Fuel 230 (2018) 319–330

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Experimental and dynamics simulation studies of the molecular modeling and reactivity of the Yaojie oil shale kerogen

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ARTICLE INFO

Keywords:
Kerogen
Molecular model
Dynamics simulation
Chemical reactivity

ABSTRACT

In this study, the chemical structural parameters of a kerogen from Yaojie oil shale were identified and investigated by using experimental data obtained from solid-state ^{13}C nuclear magnetic resonance spectroscopy, X-ray photoelectron spectroscopy, X-ray diffraction, flash pyrolysis–gas chromatography–mass spectrometry, and Fourier transform infrared spectroscopy. Twelve constitutional isomers of the Yaojie 2D models with different grids and their corresponding 3D models were constructed by the combination of molecular simulation methods and multiple testing techniques. Finally, a reasonable 3D model of Yaojie kerogen was determined by a series of anneal dynamics simulations and geometry optimization calculations. From the results obtained by Mulliken population analysis and electron density analysis, the π–π conjugation effect among the aromatic ring structures is significantly impacted by the heteroatoms, leading to the accumulation of electrons on heteroatoms. Meanwhile, sulfur, oxygen, and nitrogen in the heterocyclic structures exhibited higher electronic charge density and considerably more reactivity compared with those of other atoms. Moreover, the molecular orbitals of HOMO and LUMO were calculated to examine the properties of chemical reaction of kerogen. The HOMO–LUMO energy gap indicated that the Yaojie kerogen exhibited higher reactivities compared to Type I kerogen.

1. Introduction

Kerogen is the insoluble organic matter that generates natural gas and crude oil products during the pyrolysis [1] of sedimentary rocks. Kerogen is a complex material, which comprises various organic chemical compounds and is intertwined with inorganic minerals in organic-rich shales such as oil shale. According to the van Krevelen diagram [2], three main types of kerogen have been identified on the basis of their corresponding different sedimentary histories. Type I kerogens are immature with hydrocarbon-generation characteristics. Type II kerogens exhibit potential for oil generation. Type III kerogens are derived from higher plants, which are primarily preserved in coals or mature shales. Because of its intrinsically complex structure, early studies of kerogen mainly focused on its isolation and bulk characterization [3,4]. The physical and geochemical properties of kerogen can provide vital information for understanding the reaction mechanism for the pyrolysis of kerogen and the efficient utilization of oil shale by high-temperature processes [5].

In the past decades, with the development and comprehensive utilization of various advanced techniques, considerable information regarding the chemical structure of kerogen has been obtained by solid-state ^{13}C nuclear magnetic resonance [6–8] (solid-state ^{13}C NMR), fourier transform infrared (FTIR) spectroscopy combined with thermogravimetric analysis [9,10], gas chromatography–mass spectrometry [11,12] (GC–MS), X-ray photoelectron spectroscopy [13,14] (XPS), and X-ray diffraction [15] (XRD). Based on the experimental analysis, the statistical characteristics of kerogen can be calculated for identification and quantification. Miknis et al. [16,17] have reported a high degree of correlation between the content of aliphatic carbon in different kerogens by ^{13}C NMR spectra and the corresponding gas/genetic potential and estimated the structural features associated with the organic carbon distribution using oil shale pyrolysis models. Kelemen et al. [18] have characterized features of organic heteroatoms species of sulfur, nitrogen, and oxygen by the combination of solid-state ^{13}C NMR, XPS, and sulfur X-ray absorption near-edge structure techniques. In their study, Kelemen et al. have reported direct characterization results of kerogens on the functional group locations and carbon structural parameters. By various experimental analysis methods, the understanding of physical and chemical properties of kerogen has been significantly broadened. In 1989, Faulon et al. [19] have reported the chemical configuration of the kerogen molecule based on physicochemical analyses and integrated the kerogen model into the assembly

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https://doi.org/10.1016/j.fuel.2018.05.031
Received 7 November 2017; Received in revised form 20 April 2018; Accepted 7 May 2018

of chemical structure segments (cyclic groups, aliphatic chains, functional groups, and chemical bonds). Although their study did not include the further discussion of the kerogen chemical reactivity, the possibility of kerogen modeling was considerably explained by a useful method, which provided insight into the microstructure of the Type III kerogen carbon skeleton. In recent years, studies reported on kerogen mainly focused on the model establishment of kerogen molecules using molecular modeling and simulation. Siskin et al. [20] have classified structural fragments obtained from pyrolysis and constructed a two-dimensional (2D) model of Green River Type I kerogen (chemical formula, $C_{645}H_{1017}N_{19}O_{17}S_4$) by GC–MS and ^{13}C NMR analyses. For a three-dimensional (3D) model, Orendt et al. [21] have established a general methodology to select 3D kerogen models by an annealing procedure based on molecular mechanics and quantum mechanical calculations. In their study, the 2D kerogen model proposed by Siskin et al. was generated into a 3D model, and the effect of the size of the 3D model was examined by atomic pairwise distribution function analysis. Bousige et al. [22] have reconstructed a series of realistic molecular models of kerogens using a hybrid experimental-simulation method without considering the presence of minerals in oil shales. Their study provided details of the internal kerogen microstructure and fundamental knowledge in terms of its transport, pore distribution, and elastic properties.

On account of the application of molecular simulation technology, several successful studies have reported the evaluation of the stereostructural characteristics of a 3D kerogen model and the explanation of the chemical kinetics mechanism of kerogen at different grades of maturity [23–25]. Ungerer et al. [26] have built a series of kerogen models that vary in maturity and obtained quantitative predictions of thermodynamic properties based on the Grand Canonical Monte Carlo method and density functional theory (DFT) at the MOPAC-PM7 level. On the basis of their results, the heat of formation (ΔH_f), absolute entropy (S^0), and ideal heat capacity (C_p) were calculated and showed good agreement with the trends predicted for the kerogen density. Results of a recent study have reported the total energy and the corresponding energy components of a 3D kerogen model, which were used to perform an energy-minimum calculation [27]. The non-bond interactions (electrostatic and van der Waals forces) in kerogen are crucial for the stabilization of the model structure.

Kerogen modeling provides a new view to describe the chemical and physical behavior of the kerogen molecule; however, only a few relevant studies have been reported the reactivity of kerogen from a chemical reaction perspective. Meanwhile, few studies related to the electronic properties of the kerogen model have been reported, which are of vital importance for the determination of the pyrolysis reaction characteristics and cleavage or formation of chemical bonds in the kerogen molecule. This study proposed a novel modeling method (which provided a potential solution to aid in the consideration of constitutional isomers) via the combination of molecular simulation methods with multiple testing techniques, and a reasonable 3D kerogen model was constructed by a series of molecular dynamics (MD) and quantum chemistry methods. In addition, the chemical properties of kerogen based on the density functional-based tight binding (DFTB) method, electron density, molecular orbitals, and Mulliken population analyses using quantum chemistry and MD simulations were examined. The results from this study will provide a detailed understanding of the reaction mechanism and reactivity of kerogen, which provides explanation for the chemical behavior of the kerogen molecule from a microscopic viewpoint and supplement theoretical studies on the modeling of kerogen molecules.

2. Material and methods

2.1. Sample preparation

The oil shale sample used herein was obtained from Yaojie (YJ), China. The raw oil shale block sample was crushed and sieved to a fine powder with a size of < 0.2 mm, followed by soaking in distilled water for 2 h to eliminate the soil impurities on the sample surface. The isolated kerogen concentrate was demineralized using $HCl/HNO_3/HF$ according to the standard preparation method reported by Durand and Nicaise [28]. After the major minerals were chemically separated, the kerogen concentrate was rinsed to neutrality and extracted using analytically pure chloroform for the removal of bitumen. The treated sample of the kerogen concentrate was dried at 105 °C to remove the residual reagent and water. As kerogen tends to oxidize after exposure to air, particularly after demineralization, the kerogen sample was stored under 1 bar of N_2 for subsequent analysis.

Table 1
Elemental analysis of Yaojie kerogen.

Dry Ash-Free Basis, wt%					Atomic ratio	
C	H	O	N	S[a]	H/C	O/C
80.25	6.93	5.09	1.94	1.58	1.04	0.05

[a] Total sulfur.

Table 1 summarizes the elemental analysis data obtained for the Yaojie kerogen sample. The H/C vs. O/C atomic ratios were calculated for the classification of the types of kerogen based on the van Krevelen diagram modified by Tissot and Welte [2,29]. According to the diagram, the Yaojie kerogen is Type II. The content of carbon (wt%) in the kerogen sample was 80.25%. Owing to the intrinsically complex structure of kerogen and its intertwining in a matrix of inorganic minerals, it is difficult to completely isolate kerogen from the mineral skeleton, especially for the removal of pyrite FeS_2 [30,31]. Hence, the sum of C, H, O, N, and S observed in the elemental analysis result is 95.79 wt% rather than 100%. Although a small quantity of residual minerals possibly remains in the treated sample of the kerogen concentrate, the elemental analysis is considered to be credible if the sum of C, H, O, N, and S elements is greater than 90 wt% [32].

2.2. Structural characterization

2.2.1. Flash pyrolysis–gas chromatography–mass spectrometry (Py–GC–MS)

The kerogen sample (5 mg, < 0.2 mm) was placed in a multi-shot pyrolyzer (Frontier Laboratories EGA/PY-3030D) using a double-shot sampler, and then the kerogen pyrolysis products were directly used for GC–MS analysis (Perkin Elmer SQ8 GC–MS) coupled with the pyrolyzer using He as the carrier gas. Pyrolysis condition: Pyrolysis time = 10 s; pyrolyzer furnace temperature = 600 °C. GC–MS acquisition parameters: Oven initial temperature 50 °C for 5 min; ramp rate 10 °C/min to 280 °C; hold = 20 min; injection port temperature = 250 °C; transfer temperature = 250 °C; source temperature = 250 °C; scan range = 50 to 450 Da; and column = 30.0 m × 250 μm.

2.2.2. Solid-state ^{13}C nuclear magnetic resonance (solid-state ^{13}C NMR)

Solid-state ^{13}C NMR spectrum of the Yaojie kerogen sample was recorded on a Bruker AV-400-WB-400M spectrometer, which was equipped with a double resonance sample probe. The kerogen sample was packed into a rotor (5 mm, Kel-F ZrO_2) and spun at 12 kHz, operating at 100.637 MHz. Cross-polarization (CP) experiments were carried out at a $^1H-^{13}C$ CP contact time of 6 s, a pulse repetition delay of 6 s, and a spectral width of 3000 Hz. The acquisition time was 0.034 s, and during the total accumulation of 9000 transients, 2048 data points were collected.

2.2.3. FTIR spectroscopy

The kerogen sample was further grinded to a powder with a size of approximately 200 mesh and mixed with KBr (sample: