Biomarker characteristics of the adsorbed/occluded components of asphaltenes recovered from thermal degradation of kerogen

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Abstract. The adsorbed/occluded components of asphaltene originate from the parent kerogen. Information on the characteristics of these components is critical to the field of oil and gas geochemistry especially in the oil and source rock correlation studies. In this work, kerogen isolated from a low-matured mudstone from Lucaogou Formation, Santanghu Basin was pyrolyzed at elevated temperature for 72 hours in a semi-open system, followed by extraction with dichloromethane and precipitation of the extract to achieve the asphaltene isolation. The asphaltene was extracted by organic solvents to recover the adsorbed components while its solid residue was oxidized to release the occluded compounds. The ratios of \( \sum C_{22}/\sum C_{23} \) n-alkanes and tri/pentaterpane in the adsorbed/occluded components of the asphaltene and kerogen are similar. The distribution of C\(_{27}\), C\(_{28}\) and C\(_{29}\) regular steranes displayed a progressively increasing pattern from C\(_{27}\) \(_{10}\) C\(_{29}\) in adsorbed/occluded fractions of both the asphaltene and its kerogen precursor. This observation is also found in the terpanes distribution of the occluded components in the asphaltene and kerogen. These results showed that the biomarkers distribution in the adsorbed/occluded components of the asphaltene to some extent exhibited some level of similarity with its parent kerogen. This also showed that the occluded components in the asphaltene macromolecule are relatively intact and stable to the thermal evolutionary conversion from its kerogen precursor.

1. Introduction

Kerogen and asphaltene possess similar three-dimensional complex structures with microporous structural units \(^{1-2}\). These structures can adsorb/occlude other small molecules, such as biomarkers \(^{3-6}\). Biomarkers are useful for oil-source correlation, identification of mixed-source reservoirs, hydrocarbon-accumulation and thermal evolution. Therefore, studies on the adsorbed/occluded components of these geo-macromolecules are critical to oil and gas geochemistry field.

Asphaltene can be generated from kerogen degradation and usually considered as a soluble “fragment” of kerogen \(^{7}\). During kerogen degradation process, the adsorbed/occluded components of kerogen will form the asphaltene products \(^{8}\). However, more experimental studies are required to substantiate this assertion. In the present work, asphaltene was obtained from kerogen by thermal degradation in a simulation experiment. The biomarkers distribution in the adsorbed/occluded components of the kerogen and its degradation product (i.e. asphaltene) were investigated.

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2. Materials and methods

2.1. Sample preparation and adsorbed/occluded components release

The mudstone (Ro of 0.52%) from the upper Permian Lucaogou Formation in Yuejingou section of Santanghu Basin, China was treated by HCl and HF to obtain the kerogen according to the procedures described by Du et al.[9] The kerogen (each group having ~60 g) was pyrolyzed at elevated temperature and pressure (360°C, 50MPa) for 72 h in the semi-open system previously reported by Liao et al.[10]

The products from kerogen pyrolysis were extracted by dichloromethane. The asphaltene was precipitated from the extract by n-hexane. The adsorbed components in the asphaltene were extracted by a mixture of n-hexane and acetone for 72 h. The solid residues obtained after extraction were subjected to oxidative degradation by H2O2/CH3COOH system to release the occluded fractions as described by Zhao et al.[11] The adsorbed and occluded components extracted from the asphaltene were separately fractionated by column chromatography on silica/alumina (3:1, v/v) and the saturated fraction eluted with n-hexane.

2.2. Gas Chromatography-Mass Spectrometry (GC-MS) Analysis

Analysis of the saturated fraction was conducted by gas chromatography-mass spectrometry (GC-MS) at full scan and single ion monitoring (SIM) modes, with Thermo Scientific Trace GC Ultra gas chromatography coupled to a Thermo Scientific Trace DSQII mass spectrometer using a HD-1m fused silica capillary column (30 m × 0.25 mm i.d. × 0.25 μm film thickness). The GC oven was held isothermally at 80 °C for for 4 min, then raised to 295 °C at a rate of 4 °C / min, and held for 30 min. Helium was used as the carrier gas with a constant flow rate of 1.2 ml/min. The mass spectrometer was operated at electron energy of 70 eV and with an ion source temperature of 260 °C. The n-alkanes, terpanes and steranes were identified using m/z 85, 191 and 217, respectively.

3. Result and discussion

The majority of the adsorbed components would reside in the n-hexane/acetone extract. Therefore, the saturated hydrocarbon fraction eluted by the n-hexane from this extract was selected to represent the adsorbed component of the asphaltene.

3.1 Geochemical characteristics of adsorbed/occluded components in asphaltene

3.1.1 Adsorbed component of asphaltene. The total ion chromatogram (TIC) of the n-hexane fraction recovered from the adsorbed component of the asphaltene is represented in Figure 1a. The n-alkanes dominate the fraction and range from C_{12}-C_{33}, but with predominant peaks from C_{15}-C_{20} and maximizing at C_{17}. The n-alkanes exhibit a unimodal distribution. The concentrations of the pristane and phytane are exceptionally low while the value computed for the ratio \( \Sigma C_{23}/\Sigma C_{25} \) is 1.25 (Table 1).

Tricyclic terpanes, hopanes and regular steranes are detected in the adsorbed component of the asphaltene (Figure 1b). The C_{27}–C_{29} regular steranes display a progressive distribution pattern from C_{27}–C_{29} (Figure 1c). The values computed for the maturity parameters of Ts/(Ts+Tm) and C_{29}aaα20S/(20S+20R) are 0.77 and 0.22, respectively. The Gl (gammacerane/αβhopane) and the tri/pentaterpane ratios are 0.72 and 0.31, respectively.
Figure 1. Chromatograms of the adsorbed components in the asphaltene.

Note: (a) n-alkanes; (b) terpanes; (c) steranes. The separate numbers represent the n-alkanes with corresponding carbon number; C_{29}H — C_{31}H represent C_{29} — C_{31} hopanes; C_{31}G represents gammacerane; C_{21}S — C_{29}S represent C_{21} — C_{29} α,α,α-R-sterane.

Table 1. Some biomarker parameters from the adsorbed/occluded components of the asphaltene and its parent kerogen.

| Biomarker parameters | Asphaltene | Kerogen[12] |
|----------------------|------------|-------------|
|                      | A-H        | A-O         | K-H-raw    | K-O-raw |
| ∑C_{22}/∑C_{23}+     | 1.25       | 1.21        | <1         | ≈1      |
| C_{29}20S/(20S+20R)  | 0.22       | 0.23        | 0.44       | 0.25    |
| GI                   | 0.72       | 0.71        | 0.33       | /       |
| tri/penta            | 0.31       | 0.25        | 0.3        | 0.2     |
| Ts/(Ts+Tm)           | 0.77       | 0.79        | /          | /       |

Note: A-H is n-hexane fraction from the asphaltene (adsorbed component of asphaltene); A-O is the occluded component of the asphaltene. K-H-raw is the adsorbed component of the kerogen; K-O-raw is the occluded component of the kerogen: ∑C_{22}/∑C_{23}+ = ratio of n-alkanes below C_{22} to n-alkanes above C_{23}; C_{29}20S/(20S+20R) = ratio of α,α,α-C_{29} regular sterane 20S isomer to (20S + 20R) isomers; GI = ratio to gammacerane to αβ-hopane; tri/penta = ratio of tricyclic terpanes to pentacyclic terpanes; Ts/(Ts+Tm) = ratio of C_{27} 18α-22,29,30 norhopane isomer to C_{27} 17α-22,29,30 norhopane isomer; [12] is reproduced from (Cheng et al.).

3.1.2 Occluded component of the asphaltene. The TIC of the the n-hexane fraction obtained from the oxidative degradation products of asphaltene is shown in Figure 2a. The n-alkanes also dominate the fraction and range from C_{12}-C_{33} with predominant peaks also from C_{15}-C_{20} and maximizing at C_{17}. The distributions of n-alkanes also follow a unimodal pattern. The phytane and pristane ratio could not be computed due to their low concentrations. The computed value for ∑C_{22}/∑C_{23}, ratio is 1.21 (Table 1). The C_{29}20S/(20S+20R) ratio of the occluded components was 0.23.

Tricyclic terpanes of C_{21} to C_{23}, hopanes and C_{27}-C_{29} regular steranes have been detected from the occluded components of the asphaltenes (Figure 2b). The distribution of C_{27}, C_{28} and C_{29} regular
steranes show a similar progressive pattern from C27- C29 has previously observed in the absorbed fraction (Figure 2c). The values derived for the ratios of Ts/(Ts+Tm), GI, C29ααα20S/(20S+20R), and tri/pentaterpane are 0.79, 0.71, 0.22 and 0.25, respectively. These values and the patterns of distribution of these compounds are comparable to the adsorbed fraction of the asphaltene.

**Figure 2.** Chromatograms of the occluded components in the asphaltene.

Note: (a) n-alkanes; (b) terpanes; (c) steranes. The numbers separately represent the n-alkanes with corresponding carbon number; C29H ~ C31H represent C29 ~ C31 hopanes; C31G represents gammacerane; C21S ~ C29S represent C21 ~ C29 α,α,α-R-sterane.

### 3.2. Comparison between the adsorbed/occluded components of the kerogen and its asphaltene.

The biomarker parameters derived from the adsorbed/occluded components of the kerogen have been previously reported by Cheng et al.[12]. The biomarkers distribution and the values obtained for the various parameters are presented in Figure 3 and Table 1, respectively for comparison.

The TIC of the n-hexane fraction of the adsorbed components of the raw kerogen is dominated by n-alkanes mostly in the range of C14 to C27 and maximizing at C23 (Figure 3a). The n-alkanes distributions in the adsorbed fraction of the kerogen show little variation when compared to the adsorbed components of the asphaltene. The ratio $\Sigma C_{22}/\Sigma C_{23}$ from the kerogen is less than one, which is lower than the value derived from the adsorbed component of asphaltene (Table 1). The subtle differences in the n-alkanes distribution might have resulted from the pyrolysis of kerogen at 360 °C. Partial chromatogram of the tricyclic terpanes and hopanes determined from adsorbed components of the kerogen are displayed in Figure 3b. The values computed for C29-sterane 20S/(20S+20R), GI and tri/pentaterpane ratios are 0.44, 0.33, and 0.3, respectively. The
The tri/pentaterpane value obtained in this fraction is similar to that in the adsorbed component of asphaltene. The C_{27}-C_{29} regular steranes also display a rising trend as the same in the adsorbed component of the asphaltene.

A series of even-carbon-numbered $n$-alk-(1)-enes were detected in the occluded components of the kerogen but are absent in the occluded component of the asphaltene presently under study. This indicates that the $n$-alk-(1)-enes have undergone some reaction during kerogen pyrolysis. The $n$-alkane $\Sigma C_{22}/\Sigma C_{23+}$ ratio from kerogen in the occluded components is close to 1, which is a little lower than the value obtained in the occluded fraction of the asphaltene. The characteristics of terpanes in occluded components of kerogen are shown in Figure 3e. The C_{29}-sterane 20S/(20S+20R) and tri/pentaterpane ratios are 0.25 and 0.2, respectively. These values are lower than the value derived for the same parameters in the occluded components of the asphaltene. The distribution pattern of the C_{27}-C_{29} regular steranes in the occluded fraction of the kerogen shows similarities to that of the asphaltene.

4. Conclusion
Kerogen was thermally degraded to generate asphaltene fraction through simulation experiment. A series of biomarker compounds, including normal alkanes, terpanes and steranes were detected in the adsorbed/occluded components from the asphaltene.
The adsorbed/occluded components of the asphaltene revealed some similar geochemical characteristics with its parent kerogen. This indicates that the adsorbed/occluded components in the asphaltene structure evolve directly from the kerogen with the evolution of geomacromolecule. It also suggests that the occluded components remain intact and stable during the evolution process of kerogen to asphaltene, which can well point to the thermal evolution of the source rock and the kerogen-asphaltene-source rock relationship.

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