Full Length Article

Evaluation of the macromolecular structure of Huadian oil shale kerogen using molecular modeling

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HIGHLIGHTS

- Six constitutional isomers of Huadian oil shale kerogen molecular model were constructed.
- One model was found to have good agreement between the calculated and experimental spectra.
- Geometry optimization and molecular dynamics calculation were performed on 3D structural models.
- Several 3D structures were generated, including the energy-minimum 3D structure.
- Van der Waals interactions have a greatest effect on the physical density of this kerogen.

ARTICLE INFO

ABSTRACT

Based on chemical structure analysis, supplemented with fast pyrolysis results, six constitutional isomers of two-dimensional (2D) molecular models of the Huadian oil shale (HDOS) kerogen were constructed. One model yielded good agreement between simulated and experimental ^{13}C NMR spectra. Geometry optimization and molecular dynamics calculation were performed on three-dimensional (3D) structural models translated from the optimized 2D model. Several 3D structures were generated, including an energy-minimum 3D structure. The simulated results show that van der Waals (vdW) interactions have a greatest effect on the physical density of the HDOS kerogen. In addition, the nonbonding interactions, especially vdW interactions arisen from various flexible chains, play important role in the stabilization of the energy-minimum 3D structure.

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1. Introduction

Kerogen is the major component of organic matter in oil shale that can be converted into shale oil and various gases by pyrolysis. The yield and components of both shale oil and gases are dependent on the chemical structure of kerogen [1–3]. Over the past decades, many workers have studied the chemical structure of different kerogen using various physical and/or chemical methods [4–11] and proposed different two-dimensional (2D) [12–15] and three-dimensional (3D) [16–18] macromolecular models. Burlingame et al. published the first 2D model for Green River Oil Shale (GROS) based on the analytical data of products from CrO_3 oxidation [12]. Yen [13] and Siskin et al. [14] proposed different 2D models for GROS kerogen based on analytical data obtained from different methods. Freund et al. [3] developed a much larger 2D

model for GROS kerogen, which has been used to predict oil and gas compositional yields. Based on the results obtained from elemental analysis, electron microscopy, ^{13}C NMR, thermogravimetry, functional analysis and pyrolysis, Behar and Vandenbroucke [16] constructed three 3D models for three type kerogens. Faulon et al. [17] built the 3D models for average kerogen structures on basis of the data obtained from physicochemical analysis using the molecular modeling software Xmol. More recently, based on the data derived from chemical and physical analysis, Lille [15] proposed the 2D model for Kukersite type II/I kerogen based on chemical structural data and further evaluated this model using a simulation of ^{13}C MAS NMR spectrum. Liu et al. [18] constructed a series of possible isomers of Huadian oil shale kerogen 2D macromolecule model on the basis of the chemical structure data obtained from several physical analysis techniques. They studied these 2D models by density functional theory (DFT) calculations and proposed a relatively stable 3D model that yield a reasonably match between calculated and experimental ^{13}C NMR spectra. The

2D and 3D molecular models mentioned above can provide whole bulk structural and many molecular information; however, specific 3D structural features, intramolecular interactions and physical properties of kerogen cannot been interpreted from these models.

Recently, molecular mechanics (MM) theory and computer simulation, a powerful tool for researching the 3D structure, physical properties and various interactions of macromolecule materials (e.g., biopolymers [19]), and has been successfully applied to the fossil fuels, such as coal [20–28] and oil shale kerogen [29–35]. Carlson [20] studied the 3D structure and the energetics of four previously proposed molecular models of bituminous coal using molecular modeling techniques. The results of molecular mechanics (MM) based on the DREIDING force field and molecular dynamics (MD) calculations indicated that two non-bonding interactions (van der Waals interactions and hydrogen bonding) have an important effect on the formation and stabilization of coal macromolecular structure. The physical densities and micro porosities for these coal molecular models also were calculated and compared with the corresponding experimental values. Nakamura et al. [21,22] studied the relationship between the calculated density and the structure of the coal model molecules and found that the calculated density strongly depended on the length of the bridges of the model molecules. Takanohashi [23] evaluated association of solvent-soluble molecules of bituminous coal by the molecular mechanics and the molecular dynamics methods. The results showed that the associated structures of coal molecules through noncovalent interactions were the most stable conformation and the van der Waals and electrostatic interactions made a larger contribution to the stabilization of the associated structures than the hydrogen-bonding interaction since the number of hydrogen bonding was few. More recently, Lille [29] employed MM and MD calculations to further study the behavior of Estonian kukersite kerogen compositional 3D model, which was generated via the 2D model proposed in his previous work. Using a combination of ab initio and molecular mechanics calculations, Orendt et al. [31] obtained the 3D structural models of the Green River kerogen based on the 2D model proposed by Siskin. They also calculated the ¹³C solid state nuclear magnetic resonance spectra and the atomic pair distribution functions for several initial monomer conformations based on the above 3D models. The reasonably good agreement between calculated and experimental properties results showed that this type of 3D modeling can be of value in the evaluation of 2D models. Based on the data derived from X-ray scattering, neutron diffraction and inelastic neutron scattering experiments, Bousige et al. [32] constructed the realistic molecular models of mature and immature kerogens by using a combined technique of molecular dynamics and hybrid reverse Monte Carlo (MD-HRMC) simulations. These models can not only present a detailed nanostructure of kerogen without considering various minerals (e.g., clays) presented in shales, but predict essential features such as pore distribution, vibrational density of states and stiffness. On the other hand, many recent studies exploring both the mechanism of combustion and pyrolysis reactions for coal [24–28] and oil shale kerogen [33–35] have been carried out by a reactive force field (ReaxFF) MD simulation, which can deal with the issues concerning the bond cleavage and formation of chemical reactions.

The chemical structure of Chinese Huadian oil shale (HDOS) Type I kerogen has been studied using a combination of X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FT-IR), solid-state ¹³C Nuclear Magnetic Resonance (NMR) and elemental analysis [10]. In this paper, the initial 2D molecular model for the HDOS kerogen was constructed based on the above analytical data and the results of fast pyrolysis for HDOS published by Jiang et al. [36]. The final 2D model is a modification of the initial 2D model that optimized the similarity between the simulated and experimental ¹³C NMR spectra. MM and MD calculations were carried out to determine the energy-minimum 3D structure.

2. Construction and computation of molecular model

2.1. Determination of empirical formula for the HDOS kerogen

Kerogen is a macromolecular, insoluble organic material with no defined molecular weight. The molecular weights of the models reported in many previous studies were assumed to range from 3000 to 6000 or so [12,13,15]. On the basis of this common case, the HDOS kerogen molecular model is assumed to have an initial mass of 6000 Da in order to in corporate as many of the identified functional groups as possible.

A formula of $C_{100}H_{163}O_{7.8}N_{1.9}S_1$ can be determined for the HDOS kerogen from elemental analysis. H/C, O/C and N/C are assumed to be organic. XPS analysis indicates that most the sulfur is organic [10], hence, the S/C ratio from elemental analysis is used for the formula. Together with the molecular weight assumed above, an initial bulk formula $C_{387}H_{631}O_{30}N_7S_4$ of model molecule is determined.

2.2. Selection of a set of representative structural units

Structural units are classified into aromatic and alicyclic structures in previously reported kerogen models [12–17]. The former is mainly composed of monoaromatic, naphthalene and/or polyaromatic nuclei, as well a small number of heteroatom-containing aromatic rings; the latter mainly consists of single alicyclic and/or condensed alicyclic structures. Solid state ¹³C NMR analysis shows that the major aromatic carbons present as monoaromatic and/or naphthalene rings and the minor aliphatic carbons present as alicyclic structures in the HDOS kerogen [10]. In addition, fast pyrolysis experimental results further suggest that various alkyl benzenes have a higher proportion among aromatic compounds identified in the oils produced at temperatures above 485 °C [36]. Some aromatic species identified are probably derived from cleavage from the kerogen structure by rupture of weaker carbon–carbon bonds attaching these rings to the kerogen, since they are formed rapidly under an extremely fast heating up and are not easy to be decomposed at a low pyrolysis temperature. Hence, we selected the benzene ring as one of the representative aromatic structural units for constructing the HDOS kerogen macromolecular model.

For nitrogen and sulfur elements, XPS results indicate that in the HDOS kerogen both pyridinic and pyrrolic nitrogen forms have a more half fraction in the total organic nitrogen and the major of organic sulfur presents as aromatic and aliphatic sulfur forms [10]. Electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI FT-ICR MS) analysis for shale oil produced from the pyrolysis of HDOS also found that alkyl pyridines and indoles are more abundant in all identified nitrogen-containing aromatic compounds [37]. Many prior studies on sulfur-containing compounds suggest that alkyl thiophenes account for a larger proportion in sulfur-containing compounds in shale oil [38–40]. Therefore, pyridine, indole and thiophene rings are considered as heteroatom-containing aromatic elements for the HDOS kerogen model.

After determining the types of aromatic structural elements, we can calculate the total number of aromatic carbon using the quantitative results obtained from solid ¹³C NMR and XPS analysis [10] based on the initial bulk formula $C_{387}H_{631}O_{30}N_7S_4$ of model molecule and determine the number of each aromatic structural unit. However, it is not possible to unambiguously determine the