METHODS FOR ESTIMATING MAXIMIUM INCREMENTAL REACTIVITY (MIR) OF HYDROCARBON SOLVENTS AND THEIR CLASSIFICATION

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ABSTRACT

Hydrocarbon solvents (HCS) are complex mixtures of alkanes, branched alkanes, cycloalkanes, and aromatics that are used in manufacturing a variety of household and commercial products such as aerosol coatings. These solvents contain volatile organic compounds (VOCs) which can react photochemically in the atmosphere to contribute to ground-level ozone formation. To determine the air-quality impact of HCS, a quantitative assessment of their ozone formation potential (i.e. reactivity) is needed. At present, except for a few HCS, no experimental data are available for determining their maximum impact on urban ozone formation (i.e. maximum incremental reactivity or MIR). Although a computational method exists for determining the MIR value, the detailed chemical speciation data needed for such a calculation may not be available for all HCS. In this work, we have developed an empirical estimation method for calculating the MIRs of HCS. This method assumes that the overall reactivity of a HCS can be separated into the contribution from its chemical constituent classes such as *n*-alkanes, branched-alkanes, cycloalkanes, and substituted aromatics. A boiling point-MIR relationship was developed for each chemical class, and composition weighted *n*-alkane-branched alkane-cycloalkane-aromatics surrogate mixtures were used to calculate the reactivity of HCS with different boiling ranges. During its development, this estimation technique was tested against the hydrocarbon solvent data provided by the Chemical Manufacturing Association (CMA), and over 90 percent of the calculated and experimental MIR values of hydrocarbon solvents differed by no more than a factor of 1.15. This result suggests that the technique developed can be used for calculating the MIR values of HCS with no experimental data available. This estimation method was then used to develop a HCS classification scheme for the reactivity-based VOC regulation for aerosol coatings.

INTRODUCTION

Hydrocarbon solvents (HCS) are complex mixtures of alkanes, branched alkanes, cycloalkanes, and aromatics that are used in manufacturing a variety of household and commercial products such as aerosol coatings (Shell, 1996). These solvents contain volatile organic compounds (VOCs) which can react photochemically in the atmosphere to contribute to ground-level ozone formation. To determine the air-quality impact of HCS, a quantitative assessment of their ozone formation potential (i.e. reactivity) is needed. However, because of their complex composition, and the significant amount of time needed for conducting laboratory investigations of the ozone formation potential of these chemicals, the reactivities of only a few HCS have been studied (see, for example, Carter *et al.*, 1996, Carter, 2000).

In addition to making an experimental determination, the reactivity of a complex mixture can be evaluated using the compositional data and ozone formation potential of the ingredients (see, for example, Chang and Rudy, 1990). Ozone formation potentials are available for only about 600 compounds (Carter, 2000). However, it is not feasible to perform compositional analyses for all mixtures because of the diversity of HCS. Although hydrocarbon solvent compositions vary according to their manufacturing processes (see, for example, CMA, 1997), their production is based primarily on fractionation distillation, an industrial process for separating chemicals using their difference in boiling points, and hence, chemical structure. In this work, we have developed an empirical approach for estimating the reactivity of HCS using the boiling point-chemical structure relationship and the maximum incremental reactivity (MIR) scale developed by Dr. W.P.L. Carter at the University of California, Riverside (Carter, 2000). A HCS reactivity classification scheme (i.e. grouping of HCS of similar reactivities into “bins”) based on the method developed is proposed.

FORMULATION OF THE ESTIMATION METHOD

The proposed estimation method for hydrocarbon solvent reactivity assumes that the overall MIR can be estimated by summing the reactivity contribution from individual chemical classes. For hydrocarbon solvent mixtures composed of *n*-alkanes, branched alkanes, cycloalkanes, and mono-, di-, poly-substituted benzenes, the total MIR of a solvent mixture is then given by:

$$\begin{aligned}\text{Mixture MIR} &= \text{Sum of \% Wt MIR of all straight-chain alkanes}\\ &+ \text{Sum of \% Wt MIR of all branched alkanes}\\ &+ \text{Sum of \% Wt MIR of all cycloalkanes}\\ &+ \text{Sum of \% Wt MIR of all mono-substituted benzenes}\\ &+ \text{Sum of \% Wt MIR of all di-substituted benzenes}\\ &+ \text{Sum of \% Wt MIR of all poly-substituted benzenes}\end{aligned}$$

where % Wt = percent composition weighted. For a given carbon number, the MIR values are relatively insensitive to the position of the substituent groups (see, for example, Carter, 2000). In addition, MIR values of C_{n-1}, C_n, and C_{n+1} homologs are similar (Carter, 2000), and hydrocarbon solvent mixtures have rather narrow carbon number distributions (see for example, Carter et al., 1997). Hence, the composition weighted (% Wt.) MIR of all compounds can be approximated by, for example, for branched (Br) alkanes:

Sum of % Wt MIR of all branched alkanes
= MIR of a Br-alkane
x total Wt % of Br-alkanes in the Mixture

Thus, the MIR of a complex HCS mixture can be calculated by using a simple n-alkane-branched-alkane-cycloalkane-aromatics mixture (i.e. surrogate mixture).

Mixture MIR = MIR of a straight-chain alkane x Total Wt % alkanes
+ MIR of a branched alkane x Total Wt % branched alkanes
+ MIR of a cycloalkane x Total Wt % cycloalkanes
+ (MIRs of a mono-, di-, poly-substituted benzenes) x Total Wt % aromatics

The mid-boiling range of HCS was used as a guide for selecting a surrogate *n*-alkane, branched alkane, cycloalkane, and mono-, di-, poly-substituted aromatics (see below). Hydrocarbon solvent data provided by the Hydrocarbon Solvent Panel of the Chemical Manufacturing Association (CMA) on the mixtures' boiling ranges, carbon number distribution by weight percent, weight percentage composition of chemical classes, and MIR values were used to validate the method developed.

Surrogate Mixture Development

The method for surrogate mixture development utilizes the fact that boiling points of alkanes (normal, branched and cyclic) and aromatics increase with increasing numbers of carbon atoms (Morrison and Boyd, 1987). Figure 1 shows the plot of average carbon numbers for HSC and estimated values based on a series of carbon number-boiling point curves of C_5 or C_7 - C_{15} model *n*-alkanes, branched alkanes, and cycloalkanes (Table 1). The average carbon number of a HCS is calculated using the detailed carbon number distribution (% of mixture) data provided by CMA. Surrogate species used for constructing the carbon number-boiling curves are listed in Table 1. The boiling points of surrogates are either obtained from the literature (CRC, 1996) or estimated by using the method of Kinney (Lyman et al., 1990). Using the average boiling point of HCS as an index, an *n*-alkane, a branched-alkane, and a cycloalkane are selected from standard carbon number-boiling point curves. The average boiling point is defined as the sum of initial boiling point (IBP) plus dry point (DP) divided by two. The average carbon number of a surrogate mixture is then calculated by summing the composition weighted carbon number contributed from these species. A sample calculation is presented in Appendix 1. As can be seen in Figure 1, a good correlation ($r^2 = 0.96$) was observed between the calculated HCS average carbon numbers based on reported data and the

Table 1. Summary of Surrogate Alkane and Cycloalkane Species and Their Boiling Points.

Surrogate Species Carbon Number (CN)	Compound Used to Derive Correlation	Boiling Point (BP)[a]
Normal ALKANES		
N-C7	n-Heptane	208.4
N-C8	n-Octane	258.8
N-C9	n-Nonane	303.8
N-C10	n-Decane	345.2
N-C11	n-Undecane	384.8
N-C12	n-Dodecane	421.2
N-C13	n-Tridecane	453.2
N-C14	n-Tetradecane	487.4
N-C15	n-Pentadecane	518.0
Branched ALKANES		
BR-C5	Branched C5 Alkanes	86.0
BR-C6	Branched C6 Alkanes	140.9
BR-C7	Branched C7 Alkanes	186.8
BR-C8	Branched C8 Alkanes	236.3
BR-C9	Branched C9 Alkanes	278.0
BR-C10	Branched C10 Alkanes	322.7
BR-C11	Branched C11 Alkanes	324.7
BR-C12	Branched C12 Alkanes	366.8
BR-C13	Branched C 13 Alkanes	439.7
BR-C14	Branched C14 Alkanes	473.9
BR-C15	Branched C15 Alkanes	505.4
Cyclo ALKANES		
CYC-C7	C7 Cycloalkanes	213.8
CYC-C8	C8 Cycloalkanes	269.6
CYC-C9	C9 Cycloalkanes	312.7
CYC-C10	C10 Cycloalkanes	344.8
CYC-C11	C11 Cycloalkanes	379.5
CYC-C12	C12 Cycloalkanes	417.1
CYC-C13	C13 Cycloalkanes	474.8
CYC-C14	C14 Cycloalkanes	481.5
CYC-C15	C15 Cycloalkanes	510.7

[a] Unit = degree F; calculated value using the chemical species specified by Carter (2000); individual boiling point of each chemical was obtained from CRC (1996) or calculated using method described by Kinney (Lyman et al. 1990).

estimated values using the surrogate approach. This result suggests that a *n*-alkane-branched-alkane-cycloalkane surrogate mixture selected by using the average boiling point of a HCS can be reliably used to determine the major ingredients' carbon number in a complex HCS. A similar approach can be applied to aromatic-containing HCS for surrogate mixture development.

Calculating the Maximum Incremental Reactivity (MIR) of the Surrogate Mixtures.

Relationships Between MIR and Boiling Point of Alkanes and Aromatics

As described above, the reported mid-boiling range of a HCS can be used for selecting a *n*-alkane-branched-alkane-cycloalkane surrogate mixture. The surrogate mixture is then used to develop a method for estimating hydrocarbon solvent reactivity. Figure 2 shows the plot of MIR values of $C_5 - C_{15}$ *n*-alkane, branched-alkane, and cycloalkane surrogates versus their corresponding boiling points. The MIR values used are obtained from the latest compilation by Carter (2000). The data for cycloalkanes can be described by a nonlinear regression equation :

$$\text{CYCLO-MIR} = \alpha + \beta(\text{BP}) + \delta(\text{BP})^2$$

where α, β, and δ are regression coefficients with the values of 3.97, -0.0107, 8.14×10^{-6}, respectively, and BP is the boiling point of the surrogate. For *n*-alkanes and branched alkanes, the MIR-boiling point relationships are described by a nonlinear regression equation to reflect their similarity in reactivity [$\text{MIR} = 1.99 - 0.0034(\text{BP}) + 1.01 \times 10^{-6} (\text{BP})^2$]. Using these equations, reactivity calculations for HCS can be modeled by a hypothetical n-alkane-branched-alkane species and a cycloalkane. For determining the reactivity contribution of substituted aromatics in a solvent, ozone formation potentials of mono-, di-, and poly-substituted benzenes were calculated based on the data supplied by CMA. Using this information, together with the solvent's average boiling point, the MIR-boiling point relationships of each group of substituted benzenes were established. These relationships are:

Mono-substituted benzenes (BEN1) : MIR (BEN1) = - 0.014 (BP) + 6.94
Di-substituted benzenes (BEN2) : MIR (BEN2) = - 0.008 (BP) + 8.45
Poly-substituted benzenes (BEN3) : MIR (BEN3) = 0.013 (BP) + 4.15

MIR of Surrogate Mixtures

At a given boiling point, the MIR values of a cycloalkane (MIR_{cyc}) and a hypothetical (combined) normal- and branched-alkane (MIR_{com}) surrogate species can be determined using the MIR-Boiling Point (BP) relationship established above. The MIR of an aliphatic surrogate mixture is equal to the sum of the composition-weighted MIR of each surrogate [i.e. MIR = MIR_{cyc} x (% Wt. Cycloalkane) + MIR_{com} x (% Wt. n-alkanes +

% Wt of branched-alkanes)] (see Appendix 1: sample calculation). For representing the reactivity contribution of aromatics in a surrogate mixture, a separated estimate for a mono-, a di-, and a poly-substituted benzene was performed. This was accomplished by using the MIR-BP relationship established (see above) and the estimated fractional contribution of each substituted benzene. The fractional distribution of mono-, di-, and poly-substituted benzenes in a HCS is estimated by using a simplified form of Lorentzian distribution function, *f(x)*, and the solvent boiling range data supplied by CMA.

$$f(x) = \frac{1}{1 + (x - m)^2}$$

where m is the location of the peak boiling point. The estimated fractional distribution of total mono-, di-, and poly-substituted benzenes in a HCS is presented in Figure 3.

Figure 4 shows a plot of MIR values calculated with the method described above (i.e. surrogate mixture approach) versus the reported MIR of hydrocarbon solvent mixtures by CMA and experimental values for mineral spirits (Carter, 2000). The solid line represents perfect agreement, and the dashed lines represent disagreement by a factor of 1.15. Only 8 of 83 calculated and reported (or experimental) hydrocarbon solvent mixtures MIR values differ by more than a factor of 1.15. However, none exceed the error limits if a multiplication factor of 1.5 was used. In addition, the good fits of the calculated to experimental data for mineral spirits is gratifying. In conclusion, this estimation technique allows the reactivity of complex hydrocarbon solvent mixtures, with no experimental data available, to be reliably calculated.

Hydrocarbon Solvent Classification ("Bin" Assignment)

As described above, HCS are complex mixtures of organic compounds. For this reason, in developing a way to group HCS of similar reactivity, it is important to ensure that the MIR value assigned for the group reliably reflects the reactivity of a particular HCS mixture within the group. Using the surrogate mixture procedure developed, calculations were performed to determine the effects of hydrocarbon composition (i.e. relative percentages of *n*-alkanes, branched alkanes, cycloalkanes, and aromatics) and carbon number (as a function of boiling point) on a mixture's MIR value.

Our computational results indicate that, up to a certain temperature range, changing the mixture composition from 20 to 80 percent of total n-alkanes and branched alkanes (with the rest of the mixture being cycloalkanes) has only a minor effect on the mixture MIR value, and the coefficient of variation ranges from 8-13 percent across the temperature range studied (80 – 580 degree F). For hydrocarbon solvent mixtures containing mainly (i.e. ≥ 90 %) n-alkanes and branched alkanes or cycloalkanes, our computational results indicate that the HCS MIR value is similar to that of the major ingredient. This is consistent with the observation that a cycloalkane has a slightly higher reactivity than the *n*-alkane or branched alkane with the same number of carbons. In addition, substituted aromatic content of < 2 percent has little effect on the group MIR value of HCS. To evaluate the effect of a mixture's carbon number (i.e. chemical species composition) on HCS reactivity, calculations were performed over the average boiling points from 80 – 580 ^{o}F. This temperature range is consistent with the existing HCS data. At a particular average boiling range interval, for example, 80 to 205 ^{o}F, an increase in a mixture's carbon numbers has only a slight effect on the calculated reactivity (coefficient of variation ≤ 15 %). Therefore, using a surrogate mixture MIR's coefficients of variation of 15 percent as a grouping criterion, we have developed four HCS reactivity groups over the average boiling range of 80 – 580 ^{o}F.

Table 2 lists the four major hydrocarbon solvent groups. Within each group, five different sub-groups (or classes) are defined according to their dominant ingredients. For HCS composed of alkanes and less than 2 % aromatics, three classes are proposed: Class A (< 90 % *n*-alkanes + branched alkanes or cycloalkanes), Class B (≥ 90 % *n*-alkanes + branched alkanes), and Class C (≥ 90 % cycloalkanes (see above). For mixtures containing ≥ 2 % aromatics, 2 classes are proposed i.e. Class D with aromatic content greater than or equal to 2 percent but less than 8 percent and Class E with 8 and up to 22 percent of aromatics. The aromatics content chosen is based on the classification scheme used in American Society of Testing and Materials method (ASTM, 1995). The categorization criteria such as mid-boiling point, percent total alkanes, cycloalkanes, and aromatics are consistent with the typical solvent sales specification data.

Figure 5 shows the comparison between the assigned MIR value for *n*-alkane-branched-alkane-cycloalkane only mixture (i.e. Bin 2; average boiling point : 80 to 205 ^{o}F) to the reported HCS MIR values. The solid line represents perfect agreement, and the dashed lines represent disagreement by a factor of 1.15. As can be seen in Figure 5, these values are well within the specified uncertainty. Similar results are also obtained from the other aliphatic hydrocarbon solvent bins. For aromatic-containing hydrocarbon solvent bins (for example, bin number 15), a good agreement between the assigned and reported are also observed (Figure 6). In most cases (~70 percent), the assigned MIR is approximately ± 15 percent of the reported values, and only a few (~ 7 percent) have a discrepancy between the assigned and reported values greater than 30 percent.

CONCLUSIONS

A technique for the calculation of MIR values of HCS mixtures based on the average boiling point of the mixture and relative proportions of *n*-alkane, branched alkane, cycloalkane, and total aromatics has been developed and tested against the available database. Over 90 percent of the hydrocarbon solvent mixtures with calculated and reported MIR values disagree by a factor of 1.15 or less. Because this approach is developed without being dependent on hydrocarbon solvent compositional data, it is expected that MIR values can be calculated with similar accuracy levels for new hydrocarbon solvents which have ≤ 22 percent aromatic content. However, if the solvent mixture is made by blending HCS with distinctly different boiling points (other than using conventional distillation procedures), the calculated MIR may be erroneous because the basic assumptions used in deriving this estimation method may no longer be

Table 2. Hydrocarbon Solvent Classification (Bins) and Group MIR Values

Average BP (oF)	**CLASS**	**CRITERIA**	**MIR (g O3/ g Organics)**	**BIN NO.**
80-205	A	ALKANES (< 2% AROMATICS)	2.08	1
	B	N- & ISO-ALKANES (≥ 90% & < 2% AROMATICS)	1.59	2
	C	CYCLO-ALKANES (≥ 90% & < 2% AROMATICS)	2.52	3
	D	ALKANES (2 to < 8% AROMATICS)	2.24	4
	E	ALKANES (8 to 22% AROMATICS)	2.56	5
> 205-340	A	ALKANES (< 2% AROMATICS)	1.41	6
	B	N- & ISO-ALKANES (≥ 90% & < 2% AROMATICS)	1.17	7
	C	CYCLO-ALKANES (≥ 90% & < 2% AROMATICS)	1.65	8
	D	ALKANES (2 to < 8% AROMATICS)	1.62	9
	E	ALKANES (8 to 22% AROMATICS)	2.03	10
> 340-460	A	ALKANES (< 2% AROMATICS)	0.91	11
	B	N- & ISO-ALKANES (≥ 90% & < 2% AROMATICS)	0.81	12
	C	CYCLO-ALKANES (≥ 90% & < 2% AROMATICS)	1.01	13
	D	ALKANES (2 to < 8% AROMATICS)	1.21	14
	E	ALKANES (8 to 22% AROMATICS)	1.82	15
> 460-580	A	ALKANES (< 2% AROMATICS)	0.57	16
	B	N- & ISO-ALKANES (≥ 90% & < 2% AROMATICS)	0.51	17
	C	CYCLO-ALKANES (≥ 90% & < 2% AROMATICS)	0.63	18
	D	ALKANES (2 to < 8% AROMATICS)	0.88	19
	E	ALKANES (8 to 22% AROMATICS)	1.49	20

Average Boiling Point = [Initial boiling point (IBP) + Dry Point (DP)]/2 valid, and caution should be used. In addition, the present method has neither used oxygenated compounds for its derivation nor been tested against any oxygenated HCS data for its tolerance. Hence, this method should not be used for calculating oxygenated HCS MIR values.

As discussed previously, the proposed grouping methodology (i.e. hydrocarbon solvent binning approach) is a simplification of this estimation method for calculating hydrocarbon solvent MIR values. It is expected that the grouping method is inherently less reliable for determining MIR values of HCS. Based on the recommended uncertainty of MIR values (Stockwell, 1999), the accuracy of this method may not be improved by narrowing the group interval. Thus, additional research is needed to provide kinetic and mechanistic information for improving MIR values and to obtain information on new solvent classes, especially those with chemical ingredients other than only alkanes and aromatics.

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FIGURE CAPTIONS

Figure 1. Comparison between the hydrocarbon solvent mixture average carbon numbers and the estimated values.

Figure 2. Plot of maximum incremental reactivity values versus boiling points of cycloalkanes (Δ), branched alkanes ( ), and n-alkanes (O).

Figure 3. Plot of fractional distribution of mono-, di-, and poly-substituted benzenes versus average solvent boiling points.

Figure 4. Comparison of the calculated and reported MIR values for 54 aliphatic (O) and 29 aromatic-containing (Δ) hydrocarbon solvent mixtures. Experimental mineral spirits data are represented as a square ( ). (Solid line denotes perfect agreement; dashed lines denote disagreement by a factor of 1.15)

Figure 5. Comparison of the group assigned MIR value and reported values for 16 hydrocarbon solvents in Bin 2 classification. (Solid line denotes the assigned group MIR value of 1.59; dashed lines denote disagreement by a factor of 1.15).

Figure 6. Comparison of the group assigned MIR values and reported values for 5 aromatic-containing hydrocarbon solvents in Bin 15 classification. (Solid line denotes the assigned group MIR value of 1.82; dashed lines denote disagreement by a factor of 1.15).

Appendix 1: Sample Calculations

Sample Data:
Hypothetical Aliphatic Hydrocarbon Solvent A
Boiling Range : 300 – 415 ^{o}F (average boiling point: 357.5 ^{o}F)
Average molecular weight = 168

Carbon Number	Carbon Number Fractionation (wt %)	n-Alkane	Branched-Alkane	Cycloalkane
			(wt %)	
10	1.2	0	0	0
11	29.6	11.7	2.4	12.6
12	53.5	13.6	13.3	31.3
13	15.3	0.5	7.0	7.7
14	0.4	0	0	0
Total	100.0	25.8	22.7	51.5

Using the carbon number fractionation information, the average carbon number of solvent A is calculated as follows:

Average carbon number of the mixture:

$$\sum_{n=10}^{N}\left\{\left(\frac{\text{mol. wt. of solvent x wt \% of } C_n}{\text{mol. wt. of } C_n}\right)\text{x Carbon Number of } C_n\right\}$$
$$= 11.9$$

where n = 10,11,…14.

(A) Carbon Number Estimation

Average carbon number estimation based on wt % of n-alkanes, branched alkane, and cycloalkane:

Carbon number (CN) of a mixture can be calculated by the model species-boiling relationships of
n-alkane : CN = (BP + 85.1)/41.5
branched alkane : CN = (BP + 102.7)/40.8
cycloalkanes : CN = (BP + 28.7)/37.0
Combine with the mid-boiling range (BP) of solvent A, the calculated carbon number of n-alkane, branched alkane, and cycloalkane is 11, 12, and 11, respectively.

Estimated carbon number
= calculated CN of *n*-alkane x wt % of total *n*-alkane
+ calculated CN of branched alkane x wt % of total branched alkanes
+ calculated CN of cycloalkane x wt % of total cycloalkanes
= 11 x (25.8/100) + 12 x (22.7/100) + 11 x (51.5/100)
= 11.3

(B) Hydrocarbon Solvent MIR Estimation

Using the equations of :

$$\text{CYCLO-MIR} = 3.97 - 0.0107(\text{BP}) + 8.14 \times 10^{-6} (\text{BP})^2$$

$$\text{ALK-Br-ALK MIR} = 1.99 - 0.0034 (\text{BP}) + 1.01 \times 10^{-6} (\text{BP})^2$$

The estimated MIR of hydrocarbon solvent A

= CYCLO-MIR x Total Wt % of cycloalkanes
+ ALK-Br-ALK MIR x Total Wt % of alkanes and branched alkanes

= 1.18 x (25.8 + 22.7)/100 + 0.90 x (51.5/100)

= 1.04

Note: These calculations are used for illustrative purpose only; actual data were processed by Excel spreadsheet program. Slight difference may be due to roundoff error.