Hydrous pyrolysis of different kerogen types of source rock at high temperature-bulk results and biomarkers

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\textbf{A B S T R A C T}

Hydrous pyrolysis experiments were conducted on immature petroleum source rocks containing different types of kerogen (I and II) at a temperature range of 250–550 °C to investigate the role of kerogen type in petroleum formation at high temperature. At temperatures less than 350 °C, the bulk results and biomarker compositions were quite similar and show negligible variations for different kerogen types. However, at high-temperature, above 400 °C (400–550 °C), unexpected results were observed. The initial and peak temperature of the hydrocarbon generation of type II sources rocks is lower than the type I. The tricyclic terpenes were common in samples above 400 °C. The \( T_s/T_m \) values did not show a linear relationship with the temperature increase. The \( C_{23}/(S + R) \) values did not show significant change with temperature increase. However, a good correlation between the sterane maturity parameters and the thermal maturity were shown, especially for type I kerogen. Temperature increase resulted in significant variation in the relative contents of \( C_{27}, C_{28} \) and \( C_{29} \) steranes, suggesting that the distribution of steranes is greatly affected by thermal maturity.

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\textbf{1. Introduction}

Because of their specific genesis and structural characteristics, steranes and terpanes are widely used in petroleum exploration. They also serve as a molecular fingerprint of sedimentary organic matter (OM), indicating its origin of depositional environment, and thermal maturity (\cite{Volkman, 2006; Wang et al., 2009}). Previous studies have documented that slight enrichment in \( C_{27} \) steranes occurs with increasing thermal stress, and questioned usage of \( T_s \) to investigate the role of kerogen type in petroleum formation at high temperature. At temperatures less than 350 °C, the bulk results and biomarker compositions were quite similar and show negligible variations for different kerogen types. However, at high-temperature, above 400 °C (400–550 °C), unexpected results were observed. The initial and peak temperature of the hydrocarbon generation of type II sources rocks is lower than the type I. The tricyclic terpenes were common in samples above 400 °C. The \( T_s/T_m \) values did not show a linear relationship with the temperature increase. The \( C_{23}/(S + R) \) values did not show significant change with temperature increase. However, a good correlation between the sterane maturity parameters and the thermal maturity were shown, especially for type I kerogen. Temperature increase resulted in significant variation in the relative contents of \( C_{27}, C_{28} \) and \( C_{29} \) steranes, suggesting that the distribution of steranes is greatly affected by thermal maturity.

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Pyrolysis experiments were performed at temperatures 250, 300, 400, 450, and 500 °C, which heating rates of 10 °C/h, and kept within ±1 °C of the setting point for 24 h.

2. Samples and experimental

2.1. Samples

Two source rocks of mudstone and shale containing different types of kerogen (I and II) were used for the thermal simulation experiment. Both of the samples were collected from Shahejie Formation, Liaohe Basin, North China (Fig. 1) (Mu et al., 2008). The Shahejie Formation source rocks are comprised of black gray-dark gray mudstone, gray mudstone and oil shale, with a total thickness up to 1000 m. The depths of initial samples are 2553.6–2558 m (type II) and 1387.49–1390.19 m (type I), respectively. The present temperatures are about 93 and 51 °C, according to the average value of geothermal gradient, which reaches 36.5/km (Wang et al., 2003). The organic maturity of the two samples are relatively low, and the R₀ values are generally less than 0.6%. For hydrous pyrolysis experiments, samples were first powdered to less than 100 mesh.

2.2. Rock-eval pyrolysis

Rock-eval pyrolysis was performed using a Rock-eval II system (Delsi instrument, Suresnes, France). And organic-carbon-content (TOC) was determined using a Leco CS-344 analyzer. Group organic geochemical data for investigated samples are given in Table 1. These results indicate that source rocks contain kerogen type I and II (Espitalie et al., 1985). The T_max values of the two samples are 434 °C and 427 °C, respectively, indicating low to marginal thermal maturity (Espitalie et al., 1985).

2.3. Hydrous pyrolysis

Hydrous pyrolysis experiments were performed in a stainless steel reactor. 15–50 g of powdered sample and 50 ml of deionized water were put in the reactor, and sealed the chamber then flushed three times with pure nitrogen gas to remove the air, and then evacuated. A sensor and an external control device were used to control the temperature within the autoclave. The hydrous pyrolysis experiments were performed at temperatures 250, 300, 350, 400, 450, 500 and 550 °C.

2.4. Expelled oil and bitumen

Two organic phases were collected from the reactor after hydrous pyrolysis: expelled oil and bitumen. Expelled oil occurs in the reactor as liquid products (Lewan, 1985). The rock chips were removed from the reactor and dried in a vacuum oven at 50 °C for 24 h, and then powdered to less than 100 mesh. Bitumen was extracted from the powdered samples in a Soxhlet apparatus for 72 h with a mixture of chloroform and methanol (97:3, v-v.). After precipitation of the asphaltenes by n-hexane, maltenes were separated into three fractions by column chromatography over silica gel and aluminum oxide (3:1). The saturated hydrocarbons fraction was eluted with petroleum ether, the aromatic hydrocarbons with dichloromethane and the NSO fraction (polar fraction, which contains nitrogen, sulfur, and oxygen compounds) with methanol.

2.5. GC–MS analyses

The biomarkers in the saturated hydrocarbons fraction of the expelled oils and bitumen obtained by hydrous pyrolysis were analyzed by gas chromatography–mass spectrometry (GC–MS). A 6890 N gas chromatograph/5973 N mass spectrometer equipped with a HP-5 column (30 m × 0.32 mm i.d. × 0.25/μm film thickness) was used. The GC oven temperature was raised from 80 °C to 300 °C (held 30 min) at 4 °C min⁻¹. Helium was used as a carrier gas. MS conditions were: electron ionization (EI) at 70 eV with an ion source temperature of 250 °C. A full scan mode (m/z 20 to m/z 750) was applied.

3. Results and discussion

3.1. Amounts of expelled oil and bitumen

Group composition data for the investigated samples of expelled oil and bitumen are given in Table 2. The amount of
expelled oil and bitumen were calculated to compare TOC conversion rates of different kerogen types during hydrous pyrolysis. For both kerogen pyrolysis experiments, the amounts of expelled oil and bitumen produced (Amg/g TOC) in all experiments increased consistently from 47.76 mg/g TOC to 86.60 mg/g TOC at 250 °C to the highest 199.15–594.42 mg/g TOC at 400 °C, and then decrease to 18.04–28.35 mg/g TOC at 550 °C (Table 2; Fig. 2a). The trend of the bitumen productivity (Bmg/g TOC) and amounts productivity (Amg/g TOC) with temperature was quite similar for both kerogen types, rising to 400 °C, followed by a decrease (Table 2, Fig. 2a). At the temperature of 400 °C, samples reached the maximum bitumen productivity and total of the expelled oil and bitumen productivity. However, the total of the expelled oil and bitumen generation of type I kerogen was always higher than the type II. This result indicates that the petroleum generation potential of type I organic matter is higher in comparison to type II kerogen, which can be attributed to the differences in TOC content and kerogen structure of the initial samples.

Although the type I kerogen contains higher TOC and amount of products productivity than the type II, the productivity of expelled oil (Emg/g TOC) of the latter is higher than the former at temperatures below 350 °C (Table 2; Fig. 2b). At the temperature of 450 °C, type I kerogen attained the expelled oil generation maximum, while maximum of expelled oil productivity for type II kerogen corresponds to 350–400 °C. This result indicates that at low thermal maturity, the content of expelled oil products of type II kerogen is higher in comparison to type I (Wang et al., 1997; Wang et al., 2008).

The adsorption of organic matter on the indigenous mineral components and catalytic effect of the mineral matrix on kerogen cracking during the hydrous pyrolysis is of very low, because of the influence of water (Kooymans et al., 1998; Jovančićević et al., 1993; Huizinga et al., 1987b). TOC (total organic carbon) and the kerogen type determine the oil-generating capacity of source rocks. Especially at the lower thermal maturity, the type of kerogen has significant impact on the expelled oil productivity of source rocks. Especially at the lower thermal maturity, the type of kerogen has significant impact on the expelled oil productivity. The activation energy for conversion of OM to oil products has significant impact on the oil-generation from the source rocks at low thermal maturity (Lu et al., 2001; Huang, 1996). The observed results showed that activation energy required for hydrocarbons generation from type II kerogen is lower than for type I.

### Table 2

<table>
<thead>
<tr>
<th>Sample T (°C)</th>
<th>S_w (g)</th>
<th>Expelled oil (mg)</th>
<th>Relative content of expelled oil (%)</th>
<th>Emg/g.TOC</th>
<th>R_w (g)</th>
<th>Bitumen (mg)</th>
<th>Relative content of bitumen (%)</th>
<th>Bmg/g TOC</th>
<th>Amg/g TOC</th>
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<td>40.81</td>
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<td>8.41</td>
<td>5.42</td>
<td>50</td>
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</tr>
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<td>9.78</td>
<td>10.35</td>
<td>9</td>
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</tbody>
</table>

S_w—sample weight; R_w—residue weight; Sat—saturated hydrocarbons; Aro—aromatic hydrocarbons; NSO—nitrogen–sulphur–oxygen containing compounds (polar compounds); Asp—asphaltenes.

Emg/g TOC = Expelled oil/S_w × TOC (mg/g TOC); Bmg/g TOC = Bitumen/R_w × TOC (mg/g TOC); Amg/g TOC = Emg/g TOC + Bmg/g TOC.
3.2. Molecular composition of hydropyrolysates

The TIC, m/z 191 and m/z 217 mass chromatograms of the saturated hydrocarbons from the initial source rocks and hydrous pyrolysates at temperatures range from 250 °C to 550 °C are shown in Figs. 3 and 6 and 7. The values of the molecular parameters calculated from compositions of biomarkers are given in Table 3. As shown in Fig. 3, distribution of the saturated hydrocarbons in the bitumen isolated from initial source rocks showed similar characteristics: Both samples are characterized by a low proportion of \( n \)-alkanes. The relative abundance of isoprenoids (pristane and phytane) was higher than \( n \)-alkanes. The relative abundance of steranes and hopanes are also more abundant than \( n \)-alkanes too. These results suggest that they were immature organic matter (Tuo et al., 2007), coinciding with the maturely parameters \( T_{\text{max}} \) and \( R_c \).

3.2.1. General characteristics

At the low temperature of 250 °C, the distributions of saturated hydrocarbons of expelled oil and bitumen obtained by hydrous pyrolysis were quite similar to the original samples: lower relative abundance of \( n \)-alkanes than isoprenoids, steranes and terpanes, and a strong odd over even \( n \)-alkane predominance above \( C_{23} \) (Fig. 3; Table 3). At the temperatures of 300 °C to 450 °C, the relative abundance of \( n \)-alkanes increased gradually, and predominance of odd \( n \)-alkane homologues notably decreased (parameter OEP\textsubscript{25–29}; Table 3). Above the temperature of 450 °C, a significant difference in biomarker compositions between expelled oil and bitumen is observed (Fig. 3). The cracking of long-chain \( n \)-alkanes resulted in narrowing of the \( n \)-alkanes range in bitumen. The temperature range of maximum hydrocarbon generation for type I kerogen corresponds to 350–450 °C. Below this range, the organic matter is in the immature state, above this temperature, the cracking of long-chain \( n \)-alkanes might occur to produce gas of short-chain alkanes and methane. Main hydrocarbon generation for type II kerogen corresponds to the temperature range 300–450 °C. Those temperature ranges of hydrocarbon generation might mean the oil window’s diversity and gas window’s consistency in those two type’s kerogen. The difference of temperature range of main hydrocarbon generation of two samples, suggests that the initial temperature and the peak temperature of hydrocarbon generation of type II sources rocks is lower than type I sources rocks. (Wang et al., 1997; Wang et al., 2008).

For the all of these kerogen pyrolysis experiments, the relative abundance \( n \)-alkanes in expelled oil is always higher than in bitumen, regardless to the kerogen type. Especially at the temperature of 500 °C to 550 °C, the higher relative abundance of \( n \)-alkanes of expelled oil happened. Differences between the biomarker compositions of expelled oils and bitumens in these experiments patterned those caused by natural petroleum migration (Peters et al., 1990). Heavier, more polar compounds are preferentially retained in the bitumen, and the lighter hydrocarbons released from kerogen and expelled by hydrous pyrolysis. At the low temperature of 250 °C and 300 °C, the type of kerogen can be considered, the \( n \)-alkanes relative abundances of expelled oil for type II were higher than for type I. This result indicates that at low thermal maturity, not only the expelled oil productivity of type II kerogen is higher in comparison to type I, but also the concentrations of lighter hydrocarbons. This result confirms that at low thermal maturity the type II kerogen activation energy required to hydrocarbon generating is lower than for type I.

3.2.2. Isoprenoids, pristane and phytane

Phytane and pristane are primarily derived from the phytol side-chain on the chlorophyll skeleton in phototrophic organisms, such as cyanobacteria, most algae and higher plants (Peters et al.,
Table 3  
Basic biomarker parameters of the initial samples and hydrous pyrolysates produced at different temperatures produced at different temperatures.  

<table>
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<tr>
<th>Sample code</th>
<th>n-Alkane range</th>
<th>Pr/Ph</th>
<th>Ph/nC</th>
<th>Ph/nC18</th>
<th>C23</th>
<th>C29/GC3122</th>
<th>C29/205(R+S)</th>
<th>C29(α) + C29(β)</th>
<th>C29(R)</th>
<th>C29(β-sterane)(%)</th>
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The relative abundances of pristane (Pr), phytane (Ph) and other isoprenoids are commonly used as biomarkers of photosynthetic organisms, and to estimate the redox conditions of depositional environment of organic matter (Peters et al., 2005; Brooks et al., 1969; Powell and McKirdy, 1973).

However, the origins of pristane and phytane is much more complex than simply the reduction or oxidation of the phytol side chain in chlorophylls (Goossens et al., 1984). Previous investigations suggest that most of the pristane in crude oils originates by thermal cleavage of isoprenoid moieties bound by non-hydrolyzable C-C and/or C-O bonds within the kerogen matrix (Larter et al., 1979, 1981). In our study, for the both kerogen types, Pr/Ph values of expelled oil and bitumen produced in all pyrolysis experiments increase to 1.03 (0.78) at 400 °C and 1.67 (1.55) at 450 °C, followed by a decrease (Table 3, Fig. 4.). Increase in the relative abundances of n-alkanes with temperature, resulted in linear decrease of the Pr/nC17 and Ph/nC18 parameters (Table 3). This result seems to support previous views, for source rock samples within the oil-generative window (about 450 °C), the mixing of pristane from kerogen by thermal cleavage caused the Pr/Ph value increased with increasing temperature, and in the over-mature stage, kerogen condense as pyrobitumen and degenerating into high mature light oils (Fig. 3) and oils cracking into gases by thermal cleavage (Lu et al., 2001).

3.2.3. Terpanes

Terpanes are ubiquitous in source rocks and crude oils, and they are primarily derived from microbial (prokaryotic) membrane lipids (Ourisson et al., 1982). Numerous terpane parameters have been used to estimate the conditions of depositional environment of organic matter and assess the level of thermal maturity, such as the Gammarocene/C30 hopane ratio (G/C30H) was used to assess salinity of the depositional environment. Values of this parameter (G/C30H=0.02–0.06) suggest that the type II sample was formed in freshwater environment whereas type I sample was deposited in more saline environment (G/C30H=0.14–0.60). These results indicate that the gammacerane index has high specific for water-column stratification, and it’s unaffected by thermal effect. The T1/Tm ratio and C3122S(S+R) values were used to evaluate the level of thermal maturity. In present study, the T1/Tm ratio did not show a linear relationship with the temperature increase. The C3122S(S+R) values did not show a notable change with the temperature increase. There was a significant change of hopane composition at 400 °C and 450 °C. The relative abundance of C29-hopane increased greatly, even beyond the content of C30-hopane (C29/C30H=1.04) in the bitumen of type II at 400 °C, which can be related to the hopane demethylation resulted from thermal stress (Pan et al., 2006; Philip and Gilbert, 1984; van Graas, 1986). Besides, the previous investigations also demonstrated that C29 hopane is more stable than C30 hopane at high levels of thermal maturity (Peters et al., 2005). Thus, C29/C30 hopane ratio can be used as maturity indicator. The tricyclic terpanes were considered to originate from a regular C30 isoprenoid, such as tricyclohexaprenol, and could be constituents of prokaryote membranes (Aquino Neto et al., 1981). Also, there was an increase in tricyclic terpanes relative to hopanes in rock samples that contained elevated prasinophyte (Simoniet et al., 1986). Moreover, abundant in tricyclic terpanes commonly correlate with high paleolatitude Tasmanites-rich rocks, suggesting an origin from these algae (Peters et al., 2005). The m/z 191 mass chromatograms of saturated hydrocarbons (Fig. 5) showed that there was a trace tricyclic terpane generation below 400 °C. However, they were commonly present in the bitumen obtained at temperature above 450 °C. This data suggests that the tricyclic terpanes might be originated from regular C30 isoprenoid by thermal cleavage. It should be noticed that at temperatures above 500 °C, contents of the terpenoid biomarkers in hydroprolysates were very low, particularly in those obtained from type I kerogen.

3.2.4. Steroids

Previous studies proposed that the distributions of C27, C28, and C29 Steranes might be used to differentiate ecosystems (Huang and Meinshein, 1979). The distribution and relative abundance of...
Steranes are widely used to determine the source, type, and degree of thermal evolution of organic matter (Volkman, 2006; Farrimond et al., 1998).

Regular C27–C29 steranes have detected in all samples and their distributions are comparable as shown by the mass chromatogram of m/z 217 in (Fig. 6). There were two notable observations of the steranes: (a) maturity parameters $C_{29}\beta/((\alpha+\beta))$ and $C_{29}20S/(S+R)$ showed a linear relationship with the temperature raised, especially for the type I kerogen. However, both of the parameters showed a moderate variation. These data seem as a result of the balance between the relative rates of generation and thermal degradation of the different isomers (Farrimond et al., 1998). The type II source rock contains more C29 steranes and its precursors’ contributions from higher—plant organic matter within the kerogen.

Fig. 5. The m/z 191 mass chromatograms of saturated hydrocarbons from initial rocks and hydrous pyrolysates produced at temperature range from 250 °C to 550 °C.

Fig. 6. The m/z 217 mass chromatograms of saturated hydrocarbons from hydrous pyrolysates produced at temperature range from 250 °C to 550 °C.
matrix, as a typical of type II kerogen. Therefore the formation of secondary C_{29} steranes occurs from the kerogen by thermal cleavage, and complicates the sterane maturity parameters, C_{29}ββ/(αα+ββ) and C_{29}205/(S+R)) of type II. (b) Significant variations in the relative contents of C_{27}αα20R, C_{28}αα20R and C_{29}αα20R steranes with the temperature increase were observed (Fig. 6). The sterane distributions of Type II samples at temperatures 250–550 °C (expelled oil) and 250–550 °C (bitumen) are characterized by the predominance of biological configurations which show the follow order to abundance: C_{27}＞C_{28}＞C_{29}, indicating a typical mixture of terrigenous and aquatic OM, coincide to the type of kerogen. As the temperature increased, the relative abundance of C_{28} and C_{29} steranes gradually decreased, while C_{27} remained relatively constant increased. The line showing distribution of regular steranes of type II kerogen changed from irregular “V” to “L” (Table 3, Fig. 6). Similarly, the sterane distributions of Type I samples showed a significant variation from “anti-L” to “L”. After entering the oil-generation window, the sterane distributions are characterized by the predominance of biological configurations which are showed the following order of abundance: C_{27}＞C_{28}＞C_{29}, suggesting a typical contribution from marine OM-rich sediments. These results indicate that the distribution and relative abundance of regular steranes are effectively to determine the sediments OM source in the mature stage.

For all of the pyrolysis experiments, the trend of the C_{27}αα20R relative content with temperature was quite similar for both kerogen types, rising to temperature about 450 °C, followed by a decrease (Fig. 7). At the temperature of 450 °C, samples reached the maximum relative abundance of C_{27}αα20R. This result might indicate that formation of secondary steranes occurs by cracking the side chain and the early loss of C_{29} steranes from thermal cleavage (Lu and Kaplan 1992).

When taking into account the difference of the type, we can see that there was more significant variation of C_{27}αα20R relative content for type I than for type II kerogen (Fig. 7). This difference is supposedly due to that the type I kerogen contains more C_{27} steranes and its precursors within the kerogen matrix. The variation of C_{27}αα20R relative content for type II mostly related to the early loss of C_{29} steranes by the demethylation from thermal pyrolysis. However, at the temperature of 500 and 550 °C, kerogen condenses as pyrobitumen and degenerating into high mature light oils by thermal cleavage.

4. Conclusions

Hydrous pyrolysis experiments were conducted on immature petroleum source rocks containing different types of kerogen (I and II) at a temperature range of 250–550 °C to investigate the role of type in petroleum formation at high temperature (above 400 °C). For this purpose, the group composition, productivity of expelled oil and bitumen, and biomarker compositions (n-alkanes,
isoprenoids, terpanes and steranes) were used. The following conclusions can be drawn:

1. The trend of amounts of productivity of oil-like products (mg/g TOC) with temperature was quite similar for both types, and at temperature of 400°C, samples reached the maximum productivity. However, there were significant differences in the yield which attributed to the differences of TOC and kerogen stricture of the original samples.

2. Because of the differences of the TOC and kerogen structure, the productivity of type I kerogen is higher than type II. Nevertheless, the yield of the expelled oil of the type II kerogen was higher than the type I below 350°C, although the type I TOC was higher than the type II. This result suggests that the type of source rock is probably more important than TOC content for determining productivity at the early maturation.

3. Tricyclic terpanes were commonly present in the samples above 400°C. T/I ratios did not show a linear relationship with the temperature increase. The C19,225(S+R) values did not show significant change with the temperature increase too. These results suggest that the tricyclic maturity parameters are not reliable for thermal maturity in hydrocarbon pyrolysis. However, the gammacerane to C30 hopane ratio (G/C30H) indicate that the gammacerane index has high specific for water-column stratification, and it’s unaffected by thermal maturity.

4. As the temperature increased, significant variations in the relative contents of C27,29αβ, 27α,29αβ and 27α,29αβ steranes were occurred, showing the distribution of steranes is greatly affected by thermal maturity. However, the distribution and relative abundance of regular steranes are effective to determine the sediments OM source in the mature stage. Besides, a good correlation between the sterane maturity parameters and the thermal maturity was observed.

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References