CORRELATION OF SOOTING TENDENCIES AND MOLECULAR STRUCTURE FOR LIQUID HYDROCARBONS

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ABSTRACT

In the present analysis an effort has been made to predict the sooting tendency of hydrocarbon fuels, both in premixed and diffusion flames, by using the group additivity approach based on the molecular protons whose absorptions fall within predefined regions of the proton NMR spectra. In order to define these regions so that they may have a physical meaning, more than 200 spectra have been studied.

As a measure of the sooting tendency in premixed flames, the equivalence fuel/oxidizer ratio s_c was selected, which assumes the combustion products to be C and H_2O. This approach was applied to 69 hydrocarbon fuels (alkanes, alkenes, alkynes and aromatics); the predicted values lie in all cases within ±5% of the measured ones.

In the case of diffusion flames, the ratio used for the Threshold Soot Index (TSI) calculation, i.e. molecular weight/maximum smoke-free flame height (MW/h), has been taken as a measure of the sooting tendency. Again a large number of hydrocarbons with great variations in molecular structure was studied and the estimated values fell in most cases within ±5% of the measured ones; much better accuracy was obtained for open chain as opposed to ring hydrocarbons.

INTRODUCTION

It is generally accepted that smoke formation of hydrocarbon fuels, in both premixed and diffusion flames, depends on a number of parameters such as fuel/oxidizer ratio, temperature distribution and local mixing inside the flame[1], molecular structure etc. The quantification and dependence of the sooting tendency on these various parameters have been the subject of many studies in the past.

In premixed flames Haynes and Wagner[2] studied a number of hydrocarbons and discussed their soot threshold in terms of critical C/O ratios. Later Olson and Pickens[3] studied a large number of fuels including paraffins, olefins, alkynes and aromatics, where they investigated possible ways to define the soot values. They used two alternative equivalence ratios, the first assuming combustion to CO_2 and H_2O (φ_c) and the second to CO and H_2O (ψ_c). The former was eventually linked with the Threshold Soot Index (TSI), which Calcote and Manos[4] had previously defined. More recently, Stournas and Lois[5] discussed a simple method for predicting the sooting tendency by using the group additivity approach. They divided the carbon atoms in the molecule according to their chemical character and employed a new equivalence ratio that assumed combustion to C and H_2O (s_c) and seemed to give more consistent results.

In laminar diffusion flames, the smoke formation is an even more complex phenomenon. In the past, several investigators[6-8] have measured the sooting tendency of numerous fuels but, because of the complexity and interaction of many different factors, the prediction of their individual effects was difficult. Olson et al.[9] have reported measurements of a large number of hydrocarbons in a comprehensive list. They expressed the sooting tendency in terms of TSI, exploiting the link between TSI, molecular weight, and maximum smoke-free flame height (smoke point), as Calcote and Manos[4] suggested.

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Stournas and Lois[10], following a similar procedure as in premixed flames, propose a linear equation where TSI consists of the contributions of the saturated, unsaturated, aromatic and non-aromatic portions of the molecule.

In the present work the group additivity approach was applied, using the groups of hydrogen atoms that exist in the molecule of the hydrocarbon. On a more practical basis, the contribution of these groups can be estimated through the proton NMR spectra[11-15]. To this end, the hydrogen atoms were divided into groups according to the chemical shift of their observed absorption peaks, thus taking into account the chemical environment and stereochemical location of each hydrogen in the molecule. Our effort was focused in finding the best possible division of the generally observed chemical shifts and the weighting factor of each area of these shifts.

ANALYTICAL APPROACH

The identification of molecular structure by using NMR is mainly based on the magnetic properties of the nuclei constituting the molecule and on how they are affected by the interactions of these nuclei. Proton, unlike other nuclei that do not have magnetic properties, absorbs energy when under the influence of a strong, stable magnetic field H_o and a second, weak and at right angle oscillating field H_1 of a specific frequency.

This frequency depends upon the intensity of the main magnetic field that is finally applied on each molecular proton of ahydrocarbon; the field in the space close to the proton is affected by the existence and the density of the electronic cloud surrounding the nucleus, and as a result of induction the actual field in this area is less than H_o. This, in turn, leads to an increase in the required oscillating frequency.

In the hydrogen molecule, where the proton is completely shielded, when a field of 14.092 gauss is applied the required frequency for energy absorption is 60 MHz. In a molecule the proton becomes partially deshielded, according to its chemical and stereochemical positioning, and the frequency varies; this difference in frequency, the chemical shift, is what is mainly measured in an NMR spectrum with tetramethylsilane (TMS) as the commonly employed internal standard. In reality, neighbouring atoms and various interatomic and time-dependent phenomena affect the magnetic behaviour of the protons and complicate the appearence of the resulting spectrum but they are considered of secondary importance except for specialist work.

In hydrocarbons, the most important combinations of atoms that cause deshielding are single bonds (C-C, C-H), double bonds (C=C), triple bonds (C≡C), and aromatic and alicyclic rings. It should be remembered that the intensity of the observed peaks is proportional to the total number of magnetically equivalent protons that cause the relevant peak.

In combining the data, we observed tnat for hydrocarbons protons in similar environments can be clustered in groups, as shown in Table 1.

For premixed flames the equivalent fuel/oxidizer ratio that assumes combustion to C and H_2O (s_c)[5] was selected, whereas for diffusion flames the ratio MW/h was employed in this work. Exploiting the linear link of MW/h and TSI that Calcote and Manos[4] introduced and Olson et al.[9] examined, it proved convenient to obtain relevant data. In both cases the expressions that were selected for soot threshold quantification gave good results.

Using Table 1, the molecular structure can be quantified and expressed as numbers, indicating the amounts of molecular protons whose chemical shifts are within each area of the spectrum. As a result, the sooting tendency measure in premixed and diffusion flames can be accurately estimated, using the proton NMR spectrum of the hydrocarbon and identifying the number of the hydrogen atoms, the peaks of which are observed in each of the predefined regions.

In the case of premixed flames, s_c can be estimated accurately by the following expression:

$$s_c = C/(a_1H_1 + a_2H_2 + a_3H_3 + a_4H_4 + a_5H_5 + a_6H_6 + a_7H_7 + b) \quad (1)$$

where, a_i = the total number of protons whose absorptions lie within area i of the spectrum,
H_i = the weight factor of area i,
C = the total number of carbon atoms in the molecule,
b = a constant.

TABLE 1. Clusters of the observed chemical shifts in the proton NMR spectra of the hydrocarbons

Spectrum regions, ppm	Groups of molecular protons (H-)
0.00 - 1.00	$R\text{-}CH_3$
1.00 - 1.35	$R_1\text{-}CH_2\text{-}R_2$ $CH_3\text{-}C\text{-}Ph$
1.35 - 1.60	$R_1R_2\text{-}CH\text{-}R_3$ $R\text{-}CH_2\text{-}C\text{-}C\equiv$ $R\text{-}CH_2\text{-}C\text{-}Ph$
1.60 - 1.75	$CH_3\text{-}C=$ $CH_3\text{-}C\equiv$
1.75 - 1.95	$H\text{-}C\equiv$
1.95 - 2.05	$R\text{-}CH_2\text{-}C=$ $R_1R_2\text{-}CH\text{-}C=$
2.05 - 2.20	$R\text{-}CH_2\text{-}C\equiv$
2.20 - 2.45	$CH_3\text{-}Ph$ $CH_3\text{-}Ph\text{-}Ph$
2.45 - 3.00	$R\text{-}CH_2\text{-}Ph$ $R_1R_2\text{-}CH\text{-}C\equiv$ $R_1R_2\text{-}CH\text{-}Ph$
3.00 - 4.50	multiple and special shieldings
4.50 - 5.10	$H_2C=C$
5.10 - 6.40	$HRC=C$
6.40 - 7.50	$H\text{-}Ph$
7.50 - 8.00	$H\text{-}Ph\text{-}Ph$

where, $R_i = C_nH_{2n+1}$
Ph = aromatic ring

The spectrum areas and corresponding weight factors are defined in Table 2.

TABLE 2. Spectrum areas and weight factors, premixed flames

Area Number	Spectrum Region	Weight Factors, a_i
1	0.00 - 1.75	0.273
2	1.75 - 2.05	0.305
3	2.05 - 2.20	0.402
4	2.20 - 3.00	0.264
5	3.00 - 4.50	0.283
6	4.50 - 6.40	0.298
7	6.40 - 8.00	0.275
		b = 0.217

In diffusion flames, MW/h was estimated by the following expression:

$$MW/h = \sum_{i=1}^{n} a_i H_i + b \qquad (2)$$

where, n = the number of spectrum regions defined.

Better results were obtained when the hydrocarbons were separated into two categories, each having its own predefined regions and weight factors. The first category includes liquid, open chain hydrocarbons, and the results are shown in Table 3.

Table 3. Spectrum areas and weight factors. Diffusion flames Open-chain hydrocarbons

Area Number	Spectrum Region	Weight Factors, a_i
1	0.00 - 1.00	2.97
2	1.00 - 1.35	1.26
3	1.35 - 1.60	0.88
4	1.60 - 1.75	33.95
5	1.75 - 2.05	-120.74
6	2.05 - 5.10	92.70
7	5.10 - 6.40	83.50
		b = -20.65

In the case of ring hydrocarbons (aromatic or alicyclic) the range of the chemical shifts is divided into 9 areas, as shown in Table 4.

Table 4. Spectrum areas and weight factors. Diffusion flames Ring hydrocarbons

Area Number	Spectrum Region	Weight Factors, a_i
1	0.00 - 1.00	-0.44
2	1.00 - 1.35	5.77
3	1.35 - 1.75	3.90
4	1.75 - 1.95	8.19
5	1.95 - 2.45	5.51
6	2.45 - 3.00	5.76
7	3.00 - 4.50	38.71
8	4.50 - 7.50	12.00
9	7.50 - 8.00	26.31
		b = 91.30

RESULTS AND DISCUSSION

The procedure for estimating sooting tendency through NMR spectra that was described above is illustrated in Tables 5-7, both for premixed and diffusion flames.

In the case of premixed flames, equation (1) was applied to a total of 69 hydrocarbons, of which 25 were alkanes and cycloalkanes, 18 alkenes and cycloalkenes, 6 alkynes and 20 aromatics; the results are depicted in Fig. 1. The overall linear correlation coefficient was very good (r=0.99) and the mean error 3.4%. The computed values are all within ±5% of the experimental ones. Further splitting of the areas in the NMR spectrum does not appear to improve the yield. Some examples of the calculation procedure are shown in Table 5.

In diffusion flames, equation (2) was applied to 50 open chain and 24 aromatic hydrocarbons. The open chain hydrocarbons offer a better fit than the ones that contain one or more rings (Fig. 2) and the correlation coefficient of predicted vs. experimental values of MW/h is 0.99.

Some examples of the calculation procedure are shown in Table 6 for open-chain hydrocarbons and in Table 7 for ring-containing ones.

Table 5. Calculation Examples for Premixed Flames

Compound	C	H	Area Number 1	2	3	4	5	6	7	S_c Exp	Pred
Isopentane	5	12	12	0	0	0	0	0	0	1.45	1.44
Decaline	10	18	18	0	0	0	0	0	0	1.98	1.95
1-Butene	4	8	3	2	0	0	0	3	0	1.59	1.58
Cyclopentene	5	8	0	2	0	4	0	2	0	1.94	2.02
1-Octyne	8	14	11	1	2	0	0	0	0	1.85	1.85
Ethylbenzene	8	10	3	0	0	2	0	0	5	2.71	2.72
Indene	9	8	0	0	0	0	2	0	6	3.72	3.70

Table 6. Calculation Examples for Diffusion Flames. Acyclic Compounds

Compound	C	H	Area Number 1	2	3	4	5	6	7	MW/h Exp	Pred
3-Methylpentane	6	14	9	4	1	0	0	0	0	11.45	11.97
n-Undecane	11	24	6	18	0	0	0	0	0	19.70	19.77
1-Heptene	7	14	3	6	0	0	2	2	1	21.61	23.22
2-Octene	8	16	3	6	0	3	2	0	2	21.83	23.18
1-Octyne	8	14	3	6	2	0	1	2	0	61.22	62.22

Table 7. Calculation Examples for Diffusion Flames. Ring Compounds

Compound	C	H	Area Number 1	2	3	4	5	6	7	8	9	MW/h Exp	Pred
Ethylbenzene	8	10	0	3	0	0	0	2	0	5	0	178.4	180.1
Butylbenzene	10	14	0	5	2	0	0	2	0	5	0	187.9	192.4
Dimethyl-naphthalene	12	12	0	0	0	0	3	3	0	3	3	240.0	240.0

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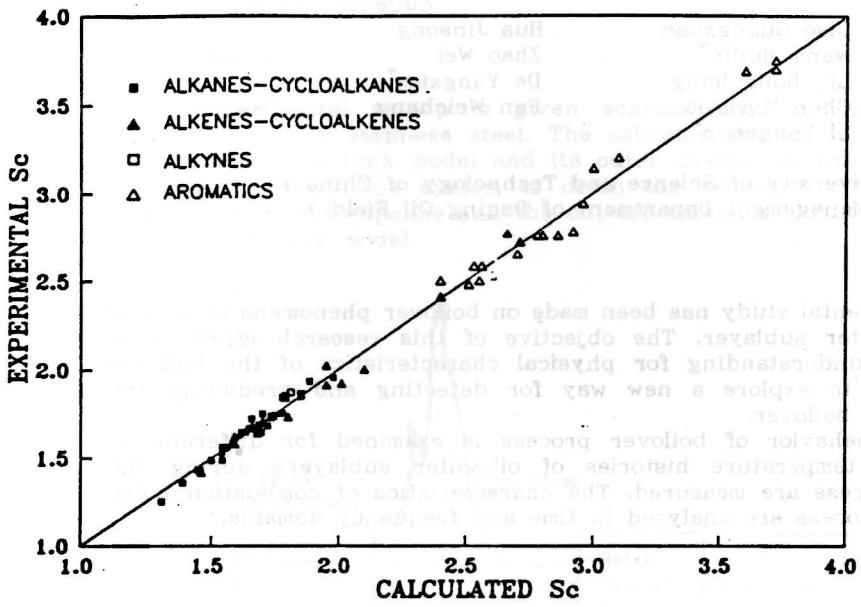

FIGURE 1. Experimental vs Calculated Sc for premixed flames

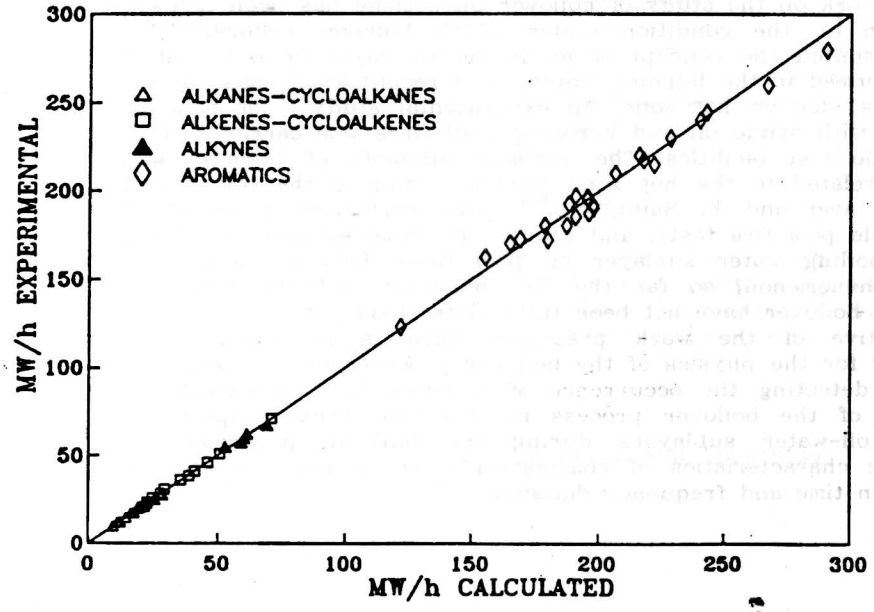

FIGURE 2. Experimental vs Calculated MW/h for diffusion