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Nitrogen Injection Pyrolysis Simulated Experiment and Pyrolysis Characteristics Analysis of Huadian Oil Shale

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In-situ conversion is a promising way to utilize oil shale and fracturing nitrogen injection technology is an effective technology of in-situ conversion. This paper analyzed and tested the pyrolysis characteristics of Huadian oil shale. In-door experiments which simulated this technology were conducted based on the pyrolysis characteristics. The effect of nitrogen injection rate on the pyrolysis efficiency of oil shale was investigated by means of indoor simulated experiments. The intention was optimizing the high temperature nitrogen injection flow rate to achieve the highest energy utilization ratio. The injection flow rate in the experiment was designed from 3m^3/h to 6m^3/h, and the best injection flow rate was 5m^3/h according to the results. The highest oil production ratio was 8.63% and 202g shale oil was collected at this injection flow rate.

1. Introduction

Oil shale is a kind of high ash sedimentary rock that contains combustible organic chemical compounds (Kök and Pamir, 1998; Na et al., 2012), including organic solvent-dissolvable asphaltene and undissolvable kerogen, which can produce combustible shale oil and gas upon high temperature heating (Martins et al., 2010; Bhargava et al., 2005; Al-Harahsheh et al., 2011). Oil shale, as an unconventional oil and gas resource, is an important alternative energy source (Akash, 2003; Lai et al., 2016). With the rising tension of the international energy landscape, oil shale has received increased attention due to its vast reserves and excellent business prospects for exploitation. The extraction technologies of oil shale are primarily classified into two types. In the first process, the extraction of oil shale is either through underground tunnel mining or open pit mining, and then directly dry distilled at the surface; this method has been widely used in China, Estonia, and Brazil. Its disadvantages include high energy consumption and high levels of environment pollution (Khalil, 2013; Liu et al., 2009; Qian et al., 2011). The second method is in-situ underground conversion and the advantages of this method include minor damage to the integral structure of the underground rock mass, lower levels of pollution and lower energy consumption. In-situ underground conversion will become the main means of large-scale commercial exploitation in the future. The in-situ conversion process (ICP) by electric heaters, which is an in-situ shale oil extraction technology, has been tested in the United States. Due to the low natural permeability of oil shale and the low thermal conductivity of rock mass, the temperature of oil shale increases very slowly. As a result, the experiment process lasts for a very long time and no desirable result can be obtained (Jiang et al., 2007). Among different types of in-situ oil shale conversion methods, one of the relatively efficient methods of in-situ conversion is to fracture the oil shale layers and then heat via heat carriers.

This paper evaluated the pyrolysis characteristics of Huadian oil shale through thermogravimetric analysis (TGA) and got the TG curve and the pyrolysis temperature range. The pyrolysis experiment was done to simulate fracturing-nitrogen injection in-situ pyrolysis process by self-made devices. From this experiment, we got the qualitative relationship between the pyrolysis efficiency and injection flow rate under the condition of the same injection quantity of heat.

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2. Materials and methods

2.1 Materials

The samples were extracted from the Huadian oil shale field in Jilin Province, which is located in northeast of China. The samples were blocky, dark brown in color without special smell. The fundamental properties of the sample were tested and the results were shown in Table 1

Table 1: Physical properties of the oil shale samples

Proximate analysis (wt%)	Volatile matter	41.9
	Ash	51.8
	Moisture	3.9
	Fixed carbon	2.4
Ultimate analysis (wt%)	C	34.5
	H	4.3
	N	0.9
	S	1.6
Fischer assay (wt%)	Solid residue	68.4
	Oil	19.6
	Gas	6.4
	Water	5.6

2.2 Apparatuses

The thermogravimetric analysis test was performed on a Netzsch STA 449C thermal analyzer system (Germany). The samples were crushed then heated at a rate of 10 ℃/min and the final temperature was 750℃. The test sample of 10mg needed to be pulverized into powder of 63um sieve for raw oil shale, and there is no need to pulverize for the extracted shale oil. In the process of testing, the sample was put into the aluminum crucible. In order to reduce the effects caused by the components of the crucible, the crucible should be dried for two hours at the high temperature of 1000℃ before used. Nitrogen was used as the carrier gas during the heating process in order to take the product out of the reactor, and the flow rate was 60ml/min.

Gas Chromatography-Mass Spectrometer (GC–MS) analysis was carried out using the Agilent 6890/5973 N GC–MS instrument (America). A DB-5MS column (0.25lm film) with an internal dimension of 30m×320um×0.25um was used to analyze the shale oil. The oven temperature was kept at 50℃ for 5min and slowly increased to 280℃ at a rate of 10℃ min^{-1}, The final temperature would be held for 12min.

2.3 Nitrogen injection pyrolysis simulated experiment of oil shale

2.3.1 Experiment equipment and principles

This part simulated the fracturing-nitrogen injection method of oil shale in-situ conversion through self-made experimental equipment. The purpose of the experiment is to find out the optimal nitrogen injection flow rate which could achieve the highest energy utility efficiency and largest quantity of products, and get the relationship between the flow rate and the energy utilization ratio under the same amount of heat injection. Figure 1 showed the principle and equipment of the experiment.

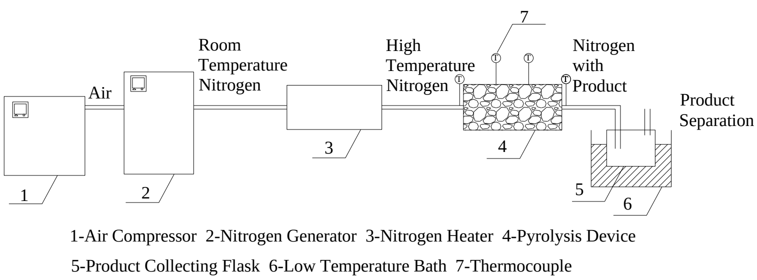

Figure 1: Principle of the pyrolysis experiment

The whole experiment equipment was consisted by six parts which included the air compressor, nitrogen generator, nitrogen heater, oil shale pyrolysis device, product collecting flask and low temperature bath. As shown in Figure 1, the air supply was provided by the air compressor. Firstly, air came into the nitrogen generator, and high purity nitrogen (>99.5%) was obtained through the separation process of nitrogen generator. Then the nitrogen was heated by the electric heater and flowed into the oil shale pyrolysis device. The oil shale samples in the pyrolysis device were in the block form and the gaps between the oil shale lumps could simulate the fractures produced by the hydraulic fracturing in the actual situation. Oil shale lumps were heated in the high temperature nitrogen flowing process and pyrolyzed to generate shale oil and gas. The nitrogen also carried the product flowing out of the pyrolysis device and flowed into the condensation collecting device. At last, the shale oil could be collected in the product collecting flask.

The oil shale pyrolysis device was made of stainless steel with the diameter of 3 inches and the length of 500 millimeters. Two temperature thermocouples were put in the device (T2 and T3), and another two thermocouples were installed on the front and rear of the pyrolysis device (T1 and T4). A total of four thermocouples were used to measure the temperature during the test process. T1 referred to the temperature of the nitrogen flowing into the reactor, and T2 and T3 referred to the temperature of nitrogen when heating the oil shale, while T4 referred to the temperature of nitrogen flowing out the reactor. Insulation treatment was performed on the pyrolysis device in order to obviate the heat loss during the experiment.Nano silica aerogel mat was used as the insulation material for its excellent heat insulated property. This material has been widely used in insulation engineering, and its thermal conductivity was only 0.017 ~ 0.023W/m•K.

2.3.2. Pyrolysis experiment procedure

Pyrolysis experiment was done as follows:

(1) The first step was to prepare the oil shale samples, and oil shale was broken to a certain size and sieved to the diameter of 10mm-20mm.

(2) The prepared oil shale samples were filled into the pyrolysis device and compacted by shaking. The mass of the oil shale samples should be recorded, and the same mass of oil shale was used in each group so as to measure and compare the experiment results. The mass of the oil shale samples used in each test group was 2.34 kg.

(3) The third step was to connect the front end of the pyrolysis device to the electric heater and rear end to the condensation collection part. Meanwhile the nano silica aerogel mat was wrapped around the pyrolysis device.

(4) The electric heater was turned on. When the heater rose to a certain temperature, the air compressor and the nitrogen generator should be turned on. The high temperature nitrogen began to flow to the pyrolysis device and heat the oil shale.

(5) After completing the test according to the planned schedule, the product mass obtained in the experiment was weighed. The weight of the shale oil was recorded, and the mass of the oil shale residue taken out from the pyrolysis device was also weighed.

The whole experiment included 4 groups, and each group corresponded to a different nitrogen flow rate. The injection flow rate of nitrogen was set to 3, 4, 5 and 6 m^3/h, respectively with the corresponding injection time of 4, 3, 2.4, 2 h. The temperature of nitrogen which flowed into the pyrolysis device was set to about 550℃ (Temperature of T1). The total amount of the injected nitrogen in each group was 12m^3, and the total injected heat was the same in each group. The weight of shale oil after the experiment could be used to evaluate the energy utilization ratio in different injection flow rate under the same heat injection amount.

3. Results and discussion

3.1 TG of the raw oil shale

The TG curve and the derivative thermogravimetric (DTG) curve of oil shale were shown in Figure 2.

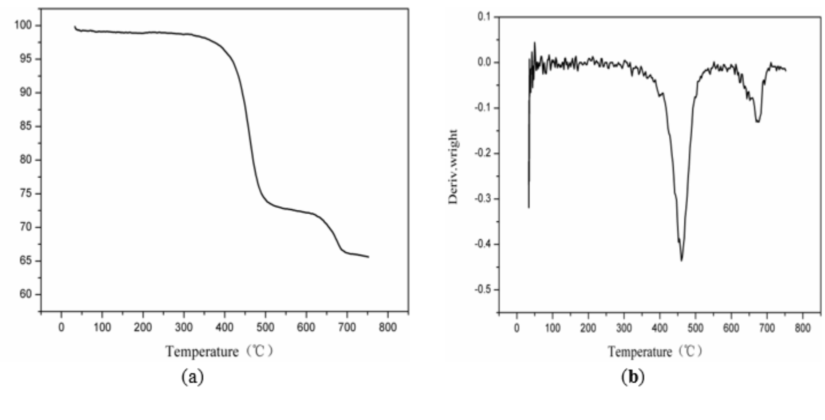

Figure 2: (a) Thermogravimetric (TG) curve of Huadian oil shale; (b) Derivative Thermogravimetric (DTG) curve of Huadian oil shale.

The TG curve indicated that the thermal weight loss of Huadian oil shale could be divided into three stages. The first stage was the temperature below 200℃, in which the weight loss of the oil shale was mainly due to the evaporation of water vapor. The second stage was from 200℃ to 600℃, in which the weight loss was primarily caused by the pyrolysis of kerogen in the oil shale. In addition, some of the clay minerals lost their bound water. For example, the kaolinite lost its bound water at approximately 430℃ (Brandt 2008; Liu et al., 2014; Ballice, 2003). In the last stage (between 600℃ and 800℃), the weight loss was caused by the decomposition of carbonate minerals at a high temperature (Kaljuvee et al., 2004). Two peaks could be found from the DTG curve, which referred to the pyrolysis of kerogen in the second stage and the decomposition of carbonate minerals in the third stage, and the kerogen was mainly pyrolyzed in the range of 400 ~500℃. In addition, the temperature of maximum weight loss was about 455℃.

3.2 Analysis of the nitrogen injection pyrolysis simulated experiment

The experiment result indicated that shale oil production ratio first rose and then fell along with the increasing injection flow rate from 3 m^3/h to 6 m^3/h under the same total amount of heat injected. The most shale oil was collected when the nitrogen flow rate was 5 m^3/h, and it reached the highest energy utilization ratio. The shale oil mass was 202g and the oil production ratio was 8.63%. Figure 3 showed the oil shale mass and the shale oil production ratio along with the nitrogen injection flow rate.

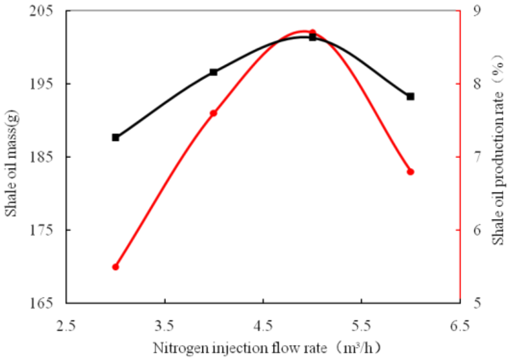

Figure 3: Shale oil mass and production rate along with nitrogen injection flow rate.

The oil production ratio of oil shale is related to the amount of absorbed heat, the highest oil production ratio indicates that the oil shale absorbs the most heat. In this experiment, the heat absorbed by oil shale was the total heat injected subtracting the heat loss. The heat loss could be divided into two parts. The first part was the heat dissipating from the pyrolysis device, and the second part was the heat carried from the pyrolysis device by nitrogen.

Small nitrogen injection flow rate led to a relatively long time of experiment, so the first part of heat loss was larger. Temperature rising rate of oil shale was higher in large nitrogen flow rate. However, nitrogen had a relatively high velocity and flowed out of the pyrolysis device without adequate heat exchange with oil shale, which led to a greater heat loss in the second aspect.

The above conclusions can also be drawn from the test data recorded by T4. For example, at the end of each group (the total volume of the injected nitrogen was 12 m^3), the temperature of T4 was 265℃ when the injection flow rate was 3m^3/h; 284℃ when the injection flow rate was 4m^3/h; 296℃when the injection flow rate was 5m^3/h; 307℃ when the injection flow rate was 6m^3/h. The first part of heat loss in the experiment can simulate the heat loss transferred to the upper and lower strata of oil shale in practical engineering, and the second part of heat loss can simulate the heat loss carried by the nitrogen flowing out from the production well in actual engineering.

To summarize what have been discussed above, when the injection flow rate was the smallest of 3m^3/h, the heat flowing out of the pyrolysis device was small but the heat dissipating from the body of the pyrolysis device to the outside air was relatively large. When the injection flow rate was the largest of 6m^3/h, the heat flowing out of the pyrolysis device was larger but the heat dissipating from the body of the pyrolysis device to the outside air was relatively small. In conclusion, when the injection flow rate was 5m^3/h, the heat loss of the addition of the two parts of was the smallest, and the oil shale samples absorbed the most heat and got the highest oil production ratio, as is shown in the curve in Figure 6.

3.3 Characteristics of the shale oil

After the pyrolysis experiment, the collected shale oil was analyzed. The first test was the simulation of steam distillation of shale oil by thermogravimetric analysis. The shale oil and the thermogravimetry curve were shown in Figure 4.

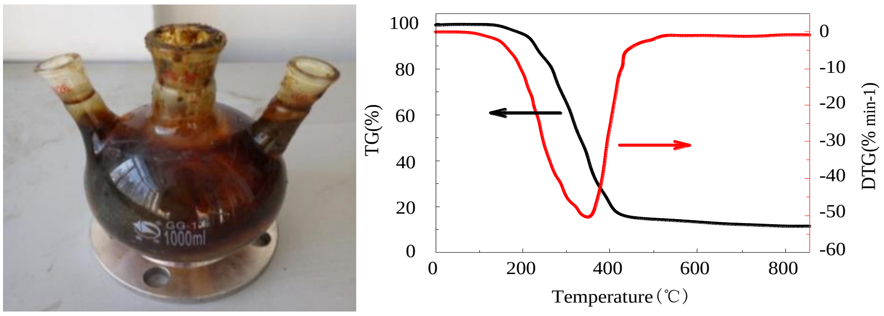

Figure 4: Shale oil and TG/DTG curves

The DTG curve of shale oil indicated that the main weight loss range was from 80℃ to 400℃, and the weight loss rate reached the maximum at about 350℃. The weight loss in this temperature range was mainly caused by volatile and low molecular weight ydrocarbons (Zhang et al., 2012; Mou et al., 2010; Chen et al., 2014). At the end of the thermogravimetry test (the heating temperature was 600℃), there was still a small amount of residue in the shale oil, accounting for about 10% of the total mass. The result was consistent with the test result of crude oil, indicating that the shale oil product collected in this experiment was basically consistent with that of crude oil.

GC-MS test was also done to the shale oil, and the spectrum was shown in Figure 5.

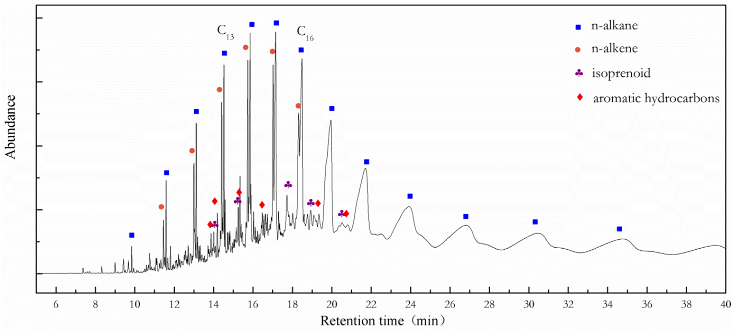

Figure 5: GC-MS spectrum of shale oil

It could be seen from the shale oil spectrum that the composition of the shale oil was complex, mainly including alkane and alkene, while aromatic hydrocarbons and isoprenoid were not so much.

4. Conclusions

(1) TGA test was done to the Huadian oil shale, and the TG curve could be mainly divided into three stages. The pyrolysis of organic matter occured in the second stage, and the temperature of maximum weight loss of was about 455℃.

(2) In-door pyrolysis experiment was done to simulate the fracturing-high temperature nitrogen injection technology. The total injected volume of nitrogen was 12m³ and the injection temperature was 550℃. The highest energy utilization ratio was achieved in the injection flow rate of 5m³/h.

(3) The highest shale oil production ratio was 8.63%. The qualitative relationship between oil production ratio and nitrogen injection flow rate was summarized. The relationship was also applicable in field engineering.

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References

Akash B.A., 2003, Characterization of Shale Oil as Compared to Crude Oil and Some Refined Petroleum Products, Energy Sources, 25(12), 1171-1182, DOI: 10.1080/00908310390233612

Al-Harahsheh M., Al-Ayed O., Robinson J., Kingman S., Al-Harahsheh A., 2011, Effect of demineralization and heating rate on the pyrolysis kinetics of Jordanian oil shales, Fuel & Energy Abstracts, 92(9), 1805-1811, DOI: 10.1016/j.fuproc.2011.04.037

Bai F., Sun Y., Liu Y., Liu B., Guo M., Lv X., Guo W., Li Q., Hou C., Wang Q., 2014, Kinetic investigation on partially oxidized Huadian oil shale by thermogravimetric analysis, Oil Shale, 31(4), 377-393, DOI: 10.3176/oil.2014.4.06

Ballice L., 2003, Classification of aliphatic hydrocarbons formed at temperature-programmed co-pyrolysis of Turkish oil shales of kerogen types I and II, Oil Shale, 20(1), 33-46.

Bhargava S., Awaja F., Subasinghe N.D., 2005, Characterisation of some Australian oil shale using thermal, X-ray and IR techniques, Fuel, 84(6), 707-715, DOI: 10.1016/j.fuel.2004.11.013

Brandt A.R., 2008, Converting oil shale to liquid fuels: Energy inputs and greenhouse gas emissions of the Shell in situ conversion process, Environmental Science & Technology, 42(19), 7489-7495.

Chen D., Zhou J., Zhang Q., 2014, Effects of Torrefaction on the Pyrolysis Behavior and Bio-Oil Properties of Rice Husk by Using TG-FTIR and Py-GC/MS, Energy & Fuels, 28(9), 5857-5863, DOI: 10.1021/ef501189p

Iscan A.G., Kök M.V., Bağct A.S., 2007, Kinetic analysis of central Anatolia oil shale by combustion cell experiments, Journal of Thermal Analysis and Calorimetry, 88(3), 653-656, DOI: 10.1007/s10973-006-8026-z

Jiang X.M., Han X.X., Cui Z.G., 2007, New technology for the comprehensive utilization of Chinese oil shale resources, Energy, 32(5), 772-777, DOI: 10.1016/j.energy.2006.05.001

Kaljuvee T., Pelt J., Radin M., 2004, TG-FTIR study of gaseous compounds evolved at thermooxidation of oil shale, Journal of Thermal Analysis and Calorimetry, 78(2), 399-414, DOI: 10.1023/B:JTAN.0000046106.53195.26

Khalil A.M., 2013, Oil shale pyrolysis and effect of particle size on the composition of shale oil, Oil Shale, 30(2), 136-146, DOI: 10.3176/oil.2013.2.04

Kök M.V., Pamir M.R., 1998, ASTM kinetics of oil shales, Journal of Thermal Analysis and Calorimetry, 53(2), 567-575, DOI: 10.1023/A:1010109929197

Lai D., Shi Y., Geng S., Chen Z., Gao S., Zhang J., Xu G., 2016, Secondary reactions in oil shale pyrolysis by solid heat carrier in a moving bed with internals, Fuel, 173(6), 138-145, DOI: 10.1016/j.fuel.2016.01.052

Liu D.X., Wang H.Y., Zheng D.W., 2009, World progress of oil shale in-situ exploitation methods, Natural Gas Industry, 5, 128-132.

Liu Q.Q., Han X.X., Li Q.Y., Huang Y.R., Jiang X.M., 2014, TG–DSC analysis of pyrolysis process of two Chinese oil shales, Journal of Thermal Analysis and Calorimetry, 116(1), 511-517, DOI: 10.1007/s10973-013-3524-2

Martins M.F., Salvador S., Thovert J.F., 2010, Debenest, G. Co-current combustion of oil shale-Part 1: Characterization of the solid and gaseous products, Fuel, 89(1), 144-151, DOI: 10.1016/j.fuel.2009.06.036

Mou Z., Chen H.P., Ying G., He R.X., Yang H.P., Wang X.H., 2010, Experimental study on bio-oil pyrolysis/gasification, Bioresources, 5(1), 135-146.

Na J.G., Im C.H., Chung S.H., Lee K.B., 2012, Effect of oil shale retorting temperature on shale oil yield and properties, Fuel, 95(1), 131-135, DOI: 10.1016/j.fuel.2011.11.029

Qian J.L., Yin L., Wang J.Q., Li S.Y., Han F., He Y.G., 2011, Oil shale-supplementary energy of petroleum, Beijing: China Petrochemical Press, 232-245.

Zhang Y., Chen D.Y., Dong Z., Zhu X.F., 2012, Tg-ftir analysis of bio-oil and its pyrolysis/gasification property, Journal of Fuel Chemistry & Technology, 40(10), 1194-1199, DOI: 10.1016/S1872-5813(12)60121-2