

PYROLYSIS AND CO-PYROLYSIS OF CHINESE LONGKOU OIL SHALE AND MONGOLIAN HUOLINHE LIGNITE

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Abstract. Chinese Longkou oil shale (LKO) and Mongolian Huolinhe lignite (HLHC) samples were subjected to pyrolysis and co-pyrolysis in a fixed bed reactor and rapid pyrolysis equipment to investigate the processes. The results indicated that both LKO and HLHC are ideal materials for oil recovery by pyrolysis with high oil yields. The fixed bed pyrolysis showed that the synergetic effect appeared with increasing oil yield and decreasing water yield, and was varying with changing mass percentage of coal. The optimum temperature of co-pyrolysis of LKO and HLHC in the rapid pyrolysis equipment was 510 °C. The synergetic effect was found to exist when the oil yield increased by 9% and water yield decreased by 36%.

Keywords: oil shale, lignite, pyrolysis, co-pyrolysis.

1. Introduction

Crude oil is an important feedstock of the petrochemical industry and a dominant source of energy driving the world economy. Oil shale mining and pyrolysis for producing shale oil have become profitable in China due to high crude oil prices. According to a conservative estimation, oil shale reserves in China make up 400 billion tons. Oil shale, a combustible solid mineral resource, is a fine-grained sedimentary rock containing organic matter called kerogen, and a large amount of minerals. Kerogen is a macro-molecular heteropolymer which is insoluble in common organic solvents [1–3].

Coal is the main energy source and resource in China. It is estimated that the minable coal reserve is about 114.5 billion tons and accounts for about 70% of the country's primary energy consumption at present. Pyrolysis, as a

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process technology, has received considerable attention from many researchers because it is not only an important intermediate stage in coal conversions, such as gasification, combustion, liquefaction, etc., but is also a simple and effective method for the clean conversion of coal. China is rich in lignite and subbituminous coal. Lignite with high volatile matter content is advantageous for retorting [4–7].

Shale oil and coal tar are produced from oil shale and coal by pyrolysis. Shale oil and low-temperature coal tar are complex compounds. Shale oil, unlike coal tar, is rich in hydrogen [8, 9]. The authors' attention has been directed towards the pyrolysis of oil shale in combination with coal, assuming that the thermal decomposition of coal as well as oil shale proceeds through a radical formation of shale oil and coal tar, respectively, in a narrow temperature range. This will allow chemical interactions between oil shale and coal intermediates, leading to an increase in the yield and quality of final products. In general, thermal processes of both oil shale and coal produce in various amounts gases, liquids or solids [10–12]. Therefore, our research was aimed at the investigation of co-pyrolysis of coal and oil shale.

2. Experimental

2.1. Materials

For experiments, the oil shale sample (LKO) was obtained from Longkou, Shandong province, China. The lignite sample (HLHC) was taken from Huolinhe district, Inner Mongolia. Immediately prior to pyrolysis, oil shale and lignite samples were crushed and sieved to 0–6 mm particles. The results of proximate and ultimate analyses of the samples are shown in Table 1.

Table 1. Proximate and ultimate analyses of oil shale and lignite, wt%

	LKO	HLHC
Proximate analysis, wt%, as received		
Moisture (M_{ad})	3.87	27.49
Ash (A_{ad})	49.92	10.72
Volatile matter (V_{ad})	35.66	56.15
Ultimate analysis, wt%, dry		
C_d	33.39	69.19
H_d	4.31	5.04
N_d	0.87	1.56
$S_{t,d}$	1.21	0.21
H/C atomic ratio	1.55	0.88
Fischer assay, wt%, as received		
Oil (tar_{ad})	14.38	8.55
Water	9.38	4.51
Residue (RC_{ad})	69.84	51.55
Gas and loss	6.40	7.90

2.2. Fixed-bed pyrolysis equipment

The schematic diagram of fixed-bed pyrolysis equipment is shown in Figure 1.

The experiments were carried out at ambient pressure in the reactor. In each run, about 20 g of sample was placed into the cylinder and the free space of the cylinder was filled with quartz wool and ceramic granules to minimize the amount of air in the cylinder. The reactor containing the sample was inserted into the preheated furnace and the coal sample was heated up and pyrolyzed. The time of heating the sample from room temperature to the desired temperature was about 10 min. The pyrolysis products, including gas, tar and water, flowed freely with N₂ out from the reactor. After reaching the required time measured from the moment the reactor was inserted into the furnace, the reactor was taken out of the furnace and cooled down to room temperature. The pyrolysis time at the reaction temperature was 20 min.

After each experiment, from the mass difference of the reactor before and after pyrolysis of the sample, the mass and/or yield of char can be obtained. The volume of gas was measured by a wet type flowmeter. From the gas volume, the gas mass and yield can be determined. From the mass difference of the collecting trap before and after pyrolysis of coal, the mass and/or yield of tar and water can be obtained. Then the water in the tar/water mixture was determined according to the method of ASTM D95-83(1990), using toluene as a solvent. In this case, the yield of tar and water can be separately obtained.

The experimental conditions of fixed-bed pyrolysis are given in Table 2.

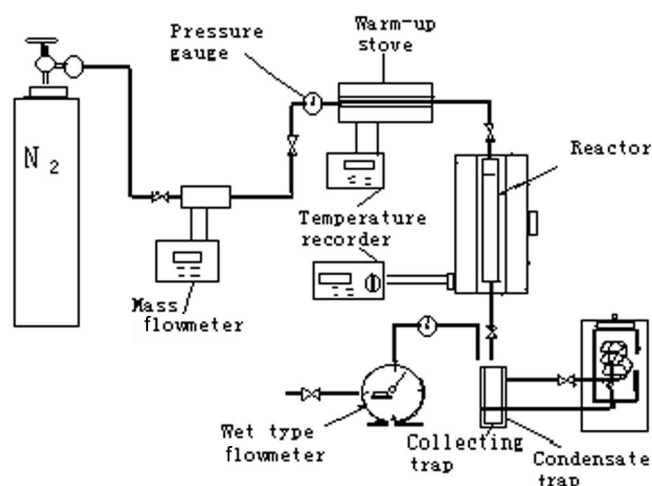


Fig. 1. Schematic diagram of fixed-bed pyrolysis equipment.

Table 2. Experimental conditions of fix-bed pyrolysis

Experimental conditions	
Sample (as received), g	20
Sample particle size, mm	1–3
N ₂ flow rate, SLM/min	0.1
Starting temperature, °C	Ambient
Ending temperature, °C	450–580
Heating rate, °C/min	40–50
Condensate trap temperature, °C	–15...–20
Pyrolysis pressure, MPa	Ambient

The calculated yield of product is obtained by the following formula:

$$Y_{product} = a \cdot Y_{product1} + b \cdot Y_{product2}$$

where $Y_{product}$ is the calculated yield of product, %; $Y_{product1}$ is the yield of product in oil shale pyrolysis only, %; $Y_{product2}$ stands for the yield of product in coal pyrolysis only, %; a denotes the percentage of oil shale in the mixture, %; b signifies the percentage of coal in the mixture, %; $a + b = 1$.

2.3. Rapid pyrolysis equipment

The rapid pyrolysis and co-pyrolysis of HLHC and LKO by using solid heat carrier were also investigated.

The flow diagram of the rapid pyrolysis process facility is shown in Figure 2.

Pyrolysis and co-pyrolysis were carried out in a 10 kg/h rapid pyrolysis equipment in a continuous mode. The equipment consists mainly of a heat carrier hopper and a pyrolysis reactor. After desiccation, the sample was mixed with hot solid heat carrier in the mixer and pyrolysis took mainly place in the reactor. Oil and water can be collected after the air cooler and water cooler. Then the water content in the oil/water mixture was determined according to the method of ASTM D95-83(1990), using toluene as a solvent. In this case, the yield of oil and water can be separately obtained. The volume of gas was measured by the wet type flowmeter. From the gas volume, the gas mass and yield can be determined.

The experimental conditions of the solid heat carrier pyrolysis process are listed in Table 3.

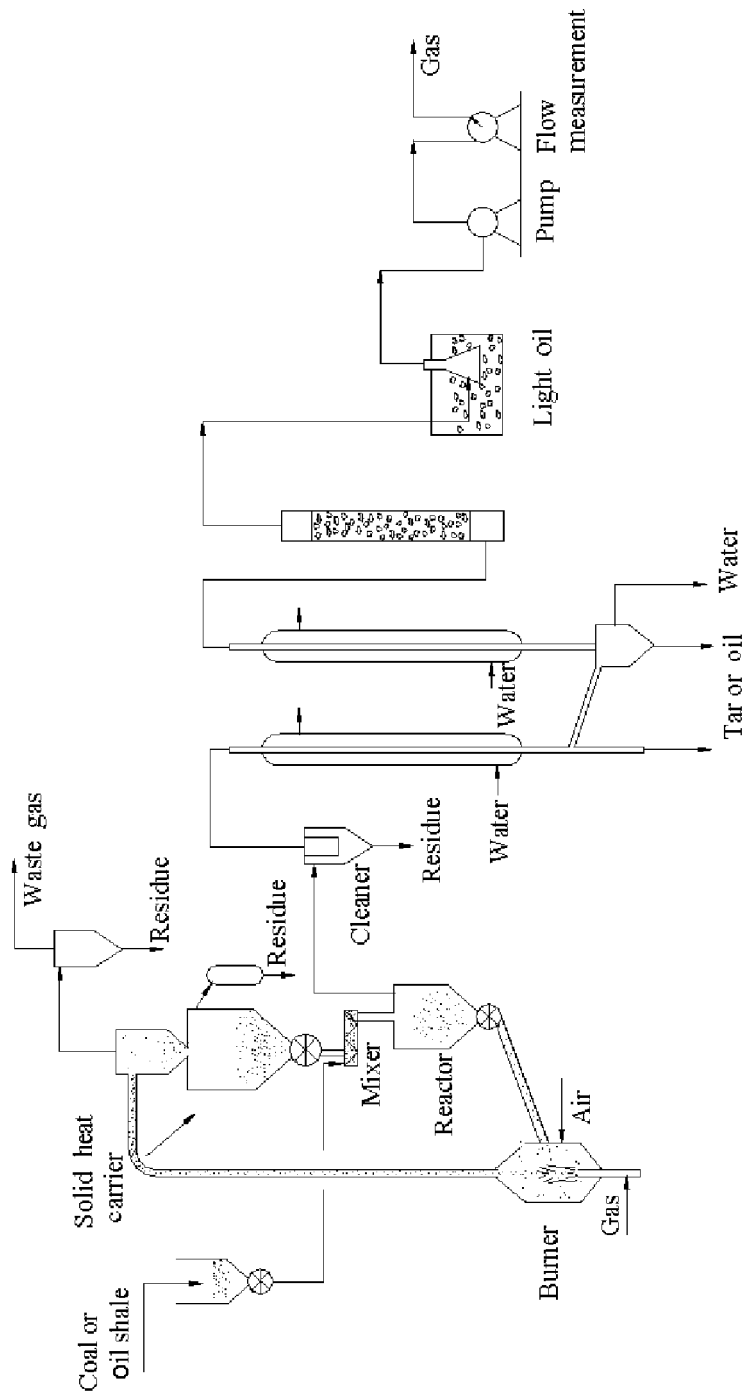


Fig. 2. Flow diagram of rapid pyrolysis equipment with solid heat carrier.

Table 3. Experimental conditions of solid heat carrier pyrolysis process

Experimental conditions	
Sample, (as received), kg/h	5–7
Sample particle size, mm	0–6
Hot heat carrier temperature, °C	560–685
Reaction temperature, °C	450–600
Sample temperature, °C	120–135
Condensate trap for light oil temperature, °C	–20...–30
Pyrolysis pressure, MPa	Ambient

3. Results and discussion

3.1. Fixed-bed pyrolysis experimental

Table 4 presents the product yields in the fixed-bed pyrolysis of LKO.

As expected, pyrolysis temperature greatly affects oil yield. The experiment results indicate that the oil yield of LKO is first increased and then decreased while pyrolysis temperature increased. It can also be seen that with increasing temperature, the char yield decreases and gas yield shows an increasing trend. The maximal oil yield of LKO is 18.9% at a pyrolysis temperature of 560 °C.

Table 5 shows the product yields in the fixed-bed pyrolysis of HLHC.

It can be seen that in pyrolysis of both HLHC and LKO the pyrolysis temperature has a similar effect on product yields. The char yield decreases with the increase of pyrolysis temperature. The tar yield in the fixed-bed pyrolysis increases with increasing pyrolysis temperature and reaches the maximum at 540 °C, and then decreases with the further increase of pyrolysis temperature.

Table 4. Product yields in the fixed-bed pyrolysis of LKO

Pyrolysis temperature, °C	Oil yield, %	Water yield, %	Char yield, %	Gas yield and loss, %
450	13.3	10.0	71.75	4.95
470	17.0	9.0	70.05	3.95
490	17.0	9.5	69.5	4.0
510	16.95	10	68.1	4.95
530	18.35	9.0	67.8	4.85
560	18.9	9.5	66.45	5.15
580	18.4	9.5	67.3	4.8

Table 5. Product yields in the fixed-bed pyrolysis of HLHC

Temperature, °C	Oil yield, %	Water yield, %	Char yield, %	Gas yield and loss, %
490	8.75	37	47.75	6.5
510	8.8	37.5	47.1	6.6
540	9.45	36.5	46.15	7.9
560	8.7	37	46.35	7.95
580	8.5	37.5	45.75	8.25

Co-pyrolysis of LKO and HLHC in the fixed-bed reactor at a temperature of 510 °C was also investigated. Table 6 shows the results.

Table 6. Product yields in the fixed-bed co-pyrolysis of LKO and HLHC

Coal in the mixture, %		0	10	20	30	40	50	100
Oil yield, %	Experimental	16.95	17.05	18.65	18.15	12.90	13.20	8.80
	Calculated	16.95	16.14	15.32	14.51	13.69	12.88	8.80
Water yield, %	Experimental	10.00	12.00	12.50	13.00	21.50	23.00	37.50
	Calculated	10.00	12.75	15.50	18.25	21.00	23.75	37.50
Char yield, %	Experimental	68.10	66.20	64.70	62.40	59.60	58.15	47.10
	Calculated	68.10	66.00	63.90	61.80	59.70	57.60	47.10
Gas yield, %	Experimental	4.95	4.75	4.15	6.45	6.00	5.65	6.60
	Calculated	4.95	5.12	5.28	5.44	5.61	5.78	6.60

These results imply that the synergetic effect existed when the oil yield increased and water yield decreased, and varied with the changing mass percentage of coal in the mixture. The oil yields of LKO and HLHC in the fixed-bed co-pyrolysis are higher than the calculated oil yield. With the increase of the percentage of coal in the mixture the char yield decreases and water yield increases. The optimum percentage of coal in the mixture is 20%.

As known, the bridge bonds rupture in coal structure results in the formation of a large amount of free radicals during coal pyrolysis. These free radicals are stabilized to form volatiles, including tar and gas products, when combining with other small free radicals such as H radical; otherwise the free radicals themselves will recombine to form char or tar [13]. The H/C atomic ratio of oil shale is higher than that of coal. In co-pyrolysis oil shale provides more H free radicals which are favourable to stabilize the free radicals from coal, so the tar yield in pyrolysis is higher than its calculated yield [14].

3.2. Continuous mode pyrolysis experimental (rapid pyrolysis process using solid heat carrier)

Pyrolysis and co-pyrolysis of LKO and HLHC were also carried out in a 10 kg/h rapid pyrolysis equipment in a continuous mode as shown in Figure 2. The sample for co-pyrolysis was a mixture with 20% of HLHC. The temperature for pyrolysis and co-pyrolysis was 510 °C. Table 7 lists product yields in the pyrolysis and co-pyrolysis of LKO and HLHC.

The results indicate that the experimental oil yields in the continuous mode co-pyrolysis of LKO and HLHC are higher than the calculated yields of oil and light oil. The synergetic effect was found to exist when the oil yield increased by 11.9% and water yield decreased by 36% compared with their calculated yields, respectively.

The composition of the gas of pyrolysis with solid heat carrier at optimum temperature is shown in Table 8.

Table 7. Product yields in pyrolysis and co-pyrolysis of LKO and HLHC in the rapid pyrolysis equipment at 510 °C

Sample	Oil yield, %	Light oil yield, %	Char yield, %	Gas yield		Water yield ¹⁾ , %	Burn-up and loss ²⁾ , %
				%	dm ³ /kg sample		
LKO	12.44	0.56	62.46	8.56	74.68	8.50 (3.33)	7.48
HLHC	5.82	0.15	42.12	14.57	115.0	34.23 (6.74)	3.11
Calculated yield from co-pyrolysis	11.12	0.48	58.39	9.76	82.74	13.45(4.0)	6.80
Experimental yield from co-pyrolysis	12.44	0.54	62.59	9.97	85.49	12.18 (2.55)	2.28

¹⁾ – in parentheses pyrolyzed water yield; ²⁾ – by difference.

Table 8. Composition of the gas of pyrolysis and co-pyrolysis in the rapid pyrolysis equipment at 510 °C, vol%

Sample	CH ₄	CO	H ₂	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	Caloric value, MJ·kg ⁻¹
LKO	19.23	8.17	24.08	33.38	4.80	5.09	5.25	21.62
HLHC	21.52	12.43	16.50	43.84	1.07	2.58	1.80	15.05
Co-pyrolysis	21.94	8.41	21.15	36.05	4.38	4.97	3.10	19.95

It can be seen that the percentage of H₂ in the gas of co-pyrolysis is less than that in the gas of pyrolysis of oil shale only. Table 8 shows that in co-pyrolysis of oil shale and coal some hydrogen may transfer from oil shale to coal.

4. Conclusions

LKO and HLHC are ideal materials for oil recovery by pyrolysis, affording high oil yields. In pyrolysis and co-pyrolysis of oil shale and coal in the fixed-bed reactor the synergetic effect existed when the oil yield increased and water yield decreased, and varied with the changing mass percentage of coal. Co-pyrolysis of LKO and HLHC in the rapid pyrolysis equipment shows the same trend, the oil yield increased by 11.9% and water yield decreased by 36% compared with their calculated yields. The results indicated that during co-pyrolysis some hydrogen may transfer from oil shale to coal.

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