EFFECT OF RESIDENCE TIME ON PRODUCTS YIELD AND CHARACTERISTICS OF SHALE OIL AND GASES PRODUCED BY LOW-TEMPERATURE RETORTING OF DACHENGZI OIL SHALE

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Abstract. Oil shale samples from Dachengzi mine located in Huadian city, Jilin province, China, were retorted in a stainless-steel cylindrical retort under argon atmosphere to determine the influence of residence time on the products yield and characteristics of shale oil and gases. It was found that the liquid yield increased with increasing residence time from 6 to 40 min, and then leveled off as the residence time further increased. The gases yield also increased with increasing residence time, while the shale char yield decreased. When prolonging the residence time from 6 to 60 min, the atomic H/C ratio of the derived shale oils decreased from 2.007 to 1.768, both the oxygen and sulfur content also decreased, while the nitrogen content slightly increased. It was also noticed that high boiling point oils were produced in the initial stage of the retorting process and low boiling point oils in its later stages. The shale oil obtained in 20 min had the lowest quantity of heavy fractions, 52.8 wt%, whilst the shale oils produced in 40 and 60 min showed similar boiling point distribution. The produced shale oils had similar atomic H/C ratio and lower heavy oil content compared to crude oils, and could be classified as sweet and high-nitrogen oil in terms of the classification method of crude oil. Extending the residence time decreased the aliphatics content and increased the aromatics content of the produced shale oil. When the residence time was 40 min, the derived oil contained the lowest amount of asphaltenes and the highest amount of non-hydrocarbons. Moreover, the produced gases contained maximum concentrations of C_1–C_4 gases (except propane) and had the lowest ethene/ethane ratio and the highest propene/propane and butene/butane ratios. The alkene/alkane gases ratio increased from 0.27 to 0.65 with increasing residence time from 6 to 60 min,

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which reflected the increasing secondary cracking reactions during a longer residence time.

1. Introduction

As the world's primary source of energy and chemicals, oil remains a dominant fuel for the many years to come, having accounted for 33.6% of global energy consumption in 2010 with the current demand of about 87.4 million barrels per day with a projection to increase to 105.5 million barrels per day by 2030 [1, 2]. The current global excessive dependence on oil may cause economic problems and instability of energy security in the high price oil period [3]. In order to keep the balance between energy supply and demand, some countries have been encouraged to explore unconventional oil sources, such as oil shale, oil sands and coal [4].

Oil shale, a fine-grained sedimentary rock containing significant amounts of kerogen, is widely distributed throughout the world. There are about 600 known oil shale deposits containing estimated 3 trillion barrels of shale oil, therefore oil shale represents a valuable potential alternative to crude oil [5]. The kerogen in oil shale can be converted by retorting into shale oil as an alternative to conventional oil [3, 6]. For the maximum and efficient extraction of shale oil from oil shales, the effect of reaction conditions, such as heating rate, retorting temperature, residence time, particle size, etc., has been investigated to determine optimal reaction parameters that would allow producing high quality shale oil [3, 7–18]. Up to now, most studies have focused on the pyrolysis kinetics of oil shale or the products yield as a function of operating variables, especially heating rate and retorting temperature, which are most studied variables affecting thermal decomposition of kerogen and as a consequence pyrolysis products and secondary reactions [3, 4, 7–15]. Such reactions are also affected by residence time. However, there are few studies in the literature about the influence of residence time on pyrolysis products [13, 14, 19, 20]. At the same time, the dependence of the properties of shale oil and gases on pyrolysis conditions has rarely been reported.

In this paper, oil shale samples from Dachengzi mine located in Huadian city of China have been retorted in a stainless-steel cylindrical retort. The effect of residence time on the products yield and properties of shale oil and gases has been investigated. Residence time here refers to the length of time (in minutes) during which an experiment is run at the final retorting temperature. The produced shale oils have been subjected to elemental analysis, high temperature simulated distillation and chemical class fractionation (aliphatics, aromatics, non-hydrocarbons, and asphaltenes). The hydrocarbon gases up to C_4 in the gases have been analyzed. Such information is needed

not only to understand the process reaction mechanisms, but also to optimize the process and enhance the shale oil yield and quality.

2. Experimental

2.1. Oil shale samples

The oil shale samples investigated in this paper were obtained from Dachengzi mine located in Huadian city, China. Table 1 shows the general characteristics of the samples. The original oil shale samples were sampled, crushed, ground and sieved to a grain size of 0–3 mm, considering the National Standards of China (GB 474-1996). All samples were dried in an oven at 105 °C for a period of 10–12 hours, and then stored in a desiccator to avoid any adsorption of water or loss of volatiles.

Table 1. Analysis of Dachengzi oil shale

Proximate analysis		Ultimate analysis, wt%, d		Retorting assay data[b], wt%, ar,	
Moisture, wt%, ar	11.54	C	30.90	Shale oil	19.20
Volatile matter, wt%, ar	36.21	H	4.058	Shale char	63.77
Ash, wt%, ar	48.24	O[a]	8.919	Water	11.88
Fixed carbon, wt%, ar	4.01	N	0.64	Gases	5.15
Low heating value, kJ/kg, ar	11076.07	S	0.95		

[a] Calclulated by difference.
[b] Under the National Standard of China (SH/T 0508-92).

2.2. Retorting system

All experiments were conducted in a stainless-steel cylindrical retort (70 mm i.d., 100 mm height). 50 grams of dried oil shale samples was placed inside the retort before each test and electrically heated from room temperature to a final retorting temperature of 430 °C at a fixed heating rate of 12 °C min^{-1} by using argon as the purge gas. The residence time at 430 °C was 6, 20, 40 and 60 min, respectively. Oven temperature controlled and monitored by a digital temperature controller was indicated by an oven thermocouple (see Fig. 1), which was situated between the external body of the retort and the inner side of the ceramic cylinder. Heating rate was controlled through changing the power supply voltage input to the retort heater. Argon sweep gas at the rate of 0.3 L min^{-1} was introduced from the top of the retort in an 8 mm pipe for preheating while passing downward to the bottom of the retort and then was allowed to disperse to sweep the generated products toward the retort side outlet to minimize secondary reactions [12]. The liquid products were trapped in a series of cold traps which were immerged in low-temperature troughs (ab 0 °C) filled with the mixture of ice and water, while the gases were directed through the U-tube and mixed with argon at the rate of
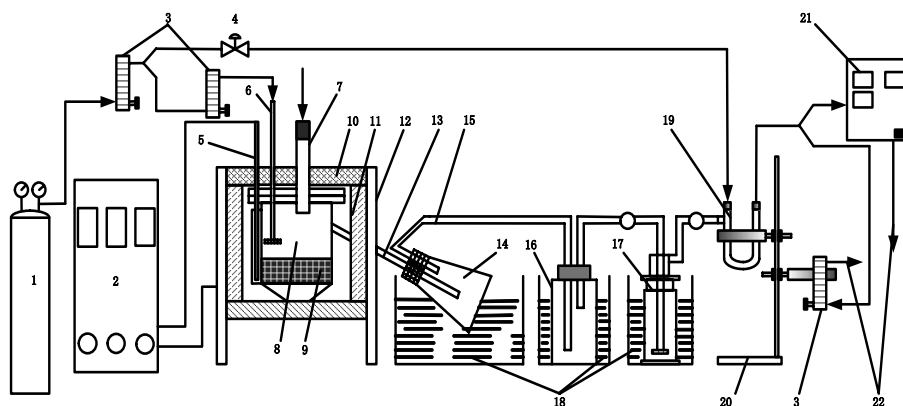
Fig. 1. Schematic diagram of the experimental retorting system of oil shales.

1 – argon cylinder, 2 – automatic temperature controller, 3 – flowmeter, 4 – flow control valve, 5 – thermocouple, 6 – gas inlet, 7 – sample inlet, 8 – retort reactor, 9 – oil shale, 10 – insulation, 11 – electric heater, 12 – steel stand, 13 – copper tube, 14 – conical flask, 15 – silicone tube, 16 – wide-mouthed bottle, 17 – gas washing bottle, 18 – water/ice condenser, 19 – U-tube, 20 – stand, 21 – gas analyzer, 22 – vent.

2.7 L min^{-1}. Part of the gas mixture was sampled into the online gas analyzer for analyzing component concentrations as a function of time and then vented from the gas analyzer outlet into the atmosphere. The rest of the gas mixture was also vented into the atmosphere via a flowmeter which kept the volume flow of gases into the analyzer constant (3 L min^{-1}). After the retorting temperature was kept constant for a specified period of residence time, the experiment ceased. The reactor was fast removed from the heating furnace and then placed in a large low-temperature trough (ab 0 °C) filled with the mixture of ice and water to be cooled. Shale char and the mixture of shale oil and water were collected and weighed, respectively. The gases yield was determined by overall material balance. The derived liquid product consisted of an aqueous phase and an oil phase. The oil was separated from the aqueous phase by centrifuging and decanting, and removing the aqueous phase by pipette for elemental analysis, high temperature simulated distillation and chemical class fractionation [21–23]. In order to assess the reproducibility, each retorting test was performed twice under identical conditions.

2.3. Gas analysis

The gas mixture sample emitted from the U-tube was continuously directed to an on-line Fourier transform infrared (FTIR) gas analyzer (GASMET DX-4000; Gasmet Technologies, USA; 8 cm^{-1} resolution, high path gas cell of length 9.8 m). The gas analyzer was composed of two units: the sampling unit for gases sampling and cleaning, and the measuring unit for continuous analysis with an FTIR analyzer. Before each test, the background spectrum

was recorded when argon flowed through the sample cell at the rate of 1.2 L min^{-1}. Then the sample was continuously measured by the analyzer at 1.046 bar and 180 °C and the sample spectra were recorded. The infra-red spectra obtained were processed by Calcmet Software 2005 which was connected to the analyzer via RS232. The FTIR spectra were recorded for the following components: NO, NO_2, N_2O, NH_3, CH_4, C_2H_6, C_3H_8, C_4H_{10}, C_2H_4, C_3H_6, C_4H_8, C_2H_2, SO_2, CS_2, CO, CO_2, and H_2O. This paper mainly investigated C_1–C_4 hydrocarbon gases.

2.4. Oil analysis

2.4.1. Elemental analysis

The shale oil samples were analyzed for CHNO using a Vario EL cube CHNOS elemental analyzer (ELEMENTAR, Germany) and for total sulfur content by a Jena EA3100 NS analyzer (Carl Zeiss, Germany).

2.4.2. High temperature simulated distillation

The boiling point distribution of liquid products was obtained by high temperature simulated distillation (HTSD), using an ASTM method HT 750 (AC Analytical Controls Method; Analytical Controls, Inc., USA). This HTSD analysis was performed with an Agilent 6890N gas chromatograph (Agilent Technologies, Inc., USA) equipped with an auto sampler and an automatic injector. The carrier gas was helium (99.999% purity) with a constant flow rate of 3 mL min^{-1}. The GC contained a 5 m × 0.53 μm × 0.09 μm capillary column (AC SIMDIS HT 750; Analytical Controls, Inc., USA) with a cool on-column injector. Temperature programming for the column was 10 °C min^{-1} from 40 °C to 430 °C (maintained for 5 min). The on-column injector was programmed from 100 °C to 430 °C (run time 22 min) with a temperature gradient of 15 °C min^{-1}. The flame ionization detector (FID) was maintained at 430 °C.

2.4.3. Chemical class fractionation

The chemical class fractionation (aliphatics, aromatics, non-hydrocarbons, and asphaltenes) of shale oil samples was carried out using the Chinese Petroleum Industrial Standard SY/T 5119-2008. A total of 30 mL of hexane was added to 50 mL of shale oil sample. The mixture sat for 12 h and then was filtered through a funnel covered with cotton wool. The hexane-insoluble matter on the cotton wool was washed with hexane until the filtrate was clear. The hexane-insoluble asphaltenes remaining on the cotton wool were dissolved and washed by dichloromethane. The hexane-soluble matter collected was subjected to aliphatic, aromatic and non-hydrocarbon fractionation. A glass column (8 mm inner diameter × 300 mm length) was packed with 3 g of silica gel (80–100 mesh, activated at 150 °C for 8 h) and 2 g of neutral alumina (100–200 mesh, activated at 400 °C for 4 h). Cotton

wool was inserted at the bottom of the column. After the hexane-soluble matter was poured through the packed column, 25 mL of hexane was added to elute the aliphatic fraction. The aromatic fraction was obtained by eluting the column with a 15 mL mixture of hexane/dichloromethane (1:1, v/v). The non-hydrocarbon fraction was obtained by eluting the column with 10 mL of ethanol, followed by 15 mL of chloroform.

3. Results and discussion

3.1. Products yield

Figure 2 presents liquid, gases, and shale char yields as a function of residence time. It can be seen that the liquid yield varies from 13.67 wt% to 24.86 wt% as the residence time increases from 6 to 60 min, and the yield obviously increases by 7.836 wt% from 6 to 20 min, by 3.288 wt% from 20 to 40 min and only by 0.066 wt% from 40 to 60 min, showing that prolonging the residence time at low retorting temperature has a limited effect on the increase in the liquid yield. The experiment showed that liquid droplets nearly disappeared and gases were continuously generated in 60 min. A similar effect of residence time on the liquid yield was found by Han et al. [13, 14] who showed that more residual organic matters had cracked to gases during the residence time of 60 min. In this paper, the gases yield increases with increasing residence time, and reaches 6.16 wt% in 60 min. In addition, it can be observed that there was no significant change in shale char yield as the residence time extended from 40 to 60 min (69.9 wt% in 40 min and 68.98 wt% in 60 min, respectively). This indicates that the complete decomposition of the sample has been achieved and the residence time
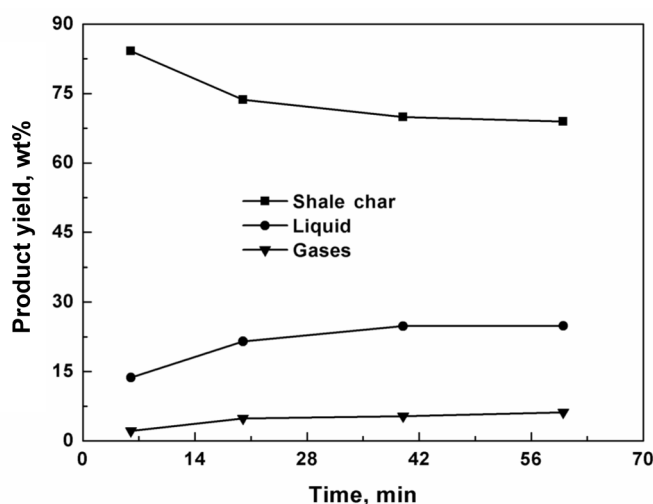

Fig. 2. Influence of residence time on the yield of products derived by retorting Dachengzi oil shale.

of 40 min is long enough for the retorting of kerogen. As reported by some authors, heat transfer in kerogen is limited and the pyrolysis process has not enough time to proceed during a short residence time, whereas for the process to proceed during a longer residence time, higher input heat is needed [24–26]. So, to ensure high shale oil yield and save on process cost, the residence time of 40 min is optimal for this stainless-steel cylindrical retort at the retorting temperature of 430 °C.

3.2. Oil analysis

3.2.1. Elemental analysis

Figure 3 shows the influence of residence time on the atomic H/C ratio, as well as oxygen, sulfur and nitrogen contents of the derived shale oil. It can
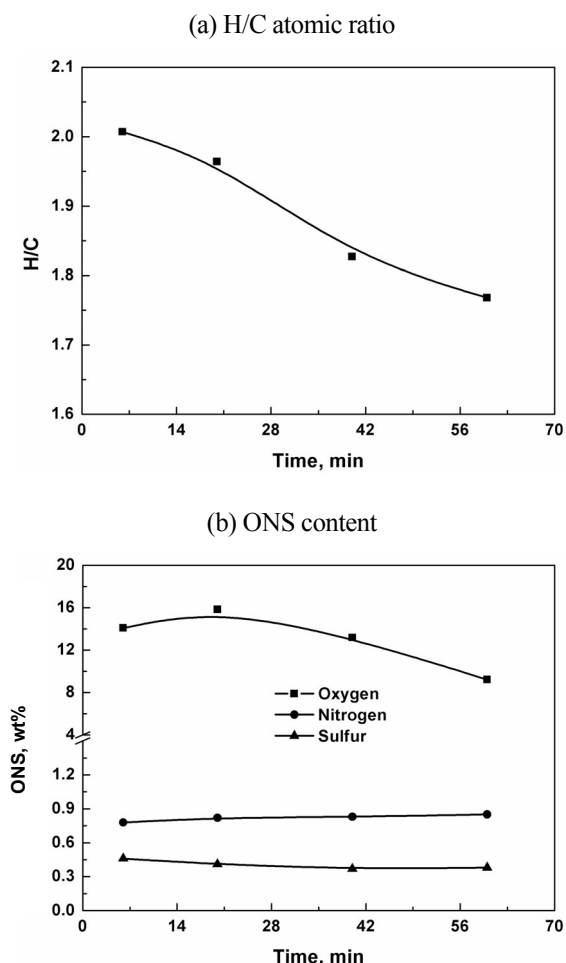
(a) H/C atomic ratio

(b) ONS content

Fig. 3. Influence of residence time on (a) the H/C atomic ratio and (b) ONS content of shale oils derived by retorting Dachengzi oil shale.

be seen in Figure 3a that the atomic H/C ratio decreases from 2.007 in 6 min to 1.827 in 40 min, which may be attributed to the obtained shale oil comprising considerable amounts of aromatic compounds. Some researchers also reported that the decrease of the atomic H/C ratio may indicate the produced oil more aromatic in nature [17]. Simultaneously, it is found that the atomic H/C ratio decreases slightly from 1.827 to 1.768 as the residence time increases from 40 to 60 min, which suggests small changes in the characteristics of shale oil after 40 min. In addition, Figure 3b shows that the nitrogen content increases from 0.78 to 0.85 wt% with increasing residence time from 6 to 60 min, while both the oxygen and sulfur content decrease. The increase in nitrogen content may be because the nitrogen in the oil is contained in aromatic molecules which are thermodynamically more stable and therefore resistant to thermal cracking [21, 27, 28]. Similar results were also reported by some researchers [4, 10], who suggested that this may result from enhanced cracking reactions of kerogen leading to aromatics and polar compounds in the obtained oil. Moreover, the decrease in oxygen and sulfur contents is possibly because more oxygen and sulfur transform to gases or shale char.

Compared to three crude oils produced in China (Daqing, Shengli, and Xinjiang) [29], the atomic H/C ratio of the derived shale oil is close to that of crude oils. However, nitrogen, oxygen and sulfur contents are higher. Moreover, the shale oil generated by retorting Dachengzi oil shale is classified as sweet and high-nitrogen crude oil in terms of the classification method of crude oil [30].

3.2.2. High temperature simulated distillation

Figure 4 compares the boiling point distributions of the recovered shale oils in 6, 20, 40 and 60 min. The final boiling point (FBP) of shale oil samples is
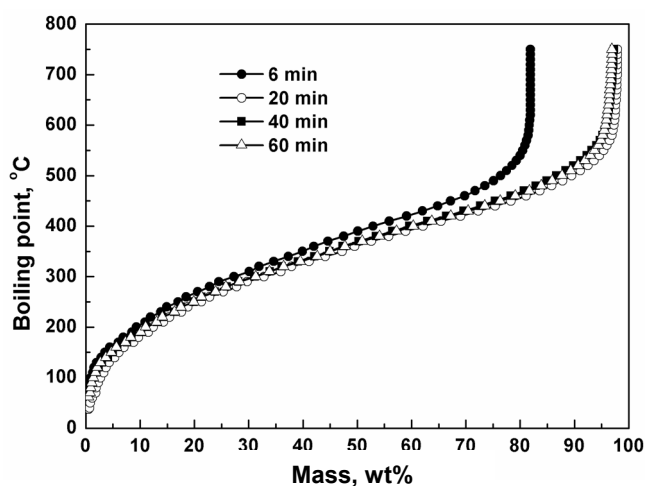

Fig. 4. Boiling point distributions of shale oils derived during different residence times.

750 °C. It is noticeable that the boiling point of the shale oil produced during the residence time of 20 min is lowest and similar boiling point distributions appear for the shale oils obtained in 40 and 60 min. In addition, the shale oil derived after 6 min contains a minimum amount of low boiling point oil. As the residence time increases, the content of low boiling point oil increases.

Table 2 further indicates that shale oils have fractions with a wide range of boiling points, mainly 9.3–12.4 wt% light naphtha (IBP ab 200 °C), 30.6–34.8 wt% medium fractions that can be used as diesel oil (200–350 °C) [31], and 52.8–60.1 wt% heavy fractions (> 350 °C). As Table 2 shows, the shale oil produced in 6 min has the highest content of heavy fraction, 60.1 wt%. At the same time, the shale oil obtained in 20 min has a minimum content of heavy fraction, 52.8 wt%, and the highest total content of light naphtha and medium fraction, 47.2 wt%. In addition, it is observed that the shale oils recovered in 40 and 60 min have a similar fractions distribution. The contents of light naphtha, medium fraction and heavy fraction of the shale oil derived in 40 min are 11.1 wt%, 33.8 wt% and 55.1 wt%, respectively, being in the shale oil obtained in 60 min 11 wt%, 34 wt% and 55 wt%, respectively. It is because of the complex nature of decomposition of kerogen as a complex heterogeneous mixture of organic compounds [32–34]. The kerogen in oil shale first breaks down into benzene soluble bitumen, and then the bitumen cracks thermally into oil, water and gases in the heating process. In the initial stage of retorting, the content of heavy oil fractions is high possibly because heavy oil fractions are stripped together with rapidly-produced oil vapor and undergo pyrolysis to a limited extent [3]. Increasing the residence time improves the heat exchanges and the transfers of heat in kerogen during the pyrolysis process. So, prolonging the residence time affords the pyrolysis process of oil shale enough time to proceed. As the retorting progresses, the amount of high boiling point oils produced is

Table 2. Distillate fractions for shale oils derived by retorting Dachengzi oil shale and crude oils produced in China, wt% of oil

Oil fraction	Oil samples	Light fraction (IBP ~200 °C)	Medium fraction (200–350 °C)	Heavy fraction (> 350 °C)
Shale oil	6 min	9.3	30.6	60.1
	20 min	12.4	34.8	52.8
	40 min	11.1	33.8	55.1
	60 min	11	34	55
Crude oils produced in China	Daqing[c]	11.5	19.7	68.8
	Shengli[d]	7.6	17.5	74.9
	Xinjiang[e]	15.4	26	59.6

[c] Daqing crude oil is obtained from Daqing oil field located in Daqing city, Heilongjiang province, China.

[d] Shengli crude oil is obtained from Shengli oil field located in Shandong province, China.

[e] Xinjiang crude oil is obtained from Xinjiang oil field located in Xinjiang Uygur Autonomous Region, China.

higher, whilst oil vapor and kerogen can be gradually pyrolyzed to become low boiling point oils [3]. For the overall recovered oil, the shale oil derived during the residence time of 20 min has the lowest boiling point.

Figure 5 shows the distillate fractions at intervals of 30 °C of the shale oils produced at different residence times. The light naphtha fractions (IBP ab 200 °C) and medium fractions (200–350 °C) have a similar boiling point distribution. The mean values of boiling points of the light naphtha fractions of shale oils produced in 6, 20, 40 and 60 min are 127.2 °C, 94.5 °C, 114.5 °C and 121.7 °C, respectively, while the respective values for the medium fractions are 242.5 °C, 242.2 °C, 241.5 °C and 241.3 °C. This distribution favors the cut of the shale oil as the naphtha and diesel oil in potential applications [31].
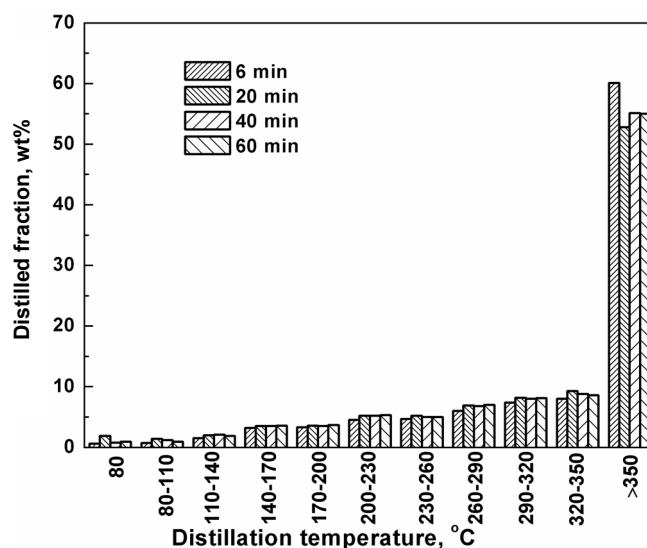

Fig. 5. Distillate fractions at intervals of 30 °C for shale oils obtained during different residence times.

In addition, Table 2 also compares the distillate fractions of the shale oil and three crude oils in China (Daqing, Shengli, and Xinjiang) [29]. The crude oil has a 59.6–74.9 wt% heavy fraction (> 350 °C), while the shale oil only contains a 52.8–60.1 wt% heavy fraction. The shale oil is much lighter than the crude oil.

3.2.3. Chemical class fractionation

Figure 6 presents the weight percent of chemical class fractionation of the derived oil as a function of residence time. It is found that the aromatics content of the obtained shale oils increases from 10.71 wt% to 16.31 wt%
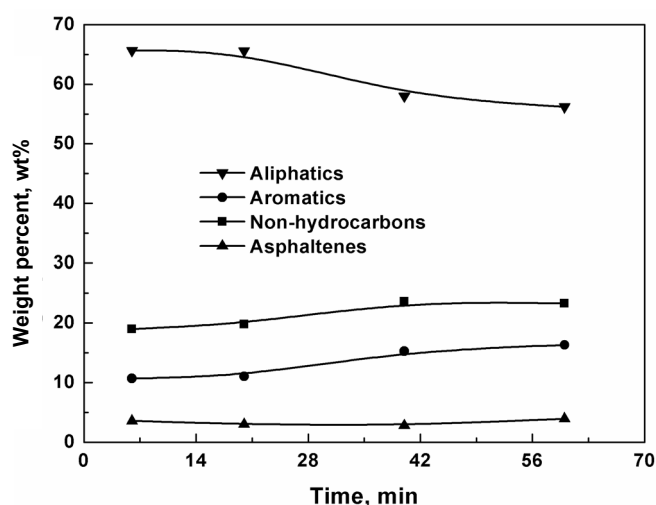
Fig. 6. Weight percent of chemical class fractionation of shale oils produced during different residence times.

with prolonging the residence time from 6 to 60 min, while the aliphatics content decreases from 65.64 wt% to 56.19 wt%. The aromatics content increases by 0.32 wt% with increasing residence time from 6 to 20 min, by 4.24 wt% from 20 to 40 min, and by 1.79 wt% from 40 to 60 min. Simultaneously, the aliphatics content decreases by 0.06 wt% from 6 to 20 min, by 7.6 wt% from 20 to 40 min, and by 1.79 wt% from 40 to 60 min. The results show that changes in aromatics and aliphatics contents are the most significant as the residence time rises from 20 to 40 min. In addition, the non-hydrocarbons content of the produced shale oils increases from 19.00 wt% to 23.61 wt% with increasing residence time from 6 to 40 min, while the asphaltenes content decreases from 3.57 wt% to 2.78 wt%. However, the opposite changes occur in the non-hydrocarbons and asphaltenes content after 40 min. The relative decrease in aliphatics concentration and increase in aromatics concentration of the shale oils suggests aromatization of oils with increasing residence time. The formation of aromatic compounds via secondary reactions during pyrolysis has been attributed to either the gas-phase cracking of aliphatic compounds [28], or to Diels–Alder type reactions resulting in the selective concentration of aromatic compounds [21, 27]. Burnham [28] has suggested that since aromatic compounds are thermodynamically more stable than aliphatic compounds and therefore more resistant to thermal cracking reactions, the gas-phase cracking reactions will selectively produce oils with an increased concentration of aromatic hydrocarbons.

In addition, Wallman et al. [34] proposed a reaction network of oil shale pyrolysis. The kerogen in oil shale first decomposes into a light hydrocarbon product and a heavy intermediate product (bitumen). Subsequently, the

bitumen is subject to two competing processes: heavy oil production and intraparticle (liquid-phase) coking. The produced oil is also subject to thermal cracking in the vapor phase surrounding the particles. The rate constants for the disappearance of bitumen are an order of magnitude smaller than the kerogen decomposition rate constant. In this work, the pyrolysis process proceeds more completely during a longer residence time, which increases the yield of aliphatics, aromatics, asphaltenes and non-hydrocarbons. On the other hand, the bitumen production rate is higher than its decomposition rate. Longer time may increase the amount of unreacted bitumen. The bitumen may be separated into asphaltenes and maltenes. Maltenes are composed of saturated and aromatic compounds, as well as non-hydrocarbons which are soluble in n-heptane [35, 36]. As the residence time increases, the asphaltenes and maltenes content increases, but that of aromatics, aliphatics and non-hydrocarbons decreases. In addition, the cleavage of the lateral alkyl chains of asphaltenes may take place during a longer residence time [15]. So, there is a transition time of 40 min for Dachengzi oil shale during which the quantity of asphaltenes is the lowest and that of non-hydrocarbons is the highest.

3.3. Gases analysis

Table 3 presents the composition of hydrocarbon gases in the produced gases as a function of residence time. The hydrocarbon gases are mainly C_1–C_4 alkanes (methane, ethane, propane and butane) and C_2–C_4 alkenes (ethene, propene and butene). It can be observed that the total content of hydrocarbon gases increases from 697.41 mg/Nm^3 to 5747.72 mg/Nm^3 as the residence time increases from 6 to 40 min, but decreases to 2643.07 mg/Nm^3 during the residence time of 60 min. The same trends are found in C_1–C_4 alkanes and C_2–C_4 alkenes gases contents, excluding propane. Accordingly, the content of this aliphatics decreases as the residence time increases from 6 to 60 min and the asphaltenes content first decreases before 40 min and then increases after 40 min in the obtained shale oils. Table 3 also shows the ratios of ethene/ethane, propene/propane, butene/butane and total alkene/alkane gases as a function of residence time. The ratio of alkene to alkane gases in the evolved pyrolysis gases has been used to determine reaction mechanisms and indicate pyrolysis conditions. Some investigators have suggested that the increase in ethene/ethane, propene/propane, butene/butane and alkene/alkane ratios reflects the increase in secondary cracking reactions [12, 21, 27, 37]. Table 3 confirms that the alkene/alkane ratio increases with increasing residence time from 6 to 60 min, which may be attributed to the increasing secondary cracking reactions during a longer residence time. However, the ratios of ethene/ethane, propene/propane and butene/butane have no conclusive trend. The ethene/ethane ratio first decreases as the residence time increases from 6 to 40 min, and then increases from 40 to 60 min. However, the opposite trend is found in the propene/propane and butene/butane ratios as a function of residence time.

Table 3. Composition of hydrocarbon gases derived by retorting Dachengzi oil shale as a function of residence time, mg/Nm³

Hydrocarbon gases	Residence time, min			
	6	20	40	60
Methane	363.63	1090.20	1834.82	436.88
Ethane	88.55	662.30	1349.68	747.47
Propane	44.19	136.75	192.75	249.26
Butane	50.90	213.68	288.89	164.77
Ethene	29.76	150.45	165.52	96.00
Propene	73.25	238.88	797.79	428.97
Butene	47.12	275.28	1118.27	519.73
Total alkanes (C_1–C_4)	547.27	2102.92	3666.14	1598.37
Total alkenes	150.14	664.61	2081.58	1044.70
Total hydrocarbon gases	697.41	2767.53	5747.72	2643.07
Ethene/ethane	0.34	0.23	0.12	0.13
Propene/propane	1.66	1.75	4.14	1.72
Butene/butane	0.93	1.29	3.87	3.15
Alkenes/alkanes	0.27	0.32	0.57	0.65

4. Conclusions

The experimental results show that residence time has a significant influence on the products yield and characteristics of shale oil and gases. The following conclusions can be inferred:

(1) Increasing residence time is helpful for the complete decomposition of kerogen as it improves the heat exchange and the transfer of heat in kerogen during the pyrolysis process; however, longer residence time will increase the input heat. As a result, the residence time of 40 min is optimal at the low retorting temperature, 430 °C, ensuring high shale oil yield and saving on process cost.

(2) Increasing the residence time decreases the atomic H/C ratio and sulfur and oxygen contents and increases nitrogen content in the recovered shale oil. This decrease of the atomic H/C ratio has been suggested to be an indication of more aromatic oil production and the slight decrease in the atomic H/C ratio after 40 min indicates that the characteristics of the shale oil after 40 min change only a little. The increase of the nitrogen content is possibly because the nitrogen in the shale char or gases participates in the aromatization process to form nitro-polycyclic aromatic hydrocarbons (NPAHs). Moreover, longer residence time enables more oxygen and sulfur to transform to gases or shale char.

(3) The atomic H/C ratio in the derived shale oil is close to that in crude oils, and nitrogen, oxygen and sulfur contents are higher. The shale oil derived from Dachengzi oil shale by retorting is characterized as sweet and high-nitrogen crude oil in terms of the classification method of crude oil.

(4) In the initial stage of retorting, high amounts of heavy oil fractions are usually produced. Increasing residence time affords the pyrolysis process of

oil shale enough time to proceed. Based on the above results, the shale oil obtained during the residence time of 20 min has the lowest quantity of heavy fractions. The shale oils obtained in 40 and 60 min show similar boiling point distributions. Moreover, the shale oil contains less heavy fractions than crude oil.

(5) Increasing the residence time from 6 to 60 min causes the increase in the aromatics content but the decrease in the aliphatics content because of the aromatization of the produced shale oils. In addition, the asphaltenes content first decreases from 6 to 40 min and then slightly increases from 40 to 60 min, while the opposite trend holds true for the non-hydrocarbons content. There is a transition time of 40 min for Dachengzi oil shales during which the quantity of asphaltenes is the lowest and that of non-hydrocarbons is the highest because prolonging the residence time enables the complete pyrolysis of kerogen; however, the cleavage of the lateral alkyl chains of asphaltenes may take place during a longer residence time.

(6) As the residence time increases, nearly all C_1–C_4 alkanes and C_2–C_4 alkenes gases contents increase as the residence time increases from 6 min to 40 min, and then decrease as the residence time increases from 40 min to 60 min. In addition, the alkene/alkane ratio increases with increasing residence time, which reflects the increasing secondary cracking reactions during a longer residence time. The residence time of 40 min is a transition time with the lowest ethene/ethane ratio and the highest propene/propane and butene/butane ratios.

Acknowledgement

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