Molecular Composition Space Boundaries for Fossil Oils

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Introduction

Analysis of complex organic mixtures provided by ultrahigh-resolution FT-ICR mass spectrometry enables assignment of elemental compositions for myriad components constituting petroleum and fuels derived from fossil resources and bio-mass [1]. With phase correction, doublets with mass difference less than the mass of an electron can be resolved [2]. The high-end edge of hydrocarbon compositional space can now be reached and the compositional space boundaries can be confirmed by experimental data [3,4]. The compositional boundary equation may be used to eliminate impossible or inaccessible chemical formulae from all possible elemental combinations found by computer matching of the measured accurate mass within a defined mass window.

The composition of petroleum fractions and hydrocarbon mixtures can be described by the distribution of components according to hydrogen-deficiency expressed through double bond equivalents (DBE = double bonds to carbon plus number of rings). FT-ICR MS analysis of petroleum enables to represent the compositional distribution by isoabundance-contoured plots of DBE versus carbon number for every heteroatom class.

In this study we use three main criteria: number of carbon atoms, number of heteroatoms (N,O,S), and number of rings plus double bonds (DBE) to determine absolute compositional boundaries for all organic compounds constituting petroleum.

Results and Discussion

We use DBE and carbon number to define the compositional boundaries for hydrocarbons and each heteroatom class (mainly $N_nO_oS_s$ in addition to hydrogens and carbons). By that definition, the low-end compositional boundary, i.e., DBE = 0, coincides with the abscissa of a plot of DBE versus carbon number and corresponds to fully saturated acyclic compounds with general formula, $C_cH_{2c+2+n}N_nO_oS_s$. The upper boundary is determined by the maximally condensed aromatic structures and defines a "planar aromatic limit".

Hydrocarbons

The lower boundary for hydrocarbons (DBE = 0) corresponds to the most saturated acyclic hydrocarbons - alkanes (C_cH_{2c+2}). Alkanes is known to present a significant part of a crude oil and its light fractions and are the main component of transportation fuels. However hydrogen deficiency (and hence DBE of petrolem compounds) increases in high boiling fractions and residues, and, for example, coke is believed to derive from highly condensed PAHs that can contain heteroatoms through depletion of hydrogen and aggregation of carbon atoms. Thus, we only consider fully aromatic hydrocarbons for the upper boundary of all possible hydrocarbons in the DBE versus carbon number plots. Beyond the boundary, the fossil hydrocarbon molecules are impossible to exist.

The smallest aromatic hyrocarbon molecule possible is benzene, C_6H_6, located at DBE = 4 and C# (carbon number) = 6 in a DBE versus carbon number plot. Its homologues, alkyl benzenes, extend the distribution from this point to higher carbon numbers at a constant DBE value of 6. Hence, the denuded benzene resides at the lowest boundary of the benzene series.

The next fully aromatic hydrocarbons of benzenes are naphthalenes of DBE = 7, C# = 10. Hydroaromatic (naphthenoaromatic) and olefinic aromatic compounds, such as indans/styrenes of DBE = 5 and indenes/cyclo-olefins/divinyl benzenes of DBE = 6, occupy the DBE versus carbon number space between benzenes and naphthalenes with the lowest carbon number members below the straight line connecting between benzene and naphthalene (**Figure 1**).

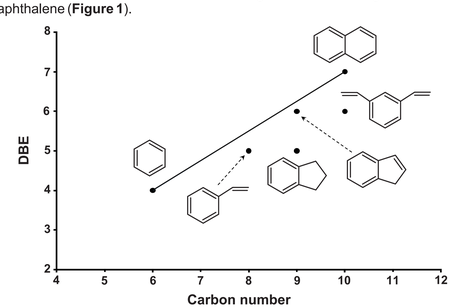


Figure 1. DBE versus carbon number plot for benzene (DBE=4), styrene (DBE=5), indane (DBE=5), indene (DBE=6), divinylbenzene (DBE=6) and naphthalene (DBE=7). The straight line sets the boundary for aromatic hydrocarbons. No aromatic compounds are possible above the line in this range of DBE and carbon number.

The PAHs beyond naphthalenes can be *cata*- and *peri*-condensed. In the *cata*-condensed PAHs, no single carbon atom is shared by more than 2 rings. In *peri*-condensed PAHs, at least one carbon atom is shared by three aromatic rings. **Figure 2** and **3** shows the schematic formation (not reaction) of next higher members of *cata*- and *peri*-condensed PAHs.

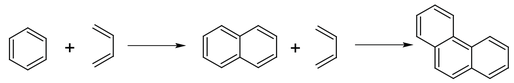


Figure 2. Next largest member of a *cata*-condensed PAH series, derived by the addition of a C_4 unit with a net gain of C_4H_2.Note that the equation shown above is conceptual for adding additional carbon skeleton unit, not representing real reaction.

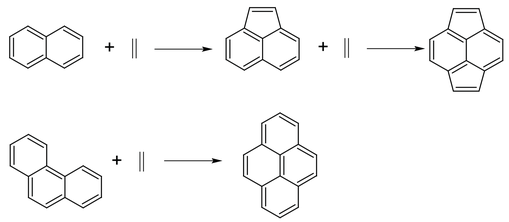


Figure 3. Derivation of a *peri*-condensed PAH from a *cata*-condensed PAH through an addition of a C_2 unit with a C_2 net gain. Note that the equations shown above are conceptual for adding additional carbon skeleton unit, not representing real reactions.

The most compact PAHs are fused *peri*-condensed species that are also the most stable, both thermodynamically and kinetically. Hence, we employ *peri*-condensed PAHs as core structures for the compositional space boundary calculations.

Figure 4 displays the most condensed bare aromatic compounds of a given DBE value, as a function of the increasing carbon number of the denuded members. $C_{112}H_{26}$ is selected as an "anchor" point because it is the most condensed PAH beyond C_{100}. Its carbon number and DBE value exceed confidently determined experimental values reported in the literature. Among several elemental compositions having the same DBE, only those compounds of the lowest hydrogen/carbon (H/C) ratio are used to define the boundary for aromatic hydrocarbons. For example, dibenzochrysene, $C_{26}H_{16}$, has the same DBE, i.e., 19, as coronene, $C_{24}H_{12}$. Thus, coronene is kept because of its lower H/C ratio as more aromatic than dibenzochrysene for setting the boundary for PAHs of DBE = 19.

The upper boundary line of the compositional space for hydrocarbons with DBEs from 0 to 100 and carbon numbers between 1 and 112 may be expressed by the following equation

$$\text{DBE} = 100/112 \times (\text{carbon number}) \sim 0.893 \times (\text{carbon number}) \qquad (1)$$

Equation 1 can be further simplified as a rule of thumb as DBE < 0.9(carbon number). That is, no hydrocarbon molecule DBE can exceed 90% of the number of carbons in its molecular formula.

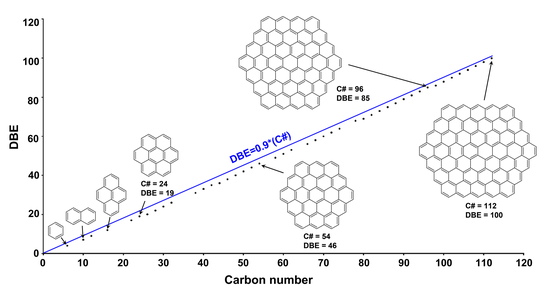
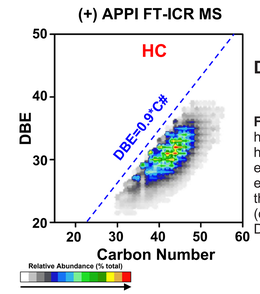


Figure 4. DBE versus carbon number for a series of the most condensed aromatic compounds. The blue line represents the upper compositional space boundary for fossil hydrocarbons defined by the **equation 2**: DBE = 0.9(carbon number) or "90% rule".



$$\text{DBE} = 0.9 \times (\text{Carbon number}) \qquad (2)$$

Figure 5. DBE versus carbon number plots for hydrocarbon class of the most severely hydrotreated asphaltene residue from an ebullated-bed reactor (positive-ion APPI data with experimental conditions described in ref 4) and for the hydrocarbon compositional space boundary (dashed blue line) based on the "90% rule", i.e., DBE = 0.9(carbon number).

However, synthetically possible non-planar aromatic structures formed by the introduction of five-member rings surrounded by six-member rings (e.g., bucky-bowls) can cross that boundary. Although no such molecules have yet been reported in petroleum mass spectra, our generalized linear equation derived for the "planar aromatic limit" is still valid for the largest known synthetic buckybowl structure (**Figure 6**).

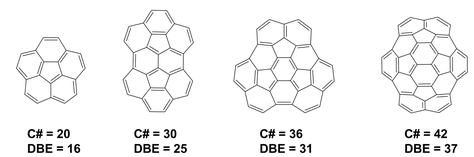


Figure 6. Non-planar polycyclic aromatic hydrocarbons with up to 4 five-member rings are still covered by the "90% rule" and generalized equation 2.

Heteroatom compounds

The first member of heterocyclic (N,O,S) aromatic compounds correspond to five-member ring (pyrrole/furan/thiophene) with C# = 4 and DBE = 3 and lie below the boundary line for the hydrocarbons (**Figure 7**). The higher aromatic members with a heteroatom in the five-member ring share the same DBE and carbon number relationship as hydrocarbons. For example, dibenzothiophene, dibenzobenzofuran and indole (C# = 12 and DBE= 9) are equivalent to acenaphthalene (C#=12, DBE=9) and do not exceed the upper limit defined for hydrocarbons. Figure 7 shows that equition 2 is still valid to define heteroatom compounds with up to 3 heteroatoms in five -membered rings.

However, heteroatom compounds containing sp^2-hybridizied nitrogen atom (basic N) results in decrease of carbon number and preservation of DBE as for the corresponding hydrocarbon (e.g., benzene→pyridine, naphthalene→quinoline). Such perturbation can be compensated by taking into account number of nitrogen atoms in a molecule. **Figure 8** schematically shows that position of aromatic compounds containing sp^2-hybridized N atoms is shifted to the left along x-axis. Thus, **Equation 3** defines the upper boundary for petroleum compounds as following: DBE = 0.9x(C#+ N#).

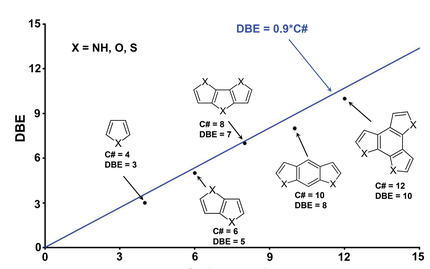


Figure 7. The hetroatom compounds with sp^3- hybridized O, S form five-member rings that are covered by the generalized equation DBE = 0.9(carbon number).

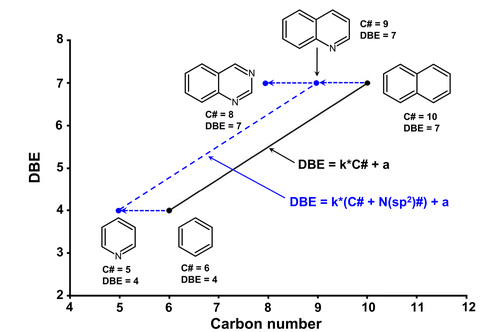
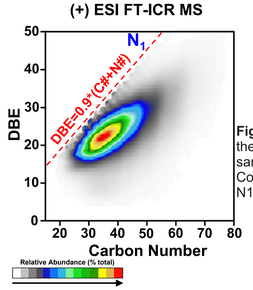


Figure 8. The substitution of CH-group(s) in a hydrocarbon molecule by sp^2-hybridizied nitrogen atom(s) causes the shift in carbon number (by one unit for each N atom) and preservation of DBE. The blue dashed line is parallel to the upper limit defined for hydrocarbons (solid black line). The number of nitrogen atoms changes the position of upper boundary according to equation DBE = 0.9x(C#+ N#).



$$\text{DBE} = 0.9\text{x}(\text{C\#+ N\#}) \qquad (3)$$

Figure 9. DBE vs. carbon number plot for N_1 class of the severely thermotreated asphaltene residue. The sample was analyzed by (+) ESI FT-ICR MS. Compositional space boundary (dashed red line) for N1 class is based on the equation 3.

Conclusions

- The compositional boundaries for petroleum compounds were established to eliminate impossible or unallowed chemical formulae found by computer matching of the measured accurate mass with those corresponding to all possible elemental combinations within the defined mass window during the search.
- The lower compositional boundary, i.e., DBE = 0, coincides with the abscissa of a plot of DBE versus carbon number and corresponds to compounds with general formula, $C_cH_{2c+2+n}N_nO_oS_s$.
- The upper boundary is determined by the maximally condensed aromatic structures (defined a "planar aromatic limit") and is described by the equation DBE = 0.9x(C#+ N#).
- The proposed equation is in the complete accordance with experimental data.

Acknowledgements

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References

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