ESTIMATING REACTIVITY OF ASPHALTENES BY A COMBINATION OF QUANTUM CHEMICAL CALCULATION AND STATISTIC ANALYSIS

Xiaoliang Ma, and Chunshan Song*

The Energy Institute, The Pennsylvania State University
409 Academic Activities Building, University Park, PA 16802
*E-mail: mxx2@psu.edu

1. Introduction

Asphaltenes are the most polar and heavy substances existing in petroleum, which cause serious problems in oil recovery, pipelines, and especially in thermal and catalytic processing of petroleum residues due to coking. Many approaches have been examined in molecular presentation of asphaltenes for several decades. Recently, some average molecular structures of asphaltenes have been constructed on the basis of elemental composition, detailed structural parameters from NMR data, pyrolysis gas chromatography/mass spectrometry and others [1-6], which allows one to estimate quantitatively the reactivity of asphaltenes at molecular level on the basis of chemical structural models of asphaltenes.

Some approaches to estimating reactivity of aromatic compounds on the basis of computational chemistry have been reported [7-11]. These approaches incorporated some quantum chemical parameters including ionization potential, bond order, π-electron density or frontier orbitals to estimate the hydrogenation reactivity and electrophilic reactivity, which allows one to compare the reactivity of a family of compounds. However, for estimating the reactivity of asphaltenes, these methods are not directly applicable because 1) asphaltenes are composed of mixtures of hundreds of organic molecules rather than a single macromolecule, 2) there are many reactive sites even in a single macromolecule in asphaltene, and 3) not only HOMO and LUMO but also HOMO-1, HOMO-2, … and LUMO +1, LUMO +2, … contribute to the reactivity of the macromolecule since the energy levels of these orbitals are close to the frontier orbitals in the macromolecule of polycyclic aromatics. Consequently, it is necessary to develop a quantitative method to estimate the reactivity of asphaltene on the basis of its chemical structural model. In the present study, we have developed an approach as a new estimation method by using a distribution function of superdelocalizability to estimate the reactivity of asphaltenes. This method combines the quantum chemical calculations and statistic analysis.

2. Structural Models of Asphaltenes

The chemical structural models for three asphaltenes, Khafji ($C_{142}H_{157}N_2O_2S_4$), Maya ($C_{125}H_{134}N_2O_3S_3$) and Iranian ($C_{109}H_{108}N_2O_3S_3$), are shown in Figure 1. The model for each asphaltene contains three macromolecules, representing an average chemical structure of the asphaltene. These models were constructed by researchers at National Institute of Advanced Industrial Science and Central Research Laboratories, Idemitsu Kosan Company, on the basis of the analytical data (including ultimate analysis, ^{1}H-NMR, ^{13}C-NMR and laser desorption mass spectrometry) of the asphaltenes obtained respectively from fractionation of Khafji, Maya, and Iranian vacuum residues using n-heptane as a solvent [2,12].

3. Computational Methods

All quantum chemistry calculations in this study were performed by using a semi-empirical molecular orbital method, the PM3 parameters, in CAChe version 5.0. Geometries of the asphaltene macromolecules and some aromatics were optimized. Bond order, net atomic charges, ionization potential, electrophilic frontier density and electrophilic superdelocalizability were calculated. The electrophilic superdelocalizability was defined as:

$$S^E(x) = 2 \sum_{i=1}^{N} [\phi_i(x)^2]/(\alpha - E_i)$$

Here, N is the total number of the occupied orbitals, $\phi_i(x)$ is the value of the filled orbital i at point x, E_i is the energy of that orbital in electron volts (eV), α is the reagent energy[13, 14]. The statistic analysis was performed by using a frequency function in Microsoft Excel.

4. Results and Discussion

Correlation of Hydrogenation Reactivity of Aromatics with the Calculated Parameters There are not many comparable quantitative data in the literature for hydrogenation reactivity of aromatic hydrocarbons. A set of pseudo–first-order rate constants for hydrogenation of benzene, biphenyl, naphthalene and 2-phenylnaphthalene catalyzed by Co-Mo/Al_2O_3 were determined by Spare and Gates [15]. In order to determine which calculated parameter is more sensitive to hydrogenation reactivity, bond order, ionization potential, electrophilic frontier density and electrophilic superdelocalizability (ESD) for the four aromatic hydrocarbons were calculated and correlated with their hydrogenation rate constants. The results revealed that ESD values of the aromatic hydrocarbons show a better correlation with their hydrogenation reactivities, indicating that we can use ESD values as an index for hydrogenation reactivity. This is probably because the π-complex intermediates formed in hydro-genation process transfer electrons from the higher occupied molecular orbitals of the hydrocarbons to an unoccupied d-orbital on the metal. The higher ESD values result in a more facile electron transfer from the hydrocarbons to the metal, and thus, a stronger adsorption of the hydrocarbons on the active sites on the catalyst surface.

Estimating Hydrogenation Reactivity of Asphaltenes by a ESD Distribution Function The EDS values for all atoms in three asphaltene models were calculated. As well known, it is unsuitable to compare the hydrogenation reactivity of asphaltenes by only comparing the reactivity of one or a couple of sites in each asphaltene model or by only comparing the reactivity of a macromolecule in each asphaltene. In order to solve this problem, we built a distribution function of ESD values for the three asphaltenes on the basis of the structural models. The higher percentage of the atoms in a range of high ESD value indicates the higher hydrogenation reactivity of the asphaltene. Percentage of the atoms in each asphaltene structural model as a function of ESD value is shown in Figure 2. The percentage of the atoms with ESD value higher than 1 increases in the order of Maya < Khafji < Iranian, indicating that the hydrogenation reactivity of the asphaltenes increases in the same order. A distribution function of the bond order for three asphaltenes were also calculated and the results imply a similar trend for hydrogenation reactivity. The distribution function of the bond order also shows that there are higher percentages of weaker C-C bonds in Khafji asphaltenes than in the others, indicating its higher thermal

creaking reactivity. The estimated hydrogenation reactivity and thermal cracking reactivity in the present study are in agreement with the experimental results obtained by Central Research Laboratories, Idemitsu Kosan Company [16]. It has been shown in previous studies that asphaltenes from different Company sources show different reactivities in catalytic and thermal hydroprocessing [17,18].

5. Acknowledgment

We gratefully acknowledge the financial support by Idemitsu Kosan Company and New Energy and Industrial Technology Development Organization (NEDO). We thank Mr. R. Tanaka, Dr. T. Takanohashi and Dr. S. Sato for providing the structural models of the three asphaltenes and for helpful discussions.

6. Reference

1. Shen, Y.; Mullins, O. C. Eds. Asphaltenes, Fundamentals and Applications, Plenum Press, New York, London, 1995.
2. Sato, S., Sekiyu Gakkaishi, 1997, 40, 46.
3. Artok, L.; Su, Y. Hirose, Y.; Hosokawa, M.; Murata, S.; Nomura, M. Energy & Fuels 1999, 13 287.
4. Groenzin, H.; Mullins, O. C. Pet. Sci. Technol. 2001, 19, 219.
5. Sheremata, J. M.; McCaffrey, W. C.; Gray, M. R. *Prepr., Div. Fuel Chem., Am. Chem. Soc*. 2001, 46, 351.
6. Sato, S.; Takanohashi, T. Tanaka, R. *Prepr., Div. Fuel Chem., Am. Chem. Soc*. 2001, 46, 353.
7. Geneste, P.; Amblard, P.; Bonnet, M.; Graffin, P. J. Catal. 1980, 61, 115.
8. Nag, N. K. Appl. Catal. 1984, 10, 53.
9. Ma, X.; Sakanishi, K.; Isoda, T.; Mochida, I. *Energy & Fuels* 1995, 9, 33-37.
10. García-Cruz, I.; Martínez-Magadá, J. M. Guadarrama, P.; Salcedo, R.; Illas, F. J. Phys. Chem. A 2003, 107, 1597-1603.
11. Marston, G.; Monks, P.; Wayne, R. P. Correlations between Rate Parameters and Molecular Properties, in *General Aspects of the Chemistry of Radicals*, Alfassi, Z. B. Ed.; John Wiley and Sons: New York, 1999, p.429.
12. Takanohashi, T. Sato, S.; Tanaka, R., Fuel Chem. Div. Preprints 2001, 46(2), 357.
13. Fukui, K.; Yonezawa, T.; Nagata, C. Bull Chem. Soc. Japan, 1954, 27, 423.
14. Fukui, K.; Yonezawa, T.; Nagata, C. J. Chem. Phys., 1957, 26, 831.
15. Sapre, A. V. Gates, B. C. Ind. Eng. Chem. Process Des. Dev. 1981, 20, 68-73.
16. Tanaka, R., personal communication, 2003.
17. Song, C.; Nihonmatsu, T.; Nomura, M. Ind. Eng. Chem. Res., 1991, 30 (8), 1726-1734.
18. Song, C.; Hanaoka, K.; Nomura, M. Energy & Fuels, 1992, 6 (5), 619-628

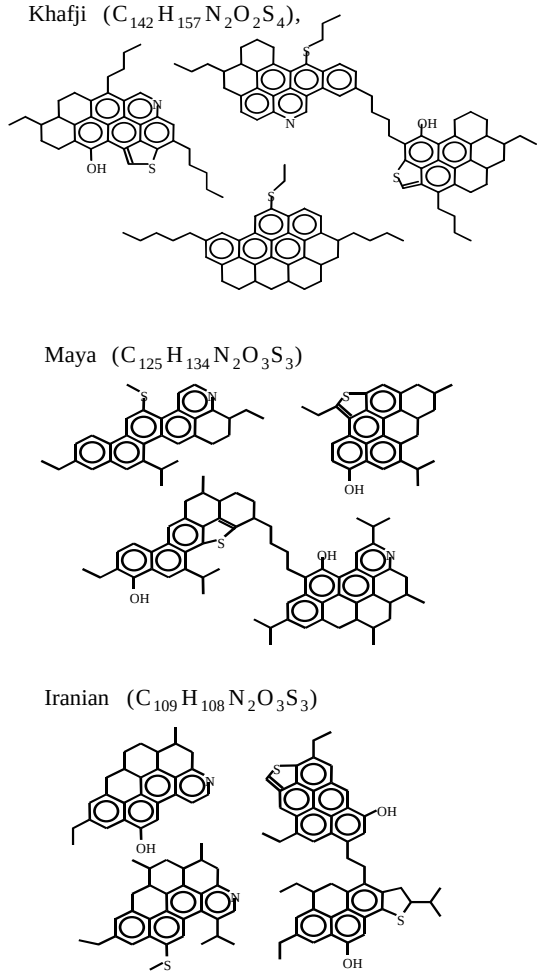

Figure 1. Chemical structural models of three asphaltenes

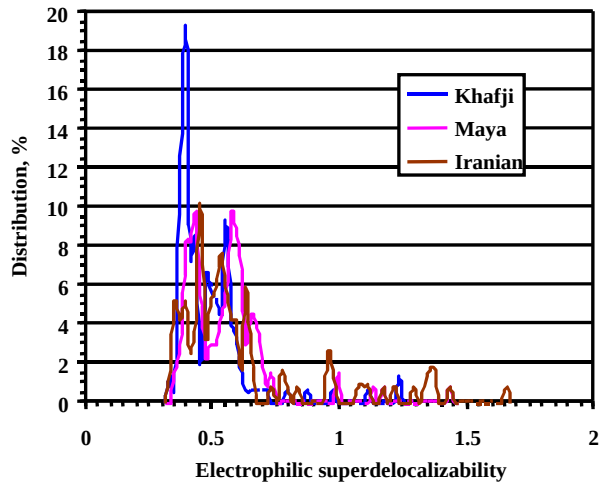

Figure 2. Distribution of electrophilic superdelocalization values on three asphaltenes