Pyrolysis characteristics of a North Korean oil shale

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Abstract: Pyrolysis characteristics of a North Korean oil shale and its pyrolysates were investigated in this paper. The pyrolysis experiments were conducted below 600 °C at a heating rate of 10, 15, 20 and 25 °C/min, respectively. The kinetics data were calculated using both integral and differential methods with the assumption of first order kinetics. The results show that the averaged oil content of the North Korean oil shale is about 12.1 wt% and its heat value is 13,400 kJ/kg. The oil yields at different retorting temperatures show that the higher the retorting temperature the greater the oil and retorting gas yields. The optimal retorting temperature for the North Korean oil shale is about 500 °C. The properties of the North Korean shale oil including density, viscosity, flash point and freezing point are found to be relatively low compared with those of shale oil from FuShun, China. The gasoline fraction, diesel fraction and heavy oil fraction account for 11.5 wt%, 41.5 wt% and 47 wt%, respectively. The major pyrolysis gases are CH₄ (the most abundant), H₂, CO₂, H₂S, CO, and C₂-C₅ hydrocarbons. The heat value of retorting gas is more than 900 kJ/mol, and the retorting gas has high sulfur content.

Key words: Shale oil, pyrolysis, properties, oil shale, retorting, kinetics

1 Introduction

Oil shale, as a source of chemical feedstocks, has attracted increasing attention due to the uncertainty of crude oil supplies and the intensification of world energy concerns (Fang et al, 2012; Sert et al, 2012; Qian et al, 2003). Oil shale is a sedimentary rock containing soluble bitumen and insoluble kerogen. Pyrolysis of oil shale can produce shale oil, water, retorting gas and semi-coke (Na et al, 2012; Martins et al, 2010; Bhargava et al, 2005). The amount and quality of the oil produced will determine process feasibility both technically and economically. The composition of the oil produced is controlled by the pyrolysis temperature and the reaction time (Williams and Ahmad, 2000; Al-Harashsheh et al, 2011).

Worldwide shale oil resources are abundant and distributed in 33 countries, and the in-place shale oil equivalent of them accounts for about 410 billion tons (Dyni, 2003; Qian and Yin, 2010; Altun et al, 2006b). So far, many investigations of oil shale have been undertaken. The pyrolysis kinetics of Chinese oil shale from different sources are studied with thermo-gravimetric analysis (TGA) (Li and Yue, 2003; Chi et al, 2007; Miao et al, 2011; Bai et al, 2006). It is found that the pyrolysis mechanisms of different oil shale are complex and their first-order kinetics parameters are different from each

other. But their plots of $\ln A - E$ (where, A is the frequency factor, min^{-1} ; E is the activation energy, kJ/mol) are straight lines according to their different kinetic models. Besides, the pyrolysis of oil shale from Spain, Jordan, Estonia have also been studied (Torrente and Galan, 2001; Al-Ayed et al, 2010; Johannes et al, 2007) and the conclusions agree well with those of Chinese oil shale. The pyrolysis characteristics of oil shale from China and Australia are studied by the topochemical reaction method and techniques including Solid-State ¹³C NMR, XPS, FT-IR, and XRD (Sun et al, 2014; Wang et al, 2012; Tong et al, 2011; Bhargava et al, 2005). It is found that in air, the topochemical reaction of oil shale generates carbon dioxide and water, and a large amount of heat simultaneously for further self-pyrolysis.

The pyrolysis characteristics of Green River oil shale (USA) are investigated with TGA-MS (Tiwari and Deo, 2012). The results show that the compositions of the pyrolysis products of Green River oil shale are affected by the compositions of the organic matter in oil shale and reaction conditions of overall system or reactor. Many investigations of oil shale from Nigeria (Ehinola et al, 2005), Morocco (El Harfi et al, 2000), and Turkey (Hascakir and Akin, 2010; Altun et al, 2006a) are reported. The dielectric properties of oil shale from Jordan and Green River (USA) have also been studied for developing in-situ electromagnetic (EM) retorting technologies (Al-Harashsheh et al, 2009; Hakala et al, 2011). China, Estonia and Brazil are producing oil from shale commercially. As an unconventional fuel resource, oil shale

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has become a part of diversified energy strategy (Wang and Zhou, 2009; Wang et al, 2010).

Although the pyrolysis characteristics of oil shale have been widely studied by many scholars, to the best of our knowledge there has not been any study on characteristics of North Korean oil shale published. This work is aimed to investigate the pyrolysis characteristics of a North Korean oil shale, including Fischer Assay, heat value, proximate analysis.

2 Experimental

2.1 Sample

The oil shale samples were from Anzhou Basin in North Korea. Before the experiments, samples were crushed and sieved to eliminate the effects of heat transfer and mass transfer of oil shale particles on pyrolysis characteristics. The oil shale particles less than 200 mesh was used as the experimental sample. Oil shale samples (about 50 g) were heated to 520 °C with the absence of air in Fischer Assay to determine the oil yield from oil shale. The heating value analysis, proximate analysis and ultimate analysis were conducted using a ZDHW-A8 analyzer (Zhengzhou Sanbo Bergwerk Instrument Co. Ltd., China), a HTGF-3000 analyzer (Hebi City HuaTai Instrument Co. Ltd., China) and a LECO CHN-2000 (LECO, USA) and LECO S-144DR analyzer (LECO, USA), respectively. Pyrolysis gases were collected and analyzed off-line by gas chromatography (7890A GC system, Agilent, USA). The analysis of shale oil was carried according to the following Chinese Standards:

GB/T265-88: Petroleum products—Determination of kinematic viscosity and calculation of dynamic viscosity;

GB/T2540-81(88): Petroleum products—Determination of density (Pyknometer method);

GB/T 510-83(91): Petroleum products—Determination of Solidification point;

GB/T261-83(91): Petroleum products—Determination of

flash point (Closed cup method);

GB/T508-85(91): Petroleum products—Determination of ash;

GB/T511-2010: Petroleum, Petroleum products and additives—Method for determination of mechanical admixtures;

GB/T260-77(88): Petroleum products—Determination of water;

SH/T0170-92: Petroleum products—Determination of carbon residue (electric stove method);

SH/T0509-92: Petroleum products—Determination of bitumen composition.

2.2 Apparatus and procedures

A thermo-gravimetric analyzer (TGA) (NETZSCH STA409PC, NETZSCH, Germany) was used for investigating the pyrolysis kinetics of the North Korean oil shale at different heating rates of 10, 15, 20 and 25 °C/min from ambient temperature to 600 °C. Experiments were performed twice to ensure repeatability.

The experimental conditions are as follows:

- Carrier gas: nitrogen with the purity of 99.99%;
- Flow rate of carrier gas: 60 mL·min⁻¹;
- Final pyrolysis temperature: 600 °C;
- Weight of the sample: 10-20 mg.

2.3 Mathematical model

It is assumed that oil shale pyrolysis is first-order reaction, so the kinetic equation of oil shale pyrolysis can be described with the following equation:

$$\frac{dx}{dt} = A \exp\left(-\frac{E}{RT}\right)(1-x) \quad (1)$$

The 3-spline interpolation equation can be used for calculation of the pyrolysis rate of oil shale samples:

$$\begin{aligned} \frac{dx}{dT}(T) = & \frac{6}{h_j^2} \left[\frac{1}{h_j} (T_{j+1} - T)^2 - (T_{j+1} - T) \right] x_j + \frac{6}{h_j^2} \left[(T - T_j) - \frac{1}{h_j} (T - T_j)^2 \right] x_{j+1} \\ & + \frac{1}{h_j} \left[\frac{3}{h_j} (T_{j+1} - T)^2 - 2(T_{j+1} - T) \right] \beta_j - \frac{1}{h_j} \left[2(T - T_j) - \frac{3}{h_j} (T - T_j)^2 \right] \beta_{j+1} \end{aligned} \quad (2)$$

When solving equation, the boundary conditions are as follows:

$$\left. \frac{d^2x}{dT^2} \right|_{x \rightarrow 0} = \left. \frac{d^2x}{dT^2} \right|_{x \rightarrow 1} = 0 \quad (3)$$

Consider constant heating rate $\beta = dT/dt$, to obtain

$$\frac{dx}{dt} = \frac{dx}{dT} \times \beta \quad (4)$$

Substituting Eq. (4) into Eq. (1) give Eq. (5):

$$\frac{dx}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right)(1-x) \quad (5)$$

2.3.1 Differential method

Taking the logarithm of Eq. (5) will give the following equation:

$$\ln \left[\frac{dx}{dt} \frac{1}{1-x} \right] = \ln A - \frac{E}{RT} \quad (6)$$

Linear regression of $\ln[(dx/dt)/(1-x)]$ vs. $1/T$ in Eq. (6), the apparent activation energy E and apparent frequency factor A can be determined from the slope and intercept of the regression line, respectively.

2.3.2 Integral method

The integral form of Eq. (5) is

$$\int_0^x \frac{dx}{(1-x)} = \int_{T_0}^T \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) dT \quad (7)$$

When $T \gg T_0$, the approximate integral of Eq. (7) will give Eq. (8):

$$\ln \left\{ \frac{-[\ln(1-x)](E + 2RT)}{T^2} \right\} = \ln \frac{AR}{\beta} - \frac{E}{RT} \quad (8)$$

The relationship of $\ln[-(E+2RT)\ln(1-x)/T^2]$ vs. $1/T$ is linear one. The slope of the plot is equal to E/R , from which the value of the activation energy can be easily estimated. The intercept of the plot allows to obtain the apparent frequency factor, A .

3 Results and discussion

3.1 Pyrolysis of oil shale

Table 1 shows the Fischer Assay analysis result of the oil shale sample. The oil yield of the oil shale sample is 12.14 wt%, higher than that of Maoming oil shale (8.80 wt %) and Fushun oil shale (6.78 wt %) (China) (Li and Yue, 2003). If our samples are representative, the oil shale deposit in North Korea has great development potential. The water content of 7.74 wt% is so high that it may result in cracking problems during the pyrolysis process. Table 1 shows that the North Korean oil shale has high oil yield, high moisture content and medium retorting gas content.

Table 1 Fischer Assay analysis of North Korean oil shale (Air Received basis, ar %)

Shale oil, wt%	Water, wt%	Semi-coke, wt%	Retorting gas, wt%
12.14	7.74	75.87	4.25

Fig. 1 shows that the oil yield and retorting gas increase with the rise of temperature. When the temperature reaches 500 °C, the oil yield has stopped increasing. So the optimum retorting temperature can be determined as about 500 °C.

Fig. 1 Fischer assay (FA) analysis of oil yield at different retorting temperatures for the North Korean oil shale

Table 2 shows that the ash content of the North Korean oil shale samples is 53 wt%, lower than that of most oil shale (with 70wt%-80wt% ash content) in China (Qian and Yin, 2010). Table 2 also shows that the fixed carbon and ash content of oil shale are lower than those of semi-coke, because of the complete combustion of combustible material and the decomposition of minerals of the oil shale.

The heat value of the North Korean oil shale in Table 3 is more than 13,000 kJ/kg, higher than the highest heat value (11,700 kJ/kg) of oil shale in China (Qian and Yin, 2010). The heat value of semi-coke is lower than that of corresponding oil shale due to the high content of ash in semi-coke in Table 2. The North Korean oil shale with the heat value of its semi-coke more than 2,000 kcal/kg can be classified as a carbonaceous oil shale. The semi-coke of North Korean oil shale not only can be used as boiler fuel for power generation, but also can be used as heating source for retorting oil shale.

Table 2 Proximate analysis results of North Korean oil shale and its semi-coke (Air received basis, ar %)

Sample	Moisture, %	Volatile, %	Ash, %	Fixed carbon, %
Oil shale	4.27	25.81	52.98	16.94
Semi-coke	0	6.92	67.22	25.86

Table 3 Heat value of North Korean oil shale and its semi-coke (Air received basis, ar %)

Sample	kJ/kg
Oil shale	13423
Semi-coke	10702

Table 4 shows that the sulfur content of North Korean oil shale is high, and that low temperature retorting of oil shale is unfavorable on environmental grounds. But there are some positive factors for the oil shale, such as low carbon content and high hydrogen/carbon ratio, which is favorable for producing high quality shale oil. The oxygen content and oxygen/carbon ratio of the North Korean oil shale are also high, similar to that of oil shale from Fushun and Maoming, China (Qian and Yin, 2010). The hydrogen content and oxygen/carbon ratio of the semi-coke decrease as the organic matter of oil shale is converted into shale oil. Table 4 also shows that the oxygen content of the semi-coke is lower than that of the corresponding oil shale sample, indicating that the oxygen of oil shale is transferred into gaseous or liquid products during the pyrolysis process. The sulfur content of the oil shale sample is lower than that of semi-coke, implying that the mineral pyrite is the main sulfur source in the oil shale.

Table 5 shows that the mechanical strength and thermal stability (BTS_{+13} and BTS_{-3}) of the oil shale from North Korea are 87.3 wt%, 84.1wt% and 5.84 wt%, respectively. The results are similar to these of Fushun oil shale in China (Qian and Yin, 2010). So the Fushun-type retort furnace and SJ-rectangular retort furnace, which are used for retorting bulk oil shale, could be used to process the North Korean oil shale.

Table 4 Ultimate analysis of North Korean oil shale, semi-coke and shale oil (Dry basis, d%)

Sample	C, wt%	H, wt%	O, wt%	N, wt%	S, wt%
Oil shale	30.56	3.25	10.19	0.90	5.59
Semi-coke	25.98	1.30	8.12	1.07	5.81
Shale oil	80.97	10.98	3.62	0.77	0.91

Table 5 Analysis of mechanical strength and thermal stability (Air received basis, ar %)

Sample	Mechanical strength ¹ , wt%	Thermal stability ² , wt %	
		BTS ₊₁₃	BTS ₋₃
Oil shale	87.3	84.1	5.84

Notes: 1 and 2 are calculated by the methods of mechanical strength and thermal stability of coal (Yang et al, 1983).

Table 6 indicates that the ash composition is mainly SiO₂, up to 60 wt%. The second largest content is Al₂O₃, about 22 wt%. The third is Fe₂O₃ with 12.6 wt%. The rest of mineral content are relatively low. The raw material for producing ceramsite, (manufactured in China) has SiO₂, Al₂O₃ and Fe₂O₃ contents of 48-68 wt%, 12-18 wt%, 5-10 wt%, respectively (Chen et al, 2004). So the North Korean shale ash is a good raw material for producing high strength ceramsite. Besides, it can also be used to produce cement and other building materials when mixed with other ingredients.

Table 6 Composition analysis for ash from North Korean oil shale

Component	Content, wt%	Component	Content, wt%
SiO ₂	60.06	K ₂ O	0.14
Al ₂ O ₃	22.01	Na ₂ O	1.87
Fe ₂ O ₃	12.6	MnO ₂	0.15
TiO ₂	0.74	SO ₃	0.75
CaO	0.63	P ₂ O ₅	0.12
MgO	0.83		

3.2 Properties of North Korean shale oil

Table 7 shows that the North Korean shale oil has the following properties: low density, low viscosity, low flash point and low freezing point compared with these of Fushun shale oil (Song, 2004). The freezing point of North Korean shale oil is 29 °C, resulting in poor fluidity. But the shale oil can be processed to produce gasoline and diesel due to its high saturated hydrocarbon and aromatic contents. So the North Korean shale oil can be considered as an important source of transportation fuels.

Table 8 shows that the initial boiling point (IBP) of North Korean shale oil is 70 °C and the final boiling point (FBP) is 558 °C. The fraction (about 11.5 wt%) obtained at the temperature lower than 180 °C is the gasoline fraction. The diesel fraction obtained at temperatures ranging from 180 °C to 360 °C is 41.5 wt%. The fraction above 360 °C is heavy

oil (47 wt%). Therefore, the North Korean shale oil can be classified as high quality light shale oil.

Table 7 Properties of North Korean shale oil

Analysis items	North Korean shale oil	Fushun shale oil
Viscosity (50 °C), mm ² ·s ⁻¹	5.45	11.22
Freezing point, °C	29	36
Density, g·cm ⁻³	0.887	0.9033
Flash point, °C	37	133
Carbon residue, wt%	1.05	-
Ash, wt%	0.008	0.08
Mechanical impurity, wt%	Trace	0.44
Water, wt%	Trace	0.24
Saturate, wt%	38.54	-
Aromatics, wt%	26.02	-
Resin, wt%	28.88	42
Asphaltene, wt%	6.55	0.85

Table 8 Simulation distillation of North Korean shale oil

Cut fraction wt%	Temperature °C	Cut fraction, wt%	Temperature °C
IBP	70	53	360
2	104	66	401
11	178	93	499
12	186	FBP	558
15	203		

3.3 Retorting gas composition

Table 9 shows the composition of retorting gas from pyrolysis of the North Korean oil shale. It can be seen that CH₄ (the most abundant), H₂, CO₂, H₂S, CO, and C₂-C₅ hydrocarbons are the major components of retorting gas. The heat value of retorting gas is more than 900 kJ/mol (The averaged heat value of retorting gas is 939.59 KJ/mol). The averaged molecular weight of retorting gas is 26.25 g/mol and the averaged specific heat is 11.34 J/(kg·°C). The H₂S content is 8.68 wt%, which is environmentally undesirable. If the retorting gas is used for oil shale pyrolysis as heat source, the exhaust gas must be desulfurized before emission.

Table 9 Composition of retorting gas from pyrolysis of North Korean oil shale

Component	Content, wt%	Component	Content, wt%
Methane	18.27	Pentane	1.43
Ethane	11.45	Hydrogen	29.92
Ethylene	4.81	Carbon dioxide	9.88
Propane	4.89	Carbon monoxide	2.84
Propene	4.94	Hydrogen sulfide	8.68
Butane	2.08		

3.4 Kinetics model

The TG curve in Fig. 2 shows that the pyrolysis of North Korean oil shale goes through two stages of mass loss. The first occurs below 200 °C with a weight loss decline from 100 wt% to 97 wt% due to the evaporation of moisture. The change is almost consistent with the moisture content (Table 2). The second stage of mass loss occurs due to the release of volatile hydrocarbons from 200 °C to 600 °C, where the sharp decline of the weight loss curve is attributed to the decomposition of bitumen and kerogen present in oil shale.

Kinetic parameters calculated by the differential (Eq. 6) and integral methods (Eq. 8) are shown in Table 10 and Table 11, respectively. It can be seen that the values of activation energies E and frequency factor A obtained by the differential method (Eq. 6) are markedly different from those obtained by the integral method (Eq. 8). The difference is attributed to the substitution for dx/dt using $\Delta x/\Delta t$ in the differential method and the approximate integration in the integral method. The results are basically identical with literature reports (Olivella and De las Heras, 2008). The relative coefficient obtained from the differential method (Eq. 6) and the integral method (Eq. 8) (Table 10 and 11) are more than 0.96 for each heating rate. Therefore, the overall first-order reaction model (including both the integral and differential methods) is valid for the temperature region below 600 °C to describe pyrolysis

Fig. 2 Thermal gravity/differential thermal gravity (TG/DTG) curves of North Korean oil shale at a heating rate of 15 °C/min

of the North Korean oil shale.

In addition, the effect of the heating rate on the activation energy values can be seen in Table 10 and Table 11. The activation energy values decrease with an increase of heating rate, in accordance with the data in literature (Torrente and Galan, 2001; Olivella and De las Heras, 2008). This is attributed to a shorter time for a particular conversion at faster heating rates and causing transport limitations due to heat transfer.

Table 10 Kinetic parameters of the North Korean oil shale calculated by the differential method

Heating rate °C / min	Conversion range	Activation energy (E) kJ/mol	Frequency factor (A) min ⁻¹	Relative coefficient
10	0.06-0.95	113.51	2.37E+06	0.9831
15	0.06-0.95	107.62	1.56E+06	0.9694
20	0.06-0.95	105.05	1.52E+06	0.9601
25	0.06-0.95	104.03	1.45E+06	0.9663

Table 11 Kinetic parameters of the North Korean oil shale calculated by the integral method

Heating rate °C/min	Conversion range	Activation energy (E) kJ/mol	Frequency factor (A) min ⁻¹	Relative coefficient
10	0.06-0.95	98.41	1.85E+08	0.9818
15	0.06-0.95	86.99	3.16E+07	0.9821
20	0.06-0.95	79.61	8.93E+06	0.9722
25	0.06-0.95	76.72	1.34E+07	0.9726

From Tables 10 and 11, $\ln A - E$ relationship equations can be described as $\ln A = aE + b$. Fig. 3 shows the curves of $\ln A$ vs. E at different heating rates by using the integral and differential methods. The equations of the linear regression analysis shown in Fig. 3 are

Differential method:

$$\ln A = 0.0517E + 8.7779 \quad (R = 0.9686) \quad (9)$$

Integral method:

$$\ln A = 0.1344E + 5.6932 \quad (R = 0.9677) \quad (10)$$

4 Conclusion

The North Korean oil shale with an oil yield of 12.1wt% indicates a potentially valuable resource. It is also characterized for high moisture content. The heat value of its semi-coke is more than 10,000 kJ/kg, so it can be classified as a carbonaceous oil shale. The mechanical strength of the North Korean oil shale is similar to that of Fushun oil shale

Fig. 3 $\text{Ln}A$ vs E curves of North Korean oil shale using integral and differential methods

in China, so that it can be processed by the Fushun-type retort. The shale oil has low density, viscosity, flash point and mechanical impurity. It can be used for producing gasoline and diesel due to the high saturate, aromatic and resin content. The retorting gas is mainly composed of CH_4 (the most abundant), H_2 , CO_2 , H_2S , CO , and $\text{C}_2\text{-C}_5$ hydrocarbons. The heat value of it is more than 900 kJ/mol, higher than that from Chinese oil shales. In addition, the retorting gas with high sulfur content must be desulfurized before it can be used to supply heat for self-retorting. Besides the shale ash with up to 60% SiO_2 is a good raw material for producing high strength artificial ceramsite. It can also be used for producing cement and other building materials when mixed with other ingredients. The overall first-order reaction model, using both the integral and differential methods, is suitable to calculate the activation energies and frequency factors. It shows that the activation energy decreases with an increase of the heating rate. $\text{Ln}A$ and E fit a good straight line.

Nomenclatures

A	Frequency factor, min^{-1} ;
E	Activation energy, kJ/mol;
R	General gas constant, 8.314 kJ/(mol·K);
t	Pyrolysis time, s;
T	Pyrolysis temperature, °C;
x	Fractional conversion of oil shale;
$\beta = dx/dT$	Constant heating rate, °C/min;
$h = T_{j+1} - T_j$	Temperature interval;
j	Number of integral

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