Article ID: 0253-2409(2007)01-0001-04

Coal pyrolysis under synthesis gas, hydrogen and nitrogen

ARIUNAA A[1,2], LI Bao-Qing[1], LI Wen[1], PUREVSUREN B[2], MUNKHJARGAL Sh[2], LIU Fen-rong[1], BAI Zong-qing[1], WANG Gang[1]

(1. *State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan* 030001, *China*; 2. *Mongolian Academy of Sciences, Ulaanbaatar* 210351, *Mongolia*)

Abstract: Chinese Xundian, Mongolian Shiveeovoo lignites and Khoot oil shale are pyrolyzed under synthesis gas (SG) at temperature range from 400 ℃ to 800 ℃ for lignite and from 300 ℃ to 600 ℃ for oil shale with heating rate of 10 ℃/min in a fixed bed reactor. The results were compared with those obtained by pyrolysis under hydrogen and nitrogen. The results showed that unlike pyrolysis at high pressure, there are only slight different in the yields of char and tar among pyrolyses under various gases at room pressure for lignite, while higher liquid yield with lower yields of char and gas was obtained in pyrolysis of oil shale under SG and H_2 than under N_2. It is found that the pyrite S can be easily removed to partially convert to organic S under various gaseous atmosphere and the total sulfur removal for oil shale is much less than lignite, which might be related to its high ash content. The higher total sulfur removal and less organic S content in the presence of SG in comparison with those under N_2 and even under H_2 in pyrolysis of Xundian lignite might result from the action of CO in SG. However, CO does not show its function in pyrolysis of Khoot oil shale, which might also be related to the high ash content. The results reported show the possibility of using synthesis gas instead of pure hydrogen as the reactive gas for coal hydropyrolysis.

Key words: pyrolysis; synthesis gas; desulfurization
CLC number: TQ530.2 **Document code**: A

China and Mongolia are the countries of lack of oil source with relative rich in coal resource. How to convert coal into oil is a major project in both countries, which will affect the national safety and the economic sustainable development.

Hydropyrolysis (HyPy) is a pyrolysis process under hydrogen. Compared with pyrolysis under inert gas, the quantity and quality of tar are improved, and low sulfur char is produced in HyPy due to that the thermally released free radicals can be stabilized by capturing hydrogen to produce tar with low molecular weight compounds and that most sulfur in coal can be removed as gaseous H_2S[1,2]. Thus, HyPy provides a route for the production of liquid from coals and extensive studies on HyPy have been reported. However, because of the high cost of pure hydrogen, HyPy is not a feasible process and coal pyrolysis using cheaper hydrogen rich gases such as coke-oven gas (COG) and synthesis gas (SG) in stead of pure hydrogen has been proposed[3]. Pyrolysis under COG was investigated more detail in our lab, however, pyrolysis under SG was less studied especially for oil shale[4,5]. For increasing coal utilization efficiency and mitigate the pollution, multi-generation process has been proposed as the future clean coal technology, which is mainly based on coal gasification with synthesis gas production[6]. Thus, it might be possible to pyrolyze coal under SG as the 1st step in the multi-generation technology.

The purpose of this work is to study the possibility of using SG instead of pure hydrogen as the reactive gas for pyrolysis of coal and oil shale. The results will be compared with those obtained in pyrolysis under H_2 and N_2. The desulfurization in pyrolysis under SG is also investigated.

1 Experimental

1.1 Samples Mongolian Shiveeovoo lignite, Khoot oil shale and Chinese Xundian lignite with particle size from 60 to 80 mesh were used in this study. Their characteristics including approximate and elemental analyses, the sulfur form and ash composition are shown in Tables 1 ~ 3.

Table 1 Proximate and ultimate analysis of samples

Sample	Proximate analysis w_{ar}/%			Ultimate analysis w_{db}/%					H/C
	M	A	V	C	H	N	S	O*	atom. ratio
Shiveeovoo	10.89	16.10	34.16	54.95	4.70	1.55	0.51	20.22	1.03
Xundian	10.00	15.92	46.42	53.39	4.39	1.09	1.64	21.79	0.99
Khoot	3.40	83.11	13.13	6.86	1.08	0.32	1.40	4.38	1.89

* -by difference

Received date: 2006-06-13; **Received in revised form**: 2006-09-08
Corresponding author: LI Bao-Qing, propessor, maijor: coal science. E-mail: libq@sxicc.ac.cn.
Author introduction: Alex Ariunaa, female, Ph.o. student, maijoring in coal chemistry. E-mail: a_a_ariunaa@yahoo.com.

Table 2 Sulfur forms of samples (w_{db}/%)

Samples	S_t	S_p	S_s	S_o
Xundian coal	1.64	1.00	0.63	0.01
Khoot oil shale	1.40	1.14	0.20	0.06

Synthesis gas was produced by methanol decomposition and provided by the Institute of Coal Chemistry with the following composition (vol%): H_2, 64.82%; CO, 31.60%; CH_4, 2.43%; CO_2, 0.64% and N_2, 0.51%.

Table 3 Ash composition of the Khoot oil shale (w/%)

SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	K_2O	P_2O_5	MgO	TiO_2
55.8	14.5	6.15	13.6	1.22	2.58	0.06	3.93	0.56

1.2 Pyrolysis Pyrolysis test was performed in a quartz tube reactor containing 5 g coal samples or 10 g Mongolian Khoot oil shale samples at temperature ranging from 400 ℃ to 800 ℃ for coal and from 300 ℃ to 600 ℃ for oil shale with a heating rate of 10 ℃/min and a flow rate of 150 mL/min under SG, H_2 and N_2 atmospheres at the atmosphere pressure. The liquid containing tar and water was collected in a cold trap. The gases were sampled regularly and analyzed by GC. After reaction the char was weighted and collected. The sulfur removal (SR) was calculated according to the following equation:

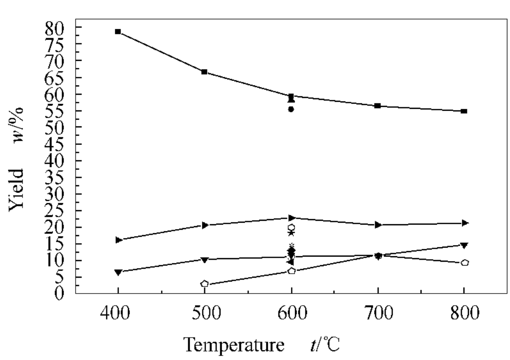
$$SR = \frac{S_{t,coal} - S_{t,char} \times Y}{S_{t,coal}} \times 100\%$$

where, $S_{t,coal}$: total sulfur in raw coal; $S_{t,char}$: total sulfur in char; Y: yield of char.

The Eschka analytical procedure was used to determine the total sulfur in coal and chars. The sulfur forms in coal and char was analyzed according to GB-215-82. Briefly, sulfate S was extracted with HCl and measured gravimetrically, and then the residue was further extracted with HNO_3 to determine pyrolytic S. The content of organic S was calculated by subtraction of the inorganic S from the total S.

2 Results and discussion

2.1 Pyrolysis under SG, H_2 and N_2 Figure 1 show the product yields in pyrolysis of Mongolian Shiveeovoo and Chinese Xundian lignites at different temperature under H_2, SG and N_2. It seems that unlike pyrolysis at high pressure[4], there are only slight different in the yields of char and tar among pyrolyses under various gases at atmosphere pressure for both lignites, indicating that gaseous hydrogen shows its notable hydrogenation ability only at high pressure. It is also found that water yield is higher for both lignites due to their high oxygen content. Compared with Shiveeovoo lignite, tar yield is higher for Xundian lignite, which should be related to its higher content of volatile matter.



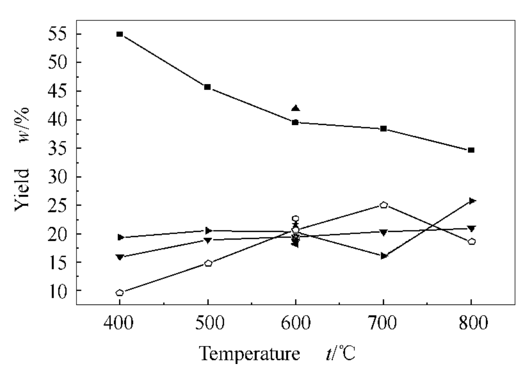


Figure 1 Product yields in pyrolysis of Shiveeovoo (left) and Xundian (right) lignites under SG, H_2 and N_2
■char under SG; ▶water under SG; ●char under H_2; ⬡water under H_2; ▲char under N_2; ★water under N_2; ▼tar under SG; ⬠gas under SG; ◆tar under H_2; ○gas under H_2; ◀tar under N_2; ✳gas under N_2;

Product yields in pyrolysis of Khoot oil shale under H_2, SG and N_2 at 600 ℃ is shown in Table 4. Due to high ash content in Khoot oil shale, the amount of liquid after pyrolysis was not enough to separate the water and tar. In comparison with lignite from Figure 1, marked difference in product yield is found in pyrolysis under various gases, i. e., higher liquid yield with lower yields of char and gas was obtained in pyrolysis under SG and H_2 than under N_2. Table 1 indicates that the molecular ratio of H/C in oil shale reaches higher than 1.8, while only about 1.0 for lignite, showing that oil shale mainly contains aliphatic structure, which can be thermally decomposed to form free radicals and then be hydrogenated easily by gaseous hydrogen at even normal pressure. The conversion of oil shale during pyrolysis is much higher than that of lignite as shown in Figure 2. It is also found that there is no significant difference between the product yields in both pyrolyses under SG and H_2, implying that SG can replace H_2 in pyrolysis of oil shale and lignite.

Table 4　Product yields in pyrolysis of Khoot oil shale under H_2, SG and N_2 at 600 ℃

Atmosphere	Product distribution w_{daf}/%		
	char	liquid	gas
SG	25.8	66.3	7.9
H_2	25.6	67.9	6.5
N_2	32.4	52.4	15.2

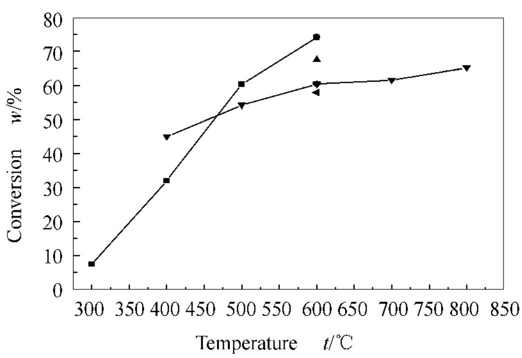


Figure 2　Comparision of conversion in pyrolysis under SG, H_2, and N_2
■Khoot in SG; ●Khoot in H_2; ▲Khoot in N_2; ▼Xundian in SG; ◆Xundian in H_2; ◀Xundian in N_2;

2.2　Desulfurization　Figures 3 ~ 4 and Tables 5 ~ 6 show the desulfurization of Xundian coal and Khoot oil shale, and the removal of various sulfur forms in pyrolysis under various gases. It is found that more than 90% of pyrite S was removed for both samples despite of different samples and various atmospheres, indicating that pyrite S can be easily removed. The total sulfur removal of oil shale is much less than that of lignite, which may be related to the high ash content especially the alkaline-earth minerals that can trap H_2S liberated during pyrolysis[7]. It is found that the organic sulfur in both samples increases in pyrolysis under various gases. The increasing trend of pyrite S removal with increasing temperatures seems to be identical with the increase of organic S in pyrolysis of oil shale and lignite as shown in Table 5 and 6, implying that the sulfur released in pyrite decomposition during pyrolysis could react with the organic char matrix and get incorporation in coal matrix[8]. It is also found that the total sulfur removal is higher in the presence of SG in comparison with that under N_2 and even under H_2 in pyrolysis of Xundian lignite. More sulfur including decomposition of pyrite S and partial organic S might react with CO to form COS[7], leading to high desulfurization in the presence of SG. The less content of organic S in lignite char obtained by pyrolysis under SG in comparison with those under H_2 and N_2 may also prove the action of CO in SG. However, CO does not show its function in pyrolysis of Khoot oil shale, which may also be resulted from the high ash content, especially its high content of CaO as shown in Table 3. It was reported that the addition of CaO had remarkable effect on reducing H_2S and COS throughout the whole pyrolysis temperature[9]. The minerals in coal may catalyze the decomposition or inhibit the formation of COS[10,11].

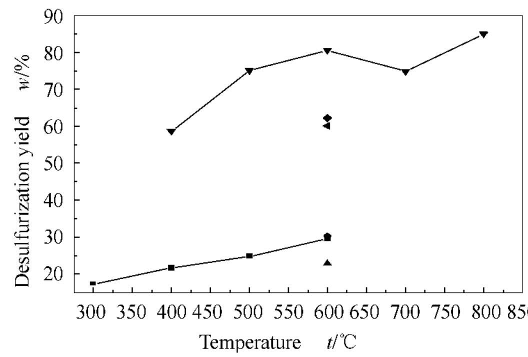


Figure 3　Desulfurization of total sulfur in pyrolysis of Khoot oil shale and Xundian lignite under SG, H_2 and N_2
■Khoot in SG; ●Khoot in H_2; ▲Khoot in N_2; ▼Xundian in SG; ◆Xundian in H_2; ◀Xundian in N_2;

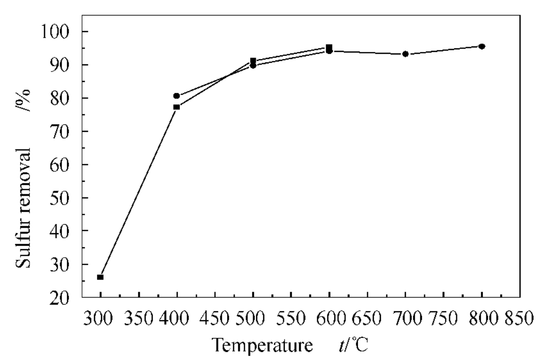


Figure 4　Desulfurization of pyrite sulfur in pyrolysis of Khoot oil shale and Xundian lignite under SG
■Khoot in SG; ●Xundian in SG

Table 5　Sulfur form and desulfurization in pyrolysis of Khoot oil shale under H_2, SG and N_2 at 600 ℃

Atmosphere	Sulfur forms w_{ar}/%				Desulfurization /%		
	S_t	S_p	S_s	S_o	SR_t	SR_p	SR_s
Raw coal	1.35	1.10	0.19	0.06			
SG	1.15	0.06	0.08	1.01	26.2	95.3	63.5
H_2	1.09	0.08	0.03	0.98	26.2	93.7	86.3
N_2	1.21	0.12	0.14	0.95	21.6	90.5	35.5

Table 6 Sulfur form and desulfurization in pyrolysis of Xundian lignite under H_2, SG and N_2 at 600 ℃

Atmosphere	Sulfur forms w_{ar}/%				Desulfurization /%		
	S_t	S_p	S_s	S_o	SR_t	SR_p	SR_s
Raw coal	1.48	0.90	0.57	0.01			
SG	0.64	0.12	0.11	0.41	80.5	94.0	91.3
H_2	1.24	0.03	0.21	1.00	62.1	98.5	83.3
N_2	1.25	0.06	0.23	0.96	60.3	96.9	81.0

3 Conclusions

Chinese Xundian lignite, Mongolian Shiveeovoo lignite and Khoot oil shale are pyrolyzed under synthesis gas atmosphere and the results were compared with those obtained by pyrolysis under hydrogen and nitrogen. Some conclusions can be drawn as follows:

(1) Unlike pyrolysis at high pressure, there are only slight different in the yields of char and tar among pyrolyses under various gases at room pressure for lignite, while higher liquid yield with lower yields of char and gas was obtained in pyrolysis under SG and H_2 than under N_2.

(2) The pyrite S can be easily removed to partially convert to organic S under various gaseous atmospheres and the total sulfur removal for oil shale is much less than lignite, which might be related to its high ash content.

(3) The higher total sulfur removal and less organic S content in the presence of SG in comparison with those under N_2 and even under H_2 in pyrolysis of Xundian lignite might result from the action of CO in SG. However, CO does not show its function in pyrolysis of Khoot oil shale, which might also be related to the high ash content, especially its high content of CaO.

(4) The results reported show the possibility of using synthesis gas instead of pure hydrogen as the reactive gas for coal hydropyrolysis.

Acknowledgements: We would like to thank the National Natural Science Foundation of China (90410017) and The Third World Academy of Sciences in Italy (Fellowship for A. Ariunaa) for their financial support..

References

[1] MASTRAL A M, PEREZ-SURIO M J. Coal hydropyrolysis in swept fixed bed reactor: Influnce of the coal bed height on the distribution and nature of the hydroconversion products[J]. Energy Fuels, 1997, **11**(1): 202-205.
[2] XU W-C, MATSUOKA K, AKINO K, KUMAGAI M, TOMITA A. High pressure hydropyrolysis of coals by using a continuous free-fall reactor[J]. Fuel, 2003, **82**(6): 677-685.
[3] CYPRES R, MINGEL W, LARDINOIS J-P, LAUDET A, MASSON H. Feasibility study of the hydropyrolysis of coal, EUR 14110[R]. Luxembourg: Commission of the European Communities, 1992.
[4] LIAO H-Q, LI B, ZHANG B. Co-pyrolysis of coal with hydrogen-rich gases: 1 Coal pyrolysis under coke-oven gas and syuthesis gas[J]. Fuel, 1998, **77**(8): 847-851.
[5] LI W, WANG N, LI B. Process analysis of catalytic multi-stage hydropyrolysis of lignite[J]. Fuel, 2002, **81**(11-12): 1491-1497.
[6] PRC STATE COUNCIL. National long-term scientific and technological development program. www.gov.cn/jrzg/2006-02/09/content_183787.htm.
[7] CYPRES R, FURFARI S. Hydropyrolysis of a high-sulphur-high-calcite Italian Sulcis coal: 1 Hydropyrolysis yields and catalytic effect of the calcite[J]. Fuel, 1982, **61**(5): 447-452.
[8] CHEN H, LI B, ZHANG B. Decomposition of pyrite and the interaction of pyrite with coal organic matrix in pyrolysis and hydropyrolysis[J]. Fuel, 2000, **79**(13): 1627-1631.
[9] GUAN R, LI W, LI B. Effects of Ca-based additives on desulfurization during coal pyrolysis[J]. Fuel, 2003, **82**(15-17): 1961-1966.
[10] CHEN H, LI B, ZHANG B. Effects of mineral matter on products and sulfur distributions in hydropyrolysis[J]. Fuel, 1999, **78**(6): 713-719.
[11] KARACA S. Desulfurization of a Turkish lignite at various gas atmospheres by pyrolysis: Effect of mineral matter[J]. Fuel, 2003, **82**(12): 1509-1516.

煤在合成气、氢气和氮气气氛下的热解研究

ARIUNAA A[1,2], 李保庆[1], 李　文[1], PUREVSUREN B[2], MUNKHJARGAL Sh[2],
刘粉荣[1], 白宗庆[1], 王　刚[1]

(1. 中国科学院山西煤炭化学研究所 煤转化国家重点实验室,山西 太原 030001;2. 蒙古科学院化学与化学工艺研究所,乌兰巴托,蒙古)

摘　要:采用固定床反应器,在合成气气氛下对中国寻甸褐煤、蒙古 Shiveeovoo 褐煤和 Khoot 油页岩进行了热解研究。升温速率 10 ℃/min,褐煤热解温度 400 ℃ ~800 ℃,油页岩热解温度 300 ℃ ~600 ℃,研究结果与氢气和氮气气氛下的热解进行了比较。结果表明,与加压热解不同,褐煤在不同气氛下常压热解半焦和焦油收率差别不大,但对油页岩,合成气和氢气气氛下热解焦油收率高于氮气,气体收率低于氮气。黄铁矿硫在不同气氛下热解均极易脱除,并部分转化为有机硫。油页岩的总硫脱除率远低于褐煤,与油页岩的高灰分含量有关。与氮气甚至氢气相比,合成气下寻甸褐煤的高总硫脱除率和低有机硫含量与合成气中的 CO 有关。但 CO 在油页岩热解脱硫中不起作用,也与油页岩高灰分含量有关。研究结果也表明合成气可代替氢气进行加氢热解。

关键词:热解;合成气;脱硫

中图分类号:TQ530.2　　**文献标识码**:A