Kerogens are extracted from deep shales to study pyrolysis of deep shale samples. The 2D molecular models of kerogens are obtained by a series of physical and chemical experiments by which the macromolecular models of kerogens are constructed. Then, the reasonable 3D macromolecular models are established by molecular mechanics and global energy minimization. The effects of temperature and heating rate on the chemical kinetics of kerogen pyrolysis are studied using reactive force field (ReaxFF). The hybrid molecular dynamics/force-biased Monte Carlo (MD/fbMC) approach is used to simulate the pyrolytic process at the experimental temperature, which is lower than the conventional one. The gaseous products and residues obtained by the simulations agree with the experimental results, which means a reliable simulation method for pyrolysis at experimental temperature is provided. This study constructs the rational macromolecular models of kerogen by experiments, and proposes the mechanisms of typical reactions of kerogen pyrolysis, which may help in understanding the formation of shale oil and gas.

1. Introduction

Nowadays, the development of shale oil and gas has brought tremendous changes to the pattern of world energy. The study of the oil/gas-forming mechanism of organic matter cracking into shale oil/gas is of great significance to the shale gas exploration, the production forecast and efficient production. Kerogen is the main organic matter and gas-generating/oil-forming parent material in sedimentary rocks. It has undergone thermal evolution and microbial transformation to form shale oil/gas over geological time. The shale oil/gas mainly exists in the form of

![Figure 1c](https://example.com/figure1c.png)

The kerogen classification defined by van Krevelen diagram is based on hydrogen/carbon (H/C) and oxygen/carbon (O/C) ratio as shown in Figure 1c. Type I kerogen (H/C > 1.25, O/C < 0.15), mainly enriched in lacustrine sedimentary rock and containing alkanes, aromatic compounds, and a small amount of oxygen functional compounds, is the most important type of oil and gas production. Type II kerogen (H/C < 1.25, O/C = 0.03–0.18) mainly comes from the ocean plankton and exists in the marine sediments, which has good oil and gas production capacity but lower than that of type I kerogen. Type III kerogen (H/C < 1, O/C = 0.03–0.3), mainly from higher plants with low hydrogen content, is with a large number of cyclic and aromatic compounds in kerogen (oil production capacity of type III kerogen is relatively low, but it is the main type of gas production when the shale is with deep burial).

The understanding of kerogen is mainly based on the 2D model of large complex carbon molecules or 3D molecular structure described by molecular dynamics (MD) simulation. Physical and chemical degradation experiments are the main methods to study the kerogen structures. The elemental analysis (EA), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR), and $^{13}$C solid-state nuclear magnetic resonance ($^{13}$C NMR) are applied to measure the compositions of elements, the elemental chemical state, types and relative abundances of functional groups in kerogen. And the micromolecular information contained in a
kerogen molecule is analyzed by pyrolysis gas-chromatogram and mass-spectrogram (PY-GC/MS). The nuclear magnetic spectra of mudstone and xylgen (the common nonhydrocarbon compounds of kerogen) have been obtained by $^{13}$C NMR. Coal structures with the high, medium, and low coal ranks have been built by XPS, $^{13}$C NMR, and EA which have been used in the study of kerogen molecular constructions. The Kimmeridge kerogen molecular formula has been constructed from the mild oxidative degradation by ruthenium tetroxide. The 2D kerogen macromolecule models of Estonian shale and Green River oil shale have been established by experimental methods.

The models of type I kerogen of Green River, type II kerogen of Paris basin, and type III kerogen of Cameroon have been built, which belong to different evolution stages (diagenetic stage, catagenetic stage, and quasi-metamorphic stage). The 3D molecular models have been established by MD simulations. The ReaxFF method has been successfully applied to reaction kinetics simulation researches, including applications of the organic micromolecular system, the polymer system, and the high energy material system. The result of ReaxFF method has been verified to be consistent with that of the quantum mechanics (QM) method and the experiment. In order to enable chemical reactions occurring in computational time which is much smaller than the experimental time scale, ReaxFF simulations take temperatures higher than that of experiments. Previous studies have confirmed the feasibility and accuracy of ReaxFF simulation of coal pyrolysis. Then the ReaxFF method has been extended and applied to the pyrolytic simulation of kerogen. However, the reaction process and intermediate products of hydrocarbon generation are rarely reported, and the simulation temperature is much higher than experimental temperature.

Figure 1. a) SEM image of shale. b) SEM image of kerogen and organic porosity. c) Van Krevelen diagram of the evolution stages and classification of kerogen types. d) The XPS spectra of Songliao and Erdos kerogens.
In this study, kerogen macromolecules (large enough) containing the functional groups that are very few in kerogen, have been established by means of physical and chemical experiments. 3D molecular models are built by MD simulations by which the pyrolytic process and the composition of kerogen pyrolysis products under different temperature control are studied using ReaxFF. The new approach of hybrid molecular dynamics/force-biased Monte Carlo (MD/fbMC) is used for kerogen pyrolytic simulations at experimental temperatures. The results of simulations and experiments are in good agreement. Our findings may expand our knowledge of kerogen pyrolysis and assist to further study of relationships of kerogen pyrolysis to the kerogen pore structure and oil/gas transportation.

2. Results and Discussion

2.1. Constructions of Kerogen Macromolecular Models

2.1.1. Classification of Kerogen Samples

As shown in Table 1 and Figure 1d, the results of XPS and EA indicated that the H/C atom ratios of two types of kerogen are 1.40 and 0.85, the O/C ratios are about 0.02–0.12 and 0.1–0.15, respectively. The two kerogen types of Erdos and Northeast China can be assigned to type I and type III kerogen, respectively, by the van Krevelen diagram.

2.1.2. Existence of Kerogen Elements by XPS

The XPS spectra were divided into several fitting peaks to calculate the relative contents of chemical states, because there are one more chemical states of these elements. The fitting peaks filled by different colors correspond to different chemical states of elements which are shown in Figure 2 and Table 2. And the simulated peaks (orange curve) are obtained by summing the fitting peaks up. As shown in Figure 2, the agreement between simulated peak points and the experimental peak points is excellent, which indicates that the peak splitting of XPS spectra is suitable. Subsequently, the peak positions and corresponding fractions of areas of each fitting peak were calculated to obtain the relative abundances of different chemical states of each element. The main chemical states and their relative contents of C, O, nitrogen (N), and sulfur (S) are listed in Table 2. The Erdos kerogen contains more aromatic groups than Songliao kerogen, which will be compared to the result of 13C NMR later. The atomic ratios of C, O, N, and S, and the relative percentages of chemical states are obtained to construct molecular models can be acquired.

2.1.3. Functional Groups of Kerogens by FT-IR

The location and relative intensity of the absorption bands of FT-IR spectra reflect the functional group composition, relative abundance, and bond properties of the kerogen. As shown in Figure 3, the kerogen is composed of aliphatic structures, aromatic structures, and heteroatomic functional groups whose main component is oxygen-containing functional groups. In conjunction with Table S1 in the Supporting Information, the kerogen functional groups reflected by the vibration frequencies are shown in Figure 3. The stretching vibration absorption bands of methyl and methylene are near 2960, 2920, and 2850 cm⁻¹ in the FT-IR spectra. The band near 1600 cm⁻¹ represents the characteristic peak of aromatic ring, and the wavenumber of ether is in 1300–1000 cm⁻¹. The –(CH₄)ₙ (n > 4) group is represented by characteristic peak near 720 cm⁻¹. The fingerprint region (880–680 cm⁻¹) of phenyl ring substitution, containing many characteristic peaks, indicates the samples have multiple substitutions. As shown in Figure 3, the spectra of two kerogen types have enormous difference. Songliao kerogen is with strong absorption peaks located in the region of 2850–3050 cm⁻¹, and the absorption peak of aromatic ring is weaker than that of saturated carbon bonds. While the infrared spectrum of Erdos kerogen has strong absorption peaks of aromatic, Songliao kerogen contains more aliphatic functional groups and less oxygen-containing functional groups than Erdos kerogen.

2.1.4. Kerogen Molecular Carbon Skeleton by 13C NMR

The 13C NMR spectra of kerogens are with mainly three bands of kerogens: the aliphatic regions at 0–90 ppm, the aromatic regions at 100–165 ppm, and carbonyl carbon regions at 165–220 ppm. As the proportions of areas in Figure 4 represent the abundances of different carbon components, Songliao kerogen contains many aliphatic carbons, while aromatic carbon is the main component in Erdos kerogen. Both samples have the smallest amount of hydroxyl carbon, while the hydroxyl carbon of Erdos kerogen is more than that of Songliao (it is consistent with the results of XPS and EA). Overlapping peak resolving of the 13C NMR spectrum is needed to obtain the fitting peaks, because the samples contain several functional groups. The fitting peaks at the corresponding chemical shift are shown in Figure 4, and the simulated peaks can be obtained by summing the fitting peaks up. In order to get reasonable carbon skeleton, the simulated peaks were compared to the entire experimental 13C NMR spectra and then parameters of the fitting peaks were adjusted, until the simulated peaks coincided with the experimental peaks. The fitting spectra and the experimental spectra are fitted very well as shown in Figure 4, which indicates the peak splitting of 13C NMR spectrums are suitable. The relative areas of fitting peaks, representing the abundance of the carbon-containin functional groups, are listed in Table 3.

Aromaticity fₐ reflects the structure of organic matter quantificationally, which is usually directly related with the degree of evolution. Aromaticity can be obtained by the high resolution 13C NMR spectra, whose value is the ratio of absorption peak area of the 100–165 ppm segment to the area of 0–220 ppm.
Figure 2. The chemical states and their content analysis of major elements in a) Songliao kerogen and b) Erdos kerogen by XPS. The fitting peaks of corresponding chemical states were filled by different colors. The red curves are the experimental results. The orange curves are the simulated peaks.
The aromaticity degrees \( f_{\text{ar}}^1, f_{\text{ar}}^3 \) of Songliao and Erdos kerogen can be calculated as

\[
f_{\text{ar}}^1 = f_{\text{ar}}^{1I} + f_{\text{ar}}^{2I} + f_{\text{ar}}^{3I} + f_{\text{ar}}^{4I} + f_{\text{ar}}^{5I} = 29.7\% \quad (1.a)
\]
\[
f_{\text{ar}}^3 = f_{\text{ar}}^{1II} + f_{\text{ar}}^{2II} + f_{\text{ar}}^{3II} + f_{\text{ar}}^{4II} + f_{\text{ar}}^{5II} = 55.9\% \quad (1.b)
\]

Another important parameter of kerogen structure is aliphaticity \( f_{\text{al}} \), which is ratio of area of 0–90 ppm segment (representing the aliphatic carbon) to the area of 0–220 ppm segment. And the aliphaticity degrees are

\[
f_{\text{al}}^1 = f_{\text{al}}^{1I} + f_{\text{al}}^{2I} + f_{\text{al}}^{3I} + f_{\text{al}}^{4I} + f_{\text{al}}^{5I} = 69.3\% \quad (2.a)
\]
\[
f_{\text{al}}^3 = f_{\text{al}}^{1II} + f_{\text{al}}^{2II} + f_{\text{al}}^{3II} + f_{\text{al}}^{4II} + f_{\text{al}}^{5II} = 42.3\% \quad (2.b)
\]

The branching degrees of alkyl chain can be obtained by the ratios of methine and quaternary carbon to aliphatic carbon, which are

\[
BI_i = f_{\text{al}}^{iI} / f_{\text{al}}^1 = 15.87\% \quad (3.a)
\]

\[
BI_i = f_{\text{al}}^{iII} / f_{\text{al}}^3 = 28.37\% \quad (3.b)
\]

The branching degree of alkyl chain of Erdos kerogen is higher than that of Songliao kerogen, which means the molecule of Erdos kerogen is more compact.

The shift of bridge aromatic carbon is near 131 ppm, and the 130–140 ppm segment represents chemical shift of alkyl substituted aromatic carbon. The contribution of oxygen to the substituted aromatic carbon is in the 155–165 ppm range. Nonprotonated aromatic carbon content is the sum of these three parts. The degrees of aromaticity substitution, which are

\[
BI_i = f_{\text{ar}}^{iI} / f_{\text{ar}}^1 = 28.37\% \quad (3.b)
\]

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\[
BI_i = f_{\text{ar}}^{iII} / f_{\text{ar}}^3 = 28.37\% \quad (3.b)
\]
the ratios of nonprotonated aromatic carbon to total aromatic carbon, can be obtained by the following equations

\[
\delta_i = \left( f_{3ii} + f_{4ii} + f_{5ii} \right) / f_{w} = 68.01\% \tag{4.a}
\]

\[
\delta_i = \left( f_{3iii} + f_{4iii} + f_{5iii} \right) / f_{w} = 59.75\% \tag{4.b}
\]

By the degrees, there are 3 to 5 aromatic hydrogen atoms are replaced by substituent groups.

Average aliphatic chain lengths are about

\[
\lambda_1 = f_{a} / f_{w}^{SL} = 8 \tag{5.a}
\]

\[
\lambda_{III} = f_{a} / f_{w}^{III} = 3 \tag{5.b}
\]

which indicates the aliphatic chain length of Songliao kerogen is longer than that of Erdos. The carbon skeletons of kerogen molecules are obtained by the analyzing of \(^{13}\text{C}\) NMR spectra.

### 2.1.5. Kerogen Macromolecular Models

The elemental ratios, the relative contents of the functional groups, and carbon skeletons are obtained by EA, XPS, FT-IR, and \(^{13}\text{C}\) NMR. Kerogen is with amorphous structure whose composition and structure are complex. The 2D macromolecular structures (statistical average) are established by setting the aromatic functional groups as the basic elements, distributing heteroatomic functional groups into the basic elements and bounding those groups by aliphatic side chains. The “average molecular structure” referring to a cluster cannot be regarded as a basic unit of any specific molecule in the whole body. Instead, it is regarded as a mathematical model containing various functional groups and could be used to reflect the typical chemical and physical properties of mixture molecular groups. As shown in Figure 5a,b, the 2D models of Songliao and Erdos kerogen samples have 29 and 114 aromatics, and the aromatic carbon numbers are 167 and 419, respectively. The ratios of aromatic carbon to aliphatic carbon of both samples are similar to the results of XPS and \(^{13}\text{C}\) NMR, and that means the elemental compositions and the aromatic degrees of kerogen models are in good agreement with the experimental results.

In order to verify the rationality of kerogen 2D molecular models, MestReNova software suite was used to calculate the \(^{13}\text{C}\) NMR spectra of the molecular models and compare them with the experimental spectra. As shown in Figure 5c,d, the fitting peaks of models were obtained by giving a linewidth to each chemical shift of the carbon atom, and assuming each peak of the \(^{13}\text{C}\) NMR simulation spectra is Gauss peak model. The superposition of the fitting peaks of the model is the simulated peak. And the simulated NMR spectra fairly correspond with the experimental spectra, by which the rationality of the kerogen molecular models used for the following studies is further verified.

#### 2.2. 3D Molecular Constructions by MD Simulations

Based on the 2D kerogen models, the 3D macromolecular models of kerogen with abundant and comprehensive functional groups were established. First, the geometric structures were modified to eliminate the irrational structure, so that the bonds, the bond angles, and the angles of torque are with chemical rationality. Then preliminary optimizations of the structures were by geometry optimization of MM to obtain the optimal geometric configuration. The smart optimization was chosen in preliminary optimization, which conjugates the steepest descent method, the gradient method, and the Newton method. While the macromolecules optimized by MM always are with local minimum energy, rather than the global minimum of the potential energy surfaces. The annealing dynamics simulations were used to optimize the model structures, to overcome the shortcoming and find out the global energy minimum. Annealing in the taskbar of the Forcite module was chosen for the annealing dynamics. The initial temperature and the midcycle temperature of annealing kinetics simulations were set
as 300 K and 600 K, respectively. The canonical (NVT, constant number of atoms, volume, and temperature) ensemble was chosen in MD simulations. The simulation times are 300 ps. The Nose–Hoover method of temperature control program was selected, as this method can couple any number of atoms with a hot bath together and eliminate local associated motion to simulate the temperature fluctuation of macro system. At last, the output structures of each annealing dynamics cycle were performed MM calculation to ensure they are in low energy state. The final outputs of the least energy configuration are selected as the optimal geometric configurations (Figure 5e,f).

2.3. Analysis of Chemical Kinetics of Kerogen Pyrolysis by ReaxFF Simulations

The NVT ensemble was selected to calculate the reactions of hydrocarbon generation from kerogen. The ReaxFF module of Amsterdam Modeling Suite software was used for the simulations, to study the effect of temperature on the pyrolytic products. HCONSB.ff was chosen as the force field. The Songliao and Erdos kerogen molecules were restricted in the 60 × 60 × 60 lattices and the simulations were calculated with periodic boundary conditions (PBC) using 0.25 fs as the time step.

The compositions of pyrolytic products of 3D model simulations were analyzed under different heating conditions as shown in Figure 6c. Kerogen can be resolved to light hydrocarbons (CH4, C2H6, etc.), heavy hydrocarbons, molecules containing heteroatoms, and inorganic small molecules (CO2, H2, etc.). To facilitate analysis, the pyrolytic products are divided into CO2, C1 hydrocarbon fragments, C2–C4 hydrocarbon fragments, C5–C12 molecular fragments, and C13–C20 molecular fragments. The gaseous hydrocarbons (C1–C4) are the main components of shale gas in shale reservoirs in which hydrocarbons of C2–C4 molecules are named as heavy hydrocarbon gas. The organic molecules of C5–C12, which boil between 30 °C and 200 °C, belong to naphtha.[40,41] And the diesel-fuel is from C13 to C20.

The results of simulations are shown in Figure S1 in the Supporting Information, which show the pyrolysis generates more pyrolytic products and is more complete at higher temperature, and Songliao kerogen is more easily pyrolysis into small molecular fragments. The typical pyrolytic process, pyrolytic temperatures, total fragments number, and pyrolytic products numerical evolutions are shown in Figure 6. Kerogen pyrolysis products are related to the bond energy of kerogen molecules. The mechanism of typical reaction of kerogen pyrolysis was shown in Figure 6a–d. The fused aromatic rings do not undergo cracking, while dehydrogenation occur in the six-membered rings. The long chain hydrocarbons will be cracked into small hydrocarbon fragments. As shown in Figure 6b, the C–C(O) band energy is higher than the C(O)–O band energy, and the reaction eventually has produced CO2. The benzene–oxygen bond is harder to be broken than methyl–oxygen bond as shown in Figure 6d, because the dissociation energy of benzene–oxygen bond (356 kJ mol−1) is higher than that of methyl–oxygen bond (247 kJ mol−1), as a result many oxygen atoms in Erdos kerogen are at the end of the fused
Figure 6. The pyrolysis process under different temperature control. a–d) The typical pyrolysis reactions of kerogen structures. e) The temperatures of simulations. f–l) Dynamic changes of the number of kerogen pyrolytic products accompanied by pyrolysis of Songliao and Erdos kerogens. The OFs is the abbreviation of organic fragments.
The total number of products increases with temperature and the number of pyrolytic products of Songliao kerogen is higher than that of Erdos at the same temperature. That means the rate of pyrolytic reaction is higher at high temperature.

The numbers of pyrolytic products obtained by simulations are listed in Table 4. At 2500 and 3000 °C, CO₂ numbers of Erdos kerogen are more than numbers of Songliao. The methane (CH₄) number of Erdos kerogen increases rapidly from 2500 to 3000 °C. And it is more than that of Songliao at 3000 °C. That means Erdos kerogen generates more CH₄ when the pyrolysis is more complete. The naphtha and diesel-fuel numbers of Erdos are less, which illustrates that Songliao kerogen is with better oil potential and proves the rationality of the kerogen molecular models from another side. The increased number of pyrolytic of Songliao kerogen simulations from 2000 to 2500 °C is more than that of simulations from 2500 to 3000 °C, while number of Erdos kerogen rises more significantly in the simulations from 2500 to 3000 °C. The results of the simulations show that the number of small molecules produced by pyrolysis does not increase linearly with the increase of temperature.

The numbers of pyrolytic products of Songliao and Erdos kerogen are detected at 1100 °C, while pyrolytic gases of Erdos kerogen are detected at 1100 °C. Therefore, the simulation temperatures of Songliao and Erdos kerogen were set as 800 °C and pyrolytic gases can be detected by the gas detector, while pyrolytic gases of Erdos kerogen are obtained in micro timescale. Similarly, the kerogen molecules were restricted in the 60 × 60 × 60 lattices by which 2 × 2 × 2 supercells are generated to get the statistical averages of pyrolytic products. The frequency of fbMC steps and number of fbMC steps were set as 10 000 steps and the heating rate was set as 0.65 K per step, using 0.25 fs as the time step. The force field of ReaxFF was consistent with the previous simulations. According to the preliminary experiments of PY-GC/MS, Songliao kerogen is pyrolyzed at 800 °C and pyrolytic gases can be detected by the gas detector, while pyrolytic gases of Erdos kerogen are obtained in micro timescale. Similarly, the kerogen molecules were restricted in the 60 × 60 × 60 lattices by which 2 × 2 × 2 supercells are generated to get the statistical averages of pyrolytic products. The frequency of fbMC steps and number of fbMC steps were set as 10 000 steps and the heating rate was set as 0.65 K per step, using 0.25 fs as the time step. The force field of ReaxFF was consistent with the previous simulations. According to the preliminary experiments of PY-GC/MS, Songliao kerogen is pyrolyzed at 800 °C and pyrolytic gases can be detected by the gas detector, while pyrolytic gases of Erdos kerogen are obtained in micro timescale. Similarly, the kerogen molecules were restricted in the 60 × 60 × 60 lattices by which 2 × 2 × 2 supercells are generated to get the statistical averages of pyrolytic products. The frequency of fbMC steps and number of fbMC steps were set as 10 000 steps and the heating rate was set as 0.65 K per step, using 0.25 fs as the time step. The force field of ReaxFF was consistent with the previous simulations. According to the preliminary experiments of PY-GC/MS, Songliao kerogen is pyrolyzed at 800 °C and pyrolytic gases can be detected by the gas detector, while pyrolytic gases of Erdos kerogen are obtained in micro timescale. Similarly, the kerogen molecules were restricted in the 60 × 60 × 60 lattices by which 2 × 2 × 2 supercells are generated to get the statistical averages of pyrolytic products. The frequency of fbMC steps and number of fbMC steps were set as 10 000 steps and the heating rate was set as 0.65 K per step, using 0.25 fs as the time step. The force field of ReaxFF was consistent with the previous simulations. According to the preliminary experiments of PY-GC/MS, Songliao kerogen is pyrolyzed at 800 °C and pyrolytic gases can be detected by the gas detector, while pyrolytic gases of Erdos kerogen are obtained in micro timescale.

Table 4. The quantitative contents of pyrolytic products.

| Simulation | CO₂ | C₁ | C₂–C₄ | C₅–C₁₂ | C₁₃–C₂₀ | Total number |
|------------|-----|----|-------|--------|---------|-------------|
| Songliao 2000 °C | 8   | 6  | 22    | 12     | 5       | 67          |
| 2500 °C | 6   | 13 | 82    | 14     | 11      | 156         |
| 3000 °C | 9   | 12 | 92    | 18     | 8       | 198         |
| Ratio | 1.075:1.125 | 1.217:2 | 1.373:4.18 | 1.171:1.5 | 1.2:2.16 | 1.233:2.96 |
| Erdos 2000 °C | 7   | 4  | 9     | 9      | 1       | 53          |
| 2500 °C | 8   | 8  | 18    | 10     | 2       | 87          |
| 3000 °C | 12  | 15 | 42    | 10     | 2       | 154         |
| Ratio | 1.14:1.71 | 1.23:75 | 1.24:67 | 1.11:11 | 1.22 | 1.64:2.91 |
Figure 7. The pyrolytic products of kerogen. Column 1 to 6 represent C₂–C₄ hydrocarbon fragments, C₁–C₄ organic heteroatomic fragments and inorganic molecules, C₅–C₁₂ organic fragments, C₁₃–C₂₀ organic fragments and C₂₀+, organic fragments in the pyrolytic products at a) 2000 °C, b) 2500 °C, and c) 3000 °C, respectively.
fractions of gases by simulations are slightly higher than the experimental results, while that of thermal residue lower than the experimental results. Some mineral impurities of the kerogen samples may contribute to this phenomenon. The mass fraction of thermal residue is chosen as the standard to calculate the impurities mass by \( \frac{m_{\text{macro}} + m_{\text{min}}}{m_{\text{sample}}} = \omega_{\text{res-expri}} \) and \( \frac{m_{\text{macro}}}{m_{\text{sample}} - m_{\text{min}}} = \omega_{\text{res-simu}} \), where \( m_{\text{macro}}, m_{\text{min}}, m_{\text{sample}}, \omega_{\text{res-expri}} \) and \( \omega_{\text{res-simu}} \) are the mass of pyrolytic products of residue, mass of mineral impurities, mass of sample, mass fraction of thermal residue by experiments, and mass fraction of thermal residue to compare with simulations. The mass of mineral impurities of Songliao and Erdos kerogens are 0.085 and 0.14 mg. Then the mass fractions of CH\(_4\), C\(_2\) hydrocarbon of Songliao kerogen are about 0.081 and 0.026, those of Erdos are 0.0054 and 0.0061. The simulation results are very similar to the experimental results.

3. Conclusions

We establish the kerogen macromolecules with abundant chemical information that are large enough to contain the functional groups presenting at low occupancy. The reliability of the molecules is verified, and the 3D molecular structures with global energy minimization are established.

By analyzing the pyrolytic process of the 3D kerogen models and the effects of temperature and heating rate on the pyrolysis of kerogen, the chemical kinetics of kerogen pyrolysis is clarified. Bond energy is the main reason that affects pyrolysis components and processes. The typical reaction mechanism of kerogen pyrolysis is found out, containing long chain hydrocarbons cracking (reaction of shale gas generation), dehydrogenation of six-membered rings and –C(0)–C to be CO\(_2\). The pyrolysis of Erdos kerogen is less affected by the rate of heating and produces fewer small molecules. Therefore, the kerogen molecule rich in fused aromatic rings is more stable, and the heteroatoms in or bonding to fused aromatic rings are distributed in large molecular structures. Erdos kerogen (rich in fused aromatic rings) generates less shale oil than Songliao kerogen, while it can produce more CH\(_4\) at high temperature. And the quantitative relationships of CH\(_4\), heavy hydrocarbon gases,
naphtha and the diesel-fuel obtained by kerogen pyrolysis of different mining areas are established at different temperature control conditions.

To carry out the simulations at experimental temperature in micro time scale, the hybrid MD/fbMC approach was used to simulate the pyrolysis of kerogen. The mass fractions of CH₄, other pyrolytic gases and residues of simulations are consistent with those of PY-GC/MS. The effectiveness and superiority of the simulation method are verified. Our findings may help to understand the oil/gas generation from the atomic level and assist in the future studies of kerogen mechanical property and oil/gas transport in micro-nanopores.

4. Experimental Section

**Kerogen Extraction**: Kerogen samples were extracted from shale to study structure and properties of kerogen. Shales were crushed and fully expanded, which lie about 3000 m underground in Erdos and 400 m underground in Songliao basin. Using GBT 19144-2010 method (Isolation Method for Kerogen from Sedimentary Rock), Kerogen samples were extracted by removing inorganic minerals through a series of chemical and physical methods. Hydrochloric acid solution (HCl) was used repeatedly for the carbonate removal, then HCl and hydrofluoric acid (HF) mixed solution was employed to remove silicate repeatedly. Sodium hydroxide (NaOH) was selected to remove silicon dioxide (SiO₂) further after taking out the centrifugal supernatant. HCl and zinc powder were added into samples repeatedly to remove pyrite. Then the halide ions were removed by eluting the remnants with water. After centrifugation, the kerogen samples were frozen and dried, the soluble halide ions were removed by eluting the remnants with water. After centrifugation, the kerogen samples were frozen and dried, the soluble organic matter was cleaned by chlorofrom, and the loss on ignition was measured. And pyrite treatment was carried out repeatedly to obtain relatively pure kerogen samples, until the loss of the extract was more than 75%.

**Experiments of Molecular Construction**: First, XPS (ESCA Lab220i-XL) was performed to analyze chemical states of elements of samples. A computation multiplex resolution method (using XPSPEAK41) was applied for the XPS intensity curves of regional XPS scans of C 1s, O 1s, S 2p, and N 1s. The XPS spectra were analyzed by XPSPEAK41, and the results of XPS were applied to establish the molecular formulas. Then, the functional groups of kerogen molecules and relative abundances can be represented by FT-IR spectrum. The main absorption frequency of each group and the vibration characteristics are shown in Table S1 in the Supporting Information. At last, cross-polarization magic angle spinning (CP/MAS) 13C NMR and magic angle spinning (CP/MAS) 19F NMR were performed to analyze the relative contents between aromatic, aliphatic, and carbonyl carbon, in order to study on the kerogen carbon skeleton. The experiments on samples were completed on BRUKER AVANCE III 400 M using 8 kHz rotation speed and adamantane (ada) as standard substance.

**Pyrolytic Experiments**: The heating rate of experiments being performed by PY-GC/MS to trap gases of H₂, CO₂, CH₄, C₂H₆, and C₂H₄ was set as 20 000 K s⁻¹ to effectively avoid secondary cracking. The 0.5 mg samples of Songliao and Erdos kerogenes were maintained at 800 °C and 1100 °C for 20 s, respectively.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

chemical kinetics, hybrid MD/fbMC approach, kerogen, macromolecular models, pyrolysis

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