

# Prediction of Sooting Tendency for Hydrocarbon Liquids in Diffusion Flames

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A theoretical method for predicting the smoke point of pure hydrocarbon liquids is presented. The method is based on a structural group contributions approach and does not require any experimental procedures or information of fuel properties, other than the molecular structure of the fuel molecules. The proposed correlation is presented in the form of a multivariable regression. The average deviation is only 1.3 TSI (threshold soot index) units for ~70 compounds from low-sooting paraffins to highly sooting aromatics, and the average relative error is 9.08%. The results of three different sets of structural groups derived from the Quann and Joback group contribution methods are tested and compared. For a mixture with a defined composition, the estimation of smoke point is also discussed. The method is of potential value for the formulation of surrogate fuels of hydrocarbon mixtures, where matching the fuel's sooting tendency is important.

## Introduction

Sooting tendency is one of the critical properties of aviation kerosene. Matching the sooting propensity of the parent jet fuel is one of the key constraints in the formulation of jet fuel surrogates.<sup>1</sup> Although considerable progress has been made in revealing the details of soot formation, there is still a lack of a widely accepted method to predict sooting tendency for any fuel from first principles. An empirical indicator of sooting tendency in diffusion flames—the smoke point—fortunately provides a simple measure in this respect.

The definition of smoke point is the maximum height (given in millimeters) of a smokeless flame of fuel burned in a specially designed lamp (ASTM D1322).<sup>2</sup> The sooting tendency is then proportional to the inverse of the smoke point. There are a few studies available with compiled smoke point data of common fuels, such as those of Hunt,<sup>3</sup> Van Treuren,<sup>4</sup> Olson et al.,<sup>5</sup> and Gulder.<sup>6</sup> Hunt's compilation of smoke point data for 75 hydrocarbons and 33 organic compounds that contain heteroatoms is probably the largest.

To better exploit the smoke point as a measure of sooting tendency, correlations between the smoke point

and other fuel properties are highly desired. API proposed an equation to estimate the smoke point with density, the Watson K factor, and a mean average boiling point as input.<sup>7</sup> Ramswamy and Singh reported a correlation between smoke point and fuel hydrogen type, based on proton nuclear magnetic resonance (NMR) spectroscopy.<sup>8</sup> Cookson et al. reported a more general correlation in predicting jet fuel properties, including the smoke point, based on <sup>13</sup>C NMR spectroscopy.<sup>9</sup> Gulder and co-workers have a similar correlation based on NMR results.<sup>10,11</sup> Unfortunately, most of these correlations cannot be applied to pure hydrocarbons or their mixtures and have a very limited range; e.g., the API correlation is only applicable to fuels that have a smoke point value of 15–33 mm. The other correlation can only be used with a kerosene fraction from a specific source of crude.<sup>8</sup>

Furthermore, smoke point results from different studies often cannot be compared directly, because of the different types of smoke lamps used, even though there is an ASTM standard smoke lamp for this test (ASTM D1322).<sup>2</sup> With the ASTM standard lamp, only liquid fuels can be tested and the smoke point measurement is limited to the range of 5–45 mm. However, lamps used in other studies have gone well beyond 100 mm.<sup>3,5</sup>

In view of the problems of inconsistent smoke point data from different studies, Calcote and Manos proposed

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the idea of the threshold soot index (TSI).<sup>12</sup> TSI provides a universal measure of fuel sooting tendency. The data in the Calcote and Manos paper and in a later publication by Olson et al.<sup>5</sup> provide the most complete TSI data and is comprised of ~100 hydrocarbons.

Because the inverse of smoke point alone will not account for the difference of oxygen required to burn a given quantity of different fuels, TSI is defined as follows:

$$TSI = a \left( \frac{MW}{SP} \right) + b \quad (1)$$

where  $a$  and  $b$  are constants for any given smoke lamp,  $SP$  is the smoke point, and  $MW$  is the molecular weight of the fuel tested. The range of TSI values is artificially assigned from 0 to 100, with ethane as the least sooting (TSI = 0) and naphthalene as the most sooting (TSI = 100). Constants  $a$  and  $b$  are first determined by selecting compounds in common with other available data sets, then adjusting with least-squares fitting to minimize the difference of TSI values of individual compounds from different sources.

The mean scatter of the data correlated by Calcote and Manos<sup>12</sup> is  $\pm 9\%$  if propane ( $\pm 117\%$ ) and propylene ( $\pm 46\%$ ) are excluded. The scatter of some aromatic compounds is also high (for instance,  $\pm 36\%$  for cymene and  $\pm 16\%$  for xylene). In that study, the TSI values of 93 compounds are listed. Olson et al.<sup>5</sup> re-evaluated this scheme and added more compounds.

TSI is a suitable choice as a sooting tendency indicator, because its data can be used to make direct comparisons. TSI would be even more useful if the TSI of new compounds encountered could be predicted (for example, sooting tendency data for compounds such as isomers of heptane, the standard diesel reference fuel  $n$ -hexadecane and its isomers, and other hydrocarbons of higher carbon number that are either incomplete or not found in the literature). Therefore, it is necessary to have a correlation that can predict the sooting tendency of unknown compounds when experimental data are not available.

In this paper, a correlation to predict sooting tendency is developed using structural group contribution methods. Both TSI and smoke point are used to develop such a relationship. Because there are many choices available in regard to presenting the molecules in terms of structural elements, comparisons are made with different sets of structural elements. The prediction of the sooting tendency of hydrocarbon mixtures is discussed as well.

### Model Description

The relation between sooting tendency and fuel structure was discussed even in the early days, when only smoke point data were available. A generally accepted statement of sooting tendency is that, in diffusion flames, soot formation increases in the following order: alkanes < alkenes < alkynes < aromatics.<sup>13</sup> In Olson's paper, some preliminary attempts on the estimation of TSI also were proposed.<sup>5</sup> Attempts were

made to fit the TSI values of paraffins, cycloparaffins, and aromatics with their carbon numbers. The results are not satisfying, except for the normal alkanes, because carbon number is far from enough to describe the molecule structure.

In terms of estimation of the chemical properties, there is a vast amount of literature available on the quantitative structure–property relationships (QSPR).<sup>14</sup> Three methods are used in developing QSPR, which are fundamental relationships using molecular dynamics, structural group/fragment contributions, and topological indices. Most QSPR are built on a structural group/fragment contribution approach (for instance, density,<sup>15</sup> boiling point,<sup>16</sup> heat capacity,<sup>17</sup> diffusivity,<sup>18</sup> vapor–liquid equilibria,<sup>19</sup> critical properties,<sup>20</sup> auto-ignition temperature,<sup>21</sup> etc.). In this paper, the idea of structural group contribution was adopted for developing the correlation for sooting tendency.

The smoke point correlations,<sup>6,8–10</sup> using the NMR spectra mentioned previously, can be viewed as examples of using the structural group contribution method. In both studies, the petroleum fraction is characterized by different hydrogen or carbon types, based on NMR data. Hanson and Rouvray estimated TSI with topological indices of hydrocarbons, which is another example of the application of QSPR by an alternative method in this respect.<sup>22</sup> However, the correlation parameter, Balaban index, or the average distance sum connectivity<sup>23</sup> is not widely used and the estimation accuracy is poor, with a standard deviation of  $\pm 5.7$  TSI units.

Pugmire obtained good correlation between TSI values and molecular structure, using bond type (e.g.,  $sp^3$ ,  $sp^2$ , and some special structural indices) as parameters.<sup>24</sup> This work is a continuation of the study of soot formation, sooting tendency prediction and soot characterization. However, instead of using bond type, a more conventional structural group contribution approach is used to describe hydrocarbons, and to use the molecular structural groups to correlate TSI.

The compounds used in this work are mainly from  $C_6$  and above, and a total of 67 compounds are used as a database. Most of these compounds are in the boiling point range of the kerosene fraction of petroleum and are used as candidates for jet fuel surrogate formulation. Light hydrocarbons having a high scatter in TSI value are excluded. Alkynes and dienes also are excluded, because of a paucity of experimental data. The selection of the compounds used in this work is not intended to limit the applicability of the correlation to be discussed.

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**Table 1. Group Contribution for Estimation of the Threshold Soot Index (TSI) with the SOL Method**

group ID	group	number of occurrences	( $sp_k$ ) <sup>b</sup>
A6	six-membered carbon aromatic ring	24	0.67641
A4	four-membered carbon aromatic increment	4	0.45433
N6	six-membered carbon cyclic ring	8	0.15239
N5	five-membered carbon cyclic ring	2	0.13594
N4	four-membered carbon cyclic ring	2	0.17762
N3	three-membered carbon cyclic ring	1	0.009381
R	aliphatic carbon chain	57	0.023252
Br	branching on the carbon chain R	22	0.085269
Me-	methyl groups on the carbon chain R	8	0.022664
IH	degree of unsaturation of hydrocarbon	29	-0.16196
AA	bridge between two nonincremental rings	2	0.12746

<sup>a</sup> The compounds for which TSI values are available did not involve the following members of the SOL methodology, A2 (two-carbon aromatic increment), N2 (two-carbon cyclic ring increment), N1 (one-carbon cyclic ring increment). Details about conventions and examples of this method can be found in the original reference.<sup>26</sup> <sup>b</sup> For use in eq 3.

Whenever more-reliable smoke point data for more compounds become available, they can certainly be added into the database and will improve the correlation.

**Selection of Structural Groups.** Many structural group contribution methods have been presented as a powerful tool for property estimation, such as those of Benson et al.,<sup>17</sup> Joback and Reid,<sup>16</sup> and Constantinou and Gani.<sup>25</sup> The major difference among them is the choice of structural groups and the sensitivity of the desired properties to change in the group's concentrations. In this study, Quann's<sup>26</sup> choice of structural groups and Joback's method are used to correlate molecular structure with TSI. Some modifications to the Joback's method are made; this revised methodology is thus called the modified Joback method.

Structural orientation lumping (SOL), which characterizes hydrocarbon mixtures by a vector whose elements represent structural features, provides an effective method for representing complex petroleum mixtures.<sup>27</sup> This also provides a basis for developing surrogate fuels from mixtures of compounds with the same structural components. The surrogate components are selected from compounds that have known kinetics and, therefore, can be easily incorporated into computer simulations. There are 22 building blocks in the SOL method, 8 of which are related to heteroatoms such as N, S, and O, which are not relevant to the hydrocarbons considered in this study. The structure groups of interest taken from the literature are summarized in Table 1.<sup>26,27</sup> A6 is a six-membered carbon aromatic ring, which is the fundamental building block for all aromatics; A4 is a four-membered carbon aromatic ring increment, such as that found in naphthalene; A2 is a two-membered carbon increment in constructing a pericondensed polyaromatic hydrocarbon (PAH) (for example, pyrene is formulated with one A6, two A4, and one A2). N6 and N5 are six- and five-membered cycloparaffin rings, respectively; N4–N1 are additional four-, three-, two-, and one-carbon cycloparaffin ring increments. R is the carbon number of aliphatic molecules

**Table 2. Group Contribution for Estimation of the Sooting Tendency with the Joback Method<sup>a</sup>**

hydrocarbon type	group ID	group	number of occurrences	(sp <sub>k</sub> ) <sub>i</sub>	
				for eq 3	for eq 5
paraffins	P-1	-CH <sub>3</sub>	56	0.073682	4.3975
paraffins	P-2	>CH <sub>2</sub>	41	0.04661	-12.573
paraffins	P-3	>CH-	21	0.071922	24.163
paraffins	P-4	>C<	5	0.43812	-21.275
olefins	O-1	=CH <sub>2</sub>	8	0.27858	0.00018
olefins	O-2	=CH	9	0.14323	6.8735
cycloparaffins	C-1	>CH <sub>2</sub>	12	0.075559	-0.02496
cycloparaffins	C-2	>CH-	7	0.21835	0.001131
cycloparaffins	C-4	=CH-	2	0.12504	0.035421
aromatics	A-1	=CH-	24	0.26922	0.07521
aromatics	A-2	>C=	23	0.28585	-0.0067

<sup>a</sup> The compounds for which TSI values are available did not involve the following members of the Joback method: O-3 (>C=), C-3 (>C<C), and C-5 (>C=). More details of the conventions used in this method can be found in the original references.<sup>14,16,28</sup>

without the presence of the ring structure or can also represent the total alkyl-group structure on ring compounds. Br indicates the number of branch points on the alkyl side chain R or on a paraffin or olefin; Me specifies the number of carbons attached as methyl groups; IH represents incremental hydrogen, which specifies the degree of unsaturation of molecules; and, finally, AA is the bridge between any two nonincremental rings (e.g., biphenyl).

There were 41 groups/atoms chosen in the Joback method. The groups containing heteroatoms and triple bonds are excluded from this work. The groups used here are shown in Table 2 and are self-explanatory. Note that there is no measure of location of alkyl branches along a chain for branched paraffins and olefins, nor for the ring size of cyclic compounds. When describing molecules with SOL, the latter issue is addressed with six naphthenic groups, i.e., N6–N1. To account for the difference of the location of alkyl branch, Albahri<sup>28</sup> added groups such as  $\alpha$  >CH-,  $\beta$  >CH-,  $\delta$  >CH- (where  $\alpha$ ,  $\beta$ , and  $\delta$  refer to the second, third, and fourth position on the carbon chain, respectively),  $\alpha$  >C<,  $\beta$  >C<, and etc.<sup>28</sup>

In this study, considering the increase in the complexity of introducing too many parameters, the Wiener index has been selected to address the issue of representing isomers of branched paraffins in this study. The definition of the Wiener index ( $W$ )<sup>29</sup> is as follows:

$$W = \frac{1}{2} \sum_{i,j}^N d_{ij} \quad (2)$$

where  $d_{ij}$  is the number of bonds in the shortest path that connects the pair of non-hydrogen atoms  $i$  and  $j$ , and  $N$  is the number of non-hydrogen atoms in the molecule. To normalize the Wiener index with the increase in carbon number, the term  $\Delta W/n^2$  instead of  $W$  is used as a parameter, where  $\Delta W = W_0 - W$  and  $W_0$  is the Wiener index of the normal paraffin with carbon number  $n$ . For example, with  $n$ -octane,  $W_0 = 84$ , the Wiener index for 2,2,4-trimethylpentane is 66, and the normalized Wiener index for 2,2,4-trimethylpentane is 0.28. The larger the number, the more branches in the structure.

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**Table 3. Group Contribution for Estimation of TSI with the Modified Joback Method<sup>a</sup>**

hydrocarbon type	group ID	group	number of occurrences	( $sp_k$ ) <sup>b</sup>
paraffins	$\Delta W/n^2$	branching	17	-3.0164
paraffins	P-1	-CH <sub>3</sub>	56	0.79888
paraffins	P-2	>CH <sub>2</sub>	52	0.088075
paraffins	P-3	>CH-	25	-0.31710
paraffins	P-4	>C<	6	-0.15031
olefins	O-1	=CH <sub>2</sub>	8	1.3480
olefins	O-2	=CH	11	0.25591
cycloparaffins	C5 c.f.	C5 ring	3	1.4699
cycloparaffins	C6 c.f.	C6 ring	9	1.7679
aromatics	A-1	=CH-	24	0.87567
aromatics	A-2	>C=	5	0.13210
aromatics	A-3	AC-C	22	0.25075

<sup>a</sup> The compounds for which TSI values are available did not involve the following members of the modified Joback method, O-3 (>C=). More details of the conventions used in this method can be found in the original references.<sup>14,16,28,29</sup> <sup>b</sup> For use with eq 3.

Two additional correction factors for five- and six-membered naphthenic ring compounds are added to address the issue of the ring size of naphthenic compounds ignored in Joback's group selection. Smaller ring increments of naphthenic compounds are neglected, because few of them have experimental data on sooting tendency. For alkyl-substituted aromatics, we have added a special group (AC-C) to address the influence of alkyl substituents on ring compounds to alkyl groups. The full list of the modified Joback's group selection used in this study is given in Table 3.

It has been noted that, when using these structural groups to represent molecules, sometimes there is more than one way to do so. This phenomenon is referred to as "Equivalent Structure Relationships" for the SOL method.<sup>26</sup> For example, toluene with the SOL method may be constructed as a benzene ring (A6 = 1) and a methyl group (R = 1). It may also be constructed with one cyclohexane ring (N6 = 1) with three double bonds (IH = -3) and one methyl group (R = 1). For this molecule, both ways are equivalent. However, as noted by the author, the A6, A4, and A2 increments are intended to indicate aromaticity, not just hydrogen deficiency, because the two structures have equivalent stoichiometry but may have different soot-forming potential.<sup>26</sup> In this work, the preferred representation of a molecule is based on convenience, with respect to the correlating properties (in this case, the sooting tendency). To get reasonable regression results, it is important to be consistent with the method of representing a family of molecules having similar structures, e.g., benzene and its derivatives.

## Results and Discussion

Several polynomial regression models have been tested for correlating the TSI for all the compounds for which the data were available. We use the polynomial regression model shown in eq 3, which is similar to that used by Albahri<sup>28</sup> to predict octane number:

$$\text{TSI} = a \left( \sum_k (N_k sp_k) \right)^{-1} + b + c \left( \sum_k (N_k sp_k) \right) + d \left( \sum_k (N_k sp_k) \right)^2 + e \left( \sum_k (N_k sp_k) \right)^3 + f \left( \sum_k (N_k sp_k) \right)^4 \quad (3)$$

where  $sp_k$  is the contribution from group  $k$  identified in the SOL method (see Table 1), Joback's method (see Table 2), and the modified Joback method (see Table 3); the values of  $a$ ,  $b$ ,  $c$ ,  $d$ ,  $e$ , and  $f$  that were fitted to the data are given in Table 4. All correlation parameters are obtained simultaneously, using all 67 compounds with a least-squares algorithm. The adequacy of the SOL and modified Joback methods for describing the sooting tendency of fuels has been tested by trying to fit the available data on TSI using polynomial regression models to determine the weighting functions for  $sp$  for any group  $k$ .

A sample calculation is provided for the prediction of the TSI for 2,2,4-trimethylpentane. The calculation is shown below and it consists of the following structural groups, as obtained from Table 3: five (-CH<sub>3</sub>), one (-CH<sub>2</sub>), one (>CH-), one (>C<), and a nonzero branching factor  $\Delta W/n^2$ :

$$\sum_k (N_k sp_k) = 5(\text{CH}_3) + 1(>\text{CH}_2) + 1(>\text{CH}-) + 1(>\text{C}<) + 1(\Delta W/n^2) = 0.5987 \quad (4a)$$

Substitution into eq 3 with the third row (set) of parameters in Table 4 yields a TSI value of 5.7. The literature value for this molecule is 6.4. The absolute error is thus 0.7 TSI units, and the relative error is 11.4%.

Another example is to estimate the TSI value of 2,2,4,4,6,6,8-heptamethyl-nonane. Unlike the example given previously, this compound does not have a known TSI value. This molecule consists of the following structural groups, as obtained from Table 3: nine (-CH<sub>3</sub>), three (-CH<sub>2</sub>), one (>CH-), three (>C<), and a nonzero branching factor  $\Delta W/n^2$ :

$$\sum_k (N_k sp_k) = 9(\text{CH}_3) + 3(>\text{CH}_2) + 1(>\text{CH}-) + 3(>\text{C}<) + 1(\Delta W/n^2) = 3.6697 \quad (4b)$$

Substitution into eq 3 with the third row (set) of parameters in Table 4 yields a TSI value of 14.6.

Table 1 clearly shows that, in terms of  $sp_k$  value, the aromatic structure has a larger contribution than the naphthenic and alkyl groups, and this is in agreement with experimental data. Among the paraffinic groups, the branched group does have a larger contribution than a straight chain group. A similar trend is observed in the value of  $sp_k$  for use with eq 3 in Joback's group selection (see Table 2). However, after the introduction of the additional three parameters, the values of  $sp_k$  in the modified Joback method do not have the apparent trend as observed previously (see Table 3). In Tables 1-3, the occurrence of each structural group in the database is also listed. For SOL and Joback methods, there are structural groups used less than three times. With the modified Joback method, the least-used group is the five-membered ring correction factor. From a statistical perspective, the more frequent the occurrence of the group, the more reliable its parameter value.

Figures 1-3 are parity plots for TSI prediction of the 67 pure hydrocarbon liquids using structural group contributions from the SOL elements (Table 1), Joback (Table 2), and the modified Joback (Table 3) methods, respectively. It can be seen that the estimation of

Table 4. Coefficients for Equations<sup>a</sup>

regression equation	structural group model	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>
eq 3	SOL	-0.0000330	2.6136	15.671	-68.986	293.11	-160.51
eq 3	Joback	-9.5414	50.729	-72.36	26.223	20.125	-6.4552
eq 3	modified Joback	297.64	-465.07	283.24	-82.709	11.685	-0.59459
eq 4	Joback	0.015548	0.00305	0.037953	0.029172	0.082134	0.19422

<sup>a</sup> The compounds for which TSI values are available did not involve the following members of the modified Joback method: O-3 (>C=).

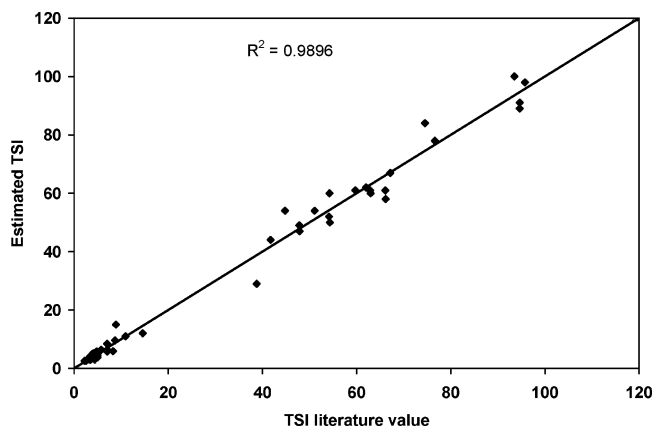


Figure 1. Threshold soot index (TSI) estimation using the SOL method, versus literature values.<sup>5,6,11,12,30</sup>

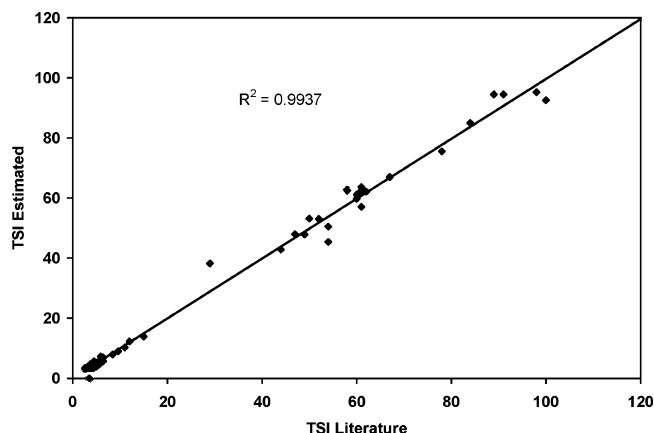


Figure 3. TSI estimation using the modified Joback method, versus literature values.<sup>5,6,11,12,30</sup>

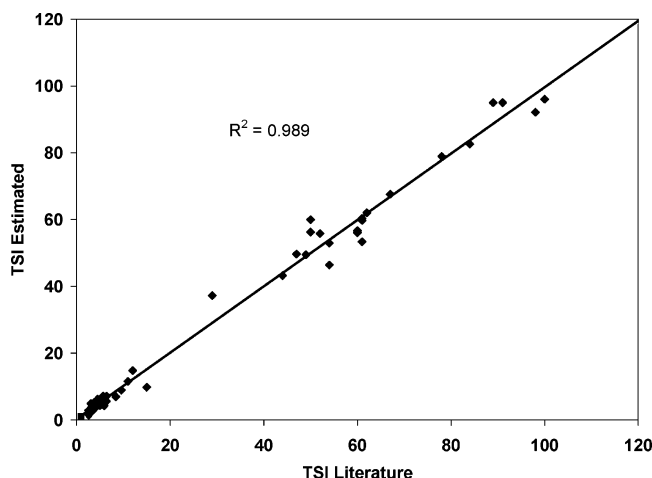


Figure 2. TSI estimation using the Joback method, versus literature values.<sup>5,6,11,12,30</sup>

sooting tendency, using all three choices of functional groups, gives acceptable results, although the best match is obtained with the modified Joback method, even though the differences between them are small.

With the error analysis shown in Table 5 it is found that, among the three choices of functional group selection, the modified Joback/Albahri method has the highest  $R^2$  value and the lowest error in every case. The difference in  $R^2$  value is small, but the differences in the average absolute error and relative error among the three methods are clear. The average deviation of the estimated TSI values with all three choices is <2 TSI units. The relative errors of the first two methods are clearly larger than those of the modified Joback/Albahri method. In short, the values of the overall correlation coefficient are all equal to 0.99 for each method, which again shows the existence of a strong correlation between the fuel molecular structure and sooting tendency, no matter which of these three structural groups

Table 5. Statistical Analysis for the TSI Prediction of eq 3

source of data	$R^2$	Deviation <sup>a</sup>		mean relative error <sup>b</sup> (%)	standard deviation
		mean	maximum		
Table 1	0.9896	1.85	9.8	11.93	3.08
Table 2	0.9890	1.62	9.9	11.32	2.76
Table 3	0.9937	1.34	9.2	9.08	2.37

<sup>a</sup> Deviation is the difference between the experimental and predicted value. <sup>b</sup> Relative error is the deviation divided by the experimental value.

are used. By contrast, the use of a simple linear additivity relation yields an  $R^2$  value of 0.951.

The statistical analysis also is performed with individual hydrocarbon classes. Among all three methods, the modified method is slightly better than the original Joback and SOL method. The correlation coefficients for each of the classes are also very close, but generally, the prediction of sooting tendency for ring compounds is higher than that of straight-chain compounds. In fact, for normal paraffins, a near-unity correlation was expected, because the sooting tendency increases linearly with chain length and no other structural factors such as branching or ring size are involved. However, the available experimental data are limited and somewhat confusing. For example, the TSI values for *n*-pentane, hexane, heptane, octane, and nonane are 2.6, 2.6, 3.2, 3.1, and 3.1, respectively. A better trend could possibly be observed if the data from both light compounds (such as ethane, propane, and *n*-butane) and heavy hydrocarbons (such as *n*-C<sub>15</sub> and above) were included.

The compounds with the highest errors from each method also are examined. When using SOL elements, benzene and *tert*-butylbenzene have the largest absolute error (9.8 and 9.5 TSI units, respectively). Decalin is the only nonaromatic hydrocarbon among the top 10 compounds with the highest error with this method.

When using Joback's selection, *sec*-amylbenzene and benzene have the largest absolute error (9.9 and 8.2 TSI units, respectively). Decalin is, again, the only nonaromatic hydrocarbon among the top 10 compounds with the highest error with this method. With the modified Joback method, the 10 compounds with the highest error are aromatics. In this sense, all three methods have limitations in predicting the sooting tendency of aromatics.

We believe the major source of error for aromatics is the inaccuracy of the smoke point data. The smoke point of most aromatic compounds is very low (usually <8 mm), and, therefore, the uncertainty of the experimental data is high. (In smoke point tests, the readings are recorded with an error of  $\pm 0.5$  mm.) For example, there are reported values of the smoke point of toluene has been given in various literature reports as 6 mm,<sup>3</sup> 7.5 mm,<sup>30</sup> and 9.8 mm.<sup>10</sup> The corresponding TSI values are 52, 47, and 39, respectively. Decalin has a similar situation. This problem could possibly be solved by measuring the smoke point of an aromatics/alkanes mixture at different concentrations, and then extrapolating the smoke point for the aromatics, assuming that a suitable mixing rule exists. This issue will be discussed further in the next section.

In terms of relative error, the compounds with the highest error are dominantly alkanes and cycloparaffins, especially the isomers of branched alkanes. It is not a surprise that alkanes have high smoke points (>50 mm) and rather low TSI values (mostly <6). Therefore, even small deviations could result in large relative error. As shown in the results, the modified Joback method has better accuracy in correlating data for branched paraffins than the SOL method. The large error with branched alkanes illustrates one shortcoming of the SOL method, as mentioned previously: i.e., it does not distinguish between primary, secondary, and tertiary carbon in a branched alkane molecule. To further reduce the error for these isomers, one could either add/replace some functional groups, which can represent the structure of the isomers better, or collect more-reliable TSI/smoke point data of branched paraffins, which can be used to improve the correlation.

In many other property estimation studies, the orientation of C atoms (such as *cis*- and *trans*-) and the location of substitution on the benzene ring ortho-, meta-, and para- isomers for aromatics have been shown to have a noticeable contribution to the chemical properties of interest. In this study, no distinction was made between these isomers. The sole reason is evident in the literature: there is no difference in their observed smoke point or calculated TSI value. The above-mentioned isomerization does not seem to affect their sooting tendency. Again, the difference in sooting tendency among them, if any, may be observed by studying their mixture with alkanes, assuming that a valid mixing rule exists. With the progress in recent years in molecular dynamics simulations, one can foresee that the soot formation from isomers with the aforementioned configurations could be simulated. Another interesting observation is the effect of alkyl substitution on aromatic rings, in terms of sooting tendency. Based on TSI data, shorter alkyl side chains have a tendency

to increase the TSI, which might be related to the formation of stable benzyl free radicals.<sup>5</sup>

McEnally et al.<sup>31</sup> measured the maximum centerline benzene (in units of parts per million (ppm)) in a methane/air flame with 5000 ppm of five heptane isomers. The ranking of the maximum benzene (given in ppm) and the maximum soot volume fraction (also given in ppm) from these flames shows that the values increase in the following sequence: *n*-heptane < 3,3-dimethylpentane < 2,3-dimethylpentane < 2,4-dimethylpentane < 2,2,3-trimethylbutane. Because TSI (smoke point) data are lacking on these isomers, it is not a certainty that this trend will hold for their sooting tendencies. With the correlation provided in this work, we projected the TSI values of these unknown compounds, and the results show that the TSI predictions are in agreement with the experimental data for these heptane isomers.

There are other compounds that also are very interesting but lack experimental data (for example, *n*-hexadecane (cetane number of CN = 100) and its isomer 2,2,4,4,6,6,8-heptamethyl-nonane (CN = 15)). The estimated TSI values for these compounds are 6.0 and 14.6, respectively. Similarly, the TSI values of *n*-dodecane and its isomer, 2,2,4,6,6-pentamethylheptane, are 4.4 and 8.2, respectively. The effect of branching on the TSI value is very evident. Derivatives of benzene, which have side chains longer than C<sub>5</sub>H<sub>11</sub>, do not have known TSI values; thus, this method can be utilized to estimate these values.

The aforementioned results demonstrate the possibility of predicting the sooting tendency by calculating the TSI, using structural group contributions. Because the TSI is proportional to the inverse of smoke point, which is highly influenced by molecular structure, the structural group contribution method will be able to estimate the smoke point. The motivation here is, if the researcher has accumulated a large amount of smoke point data, it will be useful to predict the smoke points of unknown compounds for the specific facility instead of using TSI values, which are averaged over different equipment. In this study, we use the data from Hunt<sup>3</sup> as a database to show this idea. The form of the correlation is similar to what we have used in the prediction of TSI values previously. We were able to obtain good estimation results with the following form of regression models:

$$\ln(SP) = a\left(\sum_k (N_k SP_k)\right)^{-1} + b + c\left(\sum_k (N_k SP_k)\right) + d\left(\sum_k (N_k SP_k)\right)^2 + e\left(\sum_k (N_k SP_k)\right)^3 + f\left(\sum_k (N_k SP_k)\right)^4 \quad (5)$$

where *SP* is the smoke point,  $\sum_k (N_k SP_k)$  is the sum of group contributions for smoke point from Table 2, and *a*, *b*, *c*, *d*, *e*, and *f* are correlation constants from Table 4. The mean absolute error is 2.6 mm, with a maximum error of 12.9 mm for cyclohexene and the minimum of <0.1 mm for a few aromatic compounds. The mean relative error of this correlation is 7.8% and the *R*<sup>2</sup> value of this correlation is 0.993. The calculation follows the same procedure as the samples provided previously for

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the estimation of the TSI value of iso-octane and heptamethyl-nonane. Because sooting propensity is proportional to the inverse of the smoke point, the logarithm of the smoke point is used instead of using smoke point directly. However, the estimation of the smoke point, unlike TSI, should be used with caution, because the smoke point can be operator- and location-specific (because of pressure effects), and, in some cases, non-ASTM lamps may have been used.

**Threshold Soot Index/Smoke Point of Hydrocarbon Mixtures.** Gill et al.<sup>32</sup> proposed a simple additivity rule for the sooting tendency estimation for mixtures:

$$TSI_{\text{mix}} = \sum x_i TSI_i \quad (6)$$

where  $x_i$  is the mole fraction of the  $i$ th component in the mixture and  $TSI_i$  is the TSI value of the  $i$ th component. Because TSI is proportional to the inverse of the smoke point, and the flame height is proportional to fuel mass flow rate, based on Roper's<sup>33,34</sup> equation, with some rearrangement, it can be shown that TSI is proportional to the reciprocal of the fuel volume flow rate at the smoke point. Thus, for a mixture, Markstein<sup>35</sup> derived the following relationship:

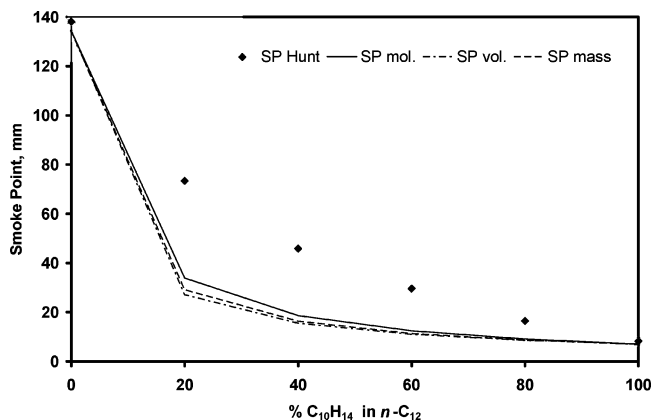
$$\frac{1}{V_{\text{SP}}} = \sum \frac{v_i}{V_{\text{SP},i}} \quad (7)$$

where  $v_i$  is the volume fraction of the  $i$ th component and  $V_{\text{SP},i}$  is the smoke-point volume flows of the  $i$ th component. Markstein demonstrated this relation for some binary fuels (for example, propylene-ethylene). However, it fails when normal alkanes (from methane to propane) are used as additives to the alkenes. The authors believe the difference in adiabatic flame temperature might be the cause of the difference in behavior when blending members of nonhomologous series.

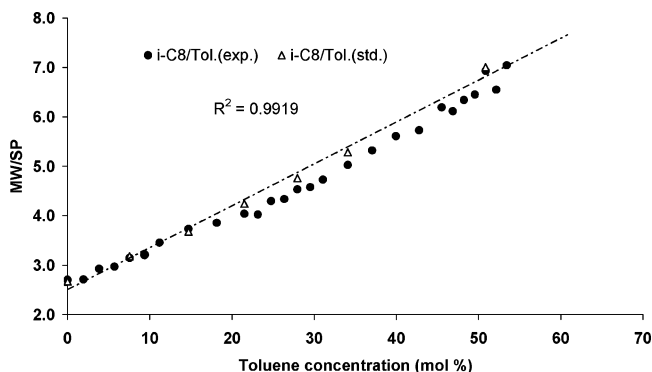
Assume that the constants  $a$  and  $b$  in the definition of TSI are only dependent on the equipment but independent of the species. With some rearrangement, one can obtain the following mixing rule for the smoke point:

$$\frac{MW_{\text{mix}}}{SP_{\text{mix}}} = \sum \frac{x_i MW_i}{SP_i} \quad (8)$$

where  $x_i$  is the mole fraction of the  $i$ th component and  $SP_i$  is the smoke point of the  $i$ th component. We first tested this relation with the mixture of *sec*-butylbenzene and *n*-dodecane, whose smoke points were plotted against the concentration of *sec*-butylbenzene in *n*-dodecane in Figure 1 from Hunt's work.<sup>3</sup> Because the original study did not state the basis of concentration, whether by volume, mole fraction, or mass fraction, we calculated the smoke point of the mixture using all three mixing modes and plotted them in Figure 4. Apparently, none of the calculated results could match the experimental data. There are three possible explanations for



**Figure 4.** Smoke point estimation of *sec*-butylbenzene/*n*-dodecane mixtures, using eq 7, in comparison to the data of Hunt.<sup>3</sup>



**Figure 5.** Smoke point measurements of iso-octane/toluene mixtures.

this discrepancy: (i) eq 6 is correct, but the assumption that the constants  $a$  and  $b$ , which were for pure compounds, that were used are the same for mixtures does not hold; (ii) eq 6, which was used to estimate the TSI of the mixture, may be wrong, and eq 8, which was used for smoke point estimation, is not correct; and (iii) the smoke point measurements of the mixtures tested in Hunt's work are not reliable.

We first calculated the TSI values of the mixture of *sec*-butylbenzene and *n*-dodecane for all three possible mixing modes with eq 6, and then interpolated the corresponding smoke point at each concentration. The results are similar to that plotted in Figure 4, based on eq 8. This suggests that the constants  $a$  and  $b$  are independent of fuel.

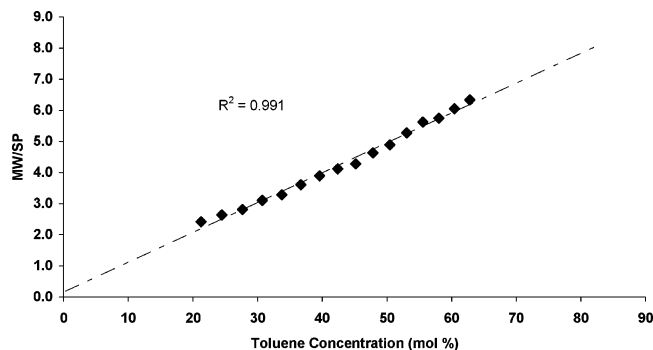
We also made some smoke point measurements of mixtures to test eqs 6 and 8. Two mixtures were chosen; one is the standard reference fuel (iso-octane and toluene) and the other mixture used is *n*-octane and toluene. The standard reference fuel is used because smoke points of this mixture at different concentrations have been tabulated and validated.<sup>2</sup> In Figure 5, it can be seen that the tabulated smoke point data from the ASTM standard is in good agreement with eq 8. The extrapolated smoke point values of pure iso-octane and toluene are 45.8 mm and 8.4 mm, respectively, which are acceptable. Our data are in general agreement with the standard, as we performed additional smoke point measurements with the standard reference fuels. The estimated results are in good agreement with experimental results, with a maximum deviation of only 1.5

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**Figure 6.** Smoke point measurements of *n*-octane/toluene mixtures.

mm. With the mixture of *n*-octane/toluene, the linear relationship seems only to hold in the measurement range of an ASTM standard smoke lamp, as shown in Figure 6. However, the extrapolated smoke points are unreasonable (for example, 695 mm for *n*-octane and 9.5 mm for toluene). For this mixture, a parabolic curve fits better, showing the approximate nature of eq 6.

We obtained the smoke points for several compounds that were tested by Hunt,<sup>3</sup> to evaluate the reproducibility of his results. Some of the data could not be duplicated. For instance, for Decalin, Hunt obtained a smoke point of 38 mm and a TSI value of 12 (cf. ref 12), compared to other values in the literature of smoke point and TSI value (23.7 mm and 18, respectively)<sup>30</sup> and our values (23.8 mm and 19, respectively). Note that a large portion of TSI data from Calcote and Manos<sup>12</sup> and Olson et al.<sup>5</sup> are based on Hunt's measurements.

Another point of note is that Gill and Olson<sup>30</sup> mentioned that mole fraction, volume fraction, or mass fraction can be used to estimate TSI using eq 6 without introducing much error. Although valid for mixtures of homologous series of compounds, this procedure will generate unacceptable errors when aromatics and paraffins are mixed, because of density differences. As an example, the smoke points for a mixture of 20% *sec*-butylbenzene and *n*-dodecane are 38 mm, 33 mm, and 30 mm when the 20% is calculated on mole basis, mass basis, and volume basis, respectively. Because TSI is well-correlated with molecular structure, we recommended the use of mole fraction in eqs 6 and 8.

Equations 6 and 8 can provide insights on the processes that govern soot formation in mixtures burned in a diffusion flame from a mixture in an ASTM-type smoke lamp. They do not allow for interactions among fuel components. Furthermore, in our laminar-flow drop-tube experiments, the amount of soot collected from a fuel is proportional to the inverse of the smoke point of that fuel.<sup>36</sup> These results suggest that the inception stage of soot formation, which is highly affected by the fuel structure, is more important than the surface growth process, in terms of the amount of soot formed. Delichatsios proposed a global soot formation model for an axisymmetric laminar diffusion flame such as that formed in a smoke point test.<sup>37</sup> The model postulated that soot formation is controlled by homo-

geneous reactions rather than soot particle surface growth, as suggested by Kennedy.<sup>38</sup> His model provides results that agree with the experimental data; however, neither the simple additivity rules nor the models allowed for interactions between components such as those found in the complex mixtures that characterize practical fuels. Comparisons of experimental and kinetic simulation studies could provide a validation of mechanisms proposed for the formation of soot.

The proposed estimation is based on TSI data for pure hydrocarbons and can be used to predict the TSI value of unknown compounds. Unlike experiments in a smoke lamp, there is no range limit for this estimation. However, note that the use of these rules for complex mixtures representing practical fuels should be used with caution. Also, the current estimation procedure does not cover any soot suppression additives, such as ferrocene.

### Conclusions and Recommendations

Limited data are available on smoke point and threshold soot index (TSI), which are used as indicators of sooting propensity. Structural group contribution methods, which have been used by others to estimate many properties, are presented here to estimate the sooting tendency of pure hydrocarbon liquids. Correlations were developed and tested, and they were observed to provide useful tools for the prediction of the TSI of pure compounds. Three choices of functional groups were compared. The groups listed in Table 3 represent a modified Joback method and were determined to give the best results. This method is useful for the automatic generation and reliable estimation of the TSI of a pure component for which no data exist in the literature. Mixing rules to estimate the sooting tendencies of hydrocarbon mixtures also were discussed.

Early work on smoke point data may not be reliable and should be used with caution. TSI is suggested as the parameter to be used in the sooting propensity estimation; however, the goal should be to replace experimental measurements of soot that are admittedly limited by the theoretical prediction of soot formation using validated chemical kinetic models.

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