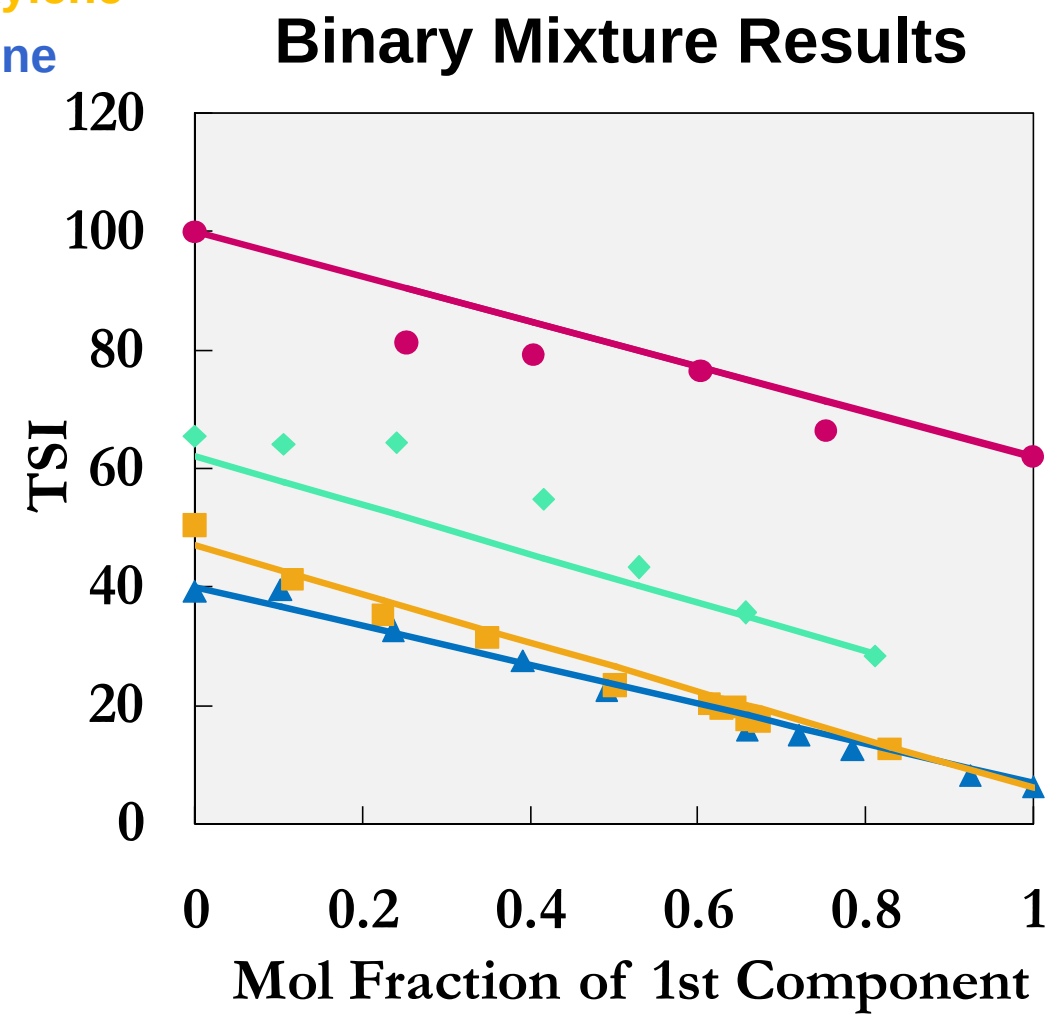
- Four binary mixtures were tested to see if they followed the mixture rule proposed by Gill and Olson, CST, (1984).

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

  - $\mathbf{x_i}$ is the component mole fraction

- Mixture volumes were measured with pipettes (resolution 0.1mL)
- Volume fractions of components were also verified by measuring component masses with a balance (resolution 0.001g).
- For all cases, mole fraction accuracy was 1%.

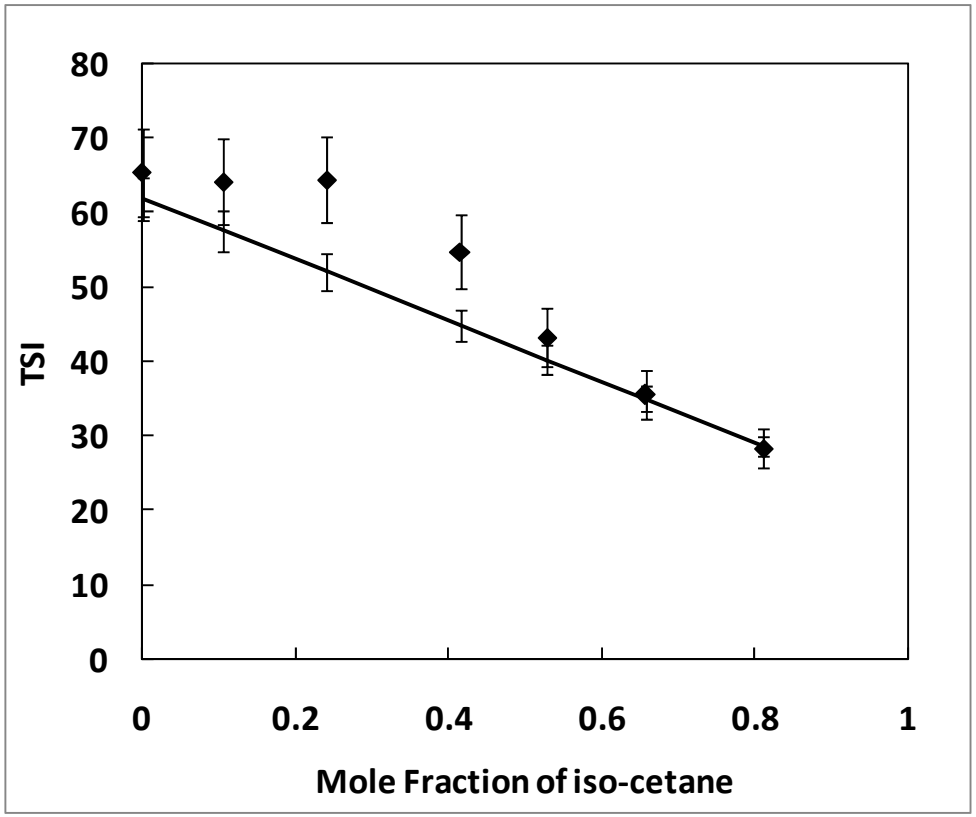
- ● Mixtures of 1,2,4-trimethylbenzene in 1-methylnaphthalene
- ♦ Mixtures of iso-cetane in 1,2,4-trimethylbenzene
- ■ Mixtures of n-dodecane in m-xylene
- ▲ Mixtures of iso-octane in toluene



Experimental uncertainties ranged from 5-11%

Iso-cetane / 1,2,4 Trimethylbenzene

- This mixture deviates from the predicted TSI line - even considering uncertainties – *for low concentrations of iso-cetane*.
- However, at 50% iso-cetane the measured TSI overlaps the predicted TSI considering the uncertainty.
  - The three surrogate mixtures we tested all have >50% iso-cetane.



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)	SP (mm)	Measured TSI = 3.9 *(MW/SP) – 4.3	Predicted TSI = $\Sigma(x_i\ TSI_i)$
3A	52% iso-cetane 23% n-dodecane 25% 1,3,5-trimethylbenzene	186.8	22.5	**27.9**	**28**
3B	64% iso-cetane 23% n-dodecane 13% 1-methylnaphthalene	202.5	24.2	**28.2**	**28**

Surrogate Mixture Results (with iso-cetane)

- Surrogate 4A achieves almost the same TSI using both aromatics.
- All three (3A, 3B, 4A) mixtures measure the same TSI as predicted to the nearest whole number.

Surrogate	Molar Composition	MW (g/mol)	SP (mm)	Measured TSI = 3.9 *(MW/SP) – 4.3	Predicted TSI = $\Sigma(x_i\ TSI_i)$
4A	58% iso-cetane 23% n-dodecane 15% 1,3,5-trimethylbenzene 5% 1-methylnaphthalene	193.9	24.0	**27.1**	**27**

JP-8 TSI

	MW (g/mol)	SP (mm)	**Measured TSI =** 3.9*(MW/SP) – 4.3
JP-8	153.3*	22.8	22
JP-8	153.3	22.2	22
JP-8	153.3	23.8	21
JP-8 average	**153.3**	**23.0**	**22**

*MW of JP-8 estimated from $C_{11}H_{21}$

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)	SP (mm)	**Predicted TSI =** $\Sigma(x_i\ TSI_i)$	**Measured TSI =** 3.9 *(MW/SP) – 4.3
JP-8 (22)	54% iso-octane 18% n-dodecane 28% 1,3,5-trimethylbenzene	125.9	17.8	**22**	**23.2**

Summary

- Completed the measurements of the TSI values for the hydrocarbons being consider the multi-component candidate surrogate fuels.
- Reviewed previous TSI/YSI studies and developed 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.

Future Work

- Investigate the deviation from a linear behavior for the iso-cetane / 1,2,4 trimethylbenzene binary mixture
- Measure the soot volume fraction at elevated pressures (~5-10 atm) for mixtures with the same TSI of JP-8 in the dump combustor.
- Investigate the autoignition of selected candidate hydrocarbons using high-pressure, high-temperature flow reactor (30 atm, 1100ºF) at Penn State

Extra Slide

Pure Compound	Formula	MW (g/mol)	TSI - Penn State	Rescaled TSI - Schalla & McDonald	Rescaled TSI - Olson et al.	Rescaled TSI – Gill & Olson	Rescaled YSI - McEnally & Pfefferle	Average Value
			a= 3.881, b= -4.282	a= 0.0438, b= 21.1	a= 0.112, b= 0.481	a= 3.612, b= -3.325		
iso-cetane	$C_{16}H_{34}$	226.45	21[b]					21
n-dodecane	$C_{12}H_{26}$	170.34			6.0 (5.4)[c]			6.0
cyclohexylbenzene	$C_{12}H_{16}$	160.26	71		82.1 (82.9)			77
1-methylnaphthalene	$C_{11}H_{10}$	142.2	100		94.2 (95.6)	101 (95)		98
n-decane	$C_{10}H_{22}$	142.29			4.5 (3.9)			4.5
decalin	$C_{10}H_{18}$	138.26	19		20.6 (20.1)	18 (18)		19
tetralin	$C_{10}H_{12}$	132.21	71		74.5 (74.2)	67 (63)	68.1 (75.1)	70
1,2,4-trimethylbenzene	C_9H_{12}	120.2	62		59.0 (57.9)		63.6 (69.8)	62
1,3,5-trimethylbenzene	C_9H_{12}	120.2	62		59.0 (57.9)		64.0 (70.3)	62
propylbenzene	C_9H_{12}	120.2	52	52 (76)	48.6 (47.6)		52.0 (55.9)	51
iso-octane	C_8H_{18}	114.23	6.2		8.6 (8.0)	6.2 (7.3)		7.0
m-xylene	C_8H_{10}	106.17	50		42.9 (42.0)		47.0 (50.0)	47
methylcyclohexane	C_7H_{14}	98.19	5		6.7 (6.0)			5.9
toluene	C_7H_8	92.14	39	39 (43)	38.7 (37.9)	41 (39)	41.6 (43.5)	40
benzene	C_6H_6	78.12	31	31 (26)		33 (32)	30.3 (30.0)	31

[a] "Rescaled" is defined as the TSI values that would be determined on the Penn State smoke point apparatus.
[b] Calculated from a mixture of 81% iso-cetane and 19% 1,2,4-trimethylbenzene by moles.
[c] TSI values originally reported by the authors or by Olson et al. in the case of the Schalla and McDonald TSI values.