Pyrolysis Products Properties from Lignite

YING XU, GUOJIE ZHANG, LEI CHEN, XIAOKUO DING and YONGFA ZHANG*

Key Laboratory of Coal Science and Technology, Ministry of Education and Shanxi Province, Taiyuan University of Technology, Taiyuan 030024, P.R. China

*Corresponding author: Tel/Fax: +86 351 601 8676; E-mail: yongfaz@tyut.edu.cn; zhgjdoc@126.com

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Temperature-programmed pyrolysis of lignite was investigated. The aim of this research was to determine the pyrolysis product distribution and product evolution rate during low temperature pyrolysis of lignite as a function of temperature. The pyrolysis products were analyzed by capillary gas chromatography, gas chromatography-mass spectroscopy (GC-MS) and Brunauer-Emmetteller method. The pyrolysis experiments were performed under a heating rate of $10^{\circ}\text{C min}^{-1}$ from room temperature to a final 600°C and kept 0.5 h at this temperature. The Hulun Bair lignite studied in this work is characterized by high content of H and O. The low rank coal of the sample influences on the low temperature pyrolysis properties. The product productivity obtained during the pyrolysis experiments show that low temperature pyrolysis process can obtain high yield of water, gas and tar.

Key Words: Lignite, Low temperature pyrolysis, Products.

INTRODUCTION

The pyrolysis process is important because of the fact that it involved in every process of coal conversion and utilization¹. Coal pyrolysis is the basic process of coke making and the initial, accompanying reaction of a number of coal conversion processes such as hydrogenation, combustion and gasification. However, because of the inherent complexity of coal composition, it is difficult to describe coal pyrolysis clearly. If, pyrolysis, performed under defined conditions, is an useful tool for the elucidation of coal structure and for the assessment of its molecular reactivity².

Products from this process are used for industrial purposes (semicoke in the steel industry, tar in the chemical, gas in the power industry) and in environmental technologies (sorbents for treatment of sewage, gas purifying, *etc.*). In all of these areas, they provide most essential materials³.

Many researches on coals have been carried out to investigate the evolutionary features of the gas, tar and char, respectively⁴⁻⁸, but researches on the evolutionary features of all products in coal pyrolysis (gas, tar, water, semi-char), especially researches on the evolutionary features of products in lignite pyrolysis were not reported to our best of knowledge.

Previous studies of low-rank lignite pyrolysis have dried the lignite at 100°C for long time before pyrolysis⁹⁻¹². This process may have a marked effect on the structure of lignites¹³ which might carry over and affect the pyrolysis products. Accordingly, in this study, raw lignite was used as the sample coals.

The aim of the present study is to obtain information for the composition of the products (gas, liquid and semi-char) and especially for the relationship between the temperature and the products releasing characteristic during the raw lignite low temperature pyrolysis.

EXPERIMENTAL

Coal sample and characteristics: The investigations were performed on lignite sample taken from the deposit near Hulun Bair of Neimen province, China. The results of proximate and ultimate analysis of the lignite are given in Table-1. For pyrolysis experiments, the samples were crushed and ground in a jaw mill until the desired particle size was obtained.

TABLE-1
PROXIMATE AND ULTIMATE
ANALYSIS OF LIGNITE (AIR DRIED)

Proximate analysis (%)			Ultimate analysis (%)				
Moisture	Ash	Volatile matter	C	H	O	N	S
18.60	11.83	35.09	50.77	3.57	14.19	0.79	0.26

Pyrolysis procedure: A schematic diagram of the experimental equipment is given in Fig. 1.

The pyrolysis was performed in an electrically heated pyrolysis stove consisting of a silex reactor tube (40 mm i.d 500-mm-long). The sample (lignite, 20 g) was transferred to

Fig. 1. Flow diagram for experimental equipment. 1. Thermograph. 2. Thermocouple. 3. Pyrolysis stove. 4. Coal charge. 5. Bottle for liquid. 6. Bottle for gas. 7. Water outlet. 8. Pressure regulator

the reactor tube. The silex reactor tube was placed in a temperature-programmable furnace. The middle zone of heater was connected to a programmer and controller. Typically, temperature-programmed pyrolysis experiments were performed under a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ from room temperature to a final $600\text{ }^{\circ}\text{C}$ and kept 0.5 h at this temperature.

Product analysis: The GC-MS analysis of liquid product was carried out by using an Agilent Technologies 6890 GC-Agilent 5973 Inert mass selective detector system. A HP-5 ms model capillary column ($30\text{ m} \times 0.25\text{ mm}$; $0.25\text{ }\mu\text{m}$ film thickness) was used in analysis. The initial oven temperature was $45\text{ }^{\circ}\text{C}$ held for 10 min and then programmed from $45\text{--}190\text{ }^{\circ}\text{C}$ at $12\text{ }^{\circ}\text{C min}^{-1}$ with an isothermal held for 2 min . Temperature was raised at $6\text{ }^{\circ}\text{C min}^{-1}$ to $225\text{ }^{\circ}\text{C}$ where it was held for 1 min . Finally, the oven temperature was increased to $250\text{ }^{\circ}\text{C}$ at $3\text{ }^{\circ}\text{C min}^{-1}$ with an isothermal held for 5 min . Helium was employed as a carrier gas at a constant flow rate of 1 mL min^{-1} . Liquid product was injected to the system. The chromatographic peaks were identified by using Nist 98 library.

Additionally, a Sorptomatic 1990 model sorptometer was used to determine the Brunauer-Emmett-Teller (BET) surface area of solid products (semi-coke). Prior to analyses, the solid products were degassed in helium atmosphere for duration of 6 h .

The concentrations of O_2 , N_2 , CH_4 , CO , CO_2 , C_2H_4 , C_2H_6 and H_2 in the reactor effluent were characterized by GC.

RESULTS AND DISCUSSION

Production of low temperature pyrolysis products: The primary volatiles are formed in the coal matrix during pyrolysis and they took part in competing recombination, cracking and de-volatilization. The primary volatile participated in transport of the volatile to the external surface of coal particles, removal of the volatile from the external surface of the coal into the bulk gas phase and transport of the volatile in the gas phase from the hot zone to cool parts of the system¹⁴. In pyrolysis, coal is converted thermally into gas, liquid and solid products through primary de-volatilization reactions. The pyrolysis products of Hulun bair lignite are shown in Table-2.

TABLE-2 ANALYSIS OF PRODUCTIVITY OF PYROLYSIS PRODUCT				
Pyrolysis product	Gas	Tar	Water	Semi-coke
Content mass fraction (%)	17.56	8.64	21.34	52.46

Table-2 shows the high yield of H_2O (21.34%) in pyrolysis process which was in agreement with Hulun Bair lignite's high

moisture ($M_{\text{ad}} = 18.60\%$) and the high yields of gas and tar products imply that using the low temperature pyrolysis process is a resultful way to upgrading lignite such as: (a) added value to the semi-char, called processes derived fuel, as the result of moisture and volatile matter removal with the accompanying increase in heating value; (b) added value in the form of the tar, called coal derived liquid, which may be refined into transportation fuels and other products; a reduction in unit transportation costs as a result of moisture and volatile matter removal and reduction in emission of sulfur dioxide, NO_x and mercury at facilities that use the processes derived fuel.

Releasing characteristic of gas products: The effects of time on the gas yield and rate of gas product evolution during the pyrolysis of lignite are shown in Fig. 2.

Fig. 2. Pyrolysis gas productivity characteristic during lignite pyrolysis

The pyrolysis gas yield can be obtained from the volume of discharged water from the cylinder while the component and content of the gas can be given from the GC analysis result. Fig. 2 showed that the gas yield raised up sharply over $400\text{ }^{\circ}\text{C}$ and the maximum gas yield rate appeared at *ca.* $520\text{ }^{\circ}\text{C}$. The gas products began to evolution at about $90\text{ }^{\circ}\text{C}$ and the final yield of gas products arrived to 17.56% during the pyrolysis. The gas between 90 and $300\text{ }^{\circ}\text{C}$ showed slowness climbing emissions accompany with a small quantity of adsorbed gases such as O_2 and N_2 in the coal. The content of O_2 and N_2 decreased along with the pyrolysis temperature and the pyrolysis gas yield rate decreased simultaneity before CO_2 , CO released. In the case of low rank coals, CO_2 is formed from aliphatic and aromatic carboxyl and carboxylate groups at a low temperature¹⁵. Ether linkages and a number of other functional groups, including phenolic-OH, quinones and epoxides, could also be expected to yield CO on thermal decomposition¹⁶.

As the pyrolysis temperature raised up to $470\text{ }^{\circ}\text{C}$, the pyrolysis gas yield rate raised sequentially, because the release of CO , CO_2 , H_2 and CH_4 increased quickly accompany with a small quantity release of C_2H_4 , C_2H_6 derived from thermally more stable ether structures, quinones and oxygen-bearing heterocycles with the subsequent condensation of aromatic structures, which is associated with the formation of mainly CO , H_2 and CH_4 ¹⁵. However, C_2H_4 and C_2H_6 began to evolve

over 500 °C, due to alkyl higher than C₃ groups breaking off from the macromolecular network, oxygen atom have been cemented out from carbon atom¹⁷.

When the lignite suffers from pyrolysis, it begin break-down thermally to form low-molecular weight fragments and the reactions involved in the process include cleavage and ring opening of large molecules¹⁴.

The gas products releasing sequence were CO₂, CO, CH₄, H₂, C₂H₄ and C₂H₆ in turn during the lignite pyrolysis process, it is corroborated by the result of GC analysis.

After temperature-programmed pyrolysis experiments, agitating the gas product with a stirring implement, the analysis of component in pyrolysis gas was presented in Table-3.

Table-3 showed that the gas yield in pyrolysis process (lignite, 20 g) was 2488.2 mL (gross calorific value 38.83 kJ). Thus the gas yield of low temperature pyrolysis was 124.41 m³ t⁻¹ raw lignite and the calorific value of the gas was 19.41 × 10² MJ t⁻¹ raw lignite. The result shows that the low-temperature lignite pyrolysis may obtain a high gas product yield with high calorific value and high CH₄ yield which are helpful in converting the gas product to substitute natural gas (SNG) and may alleviate the shortage supply of natural gas energy to some extent.

Releasing characteristic of water products: Fig. 3 displays the evolution of H₂O during thermal decomposition. It can be found that during the temperature programmed pyrolysis, water was released over a wide temperature range and the total water yield was up to 21.34 %. Simultaneously, H₂O was released in two clearly differentiated phases: the first corresponded to the 100-200 °C temperature range and the second phase took place above 200 °C and the production is decreased gently. The water yield below 200 °C reflected the moisture (M_{ad} = 18.60 %) of the samples. The evolution rate of H₂O at higher temperature was in agreement with Hulun Bair lignite's high oxygen content (O_{ad} = 14.19 %). As the pyrolysis temperature increased above 300 °C, the H₂O evolution was produced by decomposition of various oxygen-containing groups mainly OH groups¹⁸.

Fig. 3. Water generating characteristic during lignite pyrolysis

Releasing characteristic of tar products: In general, coal structures are composed of structural units (*e.g.*, aromatic and hydroaromatic clusters linked by alkyl or etheric bridges) joined together by either weak or strong linkages to form a three-dimensional macromolecular network. In pyrolysis process, the weakest bridges break in the first instance, producing molecular fragments that will be released as tar. It is well known that the lower the rank of the coals, the more dissimilar the evolved tars are to the parent coal¹⁹. However, low temperature pyrolysis tars are considered to be structurally in connection with original coals on account of they contain structures and functional groups that are present in the parent coal²⁰.

The effect of temperature and time on the rate of tar evolution during the pyrolysis of lignite was shown in Fig. 4.

Fig. 4. Tar generating characteristic during lignite pyrolysis

Fig. 4 indicates that the tar release temperature was about 350 °C and the yield of the tar was holding increasing slowly until the end of the pyrolysis processing. The tar yield rate arrived the highest value of 0.31 wt % min⁻¹ between the temperature 550 and 600 °C and the final tar yield arrived to 8.64 % in the whole pyrolysis process.

GC-MS analysis was carried out with the tar. Prior to injection, the diswater tar (85.01 wt. % of the primary tar) was distilled with different temperature region (< 170 °C, 170-220 °C, 220-270 °C, 270-310 °C, 310-340 °C and > 340 °C), among which, the distillate that >340 °C *i.e.*, asphaltum was 12.28 wt. % of the distilled tar. The major constituents of organic compounds in pyrolysis liquid products released during temperature-programmed pyrolysis of lignite were searched by GC-MS with the aid of Nist 98 library and the resulting probable compound list was given in Table-4.

The main compounds identified by means of GC-MS were: phenol, naphthalene, fluorene, phenanthrene, methyl, dimethyl and trimethyl derivatives, benzofluorene and aliphatic compounds. Because the Hulun Bair lignite is a low rank of coal with high-volatile, the GC-MS studied shows that there were a clear series of n-alkanes from C₁₀ to C₃₀ and a greater amount of aliphatic species which has been associated

TABLE-3
ANALYSIS OF COMPONENT IN PYROLYSIS GAS

	O ₂	N ₂	CH ₄	CO	CO ₂	C ₂ H ₄	C ₂ H ₆	H ₂
Content of gas volume fraction (%)	0.40	0.53	16.55	14.70	50.26	0.99	3.02	13.57

TABLE-4
ANALYSIS OF COMPONENT IN PYROLYSIS TAR

Number	Compound	Content of component in pyrolysis tar (%)				
		< 170 °C	170-220 °C	220-270 °C	270-310 °C	310-340 °C
1	Phenol	44.85	37.89	10.76	3.08	3.06
2	Alkane	13.26	17.44	36.88	74.26	47.40
3	Alkene	1.39	1.71	—	—	—
4	Cycloalkane	0.23	0.38	0.95	—	—
5	Aromatic hydrocarbon	23.59	26.33	31.15	21.89	35.33
6	Oxygenic compound(alcohol, ketone, aldehyde <i>et al.</i>)	5.94	10.20	17.96	—	7.39
7	Nitrogenous compound	1.59	1.22	—	—	6.82
8	Heterocyclic compound (indene <i>et al.</i>)	9.15	5.33	2.30	0.78	—

with the lower degree of coalification of the precursor¹⁹. This characteristic made it seem promising to utilize the low temperature pyrolysis tar into fuel.

Releasing characteristic of solid products: The effect of temperature and time on the rate of semi-char during the pyrolysis of lignite was shown in Fig. 5.

Fig. 5. Semi-coke generating characteristic during lignite pyrolysis

The yield of the semi-char was decreased evenly with the pyrolysis temperature increased. The semi-char yields were 58.08 and 52.46 wt. % while the temperature was 450 and 600 °C, respectively. Proximate and ultimate analysis of semi-char is given in Table-5.

After the two different temperature pyrolysis process, the carbon content of the semi-chars were 69.10-65.95 %, respectively, the hydrogen content and the oxygen content value were decreased slowly, while the elementary nitrogen content was not much different from that observed in the initial coal and the elementary sulfur content decreased slightly. However, both of these elements (N and S) were present in relatively small quantities in the initial coals. As might have been expected, the ash yields increased substantially because of the concentration of ash in the solid residues while the volatile yields decreased greatly.

As the result of moisture and volatile matter removal, the semi-char obtained a reduction in unit transportation costs. In addition, as a result of moisture and volatile matter removal, some facilities began to use the pyrolysis semi-char as derived fuel.

0.86, 19.23 and 52.86 m² g⁻¹ BET surface areas and 0.04, 0.05, 0.08 cm³ g⁻¹ pore specific volumes were measured for the solid products obtained at 400, 500 and 600 °C, respectively. With the increased of pyrolysis temperature, the BET surface area of semi-char correspond increased. The increase in surface area can be attributed to the more distorted surface which was caused by the removal of higher amounts of volatiles as the pyrolysis temperature increases. And the reactivity of lignite increased with the temperature similarly. To accompany the amounts of volatiles further removal, the reaction go deep into the internal of lignite. Micro-pores and capillary-pores develop further and cause the pore specific volumes increased significantly.

In accordance with the coal assumption of Van Krevelen²¹, some structural parameters and functional group concentration such as H/C, O/C H/C atomic ratios, aromatic factors (*f_a*), ring

condensation degree index $\frac{2(R-1)}{C}$ and average number of

condensation ring (*R*) can reveal the assessment of the average chemical structure of the fractions partially.

$$f_a = \frac{(100 - V_{daf}) \times 1200}{1240C_{daf}}$$

$$\frac{2(R-1)}{C} = 2 - f_a - \frac{H}{C}$$

f_a aromatic factors $\frac{2(R-1)}{C}$ ring condensation degree index,

R average condensation rings, *C*, *H* C, *H* atoms moles in per mole coal.

Table-6 shows the high H/C and O/C atomic ratios in the raw lignite; however, they decreased substantially because of the increasing amount of aliphatic in the solid residues while

TABLE-5
PROXIMATE AND ULTIMATE ANALYSIS OF SEMI-CHAR (AIR DRIED)

Sample	Proximate analysis (%)			Ultimate analysis (%)				
	Moisture	Ash	Volatile matter	C	H	O	N	S
Semi-char 500 °C	3.85	17.11	15.91	66.44	2.93	8.21	0.84	0.62
Semi-char 600 °C	2.43	23.40	10.45	64.35	2.46	6.16	0.79	0.41

TABLE-6
STRUCTURE PARAMETERS OF BROWN
COAL AND ITS PYROLYSIS SEMI-CHAR

Sample	Atomic ratios		Structure parameters		
	H/C	O/C	fa	R	$\frac{2(R-1)}{C}$
Lignite	0.84	0.21	0.50	2.52	0.50
Semi-char (500 °C)	0.53	0.09	0.92	2.93	0.55
Semi-char (600 °C)	0.46	0.07	0.96	3.10	0.58

the values of f_a and R increased greatly with the ring condensation degree index. These results shows that macromolecular network structure of the semi-char was composed of larger basic structural units instead of the smaller one which constituted the original coal, the number of the condensation rings and the dimension of the single ring became lager during the pyrolysis process. The C:H:O atomic ratio was also changed from 2.2:1:0.2 of original lignite to 1.6:1:0.4 of the 600 °C pyrolysis semi-char and this result shows that the unsaturated bonds number decreased with the pyrolysis process²².

Conclusion

The experimental results from the low temperature prolysis of the Hulun Bair lignite may be summarized as follows:

The HulunBair lignite studied in this work is characterized by high content of H and O. The low rank coal of the sample influences on the low temperature pyrolysis properties. The product productivity obtained during the pyrolysis experiments show that low temperature pyrolysis process can obtain high yield of water, gas and tar.

The gas products releasing sequence are CO₂, CO, CH₄, H₂, C₂H₄ and C₂H₆ in turn revealing from the GC analysis result. Low-temperature lignite pyrolysis seems to be a promising way to obtain a high gas product yield with high calorific value and high CH₄ yield.

The high water yield is attributed to the high moisture and high oxygen content of the lignite. The high-volatile of Hulun Bair lignite cause tar characterized by enrichment of *n*-alkanes from C10 to C30 and a greater amount of aliphatic species in the low temperature pyrolysis.

The yield of the semi-char, voliate, carbon, hydrogen and oxygen content are decreased evenly with the pyrolysis temperature while the ash yields increased substantially. The

H/C and O/C H/C atomic ratios decreased substantially while the values of f_a and R increased greatly with the ring condensation degree index. As the higher removal of amounts of volatiles with the temperature, the BET surface areas of semi-char increase gradually.

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