Molecular and carbon isotopic characteristics of C_{6-14} hydrocarbons in the condensates from Kekeya oil field, Southwest Depression of the Tarim Basin, China

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Abstract. The condensates are important oil resources generally reserved in deep layers and mainly composed of light hydrocarbons. In this study, 10 condensates samples were collected from the Southwest Depression of the Tarim Basin, and treated with the purge-and-trap and headspace single-drop microextraction (HS-SDME) techniques to study the chemical and carbon isotope composition of the C_{6-14} hydrocarbons. The relative amount of C_{6-14} hydrocarbons is significantly different between the samples. But there is still a good linear relationship between each two of the C_{6-9}/C_{10-14}, nC_{6-9}/iC_{10-14} and iC_{6-9}/iC_{10-14} ratios, indicating that the n-alkanes and isoalkanes (including aromatics) are approximately evaporated with the same ratio. And the relative amount of C_{6-14} n-alkanes in the samples is deceased as the depth increasing. The δ^{13}C values of the C_{7-14} n-alkanes are in a range of -30.5‰~−25‰, and consistent with the δ^{13}C values of C_{14+} n-alkanes that have been reported earlier. The depth might have an unpredictable effect on the δ^{13}C value when it is over 6000 m, because the samples with the highest and lowest δ^{13}C values all come from the layers at similar depths. This work might suggest that the purge-and-trap and HS-SDME techniques were practicable and reliable methods to study the light hydrocarbons in condensates, and the results could improve the understanding of the condensates from the study area.

1. Introduction

Despite the great success of unconventional oil and gas exploitation in recent ten years, the increase of global fuel demands and oil price volatility have also promoted the interest in deep and ultra-deep oil and gases \(^{1,2}\).

Condensates is one of the important deep and ultra-deep oil resources, which is dissolved in gas under the geological conditions and exists in liquid state when taken to the ground, because of the exsolution of gas hydrocarbons and the sharply decrease of temperature and pressure \(^{3}\). The condensates are dominantly composed of volatile light hydrocarbons with carbon number less than twenty, leading the accurate geochemical analysis of condensate oil to be very difficult. However, the scientific studies on condensate oil, e.g. compositional and isotope characteristics, oil-rock correlation, and oil potential evaluation, are helpful to the efficient exploitation of condensate oil reservoir, and there are still short of effective methods.

In this paper, we selected ten condensate samples from Kekeya oil field in the Southwest of the Tarim Basin, and used purge-and-trap technique to concentrate the light hydrocarbons (C_{7-20}), and
subsequently purge the light hydrocarbons into a gas chromatograph to analyse the saturated and aromatic compounds. Simultaneously, the light hydrocarbons in condensate oil were extracted by the headspace single-drop microextraction technique (HS-SDME), which has been proved to be a very efficient method to extract the volatile compounds in petroleum, and subjected to compound-specific carbon isotope analysis. Finally, the compositional and carbon isotopic characteristics of the condensates were systematically studied. We believed that the methods used for light hydrocarbons analysis in present study could suggest a practicable way for geochemical research on light oil, and the result could improve the understanding of condensate oil from the Kekeya oil field in the southwest Tarim Basin.

2. Samples and experiments

10 condensate oil samples were collected from 9 oil wells in the Kekeya field and the adjacent area in the Southwest depression of the Tarim Basin (Table 1, Figure 1-a). Most of oil samples are from the Tertiary system, e.g. N1 and E stratum, with depths of 3248–4331m, while 3 samples from 2 deep wells are from a more ancient stratum (K) and have depths between 6333–6835m (Table 1, Figure 1-b).

The oil samples were firstly dissolved in a mixture of methanol and pure water, then subjected to the Purge-and-Trap instrument to concentrate the light hydrocarbons, and an Agilent 7890 GC equipped with a HP-PONA fused silica capillary column (50 m × 0.20 mm × 0.50 μm) and a flame ionization detector (FID) was used to analyze the hydrocarbon contents. The carrier gas was Nitrogen and the flow rate was set to 1.0 ml/min. The GC inlet was operated in the split mode (split ratio of 100:1) at a temperature of 290 °C. The oven temperature was initially held at 35 °C for 5 min, then heated to 50 °C at a rate of 1.5 °C/min, further heated to 300 °C at a rate of 8 °C/min and finally held for 5 min.

| Sample No. | Well | Layer | Depth (m) | C_{6-9}/C_{10-14} | n-C_{6-9}/n-C_{10-14} | i-C_{6-9}/i-C_{10-14} | n-C_{6-9}/i-C_{6-9} | n-C_{10-14}/i-C_{10-14} |
|------------|------|-------|-----------|------------------|-----------------------|-----------------------|-------------------|---------------------|
| 1          | Ke2  | N1    | 3248-3298 | 0.31             | 0.35                  | 0.27                  | 1.00              | 0.76                |

Figure 1. Tectonic map of the Southwest Depression of the Tarim Basin showing the location of sampling area (a), and structural section of the Kekeya tectonic belt showing the sampling stratum and depths (b).
The analysis of carbon isotopic compositions of individual light n-alkanes (n-C<sub>9-14</sub>) was performed on a Delta XL Plus isotope ratios mass spectrometer connected to an Agilent 6890 GC (GC-IRMS). Prior to sample injection, HS-SDME technique was used to extract the n-C<sub>7-14</sub> hydrocarbons, and the process is briefly described as follows. 20–30 mg of oil sample was sufficiently dissolved in 2 ml of methanol, then 50 μl of the solution was transferred into a 10 ml vial preloaded with a magnetic stir bar and 5 ml of pure water. After that, the vial was sealed by a hollow cap with gasket, and placed on an electromagnetic stirrer. When the electromagnetic stirrer had been adjusted to keep the stir bar rotating at a rate of about 1000 r/min, a SGE micro-syringe (10 μl) filled with 1.2–1.5 μl of n-hexadecane was placed right upon the vial and pushed downwards until the gasket was pierced and the needle tip of the syringe was about 8 mm away from the liquid level. Then the plunger of the syringe was slowly pushed down until the n-hexadecane was hanged on the needle tip as a liquid globule. After 30 min, the n-hexadecane globule was taken back into the syringe by pulling up the plunger, and subjected to the GC-IRMS to analyze the carbon isotopic composition of the light n-alkanes dissolved in it.

The 6890 GC was equipped with a HP-5MS fused silica capillary column (50 m×0.25 mm×0.25 μm). The carrier gas was He and set at a flow rate of 1.0 ml/min. The GC inlet was operated in the split mode with a variable split ratio of 60–150:1 according to the concentration of light n-alkanes in the samples. The Oven temperature was initially kept at 40 °C for 5 min, and programed to 130 °C at a rate of 2 °C/min, then programed to 290 °C at a rate of 20 °C/min and held for 5 min.

3. Results and discussion

3.1. Compositional characteristics of C<sub>6</sub>-C<sub>14</sub> hydrocarbons
As shown in Figure 2, although the condensate oil samples are mainly composed of light hydrocarbons with carbon number less than twenty, the relative abundance of the hydrocarbons of different carbon numbers might vary within a large range. Because the light hydrocarbons are also referred to C<sub>5-9</sub> hydrocarbons at times 5, the data of C<sub>6-14</sub> hydrocarbons were divided into C<sub>6-9</sub> and C<sub>10-14</sub> to study the characteristics of the samples.

Among the 10 samples, those from the wells of Ke10, Ke20, Keshen709, Keshen101 (6807-6835m) and Kedong1 are relatively abundant in C<sub>6-9</sub> compounds, with C<sub>6-9</sub>/C<sub>10-14</sub> ratio 1.45–5.19 (Figure 2, Table 1). By contrast, other five samples are relatively rich in C<sub>10-14</sub> compounds, with C<sub>6-9</sub>/C<sub>10-14</sub> ratio 0.13–0.41 (Table 1). The distributions of the n-alkanes and isoalkanes (including aromatics) are approximately in accordance with that of the total hydrocarbons, with nC<sub>6-9</sub>/nC<sub>10-14</sub> and iC<sub>6-9</sub>/iC<sub>10-14</sub> ratios in the ranges of 0.35–12.35 and 0.27–3.79 (Table 1). And the C<sub>6-9</sub>/C<sub>10-14</sub> ratio has a significant linear correlation with C<sub>6-9</sub>/C<sub>10-14</sub> and nC<sub>6-9</sub>/nC<sub>10-14</sub> ratio respectively (Figure 3-a).

| Sample   | Carbon Number | Carbon Isotopic Ratio |
|----------|---------------|-----------------------|
| Ke10     | N<sub>1</sub> | /                     |
| Ke20     | N<sub>1</sub> | 3850-3951             |
| Ke35     | N<sub>1</sub> | /                     |
| Keshen709| /             | 3937-3952             |
| Keshen700| /             | 3861-3893             |
| Keshen103| E             | 6333-6339             |
| Keshen101| K             | 6651-6676             |
| Keshen101| /             | 6807-6835             |
| Kedong1  | K_2           | 4268-4331             |

* i-C<sub>6-9</sub> or i-C<sub>10-14</sub> refers to the sum of isoalkanes and aromatic hydrocarbons of corresponding carbon number.
In the C_{6-9} and C_{10-14} compounds, the two types of n-alkanes to isoalkanes ratios did not always agree very well with each other. The samples with relatively high C_{6-9}/C_{10-14} ratio might have a relatively low nC_{6-9}/iC_{6-9} or nC_{10-14}/iC_{10-14} ratio (Figure 3-b). For example, sample Keshen709 has the highest C_{6-9}/C_{10-14} ratio of 5.19 but low nC_{6-9}/iC_{6-9} and nC_{10-14}/iC_{10-14} ratios which are smaller than the average values (Table 1). Similarly, the condensate oil with relatively low C_{6-9}/C_{10-14} ratio might be accompanied with a relatively high nC_{6-9}/iC_{6-9} or nC_{10-14}/iC_{10-14} ratio, e.g. the sample Keshen7009 is relatively depleted in C_{6-9} hydrocarbons as suggested by the C_{6-9}/C_{10-14} ratio of 0.23, while its nC_{6-9}/iC_{6-9} and nC_{10-14}/iC_{10-14} ratios are the highest (Figure 3-b, Table 1).

![Figure 2. Gas chromatograms of C_{6-14} light hydrocarbons extracted from the condensate oil samples by purge-and-trap technique.](image)

We also studied the relationships between the molecular ratios and the depth of condensate oil samples, and found that the relative abundance of C_{6-9} compounds was independent of the depth. As shown in Figure 3-c, the ratios of C_{6-9}/C_{10-14}, nC_{6-9}/nC_{10-14} and iC_{6-9}/iC_{10-14} are not linearly correlated with the depth (R^2≈0). However, the ratio of alkanes to isoalkanes has a very good linear relationship with the depth. And this relationship could be seen in the total light hydrocarbons (C_{6-14}), C_{6-9} hydrocarbons and C_{10-14} hydrocarbons, with R^2 values of 0.59, 0.27 and 0.31(Figure 3-d). Because the 10 condensates are sampled from the wells located within one tectonic area and the adjacent area, they were supposed to be from the same source. It seems that the condensate oil from a deeper place is rich in isoalkanes (including aromatic hydrocarbons) but depleted in n-alkanes. This might indicate that the thermal maturity of the condensates would increase as the depth increasing, because the so called “isoalkanes” might mainly consist of aromatics, which are more thermally stable than n-alkanes.

3.2. Carbon isotopic characteristics of C_{6-14} n-alkanes
To analyse the carbon isotopic compositions of the individual n-alkanes, the oil generally needs pre-treatment with column chromatography to obtain the saturate fraction, and urea adduct process to isolate the n-alkanes, leading the C_{6-14} alkanes to be evaporated and thus unanalysable. In this study, the isolation of the C_{6-14} n-alkanes was directly achieved by utilizing the HS-SDME technique with n-hexadecane as extraction solvent. The extracts would be mainly composed of n-alkanes, because the solvent has a weak polarity.

As shown in Figure 4, the n-alkanes that have been successfully analysed generally have carbon numbers of C_{7-14}, because the quantities of n-C_{6} in the samples are relatively low (Figure 2). The carbon isotope ratio values ($\delta^{13}$C, PDB) of the samples are approximately in a range of -30.5‰~25‰ (Figure 4). The $\delta^{13}$C value of the individual n-alkanes generally decrease as the carbon number increasing, which
could be commonly seen in many other research papers and in accordance with the published data of Wang et al.\textsuperscript{7} The $\delta^{13}C$ values of the two samples from well Keshen101 are evidently higher than those of the other samples, and increased as the depth increased, resulting in the Keshen101 sample of depth 6807-6835m having the heaviest carbon isotopic composition. However, the Keshen103 sample, which is also collected from a depth over 6000 m, has the lightest carbon isotope composition, with $\delta^{13}C$ values of the C\textsubscript{7-14} n-alkanes in a range of -30.5‰~29.2‰ (Figure 4). On the other side, the $\delta^{13}C$ values of the 7 samples at depths of 3200 m to 4300 m are roughly consistent. This result suggests that the $\delta^{13}C$ values of the other 3 samples with depth over 6000 m could be influenced by more geochemical factors, which cause the great disparities between them.

**Figure 3.** Cross plots showing the relationships between the $C_{6,9}/C_{10,14}$ ratio and the other molecular ratios (a, b), and between the molecular ratios and depth (c, d).

**Figure 4.** Carbon isotopic compositional of C\textsubscript{7-14} n-alkanes in the condensates.
4. Conclusions
The purge-and-trap and HS-SDME techniques were successfully used in analysing the molecular and carbon isotopic composition of the C$_{6-14}$ hydrocarbons in 10 condensates collected from the Tarim Basin, in the present study. After the systematic analysis, some conclusions were reached and listed below.

1) The purge-and-trap and HS-SDME techniques are very efficient methods to study the molecular and carbon isotopic characteristics of the C$_{6-14}$ hydrocarbons in condensates.
2) The relative abundance of C$_{6-14}$ hydrocarbons was significantly different between the condensate oil samples. However, there is a good linear correlation between each two of the C$_{6-9}$/C$_{10-14}$, nC$_{6-9}$/nC$_{10-14}$ and iC$_{6-9}$/iC$_{10-14}$ ratios for all the samples, revealing the n-alkanes and isoalkanes (aromatics) are approximately evaporated or accumulated with the same degree. In addition, the relative amount of C$_{6-14}$ n-alkanes in condensates was deceased as the depth increased.
3) The $\delta^{13}$C values of C$_{7-14}$ n-alkanes in the samples fall in a range of -30.5‰~25‰, and are consistent with the $\delta^{13}$C values of C$_{14-}$ n-alkanes that have been reported earlier. The depth might have an unpredictable effect on the $\delta^{13}$C value when it is over 6000 m, as indicated by the fact that the samples with the highest and smallest $\delta^{13}$C values all came from the layers of this depth range.

Acknowledgements
This research was supported by the National Oil and Gas Major Project (2017ZX05008-002-010), the National Natural Science Foundation of China (41621062), and the State Key Laboratory of Organic Geochemistry (SKLOG2020-1).

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