Fractional composition and evolution of residual oil from coal of Early Permian Shanxi Formation (P1s), Ordos Basin (China)

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Abstract. To explore the residual oil contents and its fractional compositions changes with thermal stress, experiment of a whole coal sample from lower Permian Shanxi formation (P1sh) of Ordos Basin (China) was conducted in the grain-based micro-scale sealed vessel to explore the residual oil contents, fractional compositions and evolution at different temperatures and maturities. The residual oil of Shanxi coal reach the maximum at Ro=0.92% which was only 47.87 mg/g TOC. In oil window, the residual oil of Shanxi coal is mainly composed of asphaltenes, aromatics and resins with less saturates, showing lower oil prospective. In wet and dry gas windows, the residual oil becomes lower due to oil expulsion and cracking into gases. The main fractional compositions of residual oil are mainly aromatics and resins, which are gas-prone and can be the source of coal-bed methane at higher maturity stages.

1. Introduction
Coal is both source and reservoir rocks of large amounts of gases, which has gained increasing attention in recent years as a largely untapped potential energy resource including coal-derived gas accumulations and coal-bed methane [1]. From the previous studies, it can be found the generation and expulsion of oil from coal is controversial. Most coals are hydrogen poor and difficult to generate oil, except some unusual coals which are rich in hydrogen. The Ordos Basin is the second largest coal-bearing basin and third largest natural gas-producing basin in China[2]. The Early Permian Shanxi Formation in the Upper Paleozoic of the Ordos Basin is an important source for coal-derived gas fields and coal-bed methane [3]. The residual oil in coal will crack into gases with further thermal maturation [4]. Therefore, understanding the variation in coal properties and how the residual oil and the fractional compositions evolutions are critical for evaluating potentials of gas generation. Previous studies have been mainly conducted to make sure how oil composition changes with thermal stress on the kinetics of kerogen and oil cracking [5-12], but few studies on the residual oil and fractional compositions of coal in the process of maturation have been conducted in the Ordos Basin.

The purpose of this paper is to explore how residual oil contents and its fractional compositions change for Shanxi coal of Ordos Basin at different temperatures and maturities by using grain-based micro-scale sealed vessel pyrolysis method.

2. Samples and experiments

2.1. Samples
The whole coal sample was selected from Shanxi Formation in Ordos Basin, China. Table 1 shows the geochemical data of the Shanxi coal.

Table 1. Geochemical data for Shanxi coal used in the study

| Sample | Lithology | Age | TOC (%) | S1 (mg/g) | S2 (mg/g) | Tmax (°C) | HI (mg/g TOC) | Ro (%) |
|--------|-----------|-----|---------|-----------|-----------|-----------|--------------|--------|
| Shanxi coal | P1s | 88.37 | 9.39 | 180.07 | 454 | 204 | 0.68 |

TOC, total organic carbon; S1, free (indigenous) hydrocarbons; S2, pyrolysis of hydrocarbons; HI, hydrocarbon index; Tmax, pyrolysis temperature at maximum hydrocarbon generation.

2.2. Pyrolysis
The experimental procedures and products analysis were described in detail by our previous papers [13–14].

3. Results and discussion

3.1. Oil/gas windows of Shanxi coal
Oil window, wet gas window and dry gas window of Shanxi coal are defined according to the method presented in [13–14], which are 0.5 - 1.2%Ro, 0.8 - 2.7%Ro and 1.2 - 4.0%Ro, respectively. Figure 1 shows the variation of oil window, wet gas window and dry gas window Shanxi coal in detail.

![Figure 1](image)

Figure 1. Oil window, wet gas window and dry gas window of Shanxi coal. Figure 1a shows oil window of Shanxi coal while Figure 1b shows wet gas window and dry gas window of Shanxi coal (Solid squares in Fig.1b plots represent wet gas windows while dashed squares represent dry gas windows for Shanxi coal)

3.2. Contents and evolution of residual oil
The residual oil contents and their fractional compositions variation of Shanxi coal with increasing pyrolysis temperature are shown in Table 2. In this paper, four stages (initial maturity (Ro=0.4%), oil window (Ro=0.92%), wet gas window (Ro=1.49%) and dry gas window (Ro = 3.69%)) were selected to discuss the evolution of the residual oil and its fractional compositions.

The evolution of residual oil of Shanxi coal with increasing pyrolysis temperature is shown in Figure 2, where the residual oil of Shanxi coal has typical episodic pattern. The first peak of residual oil occurs at Ro=0.92% (oil window) and the second peak of residual oil occurs at Ro=3.09% (dry gas window). The total residual oil contents of Shanxi coal in initial maturity stage (Ro = 0.4%) is 5.86 mg/g TOC.

The total residual oil of Shanxi coal reaches the maximum (47.87 mg/g TOC) in oil window (Ro=0.92%), which means the oil generation potential is the main control of residual oil in coal. The
maximum residual oil content of Shanxi coal is 17.40 mg/g TOC at Ro=1.49% (wet gas window), while it is 0.52 mg/g TOC at Ro = 3.69% (dry gas window). The content of residual oil decreases quickly after the first peak, the reason may be the residual oil crack into wet gas or lighter components just like Pingliang and Yanchang shale in previous studies [13]. Comparing with shale, coal shows low residual oil contents in whole process of thermal evolution which may be related to its poor hydrogen contents. Previous study has suggested that hydrogen-rich coal is few. Only a few commercial oil discoveries were confidently correlated to coal. Most coals are hydrogen poor which are mainly source of gases in the process of thermal maturation [15].

Table 2. The evolution of residual oil contents and their fractional compositions of Shanxi coal with increasing pyrolysis temperature

| T(℃) | Ro(%) | residual oil (mg/g TOC) | Saturates (mg/g TOC) | Aromatics (mg/g TOC) | Resin (mg/g TOC) | Asphaltene (mg/g TOC) |
|------|-------|------------------------|---------------------|---------------------|-----------------|---------------------|
| 250  | 0.40  | 5.86                   | 0.49                | 1.78                | 1.82            | 1.76                |
| 300  | 0.60  | 37.65                  | 2.93                | 4.82                | 4.13            | 25.78               |
| 350  | 0.92  | 47.87                  | 1.27                | 5.22                | 6.60            | 34.79               |
| 400  | 1.49  | 17.40                  | 0.74                | 7.53                | 5.82            | 3.31                |
| 450  | 2.26  | 7.53                   | 0.12                | 1.19                | 1.44            | 4.78                |
| 500  | 3.09  | 12.27                  | 5.98                | 0.71                | 5.54            | 0.04                |
| 550  | 3.69  | 0.52                   | 0.13                | 0.21                | 0.17            | 0.01                |
| 600  | 3.97  | 0.71                   | 0.16                | 0.07                | 0.47            | 0.01                |

3.3. Evolution of residual oil and its fractional composition

Four fractional groups (saturates, aromatics, resins and asphaltenes) were separated by residual oil in this study. With increasing thermal temperature, the contents and proportions of saturates, aromatics, resins and asphaltenes may change accordingly. The fractional compositions of Shanxi coal at four stages were also shown in Table 2. The fractional composition variations and proportions of Shanxi coal in the whole thermal maturation were shown in Figures 2 and Figure 3.

Figure 2. The evolution of residual oil and its fractions of Shanxi coal with increasing thermal maturities and temperatures

At Ro = 0.4% (initial maturity), the contents and proportions of saturates, aromatics, resins and asphaltenes generated from Shanxi coal are 0.49 mg/g TOC (8.43%), 1.78 mg/g TOC (30.38%), 1.82 mg/g TOC (31.10%) and 1.76 mg/g TOC (30.09%), respectively. At this stage, the fractional
components of residual oil from Shanxi coal are mainly alphanenles, aromatics and resins. At Ro = 0.92% (oil window), the contents and proportions of the fractional compositions and proportions of Shanxi coal are 1.27 mg/g TOC (2.55%), 5.22 mg/g TOC (10.90%), 6.60 mg/g TOC (13.79%) and 34.79 mg/g TOC (72.67%), respectively. In oil window, the fractional components of residual oil from Shanxi coal are mainly alphanenles, resins and aromatics. At Ro =1.49% (wet gas window), the contents and proportions of saturates, aromatics, resins and alphanenles of the residual oil from Shanxi coal are 0.74 mg/g TOC (4.28%), 7.53 mg/g TOC (43.26%), 5.82 mg/g TOC (33.46%), and 3.31 mg/g TOC (19.00%), respectively. The fractional components of residual oil from Shanxi coal are mainly aromatics, resins and asphaltenes but less saturates. Compared with oil window, four fractional components contents decreased rapidly, the reason for this is mentioned in reference[14]. At Ro=3.69% (dry gas window), although the total residual oil of Shanxi coal is very low, there are still some saturates, aromatics, resins and alphanenles. At this stage, the contents and proportions of saturates, aromatics, resins and alphanenles of residual oil from Shanxi coal are 0.13 mg/g TOC (24.89 %), 0.21 mg/g TOC (40.13 %), 0.17 mg/g TOC (33.41%), and 0.01 mg/g TOC (1.57%), respectively.

Figure 3. The proportions variation of saturates, aromatics, resins and asphaltenes of Shanxi coal at different thermal maturities and temperatures

3.4. Residual oil and potentials for coal bed methane
The contents of residual oil and its fractional components of coal are important for oil and gas exploration. In this paper, the maximum residual oil yields of Shanxi coal are 47.87 mg/g TOC which occurs at Ro=0.92% (oil window). In oil window, resins and alphanenles of Shanxi coal take a large proportion which is over 50%. In low maturity (initial maturity), the residual oil content of Shanxi coal has high proportion in resins and alphanenles hydrocarbons which shows lower oil prospective. With the increasing thermal maturity, at higher maturities (wet gas window and dry gas window), the residual oil contents decrease quickly caused by expulsion and cracking. At higher maturities, the proportions of resins and asphaltenes of residual oil for Shanxi coal are more than 50%, but the contents are very low. The results show the wet gas yield and dry gas yield of residual oil of Shanxi coal are 26.50 mg/g TOC and 103.50 mg/g TOC, respectively, which suggests that Shanxi coal shows high potential of methane generation at high maturities. The study of the evolution of residual oil and their fractional compositions of Shanxi coal makes it possible to evaluate exploration prospective quantitatively of oil and gas.

4. Conclusions
To explore the residual oil contents and its fractional compositions changes with thermal stress, a whole coal sample from lower Permian Shanxi formation of Ordos Basin (China) was selected to conduct an experiment in the grain-based micro-scale sealed vessel to explore the residual oil contents, fractional compositions and evolution at different temperatures and maturities. The oil window, wet gas window and dry gas window of Shanxi coal were defined as 0.5 - 1.2%Ro, 0.8 - 2.7%Ro and 1.2 - 4.0%Ro, respectively. Coal shows broad oil window due to its early oil generation onset temperature/maturity and later oil expulsion. High porosity and higher adsorption capability to oils of coal make coal difficult to expel out oil. The maximum contents of residual oil are 47.87 mg/g TOC which occurs at Ro=0.92% (oil window). The residual oil of Shanxi coal is mainly composed of asphaltenes, aromatics and resins fractions but less saturates fraction at low maturity and mainly aromatics and resins at high thermal stages. The higher proportion of asphaltenes and resins fractions hydrocarbons in low maturity show higher gas prospective. At higher maturation stages, the contents of resins and aromatics from Shanxi coal are still high, which suggests higher generation potential of methane and other gases at higher maturities of the Shanxi coal.

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