energy&fuels ARTICLE
pubs.acs.org/EF

Compositional Boundaries for Fossil Hydrocarbons

Chang S. Hsu,*,† Vladislav V. Lobodin,‡ Ryan P. Rodgers,‡,§ Amy M. McKenna,‡ and Alan G. Marshall‡,§

†Future Fuels Institute, Florida State University, 1800 East Paul Dirac Drive, Tallahassee, Florida 32310, United States

‡Ion Cyclotron Resonance Program, National High Field Magnet Laboratory, Florida State University, 1800 East Paul Dirac Drive, Tallahassee, Florida 32310-4005, United States

§Department of Chemistry and Biochemistry, Florida State University, 95 Chieftain Way, Tallahassee, Florida 32306, United States

ABSTRACT: We have determined the absolute upper limit of hydrocarbon compositional space for petroleum and other fossil oils. The upper limit for the double-bond equivalent (DBE) to carbon is 90% of the carbon number. The DBE lower limit is zero. Any hydrocarbon molecular formula outside of those boundaries is not observed in hydrocarbon resources, petroleum, coal, and oil shale. These boundaries provide working limits for elemental compositions of fossil fuels for computer searching and model building.

INTRODUCTION

Although the general molecular nature of the components in heavy petroleum fractions, i.e., gas oils and higher boiling fractions, has been understood for some time based on bulk physical property measurements and spectroscopic results, the lack of proper analytical tools or instrumentation prohibited determination or confirmation of the elemental composition or structure of individual molecules. Recent advances in Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS), in addition to the availability of various ionization methods designed for liquid chromatography (LC), such as electrospray ionization (ESI),[1−4] atmospheric pressure chemical ionization (APCI),[5] and atmospheric pressure photoionization (APPI),[6] greatly extend the molecular characterization of hydrocarbons to petroleum fractions beyond the gas oil boiling range (>500 °C) for identification of elemental composition of individual molecules.[7] Thus, it is possible to look into the nature of the very heavy petroleum molecules in extremely complex mixtures, such as residues and asphaltenes. ESI and APCI can ionize only polar molecules, providing an opportunity to filter out the dominant and interfering nonpolar species to enhance signals of polar species.[8,9] APPI, on the other hand, can ionize less polar or nonpolar components to complement the inefficient ionization of nonpolar species by ESI.[4,6,9] However, it is more energetic and prone to fragmentation of ionic species without careful controls. In the residues and asphaltenes, it is common to detect more than 50 000 ionic species in a single sample.[10,11] The identification of these species by their molecular formulas through ultrahigh-resolution accurate mass measurement enables us to probe the previously inaccessible compositional space.

Only a handful of pure polycyclic aromatic hydrocarbons (PAHs) are commercially available through synthesis or separation from fossil fuel fractions for structural determination by various spectroscopic techniques to validate mass spectrometric and chromatographic identifications. Most of the highly condensed PAHs reported in the literature for very complex high boiling fractions can, therefore, be determined only by mass spectrometry. Their structures are inferred from lower molecular-weight-known analogues based on the elemental composition of the molecules because the pure components are impossible to synthesize or be separated from very complex mixtures.

The compositions of the components of petroleum fractions and hydrocarbon mixtures can be expressed by the distribution of components according to hydrogen-deficiency z series or double-bond equivalents (DBE = double bonds to carbon plus number of rings).[10−13] The hydrogen-deficiency z series is defined by the general formula, $C_nH_{2n+z}X$, in which X represents functional groups or heteratoms.[11,12] For example, the most saturated hydrocarbons are paraffins, for which $z = +2$. The smallest fully aromatic hydrocarbons are benzenes, for which $z = -6$. Recent FT-ICR MS experiments have made it possible to represent the compositional distribution by isoabundance-contoured plots of DBE versus carbon number.[14] Thus, it becomes convenient to determine the limit or boundary of the fully aromatic hydrocarbons, i.e., PAHs with no naphthenic (cycloparaffinic) substructures, for comparison to experimental data.

RESULTS AND DISCUSSION

Hydrocarbons. The compound type and carbon number distribution span all possible structures. The most saturated hydrocarbons are paraffins of DBE = 0. Therefore, in a plot of DBE against carbon number, the paraffin line coincides with the abscissa, providing the lower boundary. The most condensed hydrocarbons are the PAHs to define the upper boundary of all possible hydrocarbons.

The smallest aromatic molecule is benzene, C_6H_6, with DBE = 4 and carbon number = 6. Its homologues, alkyl benzenes, extend the distribution to higher carbon numbers at a constant DBE value of 4. Hence, the bare benzene molecule sets the lowest carbon number bound for the alkylbenzene series. The next largest aromatic hydrocarbons are naphthalenes, with DBE = 7. Hydroaromatic (naphthenoaromatic) and olefinic aromatic compounds, such as indans/styrenes, with DBE = 5, and indenes/cyclo-olefins/divinyl benzenes, with DBE = 6, occupy the DBE versus carbon

Received: March 22, 2011
Revised: April 19, 2011
Published: April 20, 2011

number space between benzenes and naphthalenes and are thus located below the straight line connecting benzene and naphthalene in a plot of DBE versus carbon number (Figure 1).

The PAHs beyond naphthalenes can be *cata*- or *peri*-condensed. In the *cata*-condensed PAHs, no single carbon atom is shared by more than two aromatic rings. The subsequent series of *cata*-condensed PAHs can be formed by successive addition of a C_4H_2 unit, as shown in Figure 2. Note that the transformations shown hereafter are conceptual for adding an additional carbon skeleton unit to represent subsequent condensed aromatic ring series and are not intended to represent actual chemical reactions.

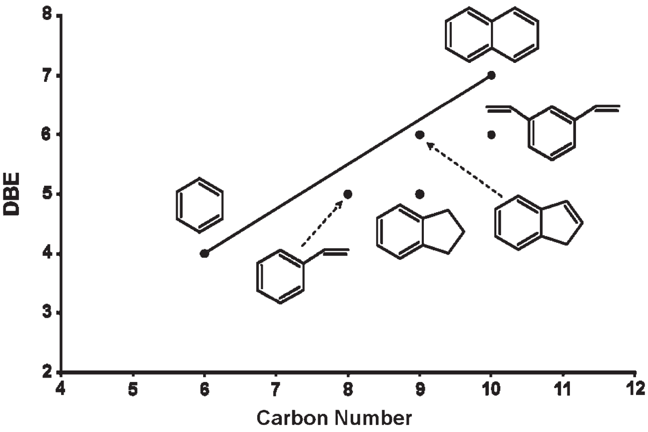


Figure 1. DBE versus carbon number plot for benzene (DBE = 4), styrene (DBE = 5), indan (DBE =5), indene (DBE = 6), divinylbenzene (DBE = 6), and naphthalene (DBE = 7). The straight line sets the upper DBE boundary for aromatic hydrocarbons. No aromatic compounds are possible above the line in this carbon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

In *peri*-condensed PAHs, at least one carbon atom is shared by three aromatic rings. Thus, the next *peri*-condensed PAH "condensation" member differs by a C_2 or C_6 unit from a *cata*-condensed PAH with a net gain of C_2 or C_6H_2, as shown in Figure 3. Another transformation is by inclusion of an additional C_4 unit, with a net gain of C_4H_2, as shown in Figure 4.

The "condensation" with a C_3 unit to represent fully *peri*-condensed PAHs is not possible because at least one carbon atom would have five covalent bonds (see the circles in Figure 5). In this case, only hydroaromatic hydrocarbons containing at least one methylene carbon in the ring are possible, a common mistake in attempts to relate the molecular structure to mass spectral interpretation.

The most compact PAHs are fused *peri*-condensed species that are also the most stable, both thermodynamically and kinetically.[15] Hence, we employ *peri*-condensed PAHs as core structures for the compositional space boundary calculations. The first (bare or C_0-substituted) members of the homologous series in the "aromatic ring condensation" series are calculated by consecutive "*cata*-condensation" of the corresponding first members shown on the left side of the tables displayed in Figure 6. For example, the next condensation series of benzenes are naphthalenes, obtained by adding one condensed aromatic ring through

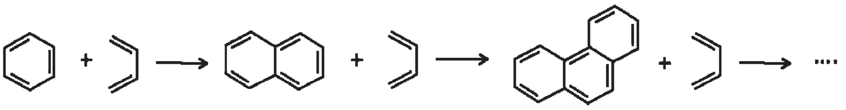


Figure 2. Next largest member of a *cata*-condensed PAH series, derived by the addition of a C_4 unit with a net gain of C_4H_2.

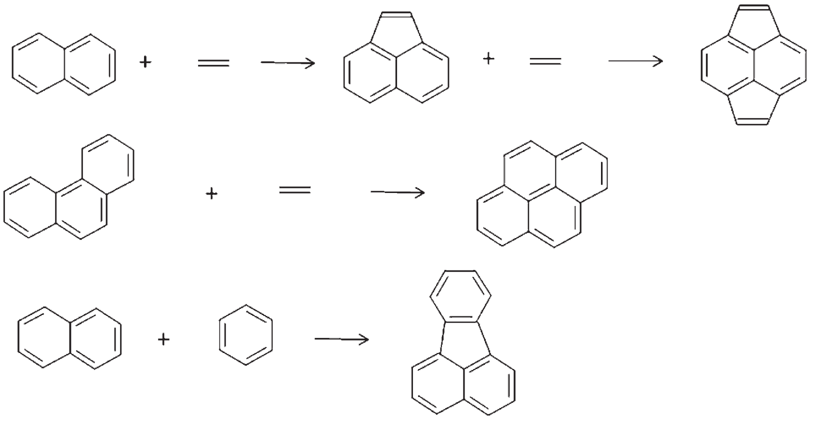


Figure 3. Derivation of a *peri*-condensed PAH from a *cata*-condensed PAH through an addition of a C_2 or C_6 unit with a C_2 or C_6H_2 net gain.

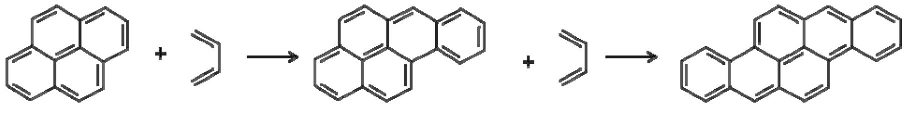


Figure 4. Derivation of next *peri*-condensed PAH member through an addition of a C_4 unit with a C_4H_2 net gain, as for "*cata*-condensation" shown in Figure 2.

cata-condensation. Only the first member of the new condensation series, namely, naphthalene itself with no substitution, $C_{10}H_8$, is listed in the table displayed in Figure 6. The tables displayed in Figure 6 list the carbon number, hydrogen number, *z* number, and DBE for the first members of condensation series.

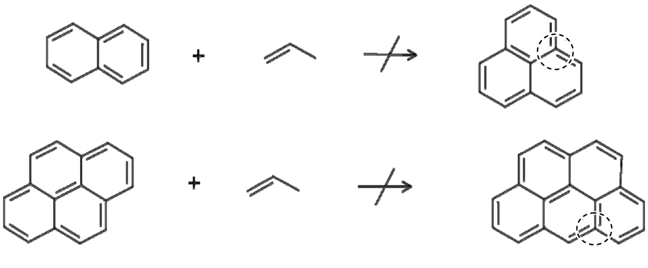
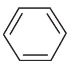
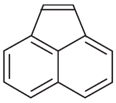


Figure 5. Unallowed *peri*-condensation forming impossible PAHs.

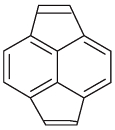
Highly condensed PAHs up to DBE = 100 provide the data points shown in Figure 7. $C_{112}H_{26}$ is selected as an "anchor" point because it is the most condensed PAH beyond C_{100}. Its carbon number and DBE value exceed confidently determined experimental values reported in the literature. Among several 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.



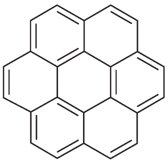
Carbon Number	6	10	14	18	22	26	30	34	38	42	46
Hydrogen Number	6	8	10	12	14	16	18	20	22	24	26
z-number	-6	-12	-18	-24	-30	-36	-42	-48	-54	-60	-66
DBE	4	7	10	13	16	19	22	25	28	31	34



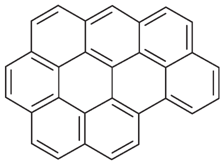
Carbon Number	12	16	20	24	28	32	36	40	44	48	52
Hydrogen Number	8	10	12	14	16	18	20	22	24	26	28
z-number	-16	-22	-28	-34	-40	-46	-52	-58	-64	-70	-76
DBE	9	12	15	18	21	24	27	30	33	36	39



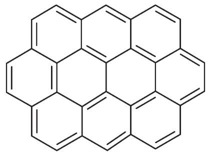
Carbon Number	14	18	22	26	30	34	38	42	46	50	54
Hydrogen Number	8	10	12	14	16	18	20	22	24	26	28
z-number	-20	-26	-32	-38	-44	-50	-56	-62	-68	-74	-80
DBE	11	14	17	20	23	26	29	32	35	38	41



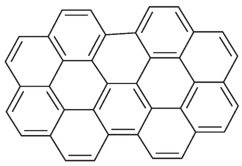
Carbon Number	24	28	32	36	40	44	48	52	56	60	64
Hydrogen Number	12	14	16	18	20	22	24	26	28	30	32
z-number	-36	-42	-48	-54	-60	-66	-72	-78	-84	-90	-96
DBE	19	22	25	28	31	34	37	40	43	46	49



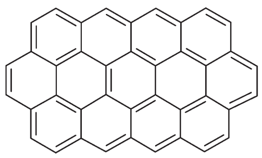
Carbon Number	30	34	38	42	46	50	54	58	62	66	70
Hydrogen Number	14	16	18	20	22	24	26	28	30	32	34
z-number	-46	-52	-58	-64	-70	-76	-82	-88	-94	-100	-106
DBE	24	27	30	33	36	39	42	45	48	51	54



Carbon Number	32	36	40	44	48	52	56	60	64	68	72
Hydrogen Number	14	16	18	20	22	24	26	28	30	32	34
z-number	-50	-56	-62	-68	-74	-80	-86	-92	-98	-104	-110
DBE	26	29	32	35	38	41	44	47	50	53	56



Carbon Number	38	42	46	50	54	58	62	66	70	74	78
Hydrogen Number	16	18	20	22	24	26	28	30	32	34	36
z-number	-60	-66	-72	-78	-84	-90	-96	-102	-108	-114	-120
DBE	31	34	37	40	43	46	49	52	55	58	61



Carbon Number	40	44	48	52	56	60	64	68	72	76	80
Hydrogen Number	16	18	20	22	24	26	28	30	32	34	36
z-number	-64	-70	-76	-82	-88	-94	-100	-106	-112	-118	-124
DBE	33	36	39	42	45	48	51	54	57	60	63

Figure 6. Calculated carbon number, hydrogen number, *z* number, and DBE for the first member of each homologous *cata*-condensation series. The structure shown on the left of each table is the base structure of the first (bare) "*cata*-condensed" member of the series.

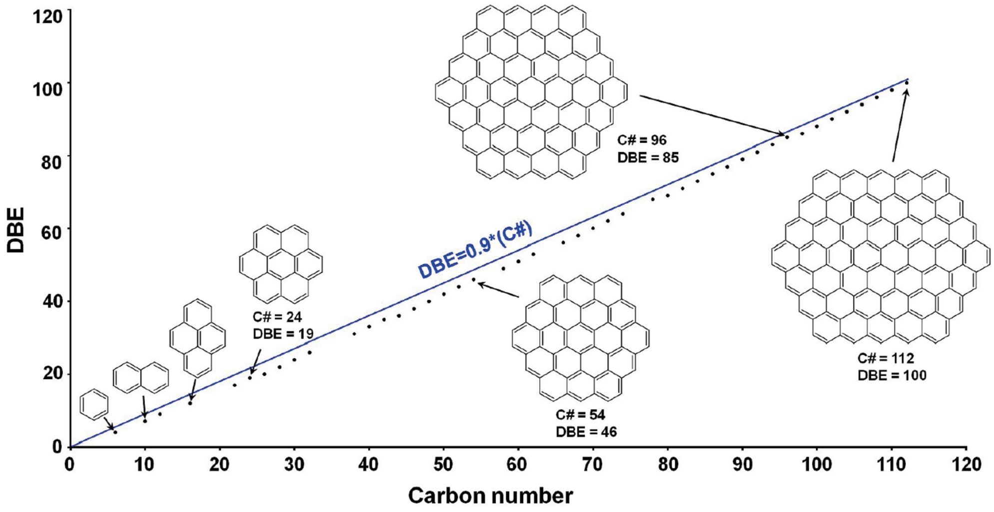


Figure 7. DBE versus carbon number for a series of the most condensed aromatic compounds.

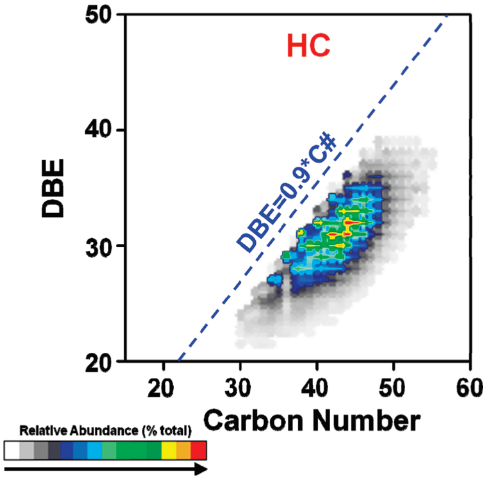


Figure 8. DBE versus carbon number plots for the most severely hydrotreated asphaltene residue from an ebullated-bed reactor (positive-ion APPI data with experimental conditions described in ref 14) and for the hydrocarbon compositional space boundary (dashed blue line) based on the "90% rule", i.e., DBE = 0.9(carbon number).

Figure 7 dislays the most condensed bare aromatic compounds of a given DBE value, as a function of the increasing carbon number of the denuded members. All of those data points fall below a straight line between the origin and the PAH of the highest DBE considered here, namely, $C_{112}H_{26}$ (DBE = 100 and carbon number = 112). Therefore, that straight line serves to represent the upper boundary for hydrocarbons because all PAHs lie below that line. Thus, 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:

$$\begin{aligned} \text{DBE} &= (100/112)(\text{carbon number}) \\ &\approx 0.893(\text{carbon number}) \end{aligned} \tag{1}$$

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.

Heteroatom-Containing Compounds. Equation 1 also holds for heteroatom (N, O, and S)-containing compounds, if each heteroatom is treated as a carbon atom, regardless of the number of heteroatoms that the molecule contains. The same is true for compounds with a carbon number smaller than benzene. For example, furan, thiophene, and pyrrole all have a carbon number of 4 with a DBE of 3. If each of these heteroatoms is replaced by a carbon atom, then the upper bound determined by the "90% rule" is valid.

Applications. ESI and APPI FT-ICR MS enable the detection and unique identification of the most highly condensed aromatics in heavy petroleum fractions, such as residues and asphaltenes.[15] Molecular compositional complexity increases rapidly with an increasing molecular weight. It is therefore important to avoid misidentification of molecules with impossible structures in the compositional analysis. The theoretical upper boundary of the DBE versus carbon number compositional space must therefore be validated from experimental data for highly condensed PAHs resulting from the most extensive hydrotreating conditions. We previously reported the presence of dealkylated highly condensed multi-ring aromatic hydrocarbons in the most severely hydrotreated asphaltene from an ebullated-bed reactor with the longest residence period.[16] Figure 8 shows similar data overlaid with the hydrocarbon compositional space boundary line (upper bound) determined from the "90% rule". Note that all of the experimental data fall below that boundary.

In conclusion, FT-ICR MS with mass resolving power, $m/\Delta m_{50\%} > 800\,000$, in which m is ion mass and $\Delta m_{50\%}$ is mass spectral peak full width at half-maximum peak height, i.e., sufficient to distinguish compositions differing in mass by less than the mass of an electron, has been used to determine elemental compositions of up to tens of thousands of components from complex hydrocarbon mixtures.[10,11] Elemental composition is determined by matching the experimental mass (to within measurement error) with that calculated for each of the possible elemental compositions containing selected elements (C, H, N, O, S, etc.). Although higher mass accuracy narrows the window for the number of putative elemental combinations, one cannot always eliminate elemental compositions whose DBE values fall above the compositional space boundary limit for a given carbon number. Thus, when impossible structures are eliminated, the presently established compositional space boundary limit will further improve the reliability and validity of elemental composition determined by mass spectrometry, for prediction of the properties and behavior of petroleum and fossil fuels based on detailed chemical composition.[17−20]

AUTHOR INFORMATION

Corresponding Author

*E-mail: hsu@magnet.fsu.edu.

ACKNOWLEDGMENT

This work was supported by the National Science Foundation (NSF) Division of Materials Research through DMR-06-54118 and the state of Florida.

REFERENCES

(1) Zhan, D. L.; Fenn, J. B. *Int. J. Mass Spectrom.* **2000**, *194*, 197–208.
(2) Marshall, A. G.; Rodgers, R. P. *Acc. Chem. Res.* **2004**, *37*, 53–59.
(3) Hughey, C. A.; Rodgers, R. P.; Marshall, A. G.; Qian, K.; Robbins, W. K. *Org. Geochem.* **2002**, *33*, 743–759.
(4) McKenna, A. M.; Purcell, J. M.; Rodgers, R. J.; Marshall, A. G. *Energy Fuels* **2010**, *24*, 2929–2938.
(5) Fukuda, E.; Wang, Y.; Hsu, C. S. *Proceedings of the 44th American Society for Mass Spectrometry (ASMS) Conference on Mass Spectrometry and Allied Topics*; Portland, OR, May 12−16, 1996; p 1273.
(6) Purcell, J. M.; Hendrickson, C. L.; Rodgers, R. P.; Marshall, A. G. *Anal. Chem.* **2006**, *78*, 5906–5912.
(7) Purcell, J. M.; Juyal, P.; Kim, D.-G.; Rodgers, R. P.; Hendrickson, C. L.; Marshall, A. G. *Energy Fuels* **2007**, *21*, 2869–2874.
(8) Klein, G. C.; Kim, S.; Rodgers, R. P.; Marshall, A. G. *Energy Fuels* **2006**, *20*, 1965–1972.
(9) Purcell, J. M.; Rodgers, R. P.; Hendrickson, C. L.; Marshall, A. G. *J. Am. Soc. Mass Spectrom.* **2007**, *18*, 1265–1273.
(10) Schaub, T. M.; Hendrickson, C. L.; Horning, S.; Quinn, J. P.; Senko, M. W.; Marshall, A. G. *Anal. Chem.* **2008**, *80*, 3985–3990.
(11) Hsu, C. S.; Hendrickson, C. L.; Rodgers, R. P.; McKenna, A. M.; Marshall, A. G. *J. Mass Spectrom* **2011**, *46*, 337–343.
(12) Hsu, C. S.; Qian, K.; Chen, Y. C. *Anal. Chim. Acta* **1992**, *264*, 79–89.
(13) Hsu, C. S. *Energy Fuels* **2010**, *24*, 4097–4098.
(14) Marshall, A. G.; Rodgers, R. P. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 18090–18095.
(15) Ruiz-Mozales, Y. *J. Phys. Chem. A* **2002**, *106*, 11283–11308.
(16) Purcell, J. M.; Merdrignac, I.; Rodgers, R. P.; Marshall, A. G.; Gauthier, T.; Guibard, I. *Energy Fuels* **2010**, *24*, 2257–2265.
(17) Quann, R. J.; Jaffe, S. B. *Ind. Eng. Chem. Res.* **1992**, *31*, 2483–2497.
(18) Jaffe, S. B.; Freund, H.; Olmstead, W. N. *Ind. Eng. Chem. Res.* **2005**, *44*, 9840–9852.
(19) Hou, Z; Bennett, C. A.; Klein, M. T.; Virk., P. S. *Energy Fuels* **2010**, *24*, 58–67.
(20) Klein, M. T.; Bertolacini, R. J.; Broadbelt, L. J.; Kumar, A.; Hou, G. *Molecular Modeling in Heavy Hydrocarbon Conversion*; CRC Press (Taylor and Francis): Boca Raton, FL, 2006.