Novel Micropyrolyis Index (MPI) to Estimate the Sooting Tendency of Fuels

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A new fuel quality indicator called micropyrolysis index (MPI) is proposed for quantifying sooting tendencies of fuels in research laboratories. The MPI has been designed with the following characteristics: (i) oxygen independence, since sooting tendencies can change dramatically with varying oxygen concentration, (ii) reduced sample volume that can be utilized on a laboratory scale, (iii) improved repeatability over traditional methods, and (iv) use of common laboratory equipment so that the method may easily be implemented in multiple laboratories. MPI measurements were conducted by pyrolyzing 20 μL of fuel across a bed of α-Al$_2$O$_3$ beads at a temperature of 850 °C. Subsequently, the carbon-containing beads were transferred to a clean reactor where the deposited carbon was burned via temperature programmed oxidation (TPO) in order to quantify the amount. The amount of deposited carbon provides an indication of the tendency of a particular fuel to form soot when pyrolyzed. The observed tendency is independent of operating conditions, such as flame temperature and stoichiometric oxygen/fuel ratios, which greatly affect the measurements in other techniques used to estimate sooting tendency. An MPI value of 5 was assigned to the amount of carbon deposited from *n*-octane, and a value of 20, to the value corresponding to decalin. These two compounds were used as reference. Repeatability tests showed that MPI measurements had a standard deviation of 1.02 MPI at MPI = 94.7 which scaled down to 0.11 at MPI = 3.3. MPI values of pure nonaromatic hydrocarbons were found to correlate well with traditional threshold soot index (TSI) values. However, MPI was found to be more differentiating than TSI among the different hydrocarbon families: *n*-alkanes, isoalkanes, and cycloalkanes. A quantitative structure–property relationship (QSPR) model was developed in order to predict the MPI of other pure compounds not measured experimentally and further expand the database. Blending issues with aromatics are discussed, as well as the effects of aromatic content in real feeds.

1. Introduction

Particulate matter (PM) emissions from soot can cause lung and heart diseases[1–6] and can potentially lead to 60 000 premature deaths per year in the United States.[7] In addition, PM emissions contribute to smog, reduce visibility, affect local climate, and could also play a significant role in the global climate.[8–12] Public concern about these serious health and environmental impacts has resulted in stricter Environmental Protection Agency (EPA) standards toward the amount of fine particulates in emissions.[13]

While the amount of particulate matter emissions that a given fuel will produce is dependent on parameters such as engine type and operating conditions, the sooting tendency associated with the chemical composition of the fuel is a critical factor. A reliable method for quantification of the sooting tendency of pure fuel components and their mixtures can be of significant help to understand and control PM emissions from different fuels. Quantitative values of sooting tendencies would also be important in upgrading of fuels to improve and model the

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sooting tendency.[14] In fact, some recent studies have made use of such numbers to create models which predict sooting tendencies under specific conditions.[15,16]

For diesel fuels, the cetane number (CN) is often mistakenly taken as an indication of the amount of PM emissions that a given fuel will produce when burned in a diesel engine. However, this has been shown to not be the case[17,18] as the PM emissions have been shown to be highly dependent on the aromatic content and operating parameters, even when the CN is kept constant. One other method which is commonly used to estimate PM emissions, especially for jet engines, is the smoke point, which is the maximum diffusion flame height obtainable before the flame begins to produce smoke. Because these measurements vary from instrument to instrument, an effort was made to correlate the various measurements by fitting them with apparatus-specific constants and defining the threshold sooting index (TSI). This also allowed the incorporation of smoke point measurements obtained by varying the fuel mass consumption rate rather than the fuel height into the TSI database. Regrettably, these measurements have been shown to have precision uncertainties of up to ±15%[19] for those measurements obtained by measuring smoke height and ±7%[20] for those measurements obtained by fuel mass consumption. Furthermore, the TSI may be more or less representative of the amount of soot that a given fuel may produce depending on the engine operating parameters as the sooting tendency largely varies with the richness of the flame and many other parameters.

One aspect that may be important to consider when evaluating a technique for determining sooting tendencies in pure compounds and prepared mixtures is the amounts of fuel required to obtain a single measurement. The current techniques require amounts that may be prohibitively large for laboratory research scale. For instance, one CN measurement requires on the order of 1L of fuel. While TSI and IQT (ignition quality test) require considerably lower amounts, e.g. on the order of 20 mL, they may still be significantly large for laboratory studies. For example, in a catalyst development study of fuel upgrading conducted in a typical laboratory reactor, collecting several mL of liquid for a single TSI or IQT measurement may take several hours. As a result, the database of pure compounds can be limited due to the large volumes needed in order to conduct a single measurement.

Another method that has recently been developed[21] involves the maximum soot volume fraction measured by laser induced incandescence in methane doped flames. This test has been named yield sooting index (YSI), for which considerable improvement has been made on the precision of the measurements to ±3% for aromatic doped flames. Furthermore, these results roughly correlate with the TSI measurements conducted by varying the mass flow rate of the fuel, but not as well with the flame height measurements. It is also claimed that because the measurements were conducted in a methane flame, the values are more representative of an alkane fueled flame, a considerable improvement over TSI measurements of pure compounds, because aromatics behave much differently in pure aromatic flames than in mixtures.

The fuel in the TSI and YSI tests is partially oxidized and partially pyrolyzed to form soot, with little information separating the two events. For this reason, we have attempted to develop a method in which the conditions are fixed and only the soot-forming pyrolysis is monitored and so the intrinsic sooting tendency of a given hydrocarbon can be analyzed. The chemistry involved with pyrolysis in oxygen-free environments is also much simpler, as the ability of molecules to oxidize, the heating value, etc. need not be taken into account. Consequently, it would be very valuable to have a fuel property which could give an indication of the nature of a particular fuel to form soot via pyrolysis which is independent of the oxygen/fuel ratio of the flame.

In designing the method presented in this contribution, we stipulated that it should be much more precise than traditional smoke point methods, it should require small sample volumes so that it can be utilized on a laboratory scale and with expensive model compounds, and it should require common laboratory equipment so that it can easily be implemented and reproduced in existing laboratories. Based on these requirements, we have developed a simple method that measures a newly defined fuel property that we have called the micropyrolysis index (MPI), which satisfies all of the aforementioned conditions.

In this contribution, we describe the experimental details of the MPI method and report measurements on pure hydrocarbon compounds. The MPI values are compared with the corresponding TSI measurements. In addition, a quantitative structure–property relationship (QSPR) has been developed between the molecular structure of each pure compound and the measured MPI. From this relationship, MPI values of unmeasured pure compounds have been estimated, leading to a large database expansion and the possibility of developing trends for various families of compounds.

2. Experimental Details

2.1. Carbon Deposition. All experiments were conducted by pyrolyzing 20 μL of a vaporized liquid sample across a hot bed of 300 mg α-Al₂O₃ beads (Purchased from Atlantic Equipment Engineers, particle size 30–50 mesh, 99.9% purity). A schematic of the reactor system can be seen in Figure 1. The alumina bed was placed at the desired height in a 1/4 in. o.d. quartz tube and held up with 15 mg of quartz wool. The reactor was placed in a Thermcraft Incorporated electric furnace (model no. 114-12-3ZV) controlled with an Omega temperature controller, model CN 3251, to keep the temperature constant at 850 °C. This temperature was chosen because it is a high enough temperature to pyrolyze hydrocarbons, but low enough to avoid alumina sintering. It is also in the range that can be used in common laboratory equipment. For the injection, 20 μL of the desired hydrocarbon sample was placed in a Hamilton 100 μL SampleLok gastight syringe (part no. 81056) with a 7 in. needle. The syringe was first filled with 20 μL of air, then 20 μL of sample, followed by 20 μL of air, and then closed off from the surrounding environment. The two air pockets were used in order to ensure that no sample was left in the needle before or after the time of injection. A gastight syringe was used in order to avoid losses of sample by vaporization before the injection. The 7 in. needle was used to ensure that entire sample was in the heating zone of the reactor when it left the syringe, so that no condensation could occur. A helium flow rate of 25 mL/min was maintained through the system as the sample was heated to

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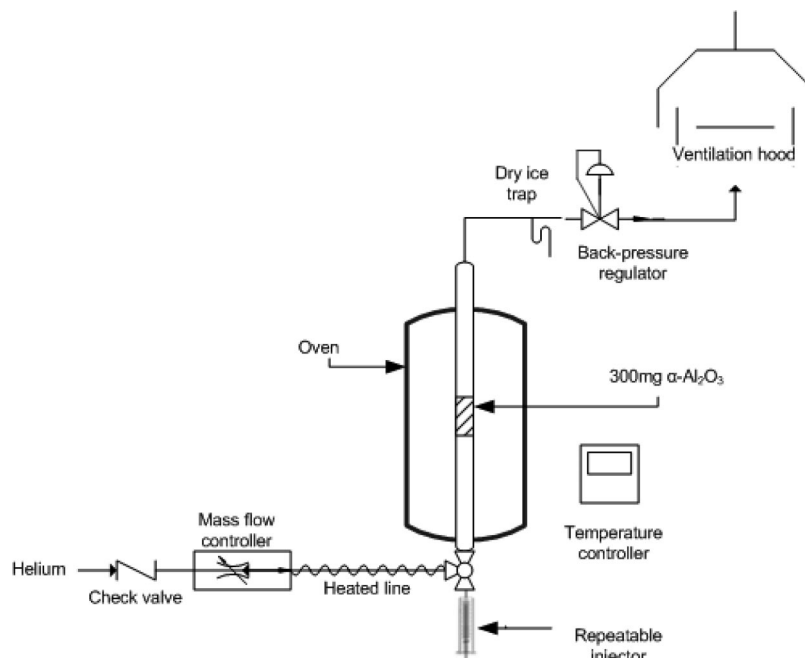
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Figure 1. Schematic description of the apparatus used to obtain MPI values by pyrolysis of a 20 μL liquid sample across an α-Al$_2$O$_3$ bed placed in a 1/4 in. o.d. quartz tube, held at 850 C. A He flow rate of 25 mL/min was maintained through the system, and a backpressure regulator was used in order to keep the pressure at 10 psig.

850 °C. A Tescom backpressure regulator (model no. 44-2361-24) was used in order to main a constant system pressure of 10 psig, and to prevent any oxygen back-diffusion into the reactor. A period of 30 min was allowed for the temperature of the catalyst bed to stabilize at the desired value. Once the temperature of the alumina bed was stabilized, the sample was injected at a constant rate over thirty seconds. This controlled injection was accomplished by using a Hamilton repeatable dispenser (part no. 83700) set to inject at a rate of 2 μL/s. Once the sample was injected on the alumina bed, the bed was maintained at 850 °C for 10 min to ensure that any light volatile hydrocarbons had passed through the reactor. After 10 min, the reactor was allowed to cool to room temperature under the same He flow rate and pressure in order to eliminate any back-diffusion of oxygen that could oxidize some of the deposited carbon. After the reactor was cooled to room temperature, the dry ice trap, and the line from the reactor to the backpressure regulator were cleaned with acetone in order to eliminate any tar buildup.

2.2. Temperature Programmed Oxidation (TPO). After the sample was cooled to room temperature, the alumina bed with a given amount of deposited carbon was transferred to a clean reactor bed. The carbon was then placed in a TPO system in order to quantify the amount of carbon deposited on the alumina during the injection. The TPO system is typically used to quantify coke deposits in heterogeneous catalysts and consists of a quartz tube containing the sample that is placed in an electric furnace while 5% O$_2$/He stream flows through the sample at a rate of 80 mL/min. The temperature of the oven is then linearly heated to 900 °C at a constant rate of 10 °C/min. The exit gas is sent through a methanator containing a 5% Ni/Al$_2$O$_3$ catalyst and a side-stream of H$_2$ to convert all of the CO and CO$_2$ into CH$_4$, which can be detected by the sensitive flame ionization detector (FID). The area of the C peak is then compared with that of a reference peak resulting from a pulse of 100 μL of CO$_2$ in order to quantify the amounts of deposited C. This setup is preferred because of the high sensitivity of the FID detector, but other systems and detectors, such as MS, or TCD, etc. might also be used. Only the carbon on the alumina was quantified because the goal of this work is to measure the kinetic tendency of a compound to form soot via pyrolysis. The alumina acts only as a mechanism of heat transfer and to provide a high surface area for deposition, so some carbon will be deposited

on the quartz wool as well as the walls of the reactor. The kinetic tendency of a compound to produce soot is captured by quantifying only the carbon deposited on the alumina as long as all of the parameters discussed in section 2.4 are carefully controlled.

2.3. Definition of MPI. We define the micropyrolysis index MPI as the amount of C deposited from injection of 20 μL of the sample, normalized to two reference compounds. The first one is *n*-octane, for which an arbitrary value of 5 was assigned, and the second is decahydronaphthalene (decalin), which was assigned a value of 20. All others were taken in reference to these values. MPI gives an indication as to how much soot a given fuel produces on a volumetric basis and is very practical from a fuels standpoint, but it may sometimes be misleading if one wants to study the chemistry because different amounts of C are being injected in each fuel due to the differences in density. In that sense, a value normalized by the number of moles of carbon injected would a give better idea of the sooting tendency of each atom of C injected. For this reason, another number may be calculated from MPI results where the number of C moles deposited on each sample are divided by the number of moles of C injected. This value typically follows very similar trends to MPI, but small differences may be observed when considering similarly sooting molecules. This fraction of injected carbon which deposits on the surface will likely be different for different systems, but the observed trends should be quite similar.

2.4. Effect of Injection Speed, Temperature, and Pressure. In order for MPI measurements to be reproducible, three factors must be carefully controlled: speed of injection, temperature, and pressure. While it is acknowledged that small deviations in these variables will likely occur as the method is repeated in other systems, the soot formation tendency of each sample with respect to that of a reference compound (hexane and decalin) should remain quite constant. What is essential, however, is that these parameters do not vary from run to run for a particular system. First, the amount of carbon deposited on the α-Al$_2$O$_3$ is highly dependent on the injection rate for multiple reasons. By varying the injection rate, both the evaporation rate and residence time through the sample can vary, leading to large differences in the observed MPI. For this reason, each sample must be injected at reproducible rates. Second, small deviations in

Table 1. MPI Values of Several Hydrocarbons (*n*-Alkanes, Isoalkanes, and Cycloalkanes) in the C_6–C_{11} Range

| name	carbons	skeletal	MPI	mol C deposited/ mol C injected
hexane	6	n-alkane	3.3	8.73E−04
2-methylpentane	6	isoalkane	6.5	1.43E−03
2,2-dimethylbutane	6	isoalkane	7.0	1.54E−03
cyclohexane	6	cycloalkane	10.8	1.81E−03
methylcyclohexane	7	cycloalkane	14.2	2.32E−03
ethylcyclopentane	7	cycloalkane	15.6	2.53E−03
1,1-dimethylcyclopentane	7	cycloalkane	19.2	3.11E−03
octane	8	*n*-alkane	5.0	1.09E−03
1,3-dimethylcyclohexane	8	cycloalkane	16.0	2.58E−03
2,2-dimethylheptane	9	isoalkane	8.4	1.61E−03
tert-butylcyclohexane	10	cycloalkane	20.5	3.07E−03
decalin	10	cycloalkane	20.0	2.68E−03
undecane	11	*n*-alkane	7.3	1.38E−03

temperature may greatly influence the rate of pyrolysis. For this reason, it is essential that the temperature of the catalyst bed is stable for the duration of the run. In most systems, additional time is required for the catalyst bed temperature to come in equilibrium with the furnace wall temperature as measured by the thermocouple. This time may vary from system to system, but can easily be measured by conducting a blank run with a thermocouple inside the catalyst bed. Third, an important variable that must be maintained constant in all measurements is system total pressure. A simple backpressure regulator can be used to maintain system pressure at 10 psig. By increasing or decreasing the system pressure, one can manipulate the amount of carbon that deposits on the alumina. If less sensitive detectors, such as TCD or MS are used, one may need to increase the pressure of the system slightly to produce more carbon per run. One further advantage of the backpressure regulator is the elimination of any possible back diffusion of oxygen from the environment that may partially oxidize some of the deposited carbon. It is essential that a dry ice trap is placed before the backpressure regulator in order to prevent any unwanted pressure increases that may be brought about by tarlike pyrolysis products building up inside the backpressure regulator. Because the MPI is a kinetic measurement, it is essential that these three variables are carefully controlled. By changing the residence time through the reactor or the pyrolysis rate, drastic differences may be observed in the amount of soot deposited on the alumina.

2.5. Repeatability. As long as the aforementioned parameters are controlled, MPI measurements can be very precise. Standard deviations of 0.11, 0.22, and 1.02 MPI were observed for sooting values of 3.3, 32.4, and 94.7 MPI, respectively. This level of reproducibility is very high compared with typical uncertainties obtained for the TSI method (e.g., 7%[20] to 15%[19]). It is also comparable to the more precise YSI method, for which an estimated ±3% inaccuracy has been reported.

3. Results and Discussion

3.1. Effects of Molecular Structure on MPI. Table 1 summarizes MPI and moles of C deposited/moles of C injected values obtained on a series of hydrocarbons. Clear trends are immediately apparent. For instance, it is observed that alkanes exhibit significantly lower MPI values than isoparaffins and naphthenic compounds. Similarly, for a given family of hydrocarbons, the MPIs clearly increase with the number of carbons in the molecule.

It is well-known that the tendency for particulate formation from hydrocarbons increases in the order: *n*-paraffins < iso-paraffins < naphthenics < aromatics. Indeed, the MPI values reported in Table 1 are in very good agreement with this trend. The increase in MPI with increasing chain length could also be anticipated and has been observed with TSI.[15] One factor that
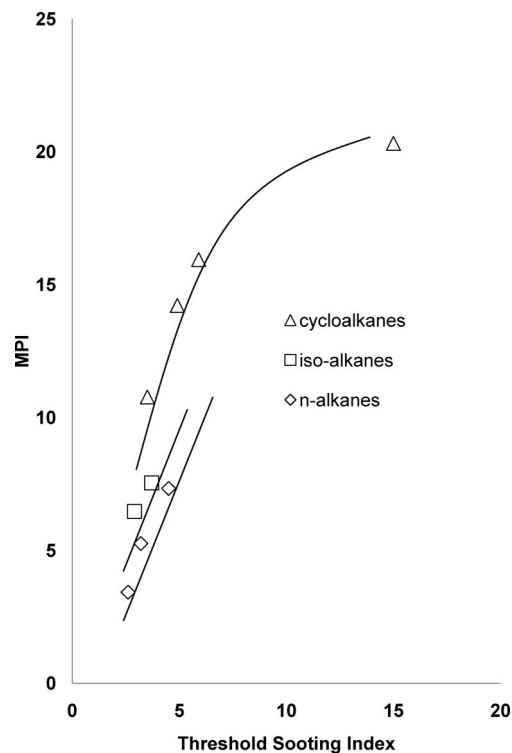
Figure 2. Comparison of MPI values obtained in this work with TSI values from the literature.[20]
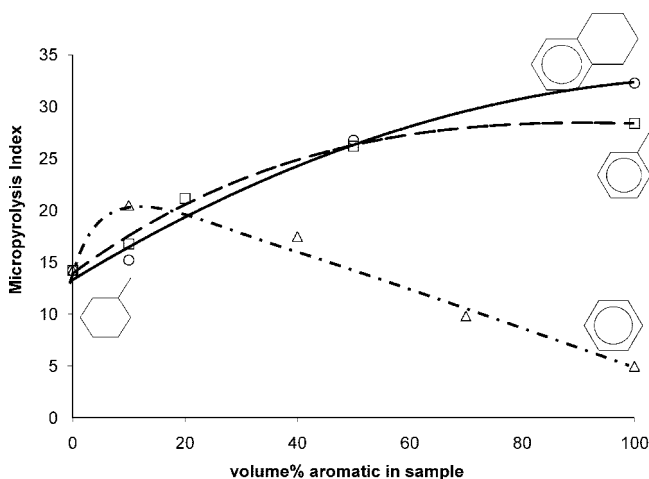
Figure 3. Effect of aromatic content in mixtures. Aromatics tetralin, toluene, and benzene were blended with methethylcyclohexane in various volume percentages. The resulting effect on MPI is shown.

is easily noted is the large effect that the degree of branching has on the MPI (e.g., hexane < 2-methylpentane < 2,2-dimethylbutane).

Since the density of isoparaffins is significantly lower than that of *n*-paraffins, MPI and the molar ratio of C deposited/ injected show considerable differences. To appreciate the need for taking into account both MPI and the molar ratio of C deposited/injected, one can compare undecane and 2,2-dimethylbutane. They both form comparable amounts of soot on a volumetric basis, but when one considers the actual moles of C that were injected, the branched molecule is seen to produce significantly more deposits, as one could have anticipated.

It is well-known that during combustion naphthenic compounds produce more soot than paraffins due to the hydrogen abstraction reactions that can take place at high
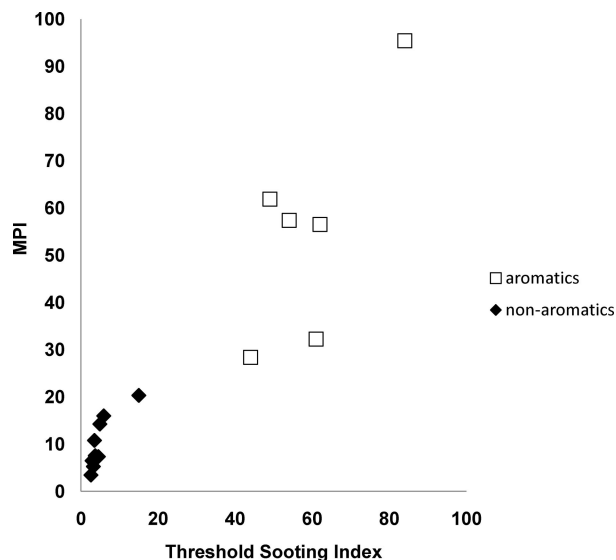
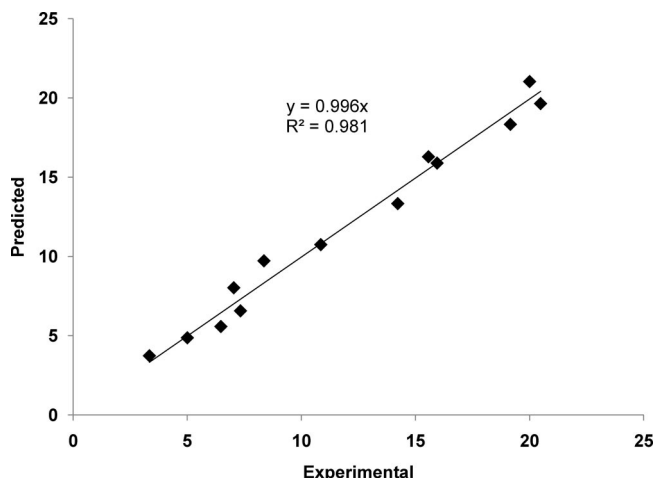**Figure 4.** Comparison between MPI values obtained in this work and TSI values from the literature.[20]

Table 2. Equation Used and Molecular Information Encoded in the Descriptors Used to Predict MPI of Unmeasured Molecules

$$\text{MPI} = -7.445k_1 + 11.33x_0 + 20.42x_{ch}^5 - 6.29804$$

descriptor	molecular information encoded
k_1 (kappa 1 shape index)	number of carbons, degree of branching, degree of cyclization
x_0 (zero-order chi index)	degree of skeletal branching
x_{ch}^5 (fifth-order chi chain index)	degree of substitution on a ring and degree of cyclization in a molecule

temperatures with the ensuing production of aromatics, which in turn are effective producers of soot. On the other hand, the explanation for the sooting trends associated with the naphthenic ring size and alkyl substituents is somewhat less straightforward. One can clearly see from the data in Table 1 that increasing the degree of branching and increasing the number of tertiary bonds in the molecule result in increases in MPI.

Overall, the trends exhibited by MPI for nonaromatic compounds seem to be consistent with those generally accepted for soot formation. For example, cyclopentane rings appear to have similar or even larger MPI values than similar cyclohexane compounds with the same number of carbon, as can be noted by comparing the MPIs of ethylcyclopentane and dimethylcyclopentane with that of methylcyclohexane. The high sooting tendency of C5 naphthenic rings can also be explained in terms of hydrogen abstraction. Through this reaction path a cyclopentane ring can lead to cyclopentadienyl radicals. Two of these radicals can then recombine to form naphthalene,[22] which is a high-sooting molecule.

3.2. Comparison with TSI. As noted in the introduction, TSI values give estimates of the sooting tendency of a flame with oxygen, and the amount of soot produced is highly dependent on the oxygen/fuel ratio. Moreover, another aspect which varies in the TSI measurements is the flame temperature. This could lead to increased nonlinearities when mixtures of pure compounds are considered. Further complications of TSI are brought about by its definition, i.e., TSI = a(MW/SP) + b.[19] In this equation, the molecular weight is introduced to offset the inherent smoke point increase brought about by increased

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Figure 5. Parity plot of predicted vs experimental values of MPI through the use of QSPR.

molecular weight and is mostly due to the larger air/fuel ratio required for stoichiometric combustion. While this effect can be relevant to some engines, this further complicates the chemistry and may not be very relevant when dealing with true fuel mixtures.

One other effect of TSI which may be misleading is that it is inversely proportional to the smoke point. This means that when dealing with any compound that has a high smoke point (e.g., alkanes), the TSI values will be very low, making it difficult to differentiate between fuels in this range, which may make up a large portion of many fuels. On the other end of the spectrum, aromatics have very low smoke points, which lead to very high TSI values. This means that a very small error, even a fraction of a mm, when reading the smoke point could lead to huge errors in TSI. Furthermore, flame temperature may have a dramatic effect on TSI values. As an example of this, Olson et al. studied the emissions temperatures of several model hydrocarbon diffusion flames.[20] It was found that the emission temperatures of cyclohexane, methyl cyclohexane, ethyl cyclohexane, and isooctane were all 1460 K, while the emission temperatures of n-paraffins were significantly higher. This indicates that multiple phenomena are involved when measuring the TSI of pure compounds. It is well-known that iso-alkanes and naphthenics have a higher tendency to produce soot under pyrolysis than *n*-paraffins, but this rate also is highly dependent on flame temperature. If *n*-paraffin flame temperatures are higher, the observed difference between sooting tendencies of the different groups may not be so straightforward. This can be illustrated by comparing the TSI values with MPI values obtained from pure pyrolysis at a uniform temperature as shown in Figure 2. Note that the MPI values for iso-alkanes and naphthenic compounds shift to higher values when compared with the corresponding TSI values. This shift can be explained by differences in flame temperatures of the three groups, which merge the TSI values closer together while MPI values distinguish the groups better. The naphthenic compound which appears to have a very high TSI value is decalin, which as indicated by Olson et al., has a uncharacteristically high emissions temperature when compared with substituted cyclohexanes as it is a very stable naphthenic, and was found to have emissions temperatures closer to those of aromatics. The differences between aromatic measurements between MPI and TSI will be discussed later in section 3.4. Overall, the scale of MPI seems to differentiate much better between low sooting nonaromatics and stoichiometric differences need not be ac-
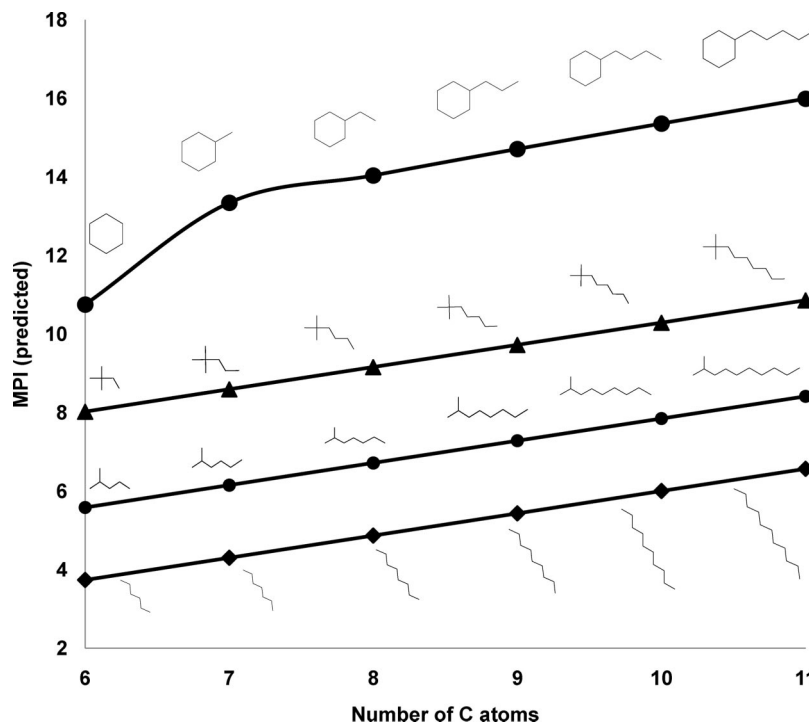
Figure 6. MPI predicted results as a function of number of carbons.

counted for as no oxygen is involved, leading to a much more straightforward fuel property.

3.3. MPI of Oxygenates. With the growing interest in renewable energy sources, the sooting tendencies of oxygenates must be well understood. It is clear that MPI values of oxygenates are lower than those of the corresponding oxygen-free hydrocarbons. For example, this trend can be seen by comparing the MPI of *n*-octane with that of octanol. Octane has an MPI of 5, while octanol has an MPI of only 3.1. This difference is likely due to the radical scavenging ability of the alcohol to eliminate radicals which are the precursors of soot. The sooting tendency of oxygenates will be the focus of future studies using MPI, since this method has the ability to probe the effects of oxygen-containing compounds on soot formation or soot reduction without the presence of oxygen in the surrounding atmosphere which further complicates the chemistry.

3.4. MPI of Aromatics. When comparing the sooting tendencies of pure aromatics, one must take caution. Aromatics in mixtures typically produce a great deal of soot when combusted in diesel or jet engines due to the fact that the formation of the first aromatic ring is the rate limiting step in soot formation. Aromatics are also very stable, so it is very unlikely that their C–C bonds will break apart at considerable rates under these pyrolysis conditions, but rather fragments of other compounds in the fuel will attach to the aromatics to form large particles. For this reason, a small amount of aromatics can lead to very large increase in soot when added to fuel mixtures. However, when tested as pure components the aromatics can only form soot by reacting with themselves, and this rate will be highly dependent on the stability of the side chains on the aromatics. An example of this is shown in Figure 3. It can be seen that the rate of soot formation for pure components is dependent on the stability and number of carbons in the side chains, which are subject to pyrolysis. For this reason, molecules with less stable side chains are more likely to produce greater amounts of carbon deposits. By contrast, in mixtures the trend is reversed as the aromatics

that form the most soot are those that had less side chains. This is because other molecules in the mixture could connect the aromatics and form soot more quickly. Because these measurements are done on a volumetric basis, the amount of aromatic rings introduced to the system typically decreases with the addition of side chains, which also will likely influence the sooting tendency in dilute mixtures for a particular volume of aromatics injected.

From the practical point of view, mixtures with small percentages of aromatics may be more representative of an actual fuel (diesel, gasoline, or kerosene) than a pure aromatic mixture. Furthermore, it is proposed that mixtures with small percentages of aromatics are the most accurate for measuring the effects of aromatics on soot formation. In order to determine the effect of aromatics in a mixture, we extrapolated the line from 0–15% aromatic content to 100% aromatics. We conclude that this is a much more accurate representation of how aromatics will influence the sooting tendency of a fuel than obtaining an MPI value of the pure aromatic compound.

The role of aromatics is different in the MPI method from the standard TSI. For TSI, oxygen is involved, which may partially oxidize some of the aromatics, making them much less stable. However, in MPI under the pyrolysis conditions alone the aromatic rings will not break in significant amounts. An example of this is shown by the MPI of pure benzene. Pure benzene alone forms far less deposited carbon than any of the other aromatics. When present in a small amount in mixtures, however, benzene produces significant amounts of carbon. This is one other inherent advantage of MPI, in which only the pyrolysis is studied. For example, the TSI values of benzene, toluene, and tetralin are 29, 44, and 61, respectively.[20] This indicates that pyrolysis plays the most important role in soot formation in flames, but by introducing oxygen the chemistry becomes much more complex. Furthermore, when introducing oxygen to aromatics, the flame temperatures and point in the flame where soot inception begins will likely change, but the effects will be dramatically different depending on the condi-

Table 3. Experimental TSI Values and Predicted MPI Values for Several Pure Hydrocarbons[a]
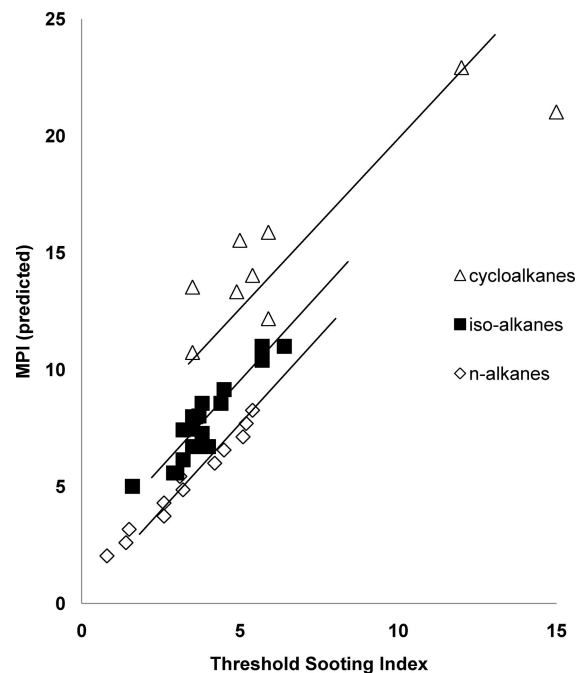
a

group	name	MPI (predicted)	TSI (from the work of Olson et al.[20])
alkanes	*n*-butane	2.6	1.4
	n-decane	6	4.2
	n-dodecane	7.1	5.1
	n-heptane	4.3	2.6
	n-hexane	3.7	2.6
	n-nonane	5.4	3.1
	n-octane	4.9	3.2
	n-pentane	3.2	1.5
	n-tetradecane	8.3	5.4
	n-tridecane	7.7	5.2
	n-undecane	6.6	4.5
	n-propane	2	0.8
iso-alkanes	2,2,4-trimethylpentane	11	6.4
	2,2-dimethylbutane	8	3.7
	2,2-dimethylhexane	9.2	4.5
	2,2-dimethylpropane	7.5	3.5
	2,3,3-trimethylpentane	11	5.7
	2,3,4-trimethylpentane	10.4	5.7
	2,3-dimethylbutane	7.4	3.2
	2,3-dimethylhexane	8.6	3.8
	2,3-dimethylpentane	8	3.5

b

group	name	MPI (predicted)	TSI (from the work of Olson et al.[20])
iso-alkanes	isopentane	5	1.6
	2-methylpentane	5.6	2.9
	3-methylpentane	5.6	3
	2-methylhexane	6.1	3.2
	3-methylhexane	6.1	3.2
	2-methylheptane	6.7	3.5
	3-ethylhexane	6.7	4
	3-methylheptane	6.7	3.7
	4-methylheptane	6.7	4
	isononane	7.3	3.8
	2,4-dimethylpentane	8	3.6
	2-methyl-3-ethylpentane	8.6	4.4
cycloalkanes	cyclohexane	10.7	3.5
	cyclooctane	12.2	5.9
	methylcyclohexane	13.3	4.9
	cyclopentane	13.5	3.5
	ethylcyclohexane	14	5.4
	methylcyclopentane	15.5	5
	1,3-dimethylcyclohexane	15.9	5.9
	trans-decalin	21	15
	bicyclohexyl	22.9	12

[a] Pure TSI values were obtained from the literature.[20]

Figure 7. Predicted MPI values vs experimental TSI values obtained from the literature.[20]

tions. Because of these issues, TSI values for pure compounds reflect both of these issues, which explains the lack of correlation between MPI and TSI values of pure aromatics, as seen in Figure 4. Aromatic species typically have MPI values greater than 30, with the exception of pure benzene (not shown). For all of the nonaromatic species, the MPI correlates with the TSI quite well as described above, but this correlation breaks apart at high sooting values. For this reason, it is proposed that the sooting tendency of a particular aromatic is more accurately estimated by investigating the effect that this compound has on the MPI of a mixture of nonaromatics.

3.5. Development of QSPR Models to Estimate MPI. Quantitative structure−property relationships (QSPR) have been used in the past to predict the values of many important fuel properties such as octane number,[16] CN,[16,23] and TSI.[24,16] QSPRs

provide a very powerful tool in fuel upgrading. Once a property is predicted, direction to desired molecules is provided as the database of fuel property values is expanded through QSPR estimation. This information helps to determine which compounds should be maximized, and which ones should be reduced in a particular fuel upgrading. The main challenge here is the limited amount of experimental data available. Furthermore, as described in the aromatic blending section, different factors influence the amount of soot that aromatics will produce when compared with nonaromatics. This means that different molecular descriptors must be used in order to quantify the MPI for aromatics. This work is in progress in our laboratory, as the aromatic database is being expanded.

In this contribution, for all of the nonaromatic compounds, a model was created in order to estimate the MPI of a pure compound which has not been previously measured. In order to accomplish this estimation, 13 nonaromatic compounds were measured and correlated with molecular descriptors to the MPI of each compound. The molecular descriptors were calculated and correlated with MDL QSAR software (version 2.2.0.0.446 (SP1) from MDL Information Systems, Inc.). This software calculates over 400 molecular descriptors of each molecule. A genetic algorithm was used in order to determine the descriptors which best described MPI by minimizing Friedman's lack-of-fit scoring. These descriptors were then correlated to MPI through an ordinary multiple regression model which involved three descriptors. Although many types of models were created, the ordinary multiple regression model was chosen based on its ability to capture the trends observed in MPI without overfitting the data. Table 2 shows the equation used to predict MPI as well as the information encoded in the descriptors which were chosen.

In prediction studies like this, it is typically recommended that a subset of data, not included in the model, be compared with the predicted values in order to validate the model and ensure that the data was not overfit. However, in this case, due

(23) Santana, R. C.; Do, P. T.; Santikunaporn, M.; Alvarez, W. E.; Taylor, J. D.; Sughrue, E. L.; Resasco, D. E. *Fuel* **2006**, *85*, 643–656.

(24) Yan, S.; Eddings, E. G.; Palotas, A. B.; Pugmire, R. J.; Sarofim, A. F. *Energy Fuels* **2005**, *19*, 2408–2415.
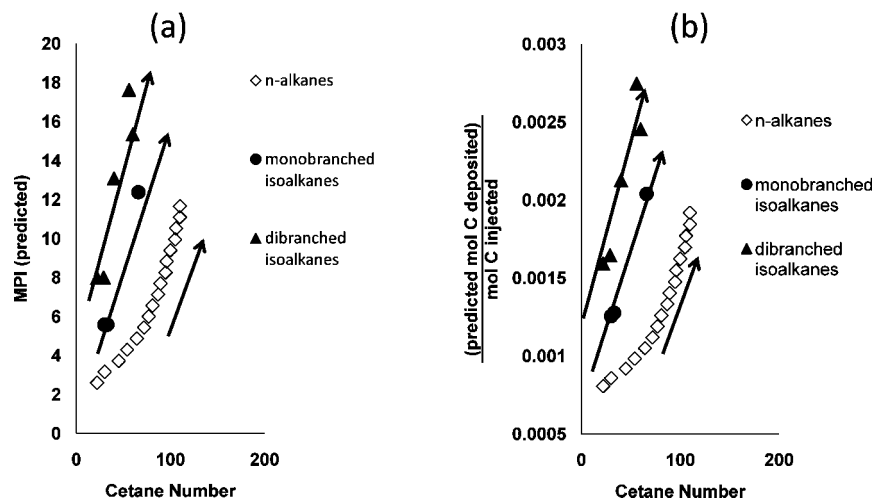
Figure 8. (a) Comparison between predicted MPI and experimental CN values obtained from the literature[23] for *n*-alkanes and isoalkanes. (b) Comparison between the (moles of carbon deposited)/(moles of carbon injected) and CN. Arrows indicate the direction of increasing number of carbons/molecule.
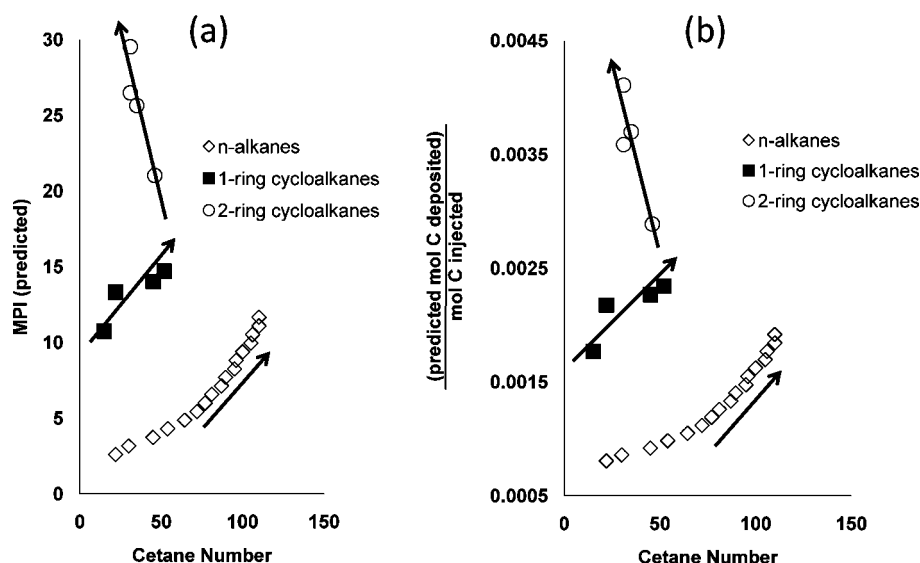
Figure 9. (a) Comparison between predicted MPI and experimental CN values obtained from the literature[23] for *n*-alkanes and cycloalkanes. (b) Comparison between the (moles of carbon deposited)/(moles of carbon injected) and CN. Arrows indicate the direction of increasing number of carbons/molecule.

Table 4. Experimental MPI and Compositional Analysis of Several Real Fuel Mixtures

	composition (wt %)						
sample	*n*-alkanes + isoalkanes	total cycloalkanes	compounds containing 1 aromatic ring	compounds containing 2 aromatic rings	substituted cyclohexanes	cycloalkanes with 2 or more rings	MPI (extrapolated)
A	26.50	60.29	12.89	0.31	33.40	26.90	65.9
B	32.19	67.81	0.00	0.00	64.00	3.80	34.6
C	39.62	48.17	12.20	0.00	44.48	3.69	43.4
D	37.12	43.62	19.16	0.10	38.76	4.85	50.8

to the small number of compounds used in the database, traditional model verification techniques could not be used as each data point was crucial. For this case, the leave-one-out method was used to find the best model. This technique involves building a model based on each compound except one in the database and then predicting the value of the last compound. This technique was repeated for each compound in the database, and the errors were summed as a form of cross validation. This technique works very well when the amount of data is limited, but as the database is expanded, the traditional method should be used. The total cross validation sum of squares added to 19.52, corresponding to an average cross validation root-mean-square (rms) error of ±1.22 MPI, which is higher, but in the

same order of magnitude as the value of the ±0.79 MPI average rms error predicted in the final model. An increase in the cross validation error is to be expected, especially with the limited number of data points in use. A parity plot of the predicted vs experimental numbers is shown in Figure 5. Note that the error is well dispersed and does not deviate to one side or the other. This is critical in order to ensure that the correct trends have been captured. Also, based on the cross validation results, as well as several parity plots for different groups which were plotted, one can conclude that the model does not overfit the data, and predictions from this model can be used to calculate MPI values in this range.

3.6. Results from Predicted MPI Values. The results from MPI prediction can be of great value. One example can be seen in Figure 6, where the predicted MPI values of various groups of compounds are plotted as a function of the number of C atoms. One can clearly see that the trends discussed earlier are captured by the predictions. As branching increases, the MPI increases, as would be expected for the pyrolysis of a mixture. Also, the addition of a ring increases the MPI even more, as expected. With this tool, one can calculate the estimated MPI for a variety of compounds and can clearly see the trends as molecular structure varies. This tool can be of great use for a variety of applications, including fuel upgrading. Table 3a and b show predicted MPI values compared with suggested experimental TSI values from Olson et al.[20] for several pure compounds. The trends discussed in section 3.2 are shown to hold for these data when compared in a much larger range of data as can be seen in Figure 7. It can clearly be seen that MPI differentiates more than TSI for the various groups of hydrocarbons. This is a very important observation as with MPI one can study the effect of pyrolysis alone, which compliments sooting tendency measurements which involve oxygen and flames. This is very important as the influence of oxygen and flame temperature on the actual sooting tendency of a fuel will vary largely depending on the combustion properties such as the oxygen/fuel ratio and other parameters. This difference gives the MPI method the advantage of discriminating between the oxygen/flame temperature effects and the intrinsic tendency to produce soot solely via pyrolysis. For a given set of molecules with the same TSI value, the MPI values follow the trend *n*-alkanes < iso-alkanes < cycloalkanes.

3.7. Comparison between Predicted MPI Values and Cetane Number. As discussed earlier in the Introduction, cetane number is often mistakenly taken as an indicator of the sooting tendency of a particular fuel. The reason for this assumption is that fuels which are more stable and less likely to combust upon compression typically contain a large degree of aromatics and highly branched compounds which result in both a low CN and a high sooting tendency. For this reason, it is generally perceived that decreasing CN will necessarily result in increasing sooting tendency. What is not so obvious is the opposite trends observed with increasing carbon numbers in many cases. By increasing the number of carbons in *n*- and isoalkanes the CN increases, but at the same time the sooting tendency also increases. These trends can be seen in Figure 8a, where predicted MPI values are compared with CN data found in the literature.[23] Arrows indicate the direction of increasing number of carbons. Among the separate groups, CN increases with increasing sooting tendency due to the higher reactivities of the larger molecules, but one can clearly see the distinction between the separate groups, with MPI differentiating more clearly between the branched molecules for a particular cetane number. One could quickly assume that the increasing in MPI for larger hydrocarbons would result from a higher density of the fuel, that is, one is injecting more carbon atoms which can form more soot. However, if we calculate the amount of carbon deposited per mole of carbon injected similar results are still obtained. To estimate the mole-based MPI, we first calculated the moles of carbon deposited on the surface from MPI values based on the moles of carbon which correspond to the MPI values of the references, 5 and 20. After these values were found, the moles of carbon injected for each pure compound could be calculated from the density,

molecular weight, and number of carbons of each molecule. Results can be seen in Figure 8b, with the overall trends being identical to those found when comparing CN to MPI alone.

In contrast, when considering cycloalkanes, the trends among the various molecular groups may not be so obvious; for instance, increasing the number of carbons may actually decrease CN in some cases. This can be seen in Figure 9a. Again, the arrows indicate the direction of increasing number of carbons. While CN trends do not remain constant across the different groups, predicted MPI values can be interpreted much more easily. For this case, the 1-ring cycloalkanes were all *n*-alkyl monosubstituted cyclohexanes (cylohexane, methylcyclohexane, ethylcyclohexane, and propylcyclohexane). In this case, the CN increased with increasing number of carbons (or length of the alkyl substituent) as did the MPI, as should be expected. For the two-ring substituted cycloalkanes, however, this trend is not so obvious. The 2 ring cycloalkane molecules shown in Figure 9 are trans-decalin, 1-propyldecalin, 1-butyldecalin, and 1-octyldecalin. In this case, even though the branch is linear, increasing numbers of carbons results in decreasing CN values. This trend is not observed with the predicted MPI values, as sooting tendency increases with an increasing number of carbons. That is, increasing the number of rings, the number of branches, or the number of carbons in the molecule increases the sooting tendency, even when it does not correlate with CN. As in the previous set of figures, when comparing MPI and CN on a per-carbon-mol injected basis, the same trends are observed (See Figure 9a and b). These results provide further evidence that CN alone does not provide a good estimate of a particular fuel's sooting tendency.

3.8. MPI Measurements of Real Fuel Mixtures. A valuable feature of MPI is its ability to measure real fuel mixtures. To test this feature, we obtained several samples of real fuels from ConocoPhillips. The compositional analysis (provided by ConocoPhillips) of each fuel along with its extrapolated MPI value can be seen in Table 4. The MPI values were calculated by diluting each sample to 10% volume in *n*-heptane and measuring the MPI of this mixture. The pure MPI values were then found by extrapolating a line from 0–10% sample in *n*-heptane to 100%; this would be the case if a pure sample were injected and no nonlinearities would exist. This approach was taken in order to eliminate any nonlinearities due to high concentrations of aromatics as discussed in section 3.4. This is a good approach if the actual fuel composition is unknown and only the sooting tendency is to be estimated. In this case, larger concentrations of sample could be used as long as the total aromatic content in the sample does not go over ~20% by volume. The observed MPI values indicate that MPI scales with aromatic content, but the presence of both large aromatic and naphthenic rings also play an important role. For instance, sample B contains no aromatics and consequently has the lowest MPI value. As aromatic content is introduced in sample C, the MPI value increases substantially, but heavier naphthenics play a significant role as well. This is indicated by the differences in samples A and D.

On the other hand, by comparing samples C and D, one can see that if the total cyclane content is kept constant, but the monoaromatic content is increased, the MPI value increases. What is not so obvious is that when comparing samples C and A, by keeping the monoaromatic content somewhat constant, but replacing a fraction of the small naphthenics and paraffins with large naphthenics, an even larger increase in MPI can occur. This means that observing

only the aromatic content of the fuel can lead to skewed interpretations of its sooting tendency.

4. Conclusions

The micropyrolysis index (MPI) proves to be a valuable tool for estimating the sooting tendency of a particular fuel component. Some advantages over more traditional measurements of sooting tendency are the following:

(a) Only pyrolysis is involved in the measurement, so this method is independent of stoichiometric oxygen ratios and flame temperatures, making it much more representative of a particular compound in a mixture, as well as very promising for fundamental studies.

(b) Only small sample volumes are required, making this method accessible for laboratory scale studies, from which small sample volumes are available.

(c) Reproducibility is much improved compared to the traditional TSI method, and equipment commonly found in conventional laboratories may be utilized to obtain the MPI values.

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