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**A STUDY ON THE SOOTING TENDENCY OF JET FUEL  
SURROGATES USING THE THRESHOLD SOOT INDEX**

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Mechanical Engineering

by

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## ABSTRACT

Currently, modeling the combustion of aviation turbine fuels is not feasible due to the complexity and variation of real fuels. Surrogates, created out of a few pure hydrocarbon compounds, are a key step toward modeling new engines and new fuels. For the surrogate to simulate the real fuel, the composition must be designed to reproduce certain pre-designated parameters. In the present research, instead of attempting to match distillation curves or estimates of the composition of the real fuel, three combustion related parameters including hydrogen to carbon (H/C) ratio, cetane number, and sooting tendency are to be reproduced. The objective of this thesis is to characterize the sooting tendency. The tendency of a fuel to produce soot in the combustor is relevant because it affects flame radiation as well as emissions. Parameters which characterize sooting tendency include hydrogen content, H/C ratio, smoke point, Threshold Soot Index (TSI), Yield Sooting Index (YSI), and others. In this work, TSI, which is derived from the smoke point measurement, is used.

Previous data on TSI had been scaled inconsistently, and widely differing values for some compounds had been reported. In addition, the TSI for a key iso-alkane, iso-cetane, had not been measured. Therefore this work sought to provide a complete and consistent set of TSI values for surrogate components. Smoke point heights of sixteen compounds were measured according to ASTM D1322, and TSI values were derived from these measurements. The soot threshold and soot yield (YSI) data from prior studies were rescaled with a correlation to the TSI values from the current study. The magnitude of the correlation coefficient was used to determine whether the data set was used in the final average TSI values. Results showed that the differences in TSI values were significantly reduced by scaling all the data sets in this manner.

Once individual TSI values are known, the resulting TSI when components are mixed together can be predicted. Previous researchers tested a mixture rule, which was

shown to hold for the mixtures investigated. In this work, it was found that six additional binary mixtures and four multi-component mixtures follow the same mixture rule. A method of calculating the TSI of a single component from the mixture TSI was used to obtain a TSI value for iso-cetane, which could not otherwise be measured, and to verify the TSI value for 1-methylnaphthalene.

Due to the complex molecular structures of aromatics, it is one of the hydrocarbon classes for which developing chemical kinetic models is difficult. Among the hydrocarbon families, aromatics also have the highest sooting tendencies, and their presence has the most effect on TSI. Due to inadequate development of some chemical kinetic models, certain aromatic compounds may need to be replaced with others for which models exist. The TSI values of three mixtures were tested to show that TSI can be replicated using different combinations of compounds for the aromatic fraction of the mixture.

The methodology of designing surrogates based on TSI was applied to JP-8, the USAF jet fuel. The smoke point height of JP-8 was measured, and the TSI was obtained using an estimated molecular weight. A surrogate, created to match the JP-8 TSI, produced the same value within the estimated uncertainty. The formation of a set of TSI values for individual compounds and the verification of a mixture rule showed that TSI can be used as a sooting tendency parameter for designing surrogate composition.

## TABLE OF CONTENTS

NOMENCLATURE .....	vii
LIST OF FIGURES .....	viii
LIST OF TABLES .....	x
ACKNOWLEDGEMENTS .....	xi
CHAPTER 1 INTRODUCTION .....	1
1.1 Motivation and Background .....	1
1.2 Objectives of the Research.....	4
CHAPTER 2 LITERATURE REVIEW .....	5
2.1 Background on Jet Fuels.....	5
2.2 Soot Threshold or Smoke Point .....	6
2.3 Threshold Soot Index, TSI.....	10
2.4 Yield Sooting Index, YSI.....	14
2.5 TSI for Mixtures .....	16
2.6 Correlations of Soot Measurements with TSI.....	17
2.7 Summary of Soot Threshold as a Measure of Sooting Tendency.....	18
CHAPTER 3 EXPERIMENTAL APPROACH .....	19
3.1 Experimental Apparatus.....	19
3.2 Experimental Procedure.....	20
3.3 Mixture Preparation .....	29
3.4 Procedure for TSI Calculation .....	30
3.5 Uncertainty Analysis.....	31
CHAPTER 4 RESULTS AND DISCUSSION.....	34

4.1 TSI for Pure Compounds .....	34
4.3 Achieving Matching TSI Values with Different Compounds .....	49
4.4 Matching the TSI of JP-8 with a Surrogate .....	51
CHAPTER 5 CONCLUSIONS .....	54
CHAPTER 6 FUTURE WORK .....	56
REFERENCES .....	57
Appendix A. <i>SP</i> , ambient conditions, and TSI for Standard Mixtures.....	59
Appendix B. <i>SP</i> and TSI Data for Binary Mixtures .....	61

## NOMENCLATURE

$a, b$	= apparatus specific Threshold Soot Index constants
$c, d$	= apparatus specific Yield Sooting Index constants
$f_{v,max}$	= the maximum soot volume fraction
$i-cet$	= iso-cetane
$K$	= smoking tendency constant
$\dot{m}$	= fuel mass flowrate
MCH	= methylcyclohexane
1-MN	= 1-methylnaphthalene
$MW$	= molecular weight
$SP$	= height of the flame at the smoke point
$S_t$	= smoking tendency
TMB	= trimethylbenzene
TSI	= Threshold Soot Index
YSI	= Yield Sooting Index

## LIST OF FIGURES

- Figure 1** Trends of TSI with carbon number for different hydrocarbon classes. Data points for aromatics are represented with the molecular structure of the specific compound. Source, Calcote and Manos 1983 [12]. ..... 12
- Figure 2** Relationship between flame height and fuel mass consumption rate of n-propylbenzene and 1-octene. Arrows point to local minimum observed at the smoke point. Source, Olson *et al.* 1985 [13]. ..... 14
- Figure 3** Drawing of ASTM standard smoke point lamp. Source, ASTM D1322-97 [4]. ..... 20
- Figure 4** Drawing of the shape of a flame: A – above the smoke point; B – at the smoke point; and C – below the smoke point. Source ASTM D1322-97 [4]. ..... 23
- Figure 5** Photograph taken of an iso-octane/toluene diffusion flame at the smoke point. ..... 23
- Figure 6** Smoke point height of a fuel mixture (20% 1-methylnaphthalene/80% decalin, by volume) changing with time before reaching a steady value of 11 mm. .... 25
- Figure 7** Calibration factor,  $f$ , plotted as a function of time. .... 27
- Figure 8** All data for smoke point heights of the standard calibration mixtures, as specified in ASTM 1322D-97 [3], plotted against ambient temperature and pressure. ... 28
- Figure 9** Scaling of TSI data. TSI values obtained in this work plotted against  $MW/SP$  data from Minchin, 1931 [7] and Clarke *et al.*, 1946 [8]. Linear fit defines TSI for a given  $MW/SP$  from those studies. .... 37



<b>Figure 10</b> Scaling of TSI data. TSI values obtained in this work plotted against $MW/SP$ data from Hunt, 1953 [12] and Gill and Olson, 1984 [19]. Linear fit defines TSI for a given $MW/SP$ from those studies. ....	38
<b>Figure 11</b> Scaling of TSI data. TSI values obtained in this work plotted against $MW/\dot{m}$ data from Schalla and McDonald, 1953 [11] and Olson <i>et al.</i> , 1985 [14]. Linear fit defines TSI for a given $MW/\dot{m}$ from those studies. ....	39
<b>Figure 12</b> Scaling of TSI data. TSI values obtained in this work plotted against YSI from McEnally and Pfefferle, 2007 [16] and 2008 [17]. Linear fit defines TSI for a given YSI from those studies. ....	40
<b>Figure 13</b> Variation of TSI with mole fraction for three binary mixtures. Points are measured TSI values, and lines are TSI values calculated from pure component values. To differentiate between the error bars, those for calculated TSI values are represented as dashed lines and are offset by 0.01 in mole fraction. ....	45
<b>Figure 14</b> Variation of TSI with mole fraction for three binary mixtures containing 1-methylnaphthalene (1-MN). Points are measured TSI values, and lines are TSI values calculated from pure component values. To differentiate between the error bars, those for calculated TSI values are represented as dashed lines and are offset by 0.01 in mole fraction. ....	46
<b>Figure 15</b> Binary mixtures containing 1-methylnaphthalene, used to calculate the TSI for pure 1-methylnaphthalene from the fit lines. ....	49

## LIST OF TABLES

<b>Table 1</b> Minimum, maximum, and average properties values of JP-8, from the 2006 PQIS report [5].	6
<b>Table 2</b> Name, chemical formula, CAS #, and purity of all pure hydrocarbons used. ...	22
<b>Table 3</b> List of binary mixture components and surrogate mixture composition. ....	30
<b>Table 4</b> Smoke point height, TSI, and relative uncertainty in TSI for pure compounds.	34
<b>Table 5</b> Sources of sooting threshold data for pure hydrocarbons, which measured two or more compounds in common with this work. ....	36
<b>Table 6</b> TSI values for compounds considered in this work. Data include TSI values measured in this study, rescaled <sup>a</sup> TSI values from studies with $R^2 > 0.95$ , Schalla and McDonald [11], Olson <i>et al.</i> [14], Gill and Olson [19], and McEnally and Pfefferle [16, 17], and an average of these TSI values. ....	42
<b>Table 7</b> Composition, smoke point height, measured TSI, and predicted TSI of three MURI [2] surrogate mixtures for JP-8.	51
<b>Table 8</b> Smoke point height and TSI results for JP-8 samples taken from the same batch of fuel.	52
<b>Table 9</b> Composition, smoke point height, measured TSI, and predicted TSI for a surrogate matching JP-8 in TSI and H/C ratio.	53

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# CHAPTER 1 INTRODUCTION

## 1.1 Motivation and Background

Combustion modeling is necessary for the development of efficient and accurate numerical design methodologies for engines. By modeling proposed changes to engine designs ahead of time, the number of costly and time consuming engine tests can be reduced. As the desire grows to employ alternative liquid fuels, energy sources such as coal and bio-feedstocks will be used. Often the alternative fuels from these sources have significantly different chemical or physical properties than the original petroleum based fuel. Modeling the combustion of the alternative fuels will become important to predict any effects on engine performance and emissions.

The concept of surrogate fuels developed from a need to model the combustion of practical liquid fuels used in existing and future engine designs. A surrogate fuel is a mixture of a small number of pure compounds that can mimic the combustion of a real fuel, whether it is derived from petroleum or an alternative source. Practical fuels are often composed of thousands of components, which can vary with location and time of year [1]. The variation is acceptable because specifications generally require fuels to meet certain values on empirical tests, but do not specify composition. The resulting multi-component and variable nature of practical fuels introduces overwhelming complexity to the modeling task. A surrogate fuel requires a much simpler chemical kinetic model than would be needed for the practical fuel. Therefore, with surrogate fuels to represent the real fuel, designing engines and developing new fuels using modeling becomes possible.

The work to be discussed is part of a Multi-disciplinary University Research Initiative (MURI) [2] to develop surrogate fuel mixtures of three to five components and related kinetic models for the United States Air Force jet fuel, JP-8. In automobile

engines, the technique of substituting surrogates for practical fuels has been used successfully to model the combustion of gasoline. However, developing functioning surrogates for aviation jet fuels is more difficult for several reasons. Jet fuel has a higher average molecular weight than gasoline, which means chemical kinetic models of the individual mixture components of a jet fuel surrogate are harder to develop. Also, the specifications for jet fuels are relatively broad and include fuels with a rather wide range of properties, implying composition can vary significantly [2].

To be useful the surrogate fuel must match key combustion processes with reasonable fidelity, and models must be carefully constructed, which presents some challenges. Rules for selecting surrogate components and matching mixtures against real jet fuels have not been previously defined. One of the goals of the MURI is to develop a methodology for designing surrogates that can be applied to any fuel. It is proposed that a surrogate must meet a few important combustion-related parameters to be considered. In addition, there is a lack of kinetic model validation data for higher molecular weight compounds and their mixtures.

The MURI has identified three combustion-related parameters as crucial parameters to be reproduced by the surrogate: hydrogen to carbon (H/C) ratio, autoignition characteristics, and sooting tendency [2]. The H/C ratio has been shown to be important for many combustion quantities, such as heat of reaction, flame temperature, flame speed, and local air-to-fuel ratio. The work here focuses on the development and use of the parameter for sooting tendency. The surrogate fuel should be able to accurately simulate in-combustor soot formation as well as soot emissions of JP-8. The sooting characteristics of JP-8 are important because radiation from soot formed in the combustor heats and stresses the combustor liner. Soot particles that escape from the combustor deposit in the turbine section or leave with the exhaust as soot emissions.

Studies of sooting tendency of hydrocarbon fuels have been done in a number of combustors and burners. A simple diffusion flame has been especially useful, as it is a

key element of the United States Air Force (USAF) specifications for jet fuel with respect to soot. In diffusion flames, the threshold of soot breakthrough is identified as the condition at which soot particles are observed to exit the flame, and is commonly referred to as the smoke point (*SP*). Measurements show that the smoke point occurs at different flame heights for different fuels. Thus, the smoke point has been used as an important predictor of soot formation for years. The Threshold Soot Index (TSI), which is a linear function of the molecular weight of the fuel divided by the smoke point defined in Eq. (2), can be used as a measure of sooting tendency for fuels for which these quantities are known [13]. Some parameters that have been used to characterize sooting tendency of fuels include hydrogen content, H/C ratio, smoke point, TSI, and Yield Sooting Index (YSI) [16, 17]. TSI has been chosen to be the sooting tendency parameter for this effort because of its consistency and relationship to the smoke point measurement. The critical parameters for the MURI methodology, such as TSI, can match those of the practical fuel by varying the composition of the surrogate once the base components have been selected.

The selection of surrogate components for the aviation jet fuel, JP-8, reflects the type of molecular structures in the real fuel, as well as the availability of chemical kinetic models for which validation data already exist, or are under investigation as part of the MURI collaborative projects [2] or elsewhere. As an initial approach, the surrogate for JP-8 is created using hydrocarbons from the three main classes of compounds present in the fuel: n-alkanes, iso-alkanes, and aromatics. Higher carbon number n-alkanes and iso-alkanes are selected in order to achieve the typical H/C ratio and autoignition properties of JP-8. Aromatic compounds, which are the most influential to TSI, are chosen with consideration of the length, location and number of alkyl branches on the benzene and naphthalene rings.

## 1.2 Objectives of the Research

The first objective was to generate a consistent set of TSI data for all the compounds that are being considered for formulating surrogate mixtures for the MURI. Creating a consistent set of TSI values required measuring the TSI values for a number of hydrocarbons. In addition to the candidate surrogate compounds, more compounds were tested for better comparison to previous studies. Previous sooting tendency measurements include the flame height and the fuel consumption rate at the smoke point, as well as the volume fraction of soot, known as soot yield, in a doped methane diffusion flame (used to derive the Yield Sooting Index). TSI data derived from all three types of measurements were incorporated into the final set of values. A second objective was to verify that for binary mixtures, TSI values were linearly related based on the mole fraction of the candidate surrogate compounds. A third objective was to verify that different hydrocarbon molecules from the same class could be used to formulate equivalent mixtures, in terms of the TSI values, using the linear mixing rule. Confirming mixture equivalence required testing the mixtures to verify that their measured TSI values were the same. The mixtures contained different compounds in proportions so that the predicted TSI values of the mixtures were equal. A final objective was to test the TSI of a surrogate mixture that was devised to match the measured TSI of JP-8. Overall, this research attempted to show that TSI is an effective method for sooting tendency prediction for real jet fuels.

## CHAPTER 2 LITERATURE REVIEW

### 2.1 Background on Jet Fuels

Jet propulsion fuels were developed for the turbojet engine used in military applications after World War II. Due to the availability of gasoline, the first jet fuels were very similar to automobile gasoline [1]. Jet fuels evolved to use more of the kerosene fraction of the petroleum distillate for improved performance in jet engine applications. For most of the 20<sup>th</sup> century the primary USAF fuel was JP-4, a mixture of the gasoline and kerosene fractions. The gasoline fraction was maintained to keep a lower freezing point leading to improved cold temperature stability and lubricity [1]. When commercial aviation developed in the 1960's a purely kerosene fuel named Jet A was developed. An advantage of Jet A over JP-4 was reduced flammability leading to safer operation. The damage and losses by the USAF due to use of the highly flammable JP-4 in the Vietnam War, motivated the switch from JP-4 to a fuel similar to Jet A [1]. The new fuel, JP-8, was practically the same as Jet A, but had an additive package to improve lubricity and prevent accidents caused by icing and static discharge during fueling. By 1995 the USAF completely converted to JP-8 for all aircraft and mobile ground equipment [1].

The specifications for JP-8 were motivated by operational parameters developed throughout the evolution of jet fuels. To specify sooting tendency, the USAF regulates hydrogen content as well as smoke point and naphthalene content. With regard to sooting tendency, specifications for JP-8 require the following [3]:

1. Minimum hydrogen content, 13.4% by mass
2. Minimum smoke point of 25 mm

OR

Minimum smoke point of 19 mm AND Maximum naphthalene 3% by volume



The first requirement establishes the H/C ratio, which has shown some correlation with sooting tendency in the literature. The second requirement specifies the minimum smoke point, which is found through a standard ASTM measurement [4] of the flame height taken at the onset of soot breakthrough of a wick-fed diffusion flame. The minimum smoke point requirement depends on the naphthalene content, because naphthalene is known to be a heavily sooting compound.

As described above, there is a wide range of acceptable fuels for JP-8. An estimate of the range of properties found in JP-8 fuels is included in the 2006 Petroleum Quality Information System (PQIS) report [5]. This report cites critical data on fuel quality and property variations for the year. Certain chemical and physical properties found for JP-8 are summarized in Table 1.

**Table 1** Minimum, maximum, and average properties values of JP-8, from the 2006 PQIS report [5].

	Min.	Max.	Avg.
Hydrogen Content (mass %)	13.40	14.78	13.81
H/C Ratio	1.844	2.067	1.909
Cetane Number	31.8	56.8	43.9
Smoke Point (mm)	19.0	31.0	22.7
Aromatics (liq. vol. %)	0.10	24.60	17.86
Density (g/ml) @ 288.15 K	0.7800	0.8325	0.8038

## 2.2 Soot Threshold or Smoke Point

The soot threshold or smoke point is the point at which any increase in flame height or fuel flow rate results in smoke emitted from the tip of the flame. Soot threshold studies of diffusion flames began in the early 20<sup>th</sup> century and continue to be relevant today in the specifications for jet fuel. The first investigators of sooting tendency were

concerned with the quality of kerosene burned in oil lamps. The smoke point was determined by observing a distinct change in the shape of the flame tip as the flame height was adjusted. It was realized that fuels which produced more soot tended to reach the soot threshold at lower flame heights than less sootier fuels. Kewley and Jackson [6] studied the soot threshold on a Weber Photometer lamp, which burned liquid fuels using a wick. The length of wick could be adjusted to find and measure the height of the smoke point. They defined a “tendency to soot” of kerosene as the measured height subtracted from 32 mm, the upper limit of the scale. Thus the higher the resulting value, the higher the “tendency to soot” was for that fuel. Minchin [7], noting that in this definition a smoke point height of 32 mm or higher would have a “tendency to soot” of zero or below, improved the parameter to an inverse relationship,

$$S_t = K / SP , \quad (1)$$

where  $S_t$  was called the smoking tendency, and  $K$  was an arbitrary constant. Minchin measured the smoke point heights of seven pure hydrocarbons and three phenol compounds using a Weber Photometer lamp. Using a correlation of the volume of the flame, estimated roughly as a cone shape, and the required molar volume of oxygen, and the molar volume of combustion products, Minchin predicted the smoke point heights of compounds that had not been measured. These calculated smoke point heights allowed Minchin to make a qualitative ranking of the sooting tendency of groups of compounds with similar molecular structure, or hydrocarbon classes: alkanes < alkenes and monocyclic cycloalkanes < di-alkenes and di-cyclic cycloalkanes < benzene series < naphthalene series. Within each hydrocarbon class, it was found that  $S_t$  had a relationship to carbon number. For paraffins,  $S_t$  decreased as carbon number increased, but for the other hydrocarbon classes,  $S_t$  increased as carbon number increased. These observations demonstrated that  $S_t$  was closely related to molecular structure.

Two other studies on smoke point were conducted on conical pool burners. Instead of burning from a wick, the flame burned from the surface of a pool of the liquid

fuel. The method of varying the flowrate of fuel was similar in concept to the wick design of exposing more or less wick surface, instead here the level of the pool in the cone was changed. Actual values of smoke point heights differed, but general trends between compounds remained the same. The smoke point data obtained by Clarke *et al.* [8] on a wickless conical burner looked at several new hydrocarbons, but the smoke points were consistently greater than the data from the wick lamp. They observed similar qualitative trends, and also noted an adequate correlation of sooting tendency with C/H ratio. However, a significant exception to the C/H ratio correlation was that branched-chain alkanes had a greater sooting tendency than normal alkanes despite having the same C/H ratio. This observation indicated the effect of increased sooting tendency with branching. Van Treuren [9] also used a conical pool burner to measure the *SP* for seven hydrocarbons and obtained similar results as Clarke *et al.* Van Treuren observed the influence of air flow and burner temperature on smoke point, which suggested that actual numerical values for smoke point were apparatus specific.

A later work by Schug *et al.* [10] concluded that C/H ratio does not have a direct effect on the smoke point. Their study looked at the smoke point of gaseous hydrocarbons in a cylindrical burner, with sufficiently large surrounding air flow. Along with testing the effect of additives on smoke point, several mixtures of acetylene plus hydrogen, methane, ethane, or ethylene, were used to match C/H ratio with different components. Their results showed that mixtures with the same C/H ratio did not display the same smoke points, and each pair of compounds followed its own distinct trend with C/H ratio.

Instead of the flame height, Schalla and McDonald [11] measured the fuel consumption rate at the smoke point. They employed a wick burning lamp, and tested 38 hydrocarbons. To calculate the burning rate, the difference in the weight of the lamp was measured after remaining at the smoke point for a given interval of time. These results for fuel consumption rate at the smoke point in a wick-fed lamp were checked against the

same fuels burned in a pressure bomb in the gaseous phase, and the fuel flowrates matched to within  $\pm 2\%$ . Schalla and McDonald represented sooting tendency as the reciprocal of the smoke point fuel flowrate, and plotted it against carbon number, as Minchin had done for the inverse of the estimated smoke point heights. Schalla and McDonald also obtained linear correlations between compounds of the same hydrocarbon class. However, the trends showed that sooting tendency increased with carbon number for all hydrocarbon classes except cycloalkanes. For normal alkanes, these findings agreed with the trend calculated by Minchin, but for alkenes and aromatics they contradicted Minchin's findings. It should be noted that it is not known exactly which compounds Minchin considered, only that they ranged from  $C_6$  to  $C_{17}$ . Schalla and McDonald measured compounds from  $C_2$  to  $C_{10}$ .

Schalla and McDonald attempted to find a parameter that would result in a single correlation with the smoke point fuel flowrates for all hydrocarbons. They tried to correlate smoke point with the average strength of the carbon-carbon bonds in the molecule. They obtained a decreasing non-linear relationship that was reasonably successful. However, some disparities remained, in particular between sooting tendencies of alkanes and iso-alkanes. Since alkanes and iso-alkanes have the same type of bonds, there should have been no difference between compounds with the same carbon number, but their smoke point fuel flowrates were different. This meant branching had an effect that was still not taken into account, as Clarke *et al.* had also found.

The smoke point study performed by Hunt [12] provided the smoke point for 74 hydrocarbons, the most comprehensive set of data up to this point. Hunt used felt wicks in a Davis Factor lamp, which had been designed as an improvement over the Weber Photometer lamp used by earlier researchers. Also tested were two binary mixtures consisting of an aromatic, either 1-methylnaphthalene or sec-butylbenzene, and a normal alkane, n-dodecane. It was found that the smoke point of the mixtures decreased continuously as more aromatic was added, but the trends were not linear. The initial drop

in smoke point was more drastic for small amounts of 1-methylnaphthalene than for sec-butylbenzene.

### 2.3 Threshold Soot Index, TSI

Calcote and Manos [13] recognized that previous smoke point studies all demonstrated that a similar qualitative ordering of hydrocarbon classes (e.g. alkanes < iso-alkanes < cycloalkanes < alkenes < alkynes < benzenes < naphthalenes) could be reproduced in different studies, but actual values of smoke points and trends with carbon number were not consistent. The trends for some hydrocarbon classes were increasing with carbon number and others decreasing, and even these trends were not the same in all cases. Previous studies had also concluded that sooting tendency exhibited trends with C/H ratio and carbon-carbon bond strengths, but the relationships did not apply to all compounds. In addition, the accepted definition of tendency to soot,  $K/SP$ , did not take into account the effect of fuel molecule size on flame height. As the molecular weight increases, the flame height increases because more oxygen must diffuse into the flame to consume a unit volume of fuel [13]. Calcote and Manos [13] noted that the molecular weight of a fuel was approximately linearly proportional to the number moles of air needed to consume a mole of fuel and was a convenient proxy for moles of air per mole of fuel.

Calcote and Manos [13] attempted to resolve these issues by defining the Threshold Soot Index (TSI), which considered all the literature data on smoke point and accounted for the differences in each smoke point apparatus used. To quantitatively compare sooting tendencies between hydrocarbons, they proposed that TSI have a scale from 0 to 100. The molecular weight,  $MW$ , of the fuel tested was incorporated into the definition for TSI,

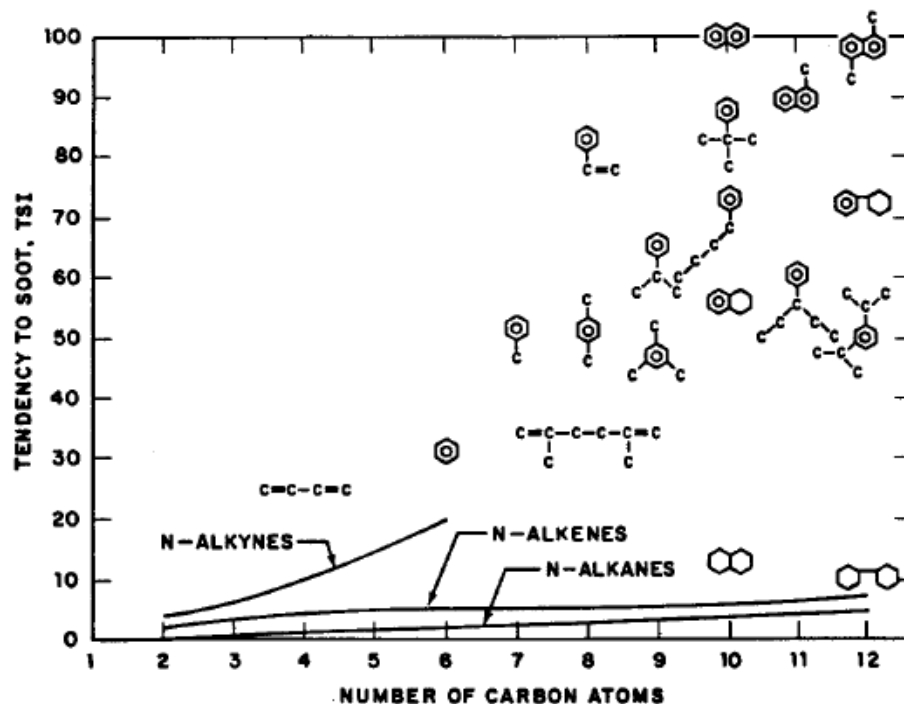
$$TSI = a(MW/SP) + b, \quad (2)$$

to account for the change in flame height with larger molecules. The constants,  $a$  and  $b$ , were used to put the TSI on a uniform scale and compare results from different experiments. The units of  $a$  were  $[\text{mm} \cdot (\text{g/mol})^{-1}]$ , and  $b$  was unitless. The constants were changed for each study in order to minimize differences in TSI scales. Since Schalla and McDonald measured the mass flowrate ( $\dot{m}$ ) at the smoke point, and the inverse of this parameter also characterized sooting tendency, an alternate definition of TSI was

$$TSI = a'(MW/\dot{m}) + b' . \quad (3)$$

The units of  $a'$  were  $[(\text{mg/s}) \cdot (\text{g/mol})^{-1}]$ , and  $b'$  was unitless.

The TSI correlation resulted in improvements for the representation of pure hydrocarbon sooting tendencies. With TSI, a distinction was made between sooting tendencies of compounds with the same smoke point but different molecular weights, which occurs with a number of aromatics. Also, the direction of trends with carbon number became consistent for all classes of hydrocarbons as shown in Figure 1. The TSI of all hydrocarbon classes increased with carbon number, although the effect of carbon number on alkanes and alkenes was not large. No single trend line of TSI versus C/H ratio for aromatics could be drawn that would give a good fit to the data.



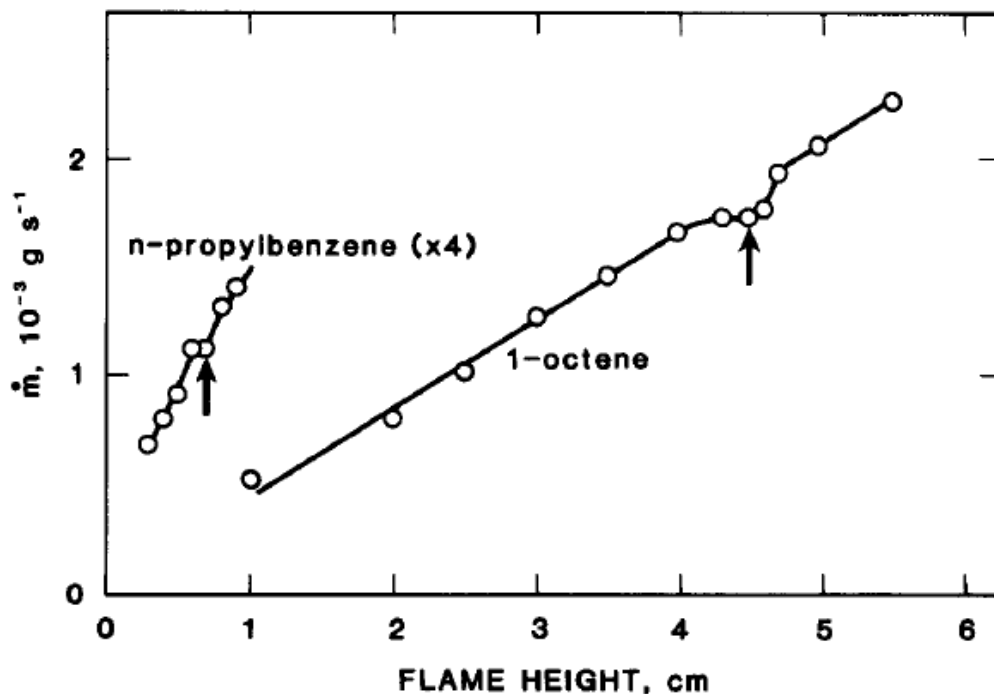
**Figure 1** Trends of TSI with carbon number for different hydrocarbon classes. Data points for aromatics are represented with the molecular structure of the specific compound. Source, Calcote and Manos 1983 [12].

Calcote and Manos presented a procedure for defining a single TSI scale for the multiple sources of data available. In this procedure, the TSI was defined for the first set of data, Ref. 12, by arbitrarily assigning TSI values to the compounds with the highest and lowest values of  $MW/SP$  for that first data set. This gave two equations in the form of Eq. (2), where only  $a$  and  $b$  were unknown. After solving for  $a$  and  $b$ , the TSI for every compound measured in that data set could be found from Eq. (2). The constants for subsequent data sets were found by finding two compounds that were measured in both data sets. TSI values from the first data set were assigned to these two compounds. Then preliminary constants ( $a$ ,  $b$ ) for the second data set could be found, allowing calculation of preliminary TSI values for the rest of the compounds. The preliminary TSI values were rescaled to minimize the differences from the first data set using a least-squares

linear correlation. Finally, because naphthalene had a TSI higher than 100, a linear adjustment was applied to all the TSI data to ensure the scale ranged from 0 to 100.

Olson *et al.* [14] applied the TSI model to smoke point data taken on a custom built wick-fed laminar diffusion flame apparatus. In addition to measuring the smoke point, the apparatus was mounted on a balance which allowed measurement of the fuel mass consumption rate,  $\dot{m}$ . When  $\dot{m}$  was plotted versus the flame height, a linear relationship was observed, except for a local minimum at the smoke point height as shown in Figure 2. Olson *et al.* suggested that determining the smoke point from this local minimum in  $\dot{m}$  was a more repeatable and objective method than traditional visual inspection of the flame shape. The average TSI values reported in the work by Calcote and Manos [13] were plotted against the  $(MW/\dot{m})$  data measured by Olson *et al.*, and a linear regression was applied to all the compounds tested. The linear regression solved for the constants  $a$  and  $b$ , and provided a linear correlation coefficient, which indicated how well their TSI values correlated to the values Calcote and Manos reported. Examples of this procedure are given in the experimental section. To summarize the data, Olson *et al.* provided a list of “Suggested Values” for TSI as averages of the TSI values from all the previous studies, Refs. 7-12, 14, and their study.





**Figure 2** Relationship between flame height and fuel mass consumption rate of n-propylbenzene and 1-octene. Arrows point to local minimum observed at the smoke point. Source, Olson *et al.* 1985 [13].

Yan *et al.* [15] applied a structural group contribution method to predict TSI values. The approach used a multivariable regression model, based solely on molecular structure. The results predicted the TSI values of about 70 compounds with a standard deviation of 1.3 TSI units. The structural group contribution method could also estimate the TSI values for certain compounds which lacked experimental data. An example of one of these compounds is iso-cetane, for which the TSI value was estimated to be 14.6.

## 2.4 Yield Sooting Index, YSI

Despite the scaling procedures used by Calcote and Manos and by Olson *et al.* to minimize differences between sources, TSI data varied considerably for certain compounds, especially aromatics. The values of smoke point and  $\dot{m}$  at the smoke point are small for these heavily sooting compounds, and smoke point data are inversely

proportional to sooting tendency. As a result, small variations in these measurements can result in large differences in TSI values. Because most TSI data have been based on the more subjective, visual determination of smoke point, the uncertainty in TSI can be large.

McEnally and Pfefferle [16, 17] pointed out these limitations of creating a sooting index based on measurements at the smoke point. They proposed a similar scale based on the soot yield of a diffusion flame rather than the soot threshold. The maximum soot volume fraction,  $f_{v,max}$ , was measured along the centerline of a nitrogen-diluted methane diffusion flame doped with small quantities of the compound of interest, which vaporized once introduced into the heated fuel stream. Using this technique, the flame conditions, such as temperature, residence time, and concentration of radicals, stayed relatively constant for each compound tested. Laser induced incandescence (LII) intensities, which have been shown to be proportional to soot volume fraction [18], were measured at different heights of the flame, and the highest value was taken as  $f_{v,max}$ . Since  $f_{v,max}$  is proportional to sooting tendency, the definition of the Yield Sooting Index (YSI) is

$$YSI = c(f_{v,max}) + d \quad (4)$$

where  $c$  and  $d$  are experiment specific constants used to scale the YSI from 0 to 100. In the first of two studies, 400 ppm of the fuel was introduced into the methane fuel stream. This requirement limited the selection of compounds that could be tested to fuels with relatively high volatilities. YSI values were measured for 68 hydrocarbons, most of which were aromatics. The compounds used to scale YSI were benzene, which was set to 30, and 1,2-dihydronaphthalene, which was set to 100. The value assigned to benzene was the previously reported average TSI, but the TSI of 1,2-dihydronaphthalene had not been measured. Instead, through mixtures with 2-heptanone, it was shown that the YSI of 1,2-dihydronaphthalene was equivalent to naphthalene, which had a previously reported TSI of 100.

In the second study, the YSI values of 72 non-volatile aromatics were measured by dissolving each compound into a solvent (2-heptanone), and injecting the solution in the same manner as the pure fuels in the first study. Six compounds tested in the first study were able to be retested in the second study. The constants from the second study were defined so that the YSI values for these compounds matched as well as possible. This resulted in endpoint compounds, 2-heptanone and phenanthrene, with YSI values of 17 and 191, respectively.

McEnally and Pfefferle calculated the uncertainty in YSI to be only  $\pm 3\text{-}10\%$ , depending on the amount of compound injected, as compared to  $\pm 15\%$  for TSI values based on *SP* (from Ref. 10), and  $\pm 7\%$  for the TSI values based on *m* (from Ref. 13). The YSI agreed with TSI values from Hunt and Olson *et al.* for most compounds within the estimated uncertainties. Therefore, McEnally and Pfefferle concluded that the YSI was a preferred sooting tendency index over the TSI because the YSI had better accuracy for heavily sooting compounds, and the YSI ranks sooting tendency according to the soot yield at the same conditions, as opposed to the soot threshold. Although the YSI has been valuable for measuring the sooting tendency of many aromatic compounds, YSI values have not been measured for many n-alkanes or iso-alkanes, which make up a large portion of jet fuels. Therefore, an attempt will be made to use both TSI and YSI values in this study.

## **2.5 TSI for Mixtures**

In the smoke point study performed by Gill and Olson [19], a possible TSI mixture rule for diffusion flames was investigated. The smoke point data from ten pure compounds, measured on an ASTM (1980) smoke point wick lamp, were compared to the suggested TSI values reported in Ref. 13, using a linear regression to obtain the apparatus-specific constants for TSI. Gill and Olson assessed the validity of the mixture rule of a linear sum of the component TSI values weighted by their mole fractions,  $x_i$ ,

$$TSI_{mix} = \sum_i x_i TSI_i, \quad (5)$$

using six binary fuel blends and two tertiary fuel blends. The binary mixtures were decalin/1-methylnaphthalene, iso-octane/tetralin, iso-octane/decalin, ethylbenzene/cumene, iso-octane/cumene, and iso-octane/cyclooctadiene. There was good agreement between the TSI values measured on the smoke point lamp and those predicted with Eq. (5). This work provided another benefit for using TSI over smoke point, a method to predict the sooting tendency of mixtures. Recall that the binary mixtures tested by Hunt had smoke points varying nonlinearly and inconsistently with composition.

Yan *et al.* [15] tested the linearity of the TSI parameter,  $MW/SP$ , on two other binary mixtures, n-octane/toluene and iso-octane/toluene. They did not go through the process to find the constants specific for their experiment, so actual TSI values could not be calculated. However, when comparing values of  $MW/SP$  measured on their apparatus, the results showed that both mixtures obeyed a linear relationship with mole fraction within the range of data taken, supporting the results of Gill and Olson. The correlation coefficients were both  $R^2 > 0.99$ .

## 2.6 Correlations of Soot Measurements with TSI

The correlation of TSI with actual soot formation in the smoke point flame was examined by Olson *et al.* [14]. Line-of-sight multiwavelength light extinction was used to measure the maximum soot volume fraction,  $f_{v,max}$ , in the same diffusion flames used to measure their TSI values. At the soot threshold, the  $f_{v,max}$  height, was consistently around half the height of the smoke point. The  $f_{v,max}$  in the diffusion flame was found to have a nonlinear relationship with the TSI. However, since the measurements were taken with each compound at its own soot threshold, the temperatures in each flame were different, which also has an effect on the amount of soot produced.

Yang *et al.* [20] tried to correlate TSI with the relative flame radiation and relative exhaust soot in a Rolls Royce Tyne combustor measured by Pande and Hardy [21]. The fuels tested were JP-8, JP-8+100, and various coal-derived liquid fuels. Results of GC-MS analyses provided the paraffin, naphthene, monoaromatic, and diaromatic content, which accounted for a rough composition of the fuels. The TSI values of the practical fuels were calculated by selecting a representative compound for each hydrocarbon class, and applying Eq. (5) using the suggested TSI value from Ref. 14. The relative flame radiation and exhaust soot were found to correlate with the calculated TSI, with  $R^2$  values of 0.989 and 0.867 respectively. It was concluded that as a predictor of sooting tendency, TSI performed better than hydrogen content and smoke point. This work indicated that TSI has merit as a predictor of sooting tendency in actual engines.

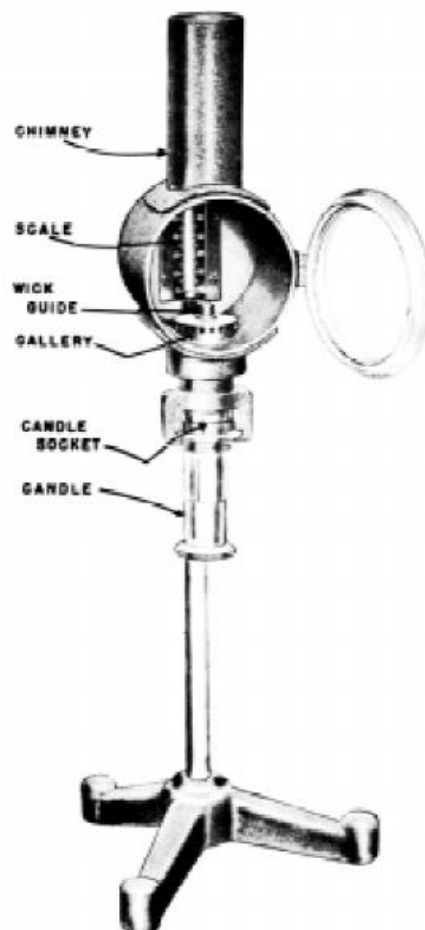
## **2.7 Summary of Soot Threshold as a Measure of Sooting Tendency**

Many researchers have attempted to correlate measurements at the soot threshold with aspects of molecular structure to predict the sooting behavior of fuels in different applications. Originally, the burning of oil in lamps motivated these studies; later the motivation shifted to diesel and jet fuel in engines. Developments in understanding the soot threshold had been achieved, but not until the 1980's was it recognized that molecular weight was a missing factor in the correlation for sooting tendency. Once this link was made, a relative scale ranking sooting tendency of all hydrocarbons was created, similar to the octane number (ranking resistance to autoignition) for gasoline or the cetane number (ranking ignition delay time) for diesel. In more recent work, an effort has been made to show that the sooting tendencies measured in the laboratory correlate to the amount of soot produced in real applications.

## CHAPTER 3 EXPERIMENTAL APPROACH

### 3.1 Experimental Apparatus

A standard smoke point lamp for liquid fuels as specified by ASTM D1322-97 *Standard Test Method for Smoke Point of Kerosine and Aviation Turbine Fuel* [4] was used for measurements of smoke point height. The lamp is pictured in Figure 3. The fuel was stored in the reservoir labeled “candle” and burned from a cotton wick. The specifications for the standard wick are listed in ASTM D1322 [4]. The wicks used were obtained from Koehler Instrument Company, Inc., part no. K27021. The candle assembly could be raised and lowered to expose more or less of the wick through a screw mechanism. This allowed for reasonable control of the flame height. The height of the flame was measured along a 50 mm scale mounted on the surface behind the flame. The top of the wick guide was level with the zero mark on the scale. The glass door on the front of the apparatus was curved to prevent the formation of multiple images. The chimney, as well as an outer black painted steel frame surrounding the apparatus on three sides, acted to minimize disturbances in the air and stabilize the flame.



**Figure 3** Drawing of ASTM standard smoke point lamp. Source, ASTM D1322-97 [4].

### 3.2 Experimental Procedure

Smoke point measurements were made according to the procedure in ASTM D1322-97 [4] for the compounds listed in Table 2. First a 15-20 mL sample was obtained and poured into a 25 mL graduated cylinder. A new cotton wick was dipped into the sample so that the entire wick was submerged. Then a wick trimmer assembly was used to pull the soaked wick through the lid of the candle. The excess wick was cut off cleanly with a razor blade so that 6 mm protruded from the end of the candle. The end of the wick was dipped back into the sample to ensure it had not dried out. The rest of the sample was poured into the candle reservoir. Once the reservoir and wick were

assembled, the candle was locked into place on the apparatus. After the flame was lit, the door was immediately closed, and the wick was lowered until the flame stopped emitting smoke. To find the precise location of the smoke point, the wick needed to be raised just above the smoke point, and then lowered back to the smoke point. The smoke point was reached when the shape of the flame tip changed from elongated with concave upward edges, to a very slightly blunted tip with straight (not concave downward) edges. This change of shape is depicted in Figure 4. In some cases the elongated tip, observed above the smoke point, included soot “wings” on the sides, where soot “breakthrough” was clearly visible. At the smoke point, the soot “wings” merged smoothly with the rest of the flame. In general, the smoke points of heavily sooting compounds were short, and easy to identify. This was due to the low flowrate associated with a smoke point of this height, leading to a stable flame with well defined edges. The height of the flame was measured by lining up the top of the flame with its reflection on either side of the vertical line in the scale as shown for a typical smoke point flame in Figure 5. The value was recorded to the nearest millimeter. Following the completion of the test, the remaining fuel was removed and either discarded or saved in sample bottles for further tests. The metal parts comprising the candle and wick trimmer assembly were washed in n-heptane. All used glassware was rinsed with dichloromethane. If a second smoke point test was to be done the same day, the rinsed parts were blown dry with compressed air.



**Table 2** Name, chemical formula, CAS #, and purity of all pure hydrocarbons used.

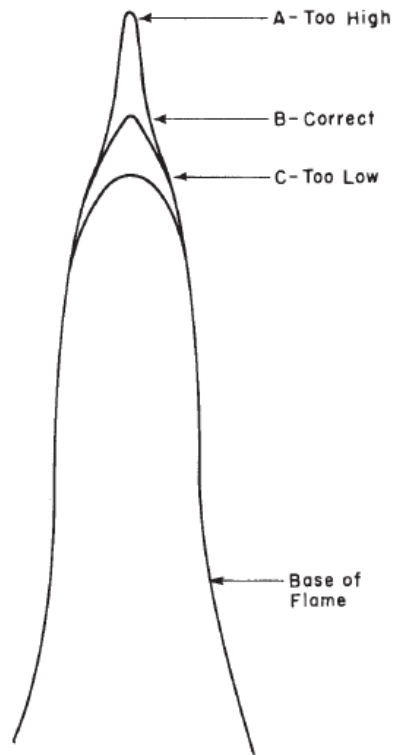
IUPAC name (common name)	Formula	CAS #	Purity
2,2,4,4,6,8,8-heptamethylnonane (iso-cetane)	C <sub>16</sub> H <sub>34</sub>	4390-04-9	98%
n-dodecane	C <sub>12</sub> H <sub>26</sub>	112-40-3	99%
cyclohexylbenzene	C <sub>12</sub> H <sub>16</sub>	827-52-1	97%
n-decane	C <sub>11</sub> H <sub>10</sub>	124-18-5	99%
1-methylnaphthalene	C <sub>10</sub> H <sub>22</sub>	90-12-0	97% <sup>a</sup>
1,2,3,4-tetrahydronaphthalene (tetralin)	C <sub>10</sub> H <sub>18</sub>	119-64-2	99%
decahydronaphthalene (decalin)	C <sub>10</sub> H <sub>12</sub>	91-17-8	98%
1,2-dihydronaphthalene	C <sub>10</sub> H <sub>10</sub>	447-53-0	98%
1,2,4-trimethylbenzene	C <sub>9</sub> H <sub>12</sub>	95-63-6	98%
1,3,5-trimethylbenzene	C <sub>9</sub> H <sub>12</sub>	108-67-8	99%
propylbenzene	C <sub>9</sub> H <sub>12</sub>	103-65-1	98%
2,2,4-trimethylpentane (iso-octane)	C <sub>8</sub> H <sub>18</sub>	540-84-1	99.8% <sup>b</sup>
1,3-dimethylbenzene (m-xylene)	C <sub>8</sub> H <sub>10</sub>	108-38-3	99% <sup>c</sup>
methylcyclohexane	C <sub>7</sub> H <sub>14</sub>	108-87-2	99%
1-methylbenzene (toluene)	C <sub>7</sub> H <sub>8</sub>	108-88-3	99.9%
benzene	C <sub>6</sub> H <sub>6</sub>	71-43-2	99% <sup>d</sup>

<sup>a</sup> Impurities include 2-methylnaphthalene.

<sup>b</sup> Impurities include water.

<sup>c</sup> Impurities include o-xylene, p-xylene, and toluene.

<sup>d</sup> Impurities include H<sub>2</sub>SO<sub>4</sub>, thiophene, sulfur compounds, and water.



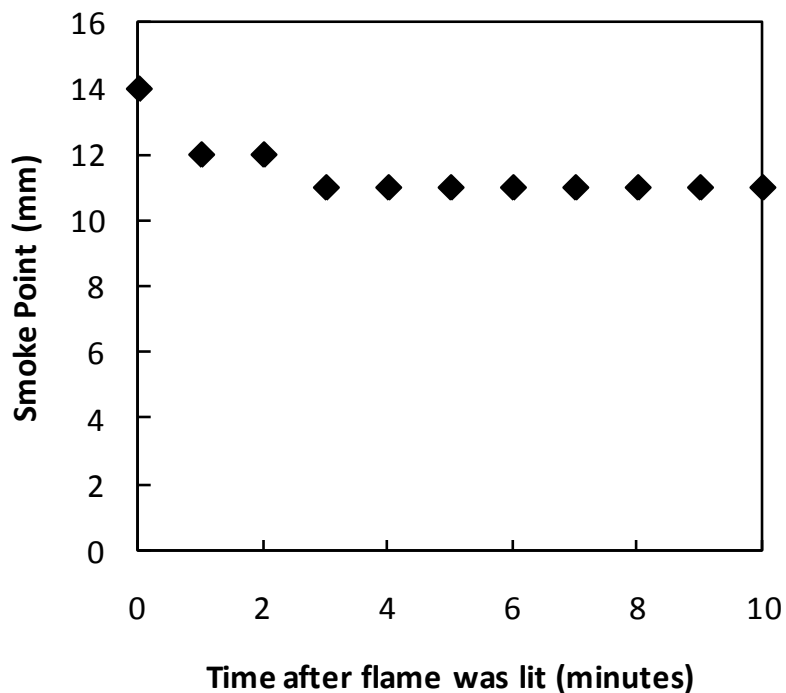
**Figure 4** Drawing of the shape of a flame: A – above the smoke point; B – at the smoke point; and C – below the smoke point. Source ASTM D1322-97 [4].



**Figure 5** Photograph taken of an iso-octane/toluene diffusion flame at the smoke point.

During some experiments, most noticeably with mixtures, it was found that the smoke points changed over time. For example, Figure 6 shows the raw smoke point

readings for a mixture of 20% 1-methylnaphthalene and 80% decalin (by volume) taken every minute during one smoke point test. In the case of this mixture, the smoke point reached the final value after three minutes. However, this length of time varied for different fuels, from less than one minute for pure compounds, up to five minutes for certain mixtures. Furthermore, the smoke points of some fuels increased to a final value, and others decreased. A change in smoke point for pure compounds can be attributed to the time to reach steady state. In the case of mixtures, it is possible that the composition of the gaseous fuel just above the wick is not the same as the composition of the liquid mixture in the candle during this transient period. This could occur due to differences in boiling points of the mixture components. Consequently, as the composition of the gaseous fuel mixture adjusts, the smoke point would change. To avoid the issue of recording transient data, only the values measured after the system reached steady state were recorded as actual smoke points. It was found that waiting five minutes was sufficient time to reach steady state.



**Figure 6** Smoke point height of a fuel mixture (20% 1-methylnaphthalene/80% decalin, by volume) changing with time before reaching a steady value of 11 mm.

Because it was possible that during the first five minutes of burning, the vapor composition varied from the mixture composition, a test was done to find out whether the remaining liquid composition was affected. The smoke point of a mixture of 40% iso-octane/60% 1,2,4 trimethylbenzene was observed to increase from 9 to 10 mm after a few minutes. Ten milliliters of this mixture were prepared and burned on the smoke point lamp for 20 minutes. Then the flame was extinguished, relit and burned for another 20 minutes. In the first few minutes after the flame was lit both times, it was observed, as before, that the smoke point increased from 9 to 10 mm. About half of the original 10 mL sample remained in the fuel reservoir, and about 2 mL was absorbed into the wick. Therefore, it is estimated that about 3 mL, or 30%, was consumed. Since 1,2,4 trimethylbenzene has a lower boiling point it would be expected that there more than 60% 1,2,4 trimethylbenzene was burned in the initial transient period. In addition, the

transient smoke point is closer to the smoke point of 1,2,4 trimethylbenzene, supporting the hypothesis that there would be less 1,2,4 trimethylbenzene in the remaining fuel, if a difference was observed. A GC-MS analysis, performed on a Shimadzu QP-5000, of the remaining fuel revealed an approximate composition of 39% iso-cetane/61% 1,2,4 trimethylbenzene. The difference of 1% from 40/60 is not in the expected direction, and so within the accuracy of this technique, the composition of the remaining fuel was not affected by the transient behavior after the flame is lit.

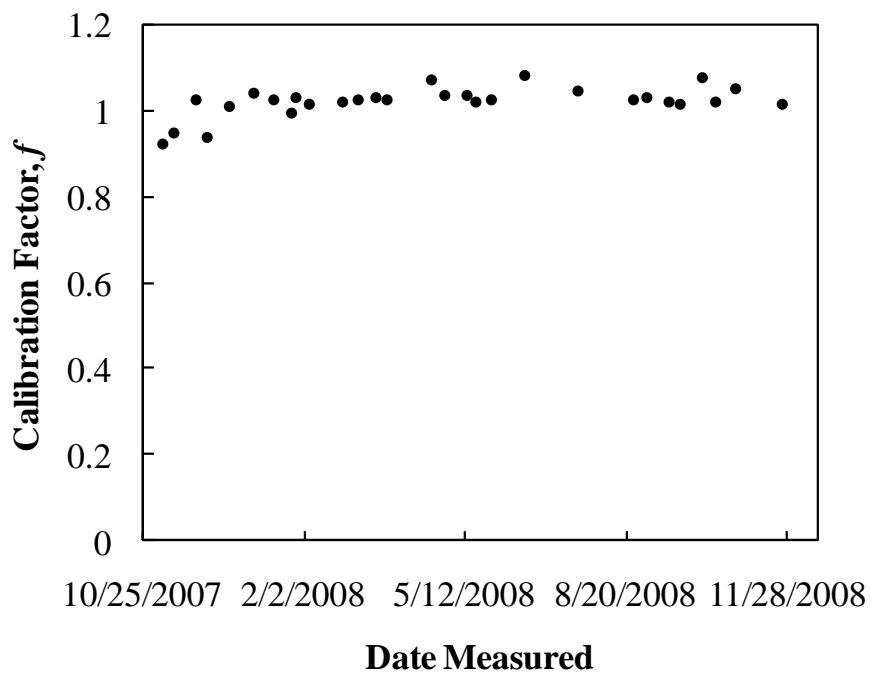
Calibration of smoke points was achieved by multiplying the average of three smoke point readings, taken after the specified five minute transient period, by a calibration factor. This calibration factor was obtained for each set of data by measuring the smoke points of two of the six recommended reference fuel blends of toluene and 2,2,4-trimethylpentane (iso-octane). The smoke points for the reference blends were specified in ASTM D1322-97 [3] for standard pressure of 101.3kPa. The calibration factor,  $f$ , was calculated using Equation (6),

$$f = \frac{1}{2} \left[ \left( \frac{SP_{1,std}}{SP_{1,meas}} \right) + \left( \frac{SP_{2,std}}{SP_{2,meas}} \right) \right] \quad (6)$$

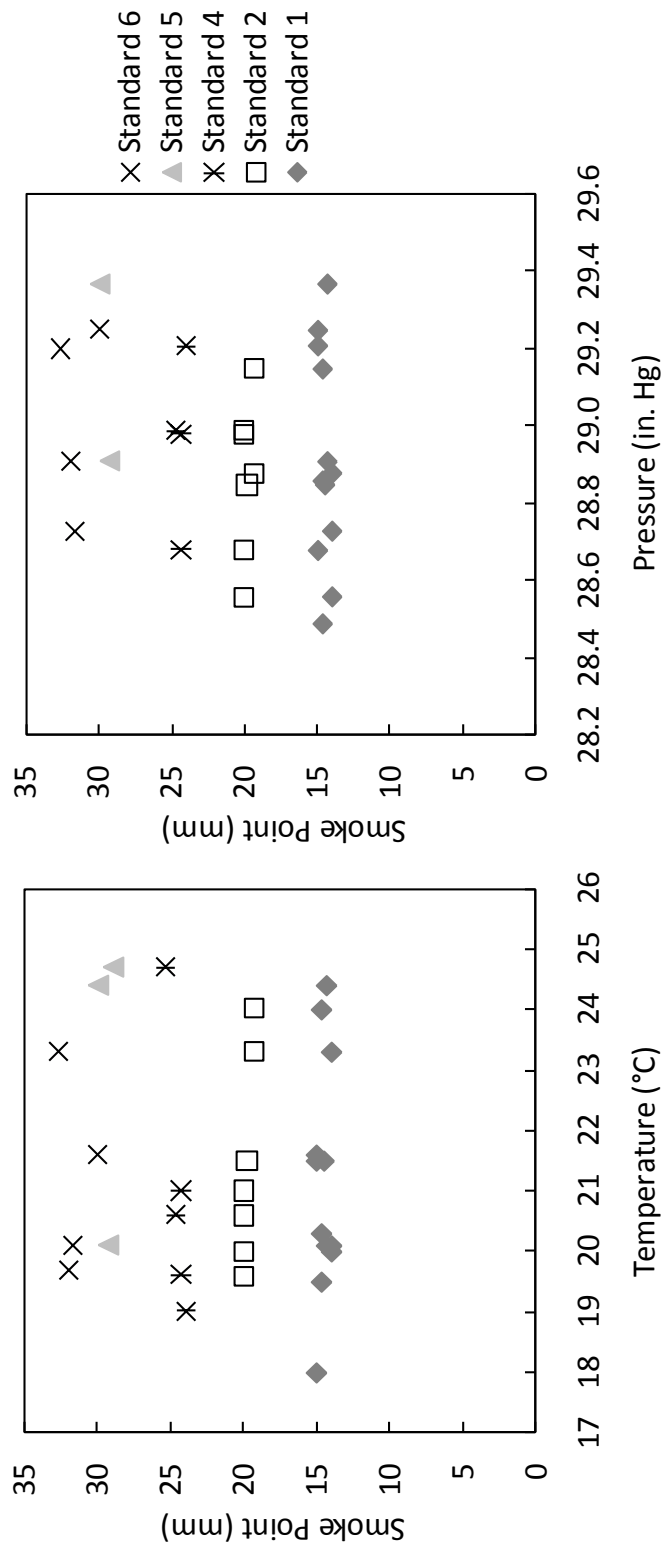
where  $SP_{1,std}$  and  $SP_{1,meas}$  are the standard and measured smoke point values for the first reference blend, and  $SP_{2,std}$  and  $SP_{2,meas}$  are for the second reference blend. If possible, the reference blends were chosen so that their smoke points bracketed the smoke points of the samples for that data set.

Figure 7 shows the calibration factors obtained as a function of time over somewhat more than a year. Generally these values were close to one. The largest deviations were within 8%. To investigate whether slight fluctuations in ambient conditions caused the variation in the calibration factor, the ambient temperature and pressure were monitored. The ambient temperature ranged from 18-25°C, and the ambient pressure ranged from 28.5-29.4 inches Hg. Figure 8 plots the smoke points of the reference blends as functions of the ambient temperature and pressure. Appendix A

lists the raw data. It can be seen that the smoke points of the reference blends were not affected by the small changes in ambient conditions, because no trend with these parameters was observed. It is concluded that the variations in the calibration factor for each experiment were related to the specific standards used in that experiment.



**Figure 8** All data for smoke point heights of the standard calibration mixtures, as specified in ASTM 1322D-97 [3], plotted against ambient temperature and pressure.



### 3.3 Mixture Preparation

Reference fuel blends, binary mixtures, and surrogate mixtures, all were prepared from pure compounds in the same manner. The appropriate volumes and masses of each component were calculated according to the desired composition for batches of 20-25 mL. Pipettes of different sizes, 2 mL, 10 mL, and 25 mL, but the same accuracy,  $\pm 0.05$  mL, were used to measure the volume of each component. In addition, a Sartorius Analytic Balance, Type A200S, with a standard deviation of  $\pm 0.1$  mg, was used to measure the mass of each component. The mass readings, the more accurate of the two methods, were used to verify that the desired composition was achieved with the pipettes. Before the smoke point of the mixture could be tested, the mixture had to be completely uniform. It was observed that all compounds tested dissolved in one another in time and did not separate. Sufficient time for mixing was observed to be four hours, during which the mixtures were left in a closed bottle. Before a test, the sample was checked for any non-uniformities visible in the liquid. These non-uniformities were easily seen as lines when the sample was shaken or stirred. Table 3 lists the mixtures that were studied.



**Table 3** List of binary mixture components and surrogate mixture composition.

Binary Mixture Components	Surrogate Mixture	Liquid Volume Fraction
1,2,4-trimethylbenzene / iso-cetane	3-component A	63.2% iso-cetane
		22.0% n-dodecane
toluene / iso-octane	3-component B	14.8% 1,3,5-trimethylbenzene
		62.4% iso-cetane
n-dodecane / m-xylene	3-component B	20.4% n-dodecane
		7.2% 1-methylnaphthalene
1-methylnaphthalene / 1,2,4-trimethylbenzene	4-component A	67.8% iso-octane
		21.1% n-dodecane
1-methylnaphthalene / decalin	4-component A	8.3% 1,3,5-trimethylbenzene
		2.8% 1-methylnaphthalene
1-methylnaphthalene / methylcyclohexane	JP-8 surrogate (22)	53.0% iso-octane
		24.0% n-dodecane
		23.0% 1,3,5-trimethylbenzene

### 3.4 Procedure for TSI Calculation

Following the method described by Calcote and Manos [13], the set of TSI values was based on the highest and lowest values of  $MW/SP$  from the measurements. A TSI value of 100 was assigned to 1-methylnaphthalene, which had the highest  $MW/SP$ . The lowest  $MW/SP$  from the data was for methylcyclohexane. The TSI value for methylcyclohexane was chosen to be 5 because the suggested value reported in Ref. 13 for  $TSI_{MCH}$  was  $4.9 \pm 1.1$ . The apparatus specific constants could be found by solving for  $a$  and  $b$  in the TSI equations for 1-methylnaphthalene and methylcyclohexane, Eq. (7),

$$\begin{aligned}
 100 &= a \left( \frac{MW}{SP} \right)_{1-MN} + b \\
 5 &= a \left( \frac{MW}{SP} \right)_{MCH} + b
 \end{aligned} \tag{7}$$

Once  $a$  and  $b$  were known, the TSI value for any other compound or mixture with a known  $MW$  and a  $SP$  measured on the same apparatus could be found with Eq. (2).

### 3.5 Uncertainty Analysis

For pure compound smoke points, the experimental uncertainty was calculated by taking the root mean square of the bias and precision uncertainties. The bias uncertainty was 0.5 mm due to the resolution of the scale. The precision uncertainty was estimated as the confidence interval based on the standard deviation of the measured values. For each compound tested, an individual standard deviation was found. Then an average of these standard deviations, weighted by the number of readings for each compound, was taken to calculate the overall standard deviation. Considering all the smoke point readings taken, the sample size was well over 30, which was the minimum for a large sample size. Therefore, the 95% confidence interval was found assuming a normal distribution using Equation (8),

$$Confidence\ Interval = z_{(0.95/2)} \frac{S_x}{\sqrt{n}} = 1.96 \left( \frac{0.70mm}{\sqrt{138}} \right) = 0.12mm, \quad (8)$$

where  $z_{(0.95/2)}=1.96$  was the value of the z-distribution (normal distribution) for 95% confidence,  $S_x$  was the overall standard deviation, and  $n$  was the total number of smoke point readings. The root mean square of the total uncertainty, the precision uncertainty ( $\pm 0.12$  mm) and the bias uncertainty ( $\pm 0.5$  mm), was  $\pm 0.51$  mm and for the most part a result of the bias uncertainty. To calculate uncertainty in TSI values, the same value of uncertainty in smoke point measurement,  $\pm 0.51$  mm, was used for all compounds.

The uncertainty in TSI values was calculated through an analysis of the propagation of uncertainty of the constants ( $a$ ,  $b$ ), the  $MW$ , and the  $SP$ . The equation for the uncertainty in TSI involves the partial derivatives of TSI with respect to these quantities as well as the uncertainties in the quantities themselves, as shown in Equation (9),

$$\delta TSI = \sqrt{\left(\frac{\partial TSI}{\partial a} \delta a\right)^2 + \left(\frac{\partial TSI}{\partial MW} \delta MW\right)^2 + \left(\frac{\partial TSI}{\partial SP} \delta SP\right)^2 + \left(\frac{\partial TSI}{\partial b} \delta b\right)^2}, \quad (9)$$

where the symbol  $\delta$  designated the uncertainty in a particular quantity. The partial derivatives were as shown in Equation (10),

$$\begin{aligned} \frac{\partial TSI}{\partial a} &= \frac{MW}{SP} \\ \frac{\partial TSI}{\partial MW} &= \frac{a}{SP} \\ \frac{\partial TSI}{\partial SP} &= -\frac{aMW}{SP^2} \\ \frac{\partial TSI}{\partial b} &= 1 \end{aligned} \quad (10)$$

The uncertainty in the smoke point,  $\delta SP$ , had already been calculated to be  $\pm 0.51$  mm. For pure compounds there was no uncertainty in  $MW$ . The uncertainties in the constants,  $a$  and  $b$ , needed to be found. This was calculated by the method of propagation of errors of the TSI equations, Eq. (7), for 1-methylnaphthalene and methylcyclohexane used to find the constants. Solving these equations for  $a$  and  $b$ , gave Equation (11),

$$\begin{aligned} a &= \frac{95}{\left(\frac{MW}{SP}\right)_{1-MN} + \left(\frac{MW}{SP}\right)_{MCH}} \\ b &= \frac{100\left(\frac{MW}{SP}\right)_{MCH} + 5\left(\frac{MW}{SP}\right)_{1-MN}}{\left(\frac{MW}{SP}\right)_{1-MN} + \left(\frac{MW}{SP}\right)_{MCH}} \end{aligned} \quad (11)$$

The equations for  $\delta a$  and  $\delta b$  were found in the same form as Eq. (9), but these only had terms for the uncertainty of  $MW/SP$ , which were known. The uncertainties for the constants were found to be  $\delta a = \pm 0.4 \text{ mm}(\text{g/mol})^{-1}$  and  $\delta b = \pm 2.3$ .

The absolute experimental uncertainties in pure compound TSI values varied from  $\pm 0.6$  TSI units for methylcyclohexane (TSI = 5.0) to  $\pm 10.1$  TSI units for 1-methylnaphthalene (TSI = 100). This translated into an approximate value of  $\pm 10\%$  regardless of the compound. Compounds with low smoke points, such as 1-

methylnaphthalene, tended to have larger absolute experimental errors, but these same compounds tended to have larger TSI values. Conversely, compounds with high smoke points, such as methylcyclohexane, tended to have smaller absolute experimental errors and smaller TSI values.

For binary mixtures there was an uncertainty in the molecular weight due to the measured composition because the mixture molecular weight,  $MW_{mix}$ , was calculated from Equation (12),

$$MW_{mix} = \sum_i x_i MW_i, \quad (12)$$

Since there was no uncertainty in  $MW$  of pure compounds, the uncertainty in  $MW_{mix}$ , defined in Equation (13), was only dependent on the molecular weights of the components and the uncertainty in the mole fractions.

$$\delta MW_{mix} = \sqrt{\sum_i \left( \frac{\partial MW_{mix}}{\partial x_i} \delta x_i \right)^2} = \sqrt{\sum_i (MW_i \delta x_i)^2} \quad (13)$$

The uncertainty of the mole fractions was calculated from the accuracy of the balance ( $\pm 0.0001$  g) in measuring the mass of the components. The absolute masses were converted to mass fraction and then ultimately to mole fraction. This calculation typically gave an uncertainty in  $MW_{mix}$  on the order of 0.01 g/mol, which was negligible compared to the uncertainties in the smoke points. Therefore, the uncertainties for the TSI values of mixtures turned out to be comparable to those of pure compounds at around  $\pm 10\%$ .

## CHAPTER 4 RESULTS AND DISCUSSION

### 4.1 TSI for Pure Compounds

The smoke point heights were measured for the pure hydrocarbon compounds listed in Table 2 with the exception of iso-cetane, n-decane, and n-dodecane. Pure iso-octane could not be measured because the wick began to burn before the flame height could be increased to the smoke point. In the cases of n-decane and n-dodecane, the smoke point height exceeded the maximum range of the smoke point lamp (50 mm). The smoke points and TSI values found are given in Table 4. The experiment specific constants were calculated to be  $a = 4.07 (\pm 0.4) \text{ mm} \cdot (\text{g/mol})^{-1}$  and  $b = -4.8 (\pm 2.3)$ . The relative uncertainty in TSI is also reported.

**Table 4** Smoke point height, TSI, and relative uncertainty in TSI for pure compounds.

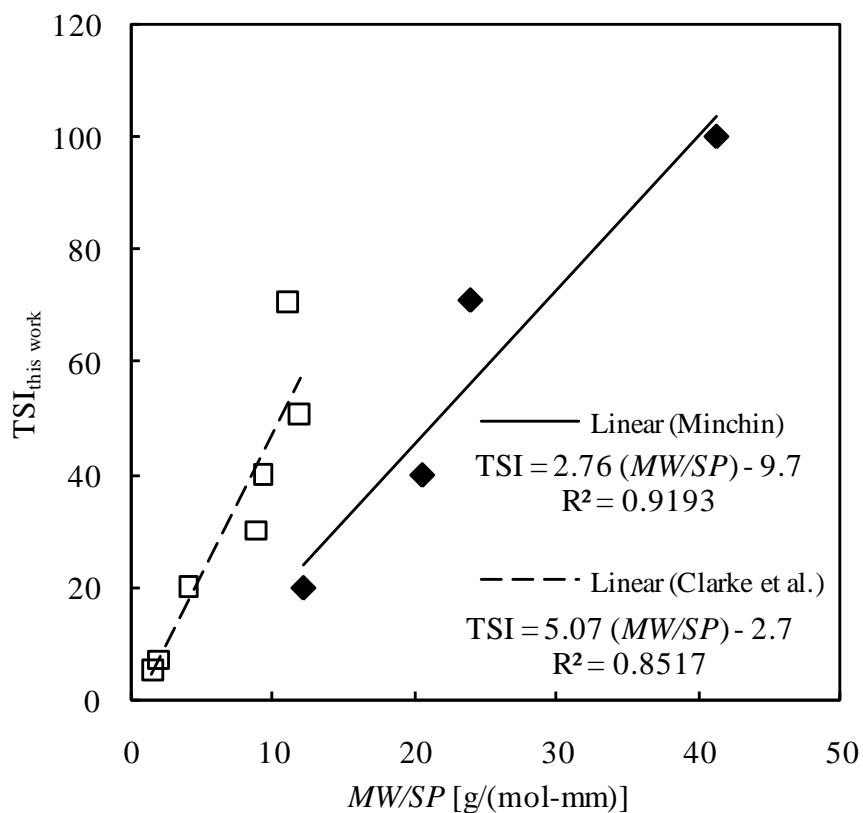
Pure Compound	Formula	<i>MW</i> (g/mol)	<i>SP</i> (mm)	TSI = 4.07 * ( <i>MW/SP</i> ) - 4.8	Uncertainty, $\delta\text{TSI}/\text{TSI}$
cyclohexylbenzene	C <sub>12</sub> H <sub>16</sub>	160.26	8.9	69	7%
1-methylnaphthalene	C <sub>11</sub> H <sub>10</sub>	142.20	5.5	100	10%
decalin	C <sub>10</sub> H <sub>18</sub>	138.26	22.7	20	5%
tetralin	C <sub>10</sub> H <sub>12</sub>	132.21	7.1	71	8%
1,2-dihydronaphthalene	C <sub>10</sub> H <sub>10</sub>	130.19	5.8	87	10%
1,2,4-trimethylbenzene	C <sub>9</sub> H <sub>12</sub>	120.20	7.2	63	8%
1,3,5-trimethylbenzene	C <sub>9</sub> H <sub>12</sub>	120.20	7.3	62	8%
n-propylbenzene	C <sub>9</sub> H <sub>12</sub>	120.20	8.5	53	7%
iso-octane	C <sub>8</sub> H <sub>18</sub>	114.23	40.0	6.8	10%
m-xylene	C <sub>8</sub> H <sub>10</sub>	106.17	7.8	51	8%
methylcyclohexane	C <sub>7</sub> H <sub>14</sub>	98.19	40.8	5.0	13%
toluene	C <sub>7</sub> H <sub>8</sub>	92.14	8.4	40	8%
benzene	C <sub>6</sub> H <sub>6</sub>	78.12	9.1	30	7%

To supplement the set of TSI values for potential surrogate components, previous TSI and YSI data sets were also considered. However, TSI values from the present study were not directly comparable because the previously reported TSI and YSI values were scaled differently. The first TSI scale, defined by Calcote and Manos [13], was based on two compounds tested by Hunt [12], and subsequent data sets were scaled from the initial TSI values corresponding to the Hunt data. Following the work by Calcote and Manos [13], researchers scaled new TSI data based on the average of previously reported values. To ensure consistent comparison of previous TSI results to those of this study, the scaling procedure was redone based on the TSI data set shown in Table 4. To compare separate data sets, it was required that at least two compounds be common to both studies. The studies which fit this criterion are shown in Table 5. These sources measured different parameters, including flame height at the smoke point, fuel mass flowrate at the smoke point, and maximum soot volume fraction in the doped methane flame studied by McEnally and Pfefferle [16, 17]. Table 5 also lists the units in which the data were measured. The measured quantities were rearranged into parameters proportional to sooting tendency (TSI or YSI), which are listed in the "TSI or YSI Parameter" column in Table 5. The TSI values were determined using the method, described by Olson *et al.* [14], of performing a linear regression between the TSI values in Table 4 and the corresponding TSI or YSI parameters from each prior study. The resulting regression equation defined the apparatus specific constants,  $a$  and  $b$ , and the  $R^2$  correlation coefficient for each data set.

**Table 5** Sources of sooting threshold data for pure hydrocarbons, which measured two or more compounds in common with this work.

Sources	Measured Quantity	Units	TSI or YSI Parameter
Minchin, 1931 [7]	$SP$	mm	$MW/SP$
Clarke <i>et al.</i> , 1946 [8]	$SP$	mm	$MW/SP$
Hunt, 1953 [12]	$SP$	mm	$MW/SP$
Schalla & McDonald, 1953 [11]	$\dot{m}$	mg/s	$MW/\dot{m}$
Olson <i>et al.</i> , 1985 [14]	$\dot{m}$	mg/s	$MW/\dot{m}$
Gill and Olson, 1984 [19]	$SP$	mm	$MW/SP$
McEnally & Pfefferle, 2007 [16]	$f_{v,max}$	--	$f_{v,max}$
McEnally & Pfefferle, 2008 [17]	$f_{v,max}$	--	$f_{v,max}$

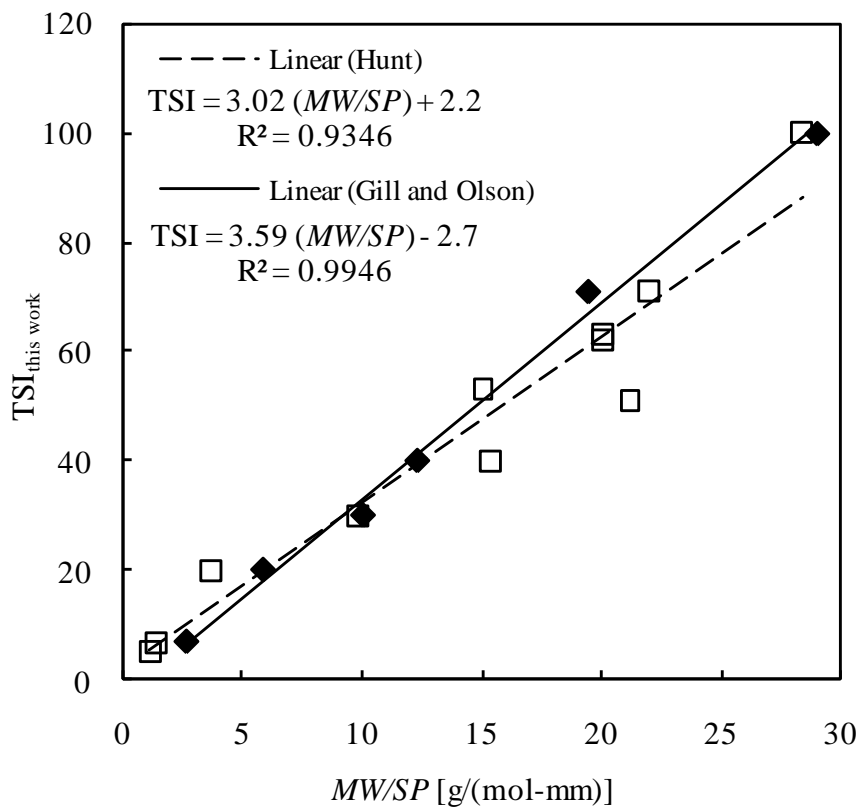
An example of such a regression is presented in Figure 9, with the measured TSI values in Table 4 plotted against the equivalent TSI parameter,  $MW/SP$ , from Minchin [7] and Clarke *et al.* [8]. The regression line, with the equation  $TSI = 2.76*(MW/SP) - 9.7$ , defines the TSI scale for data from Ref.7, and the points represent the corresponding TSI values from Table 4 for the same compounds. The TSI scale for data from Clarke *et al.* lies along the line defined by equation  $TSI = 5.07*(MW/SP) - 2.7$ . The closer the  $R^2$  value is to one, the smaller the differences between TSI values in Table 4 and those from the previous study. The agreement between TSI values in Figure 10 is reasonable; however, there are some considerable differences between the data points and the line for a given  $MW/SP$ .



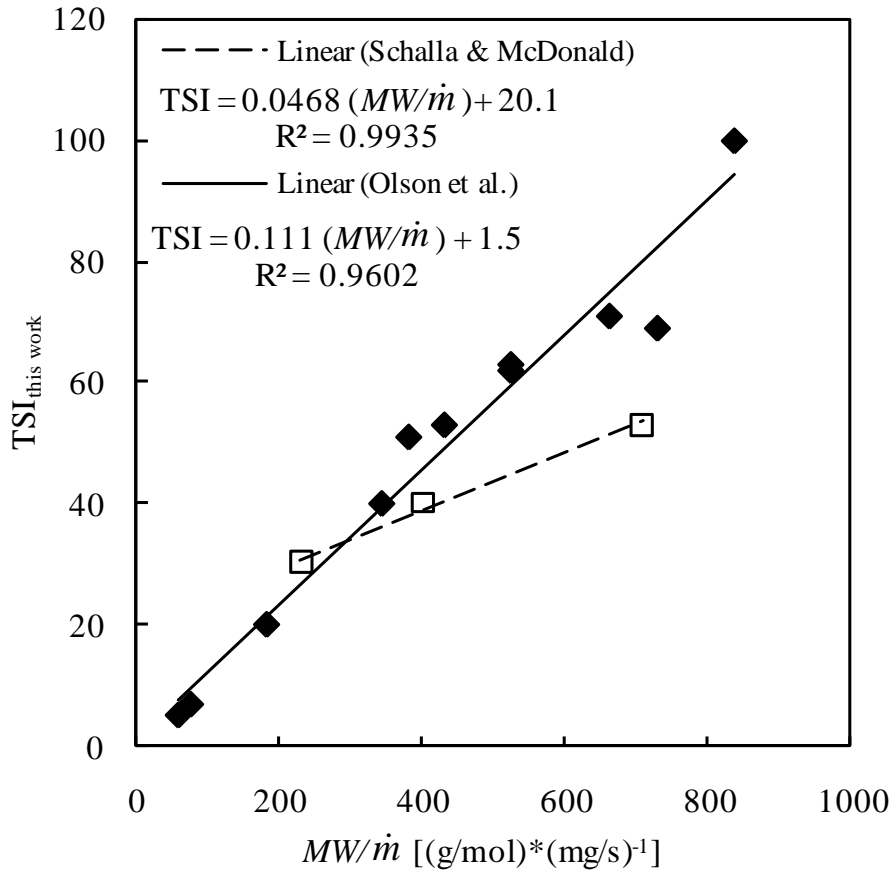
**Figure 9** Scaling of TSI data. TSI values obtained in this work plotted against  $MW/SP$  data from Minchin, 1931 [7] and Clarke *et al.*, 1946 [8]. Linear fit defines TSI for a given  $MW/SP$  from those studies.

The plots, which scale the remaining sources of soot threshold data, are shown in Figures 11 and 12. As can be seen in these plots, the TSI constants differ for each study, even for studies which measure the same quantity, confirming that the constants are experiment dependent. Also, the agreement between the TSI values varies and is reflected in the  $R^2$  value.





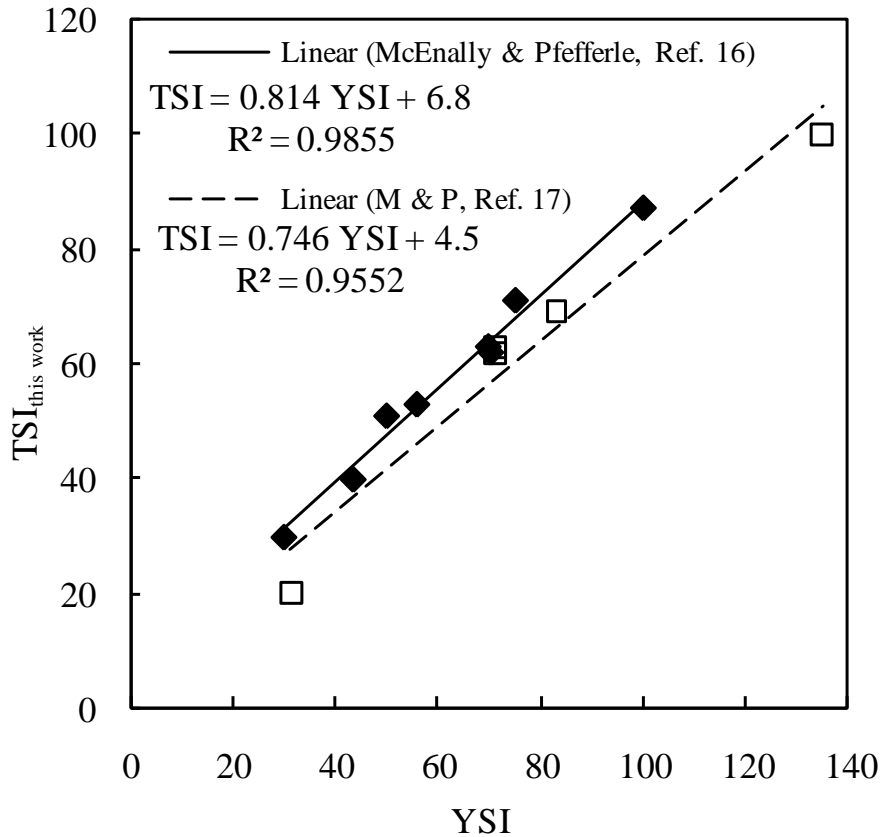
**Figure 10** Scaling of TSI data. TSI values obtained in this work plotted against *MW/SP* data from Hunt, 1953 [12] and Gill and Olson, 1984 [19]. Linear fit defines TSI for a given *MW/SP* from those studies.



**Figure 11** Scaling of TSI data. TSI values obtained in this work plotted against  $MW/\dot{m}$  data from Schalla and McDonald, 1953 [11] and Olson *et al.*, 1985 [14]. Linear fit defines TSI for a given  $MW/\dot{m}$  from those studies.

Since McEnally and Pfefferle [16, 17] only reported YSI values, the raw  $f_{v,max}$  data were not available to be scaled using the same procedure as the soot threshold data. Instead the YSI values were directly rescaled to minimize the differences from the measured TSI values in Table 4. Figure 12 shows the measured TSI values in Table 4 plotted against the reported YSI values from Refs. 16 and 17. The equations from the linear regressions convert YSI to the same scale as the TSI values in Table 4. The two YSI studies are treated separately because the experimental conditions were slightly different. In the first study, the pure fuel vapor was introduced directly into the methane

fuel stream. By contrast, in the second study less volatile compounds were able to be tested because the pure fuel was dissolved into a solvent, 2-heptanone, and then vaporized and introduced into the fuel stream. As Figure 12 shows, the conversions to TSI are slightly different for each YSI study.



**Figure 12** Scaling of TSI data. TSI values obtained in this work plotted against YSI from McEnally and Pfefferle, 2007 [16] and 2008 [17]. Linear fit defines TSI for a given YSI from those studies.

The  $R^2$  value was used as the criterion to determine which data sets to include in the final compilation of TSI values. Only the data sets that had  $R^2 > 0.95$ , namely Refs. 11, 14, 16, 17, 19, along with data from Table 4 were included in the average values. An encouraging fact is that all of the sooting tendency data taken since the 1980's correlated

well with the data measured here. With the exception of the work of Schalla & McDonald, the older studies did not correlate as well.

The rescaled TSI values, the experimental constants, and the average TSI values, are shown in Table 6. The TSI values for the compounds for which smoke points could not be measured with the ASTM standard apparatus were obtained other ways. The TSI values of n-decane and n-dodecane were found from the study by Olson *et al.* [14], in which they measured the smoke point mass flowrate in an apparatus that could handle higher smoke points than the ASTM apparatus. As for iso-cetane, no smoke point measurements were found in the literature. However, Yan *et al.* [15] did provide an estimated TSI value of iso-cetane based on a polynomial regression model that correlated known TSI values with structural groups present in the fuel molecule. From the correlation, they estimated iso-cetane had a TSI of 14.6. In the present study, a method was developed using binary mixtures to check the estimated TSI from Yan *et al.*, as discussed in section 4.2.

**Table 6** TSI values for compounds considered in this work. Data include TSI values measured in this study, rescaled<sup>a</sup> TSI values from studies with  $R^2 > 0.95$ , Schalla and McDonald [11], Olson *et al.* [14], Gill and Olson [19], and McEnally and Pfefferle [16, 17], and an average of these TSI values.

Pure Compound	Formula	MW (g/mol)	TSI - Penn State	Rescaled TSI - S&M [11]		Rescaled TSI - Olson <i>et al.</i> [14]		Rescaled TSI - G&O [19]		Rescaled TSI - M&P [16]		Rescaled TSI - M&P [17]		Average Value
				a=4.07, b=-4.8	a=0.0468, b=21.1	a=0.111, b=1.5	a=3.59, b=-2.7							
iso-cetane	C <sub>16</sub> H <sub>34</sub>	226.45		22 <sup>b</sup>									22 (14.6) <sup>d</sup>	
n-dodecane	C <sub>12</sub> H <sub>26</sub>	170.34			7.0 (5.4) <sup>c</sup>								7.0 (5.1)	
cyclohexylbenzene	C <sub>12</sub> H <sub>16</sub>	160.26		69	82.4 (82.9)						66 (83)		72 (78)	
n-decane	C <sub>10</sub> H <sub>22</sub>	142.29			5.4 (3.9)								5.4 (4.2)	
1-methylnaphthalene	C <sub>11</sub> H <sub>10</sub>	142.20		100	94.4 (95.6)		101 (95)				105 (135)		100 (91)	
decalin	C <sub>10</sub> H <sub>18</sub>	138.26		20	21.4 (20.1)		18 (18)				28 (31)		22 (15)	
tetralin	C <sub>10</sub> H <sub>12</sub>	132.21		71	74.9 (74.2)		67 (63)				67.9 (75.1)		70 (61)	
1,2-dihydronaphthalene	C <sub>10</sub> H <sub>10</sub>	130.19		87						88.2 (100.0)			88 (100)	
1,2,4-trimethylbenzene	C <sub>9</sub> H <sub>12</sub>	120.20		63	59.5 (57.9)					63.6 (69.8)		57 (71)	61 (52)	
1,3,5-trimethylbenzene	C <sub>9</sub> H <sub>12</sub>	120.20		62	59.5 (57.9)					64.0 (70.3)		57 (71)	61 (52)	
n-propylbenzene	C <sub>9</sub> H <sub>12</sub>	120.20		53	53 (76)		49.1 (47.6)			52.3 (55.9)			52 (47)	
iso-octane	C <sub>8</sub> H <sub>18</sub>	114.23		6.8		9.6 (8.0)	6.7 (7.3)						7.7 (6.4)	
m-xylene	C <sub>8</sub> H <sub>10</sub>	106.17		51	43.6 (42.0)					47.5 (50.0)			47 (49)	
methylcyclohexane	C <sub>7</sub> H <sub>14</sub>	98.19		5.0	7.7 (6.0)								6.4 (4.9)	
toluene	C <sub>7</sub> H <sub>8</sub>	92.14		40	39 (43)		39.4 (37.9)		41 (39)	42.2 (43.5)			40 (44)	
benzene	C <sub>6</sub> H <sub>6</sub>	78.12		30	31 (26)				33 (32)	31.2 (30.0)			31 (29)	

<sup>a</sup>“Rescaled” is defined as the TSI values that would be determined on the Penn State smoke point apparatus.

<sup>b</sup>Calculated from a mixture of 81% iso-cetane and 19% 1,2,4-trimethylbenzene by mole.

<sup>c</sup>Individual TSI values in parentheses are those originally reported by the authors or in Ref. 14 in the case of the Schalla and McDonald TSI values.

<sup>d</sup>Average TSI values in parentheses are those most often cited in the literature. They are the average TSI values as suggested in Ref. 14, with the exception of iso-cetane (from Ref. 15) and 1,2-dihydronaphthalene (Ref. 16).

In Table 6, the previous TSI values as they were reported in Refs. 14, 16, 17, and 19 are shown in parentheses for comparison. Although the data sets from Refs. 14 and 19 have not changed much from their original values, the other three data sets did change significantly with the rescaling. Because TSI and YSI are relative parameters, the absolute quantities depend on the compounds and original values used to define the scale.

For Schalla and McDonald [11], the TSI was originally scaled using more compounds than the ones listed, and TSI is sensitive to the quality of *each* data point included. Because of the inherent subjectivity of the smoke point measurement, this could be an issue. The quality of any of these data is unknown, and the best way to assess whether two studies obtained similar results is to find the correlation between the compounds in common, as was done here. The rescaling of the three compounds in common with this work, acted to shift the TSI values of the aromatics tested by Schalla and McDonald almost exactly to the TSI values measured here, and therefore meeting the criterion that had been set.

The differences observed for the YSI data sets can be explained by the original values used to define the scale. For the first YSI data set, the original scale was defined assuming a TSI of 100 for 1,2-dihydronaphthalene. By contrast, here the TSI of *1-methylnaphthalene* was set to 100. In the second YSI data set, 1-methylnaphthalene turned out to have a higher TSI than 1,2-dihydronaphthalene. Therefore, in the rescaling both YSI data sets are lower than the original reported values.

In parentheses next to the average TSI values in Table 6 are the TSI values suggested by Olson *et al.* [14], except for iso-cetane and 1,2-dihydronaphthalene, which were not included in Ref. 14. For iso-cetane, it is the TSI estimated in Ref. 15, and for 1,2-dihydronaphthalene, it is the YSI measured in Ref. 16. The set of TSI values in parentheses is the set of TSI values most often cited in the literature. To show that the rescaling procedure has reduced deviations in TSI values, the total root mean square deviation from the average TSI values was calculated. For the rescaled TSI values, the

root mean square deviation was 3.0 TSI units, as compared to 7.5 TSI units for the values in parentheses.

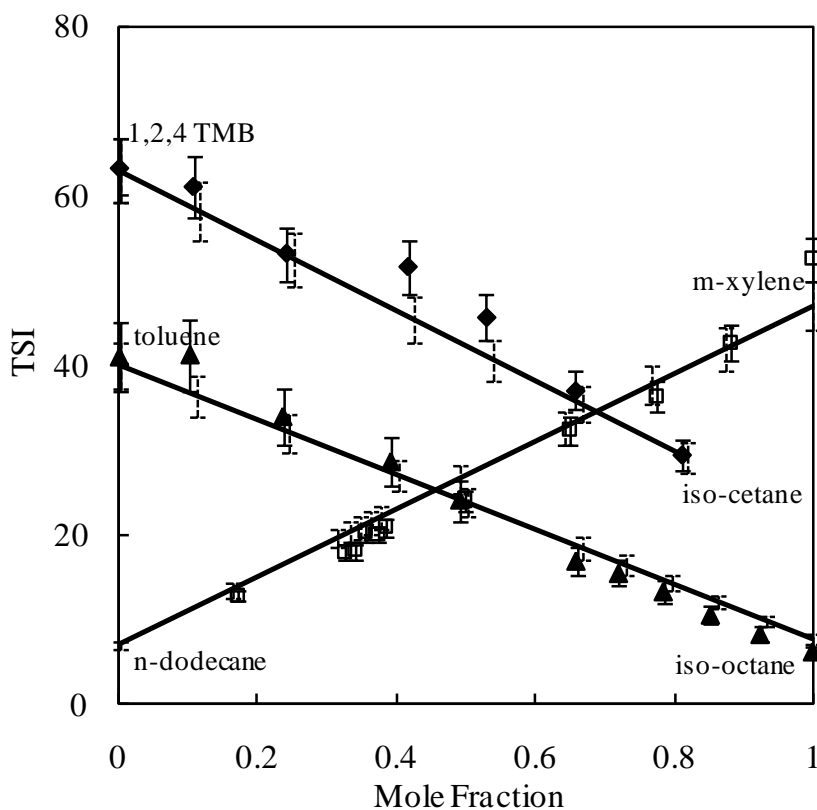
Some of the major changes in average TSI values were for the three C<sub>9</sub>H<sub>12</sub> aromatic compounds, 1-methylnaphthalene, and 1,2-dihydronaphthalene. The TSI values for propylbenzene and both trimethylbenzenes increased by more than 10%. The deviation between studies in Table 6 was  $\pm 4$  TSI units for four studies, rather than  $\pm 6$  TSI units for two studies cited in Olson *et al.* [14].

The average TSI for 1-methylnaphthalene, 100, as opposed to 91 from Ref. 14, reflects the original TSI assigned to it. In Calcote and Manos, a linear adjustment that reduced the TSI of 1-methylnaphthalene, was made to keep the scale within 0 and 100. Although not included in the previous TSI average suggested by Olson *et al.*, the YSI of 1-methylnaphthalene was 135 when McEnally and Pfefferle chose to assign 1,2-dihydronaphthalene a YSI of 100. With the YSI studies rescaled using more than two compounds, the YSI of 1-methylnaphthalene reduced to within  $\pm 10\%$  of 100. Since the previously reported average TSI (91) and YSI (135) for 1-methylnaphthalene were so different, it could have been argued that the two sooting tendency parameters were not comparable. However, the rescaling of these studies shows that TSI and YSI are complementary measures of sooting tendency, when considering the compounds in Table 6.

Another consequence of the rescaling of the YSI data was that the TSI of 1,2-dihydronaphthalene reduced from 100 to 88. However, according to Hunt's results, the TSI of naphthalene was *higher* than 1-methylnaphthalene, and McEnally and Pfefferle showed that 1,2-dihydronaphthalene and naphthalene were equivalent in YSI. Therefore, either the smoke points found by Hunt are not correct, or the TSI values of 1,2-dihydronaphthalene and naphthalene are not equivalent. Further studies on the TSI of naphthalene, which is a solid at room temperature, are needed to confirm this.

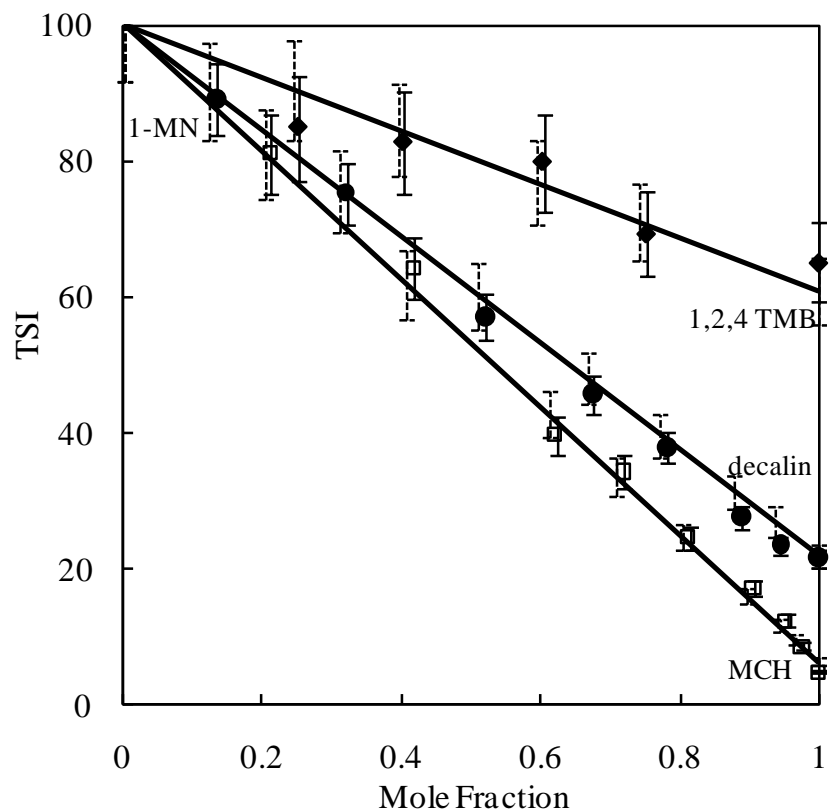
## 4.2 TSI for Binary Mixtures

The TSI values of binary mixtures were studied to verify the mixture rule proposed by Gill and Olson [19], Eq. (5), as well as to verify the TSI values of certain compounds, such as iso-cetane and 1-methylnaphthalene. A total of six binary mixtures, which are listed in Table 3, were studied. The component composition in terms of mole fraction ranged from zero to one in all cases where the smoke points could be measured. The binary mixture data are plotted versus mole fraction in Figures 13 and 14. The points represent the measured TSI values, which were calculated from the  $MW/SP$  of each mixture. Appendix B lists the measured smoke points and TSI values.



**Figure 13** Variation of TSI with mole fraction for three binary mixtures. Points are measured TSI values, and lines are TSI values calculated from pure component values. To differentiate between the error bars, those for calculated TSI values are represented as dashed lines and are offset by 0.01 in mole fraction.





**Figure 14** Variation of TSI with mole fraction for three binary mixtures containing 1-methylnaphthalene (1-MN). Points are measured TSI values, and lines are TSI values calculated from pure component values. To differentiate between the error bars, those for calculated TSI values are represented as dashed lines and are offset by 0.01 in mole fraction.

As described in the uncertainty analysis, the error bars for the measured TSI values, which range from  $\pm 5-8\%$ , largely represent the uncertainty due to the smoke point measurement. Because the uncertainty in composition was so small, error bars for mole fraction are not shown. Using the pure component average TSI values from Table 6 in the mixture rule, Eq. (5), the lines, representing the calculated TSI values, were constructed. The uncertainties associated with the calculated TSI values are shown as dashed error bars, and are due to the uncertainty in the individual component TSI values and mole fraction. Since the uncertainty in mole fraction is small, the error bars are dominated by the uncertainty in individual component TSI values. Although the

individual component TSI values used were the average values listed in Table 6, the uncertainty was taken to be the same as the uncertainty estimated for the data found in this study. The total uncertainty in the predicted mixture TSI values ( $\pm 6-9\%$ ) was generally about the same as the measured TSI mixture uncertainty. For all the mixtures tested, the error bars of the measured TSI points lie within the error bars of the calculated TSI line. It can then be concluded that the linear mixture rule, Eq. (5), applied to these mixtures in addition to the mixtures already reported in Ref. 19.

One binary mixture, 1-methylnaphthalene/decalin was also studied in Gill and Olson [19]. Examination of the three mixture data points taken in Ref. 19 to the TSI values found for comparable mixtures shows that they are very similar to those found here. The experimental constants that were used,  $a = 3.32 \text{ mm}^*(\text{g/mol})^{-1}$ ,  $b = -1.47$ , are similar to the rescaled constants found in this study for Ref. 19,  $a = 3.59 \text{ mm}^*(\text{g/mol})^{-1}$ ,  $b = -2.7$ . Therefore the TSI values using the new scale are similar to the TSI values reported using the original Gill and Olson scale.

To derive a TSI value for pure iso-cetane, a binary mixture containing as much iso-cetane as possible without losing the ability to measure the smoke point was tested. The mixture contained 81% iso-cetane and 19% 1,2,4-trimethylbenzene, molar mixture. Based on the linear mixture rule, Eq. (5), the TSI of the mixture was equal to the linear sum of the component's individual TSI values weighted by their mole fractions, called  $TSI_{calc}$ , defined for this mixture in Eq. (13). The TSI of the mixture was also found from the  $MW$  and  $SP$  of the mixture, called  $TSI_{meas}$ , defined in Eq. (14). As a component of the mixture, iso-cetane's TSI was found by equating the  $TSI_{meas}$  to the  $TSI_{calc}$ , and solving for  $TSI_{i-cet}$  in Eq. (13).

$$TSI_{calc} = TSI_{1,2,4TMB}x_{1,2,4TMB} + TSI_{i-cet}x_{i-cet} \quad (13)$$

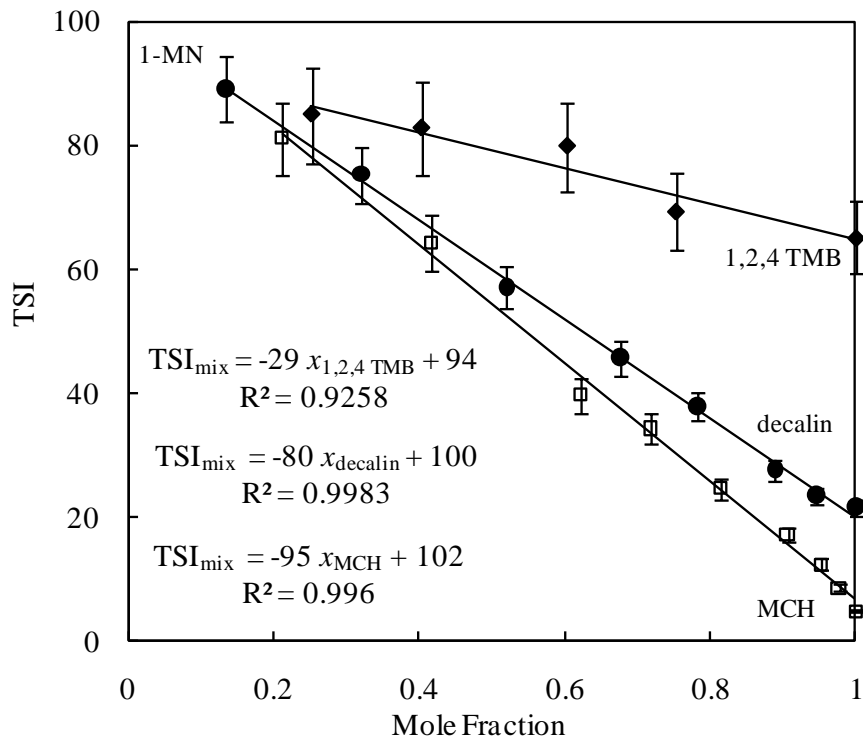
$$TSI_{meas} = a(MW_{mix}/SP_{mix}) + b \quad (14)$$

This calculation yielded a TSI for iso-cetane of 22. This is about seven TSI units (51%) higher than the value estimated by Yan *et al.* [15]. When the measured TSI values were

compared with the calculated TSI values using 22 for iso-cetane, the error bars overlapped as seen in Figure 13.

Three binary mixtures containing 1-methylnaphthalene were tested to obtain additional data on its pure compound TSI value. Since 1-methylnaphthalene had the highest *MW/SP*, it was one of the two compounds that were assigned a TSI value. Therefore, the *MW/SP* for 1-methylnaphthalene partly defined the scale for the rest of the compounds. Unlike the other end point of the scale, methylcyclohexane, 1-methylnaphthalene had a very small smoke point height, around 5 mm. Because of the low flowrate associated with a smoke point of this height, this short flame was very stable, and the smoke point was easy to identify. However, the uncertainty was large because the resolution of the scale was only 1 mm. By mixing 1-methylnaphthalene with compounds that have a higher smoke point, the relative error in the smoke point measurement could be reduced. Because the mixture points with the highest 1-methylnaphthalene content still had very low smoke points, all the mixtures containing any 1-methylnaphthalene were used to derive its TSI.

A TSI value was obtained for 1-methylnaphthalene by taking linear fits to all the measured points for the three binary mixtures, as shown in Figure 15. If the fit line is extrapolated back to the point where the mixture is entirely 1-methylnaphthalene, a TSI for 1-methylnaphthalene can be obtained. This is equivalent to inserting zero for the mole fraction of the other component in the equations of the fit lines in Figure 15. For the mixtures with 1,2,4-trimethylbenzene, decalin, and methylcyclohexane, the calculated TSI values for 1-methylnaphthalene were 94, 100, and 102, respectively. These values were well within the estimated uncertainty of  $\pm 10\%$  of 100, the TSI found for the pure compound. Therefore, the calculated TSI values were consistent with its assigned TSI of 100.



**Figure 15** Binary mixtures containing 1-methylnaphthalene, used to calculate the TSI for pure 1-methylnaphthalene from the fit lines.

### 4.3 Achieving Matching TSI Values with Different Compounds

Three mixtures were investigated to evaluate the effect of different aromatic compounds on the match between predicted and measured TSI values. N-dodecane, a normal alkane with 12 carbon atoms, and iso-cetane, an iso-alkane with nine carbon atoms on the base chain and seven branches of methyl groups, were used as the base components in these mixtures. The aromatic compounds chosen were 1-methylnaphthalene and 1,3,5-trimethylbenzene. Although 1-methylnaphthalene could be used to achieve sooting characteristics in a surrogate, the chemical kinetic models for the trimethylbenzenes are further along in development than those for naphthalene compounds. Therefore, it was of interest to demonstrate that either or both of these compounds could be used to formulate surrogate mixtures.

The composition of the mixtures, as listed in Table 7, was designed by the MURI team [2] to match the three parameters of H/C ratio, TSI, and cetane number (used to characterize auto-ignition) of JP-8. The first two surrogates, referred to as “3-component A” and “3-component B,” contain a different aromatic compound in proportions required to maintain the three parameters. In the same manner, the surrogate called “4-component A” was made containing both aromatic compounds. The mixture compositions were selected by the MURI team before any of the TSI values in this study were measured, so the TSI values for individual components at that time were taken from Refs. 14 and 15 to calculate predicted TSI values of the mixtures, using Eq. (5). The MURI team’s target TSI for the surrogates was 22, the TSI for JP-8. The TSI of JP-8 was estimated from the average JP-8 smoke point from Table 1, the average JP-8 composition [3] leading to a *MW* of 153.3 g/mol, and the experiment specific constants reported in Gill and Olson [19]. In Table 7 the predicted TSI values listed are instead calculated using the average TSI values reported in Table 6, so the predicted TSI values are higher than the originally intended TSI of 22. The increase in TSI is mainly due to an increase in the TSI used for iso-cetane from 14.6 to 22, and an increase in the TSI used for 1,3,5-trimethylbenzene from 52 to 61. Still, the predicted TSI values of the three mixtures differ from each other only by one TSI unit. Thus the predicted TSI values of the mixtures are still equivalent within the accuracy of the TSI method,  $\pm 10\%$ .

The H/C ratio, measured smoke point, as well as calculated and measured TSI values for the surrogates are listed in Table 7. The measured TSI values were calculated from the smoke point of the mixture, using the constants obtained for this study,  $a = 4.07 \text{ mm}^*(\text{g/mol})^{-1}$  and  $b = 4.8$ . The data for both three-component mixtures and the four-component mixture showed good agreement between the predicted and measured TSI values. Again, a difference of one TSI unit is within the uncertainty for TSI measurement. The surrogate mixture results in Table 7 successfully demonstrated that either or both aromatic compounds can be used to match a specified TSI value.

**Table 7** Composition, smoke point height, measured TSI, and predicted TSI of three MURI [2] surrogate mixtures for JP-8.

Surrogate	Molar Composition	<i>MW</i> (g/mol)	H/C ratio	<i>SP</i> (mm)	Measured TSI	Predicted TSI
3- component A	52% iso-cetane	186.8	2.00	22.5	29.0	28
	23% n-dodecane					
	25% 1,3,5-trimethylbenzene					
3- component B	64% iso-cetane	202.5	2.00	24.2	29.3	29
	23% n-dodecane					
	13% 1-methylnaphthalene					
4- component A	57.6% iso-octane	193.9	2.01	24.0	28.1	28
	22.8% n-dodecane					
	14.7% 1,3,5-trimethylbenzene					
	5% 1-methylnaphthalene					

#### 4.4 Matching the TSI of JP-8 with a Surrogate

A drum of JP-8 was obtained for use in the MURI program, and its smoke point height was measured on three different occasions. The results, as shown in Table 8, are within the range of JP-8 smoke points (19-31 mm) as reported in Ref. 5 and shown in Table 1. Assuming an average composition of  $C_{11}H_{21}$  as reported in Ref. 3, an average TSI value of 22 was obtained for this batch of JP-8. The measured TSI of 22 was the same as the original JP-8 TSI estimated by the MURI team [2].

**Table 8** Smoke point height and TSI results for JP-8 samples taken from the same batch of fuel.

	<i>MW</i> (g/mol) estimated	<i>SP</i> (mm)	Measured TSI
JP-8	153.3	22.8	22.6
JP-8	153.3	22.2	23.3
JP-8	153.3	23.8	21.4
<b>Average</b>	<b>153.3</b>	<b>23.0</b>	<b>22</b>

A fourth surrogate mixture was devised with a target TSI of 22, and a target H/C ratio between 1.844 and 2.067 [5]. This mixture, called “JP-8 surrogate (22),” is defined in Table 9. This mixture was comprised of n-dodecane, iso-octane, and 1,3,5-trimethylbenzene. Although these three components were chosen, it would have been possible to design the surrogate with other components, e.g. n-dodecane, iso-cetane, and 1-methylnaphthalene. Iso-octane was used because it has a lower TSI value than iso-cetane. In addition to iso-cetane, iso-octane was also being considered as a potential base iso-alkane, and it was desired to show that measured and predicted TSI would still match with an iso-octane surrogate. As shown in Table 9, the measured and predicted TSI values differ by two TSI units. Although this difference is larger than the mixtures presented in Table 7, it is within  $\pm 10\%$ . These results indicated that a surrogate fuel composed of only a few components can be formulated to match the sooting tendency of JP-8.

**Table 9** Composition, smoke point height, measured TSI, and predicted TSI for a surrogate matching JP-8 in TSI and H/C ratio.

Surrogate	Molar Composition	<i>MW</i> (g/mol)	H/C ratio	<i>SP</i> (mm)	Measured TSI	Predicted TSI
JP-8 surrogate (22)	54% iso-octane	125.9	1.98	17.8	24.0	22
	18% n-dodecane					
	28% 1,3,5-trimethylbenzene					

One drawback of including iso-octane in “JP-8 Surrogate (22)” is the effect of lowering the mixture *MW*. Although TSI and H/C ratio can be maintained, further research is needed to show that differences in *MW* are not important to the combustion characteristics.



## CHAPTER 5 CONCLUSIONS

Sooting tendency is an important parameter to consider in the design of jet fuel surrogates. TSI was used to characterize sooting tendency for potential surrogate components and their mixtures. Measurements of smoke point heights were taken according to ASTM D1322 for sixteen pure hydrocarbons, including most of the potential surrogate components being considered by the MURI team. From these data, TSI values were derived, and the uncertainty was calculated to be approximately  $\pm 10\%$ . Previous literature data on soot threshold and soot yield of pure hydrocarbons were brought together and compared on a common scale defined by the TSI values obtained in this study. Previous data sets that had a satisfactory  $R^2$  correlation were retained to be averaged into a consistent set of TSI and YSI values for pure hydrocarbon compounds. In some cases, the scaling procedure had a significant effect on the TSI values previously reported, to the point where the average TSI values changed by as much as 47%. The scaling procedure resulted in better agreement between TSI values from different studies. Therefore, when properly rescaled, a consistent set of TSI values can be assembled that uses results from different studies. Although YSI values for sooting tendency are obtained by a very different approach than TSI, both TSI and YSI data can be included in the consistent set of sooting tendency values when rescaled.

The TSI values of several mixtures were determined to verify the rule used to predict TSI values of mixtures, that the mixture TSI is the linear sum of the component TSI values weighted by mole fraction. Within the estimated uncertainty, the experimental TSI values of the binary mixtures as well as three and four component mixtures matched the predicted TSI values. Therefore, using the consistent set of TSI values obtained in this study, the TSI of a mixture can be specified and evaluated. The TSI values of iso-cetane and 1-methylnaphthalene were calculated using mixture TSI values containing these compounds. The technique of calculating individual TSI values

from their mixtures can be useful for obtaining TSI values for compounds which cannot be measured as pure compounds (e.g. iso-cetane), or for verifying TSI values for compounds which have very short smoke points and large relative uncertainties as pure compounds (e.g. 1-methylnaphthalene).

Three surrogates containing different aromatic compounds were formulated to have the same TSI and H/C ratio with slightly different compositions. Measuring the TSI values confirmed that either 1,3,5-trimethylbenzene, 1-methylnaphthalene, or both could be used to attain the same TSI. Also, the TSI of JP-8 was measured assuming a *MW* corresponding to the reported average JP-8 composition in 2006 [3]. The resulting value of 22 was used as a target to design the surrogate, “JP-8 surrogate (22).” Although this surrogate had a lower *MW* than JP-8, the surrogate matched in TSI and H/C ratio. The method for evaluating the TSI values of mixtures allows the selection or exclusion of certain compounds, according to considerations such as availability of chemical kinetic models.

## CHAPTER 6 FUTURE WORK

The range of smoke points that can be measured on the ASTM standard apparatus is restricted to a maximum of 50 mm because the apparatus was designed to be able to measure the smoke points of kerosene and aviation fuels. To gain more data on the TSI values for n-alkanes, and to be able to test Fischer-Tropsch type fuels, an apparatus with a taller chamber is necessary.

Since iso-cetane is expected to be an important component of jet fuel surrogates for the MURI, its TSI could be confirmed by mixing iso-cetane with another hydrocarbon besides 1,2,4-trimethylbenzene and deriving the TSI based on the mixture rule. Mixtures of naphthalene with liquid hydrocarbons should be tested to obtain naphthalene's TSI for comparison to the TSI of 1,2-dihydronaphthalene, since the YSI values of these compounds were found to be equal.

In previous studies and in the results presented, no mixture has proved to violate the mixture rule. However, the rule has only been tested on a limited number of mixtures, and so has not been proven for all combinations of compounds. It is suggested that when working with compounds or combinations of compounds other than those tested, it should be verified that the measured TSI matches the predicted TSI.

Although the results support the concept that TSI and YSI can be used as predictors of sooting tendency, it has not been verified that these quantities actually reflect the amount of soot formed in the real application. It is promising that the in-combustor soot formation is related to TSI, since Yang *et al.* correlated relative flame radiation with TSI [20]. Future studies include plans to measure soot volume fraction of JP-8 and surrogate fuels with various TSI values in a model combustor to compare trends in volume fraction and TSI.

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## Appendix A. *SP*, ambient conditions, and TSI for Standard Mixtures

Date	<i>SP</i> (mm)	Temp. (°C)	Pressure (in. Hg)	<i>MW</i> (g/mol)	TSI measured
<b>Standard 1, 60% iso-octane/40% toluene, by liquid volume</b>					
11/27/2007	14.3			103.0	24
12/12/2007	15.3			103.0	23
1/3/2008	14.3			103.0	24
1/25/2008	15.0			103.0	23
1/28/2008	14.7			103.0	24
2/6/2008	14.3			103.0	24
3/7/2008	14.7	19.5	28.86	103.0	24
3/18/2008	14.0	20.0	28.56	103.0	25
3/25/2008	15.0	18.0	29.21	103.0	23
5/19/2008	14.7	20.3	28.49	103.0	24
6/18/2008	14.0	20.1	28.73	103.0	25
7/22/2008	14.0	23.3	28.88	103.0	25
8/25/2008	14.3	20.1	28.91	103.0	24
9/17/2008	14.7	24.0	29.15	103.0	24
9/23/2008	14.3	24.4	29.37	103.0	24
10/7/2008	15.0	21.6	29.25	103.0	23
10/16/2008	14.7			103.0	24
10/28/2008	15.0	21.5	28.68	103.0	23
11/26/2008	14.5	21.5	28.85	103.0	24
<b>Standard 2, 75% iso-octane/25% toluene, by liquid volume</b>					
11/27/2007	19.7			106.7	17
12/12/2007	22.0			106.7	15
12/18/2007	20.0			106.7	17
1/3/2008	19.0			106.7	18
1/14/2008	20.0			106.7	17
1/25/2008	20.0			106.7	17
2/6/2008	20.0			106.7	17
2/26/2008	20.0			106.7	17
3/18/2008	20.0	20.0	28.56	106.7	17
4/30/2008	20.0	21.0	28.98	106.7	17
5/9/2008	20.0	19.6	28.68	106.7	17
5/29/2008	20.0	20.6	28.99	106.7	17
7/22/2008	19.3	23.3	28.88	106.7	18
9/17/2008	19.3	24.0	29.15	106.7	18
10/16/2008	19.3			106.7	18
11/26/2008	19.8	21.5	28.85	106.7	17

Date	SP (mm)	Temp. (°C)	Pressure (in. Hg)	MW (g/mol)	TSI measured
<b>Standard 3, 80% iso-octane/20% toluene, by liquid volume</b>					
1/14/2008	21.7			108.1	16
<b>Standard 4, 85% iso-octane/15% toluene, by liquid volume</b>					
2/26/2008	25.0			109.5	13
3/25/2008	24.0	19	29.21	109.5	14
4/30/2008	24.3	21	28.98	109.5	14
5/9/2008	24.3	19.6	28.68	109.5	14
5/29/2008	24.7	20.6	28.99	109.5	13
9/3/2008	25.3	24.7		109.5	13
<b>Standard 5, 90% iso-octane/10% toluene, by liquid volume</b>					
8/25/2008	29.3	20.1	28.91	111.0	11
9/3/2008	29.0	24.7		111.0	11
9/23/2008	30.0	24.4	29.37	111.0	10
<b>Standard 6, 95% iso-octane/5% toluene, by liquid volume</b>					
4/22/2008	32.7	23.3	29.20	112.6	9.2
6/18/2008	31.7	20.1	28.73	112.6	9.7
6/23/2008	32.0	19.7	28.91	112.6	9.5
10/7/2008	30.0	21.6	29.25	112.6	10.5

## Appendix B. *SP* and TSI Data for Binary Mixtures

Mole Fractions		<i>MW</i> (g/mol)	<i>SP</i> (mm)	TSI measured	TSI calculated
iso-cetane	1,2,4 TMB				
0.11	0.89	131.48	8.1	61	59
0.24	0.76	145.76	10.2	53	53
0.42	0.58	164.36	11.9	52	46
0.53	0.47	176.39	14.2	46	41
0.66	0.34	190.00	18.5	37	36
0.81	0.19	206.30	24.5	30	30
iso-octane	toluene				
0.10	0.90	94.39	8.4	41	37
0.24	0.76	97.35	10.2	34	32
0.39	0.61	100.79	12.3	29	27
0.49	0.51	102.99	14.5	24	24
0.66	0.34	106.69	20.0	17	19
0.72	0.28	108.05	21.7	15	17
0.78	0.22	109.48	24.6	13	15
0.85	0.15	110.98	29.4	11	12
0.92	0.08	112.56	35.0	8.3	10
m-xylene	n-dodecane				
0.17	0.83	159.35	36.9	13	14
0.33	0.67	149.43	26.8	18	20
0.34	0.66	148.43	26.4	18	21
0.36	0.64	147.49	23.9	20	21
0.37	0.63	146.52	24.0	20	22
0.39	0.61	145.61	23.0	21	22
0.50	0.50	138.31	19.5	24	27
0.65	0.35	128.57	14.1	32	33
0.78	0.22	120.58	11.9	36	38
0.88	0.12	113.68	9.8	43	42
1,2,4 TMB	1-MN				
0.75	0.25	125.64	6.9	69	71
0.60	0.40	128.92	6.2	80	76
0.40	0.60	133.32	6.2	83	84
0.25	0.75	136.64	6.2	85	90



Mole Fractions		<i>MW</i> (g/mol)	<i>SP</i> (mm)	TSI measured	TSI calculated
decalin	1-MN				
0.95	0.05	138.47	20.0	23	26
0.89	0.11	138.69	17.4	28	31
0.78	0.22	139.12	13.3	38	39
0.68	0.32	139.53	11.3	46	47
0.52	0.48	140.15	9.2	57	59
0.32	0.68	140.94	7.2	75	75
0.13	0.87	141.67	6.1	89	90
MCH	1-MN				
0.98	0.02	99.20	29.9	8.7	8.6
0.95	0.05	100.24	23.7	12	11
0.91	0.09	102.31	18.9	17	15
0.81	0.19	106.39	14.7	25	24
0.72	0.28	110.54	11.5	34	33
0.62	0.38	114.82	10.5	40	42
0.42	0.58	123.83	7.3	64	61
0.21	0.79	132.85	6.3	81	80