Study on microwave induced pyrolysis of low metamorphic coal and liquefaction residue

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Abstract. This paper mainly studies pyrolysis characteristic in the different heating of microwave of low metamorphic coal and Liquefaction Residue, which was focused on the effects of particle sizes, pyrolysis reaction time, and microwave powers. The product are analyzed by Gas chromatography- mass spectrometry (GC-MS), etc. The results showed that when heating time is 40 min and 800 W, yield of tar is about 15.51%.

1. Introduction

China’s energy is featured with large quantity of coal but small quantity of oil and gas. With rapid development of China’s economy, there is an enormous demand for energy especially for petroleum. Import of crude oil will not only increase our reliance on foreign energy resources, but also will directly affect safety of our economic development and energy supply. Therefore, the coal-to-oil project is of vital importance to development of our national economy. Low metamorphic coal accounts for an extremely large proportion in China’s coal resources. The technology of retorting low metamorphic coal in Northern Shaanxi, which prioritizes comprehensive utility rate of resources, is of great significance to quality improvement and comprehensive process & utility of low metamorphic coal in Northern Shaanxi. At the same time, it can reduce environmental pollution. So in recent years, it has received wide attention as a special technology in the field of clean coal technology.

Production of tar and combustible gases by coal pyrolysis has evoked interest in science researchers. Microwave heating, as a volumetric heating, can turn microwave energy absorbed by materials in the electromagnetic field into thermal energy. As compared with conventional heating, microwave heating has the following advantages: instant and pollution-free. As an all-new heating method, microwave heating has been widely used in many fields. Huang Xin, etc examined effect of pyrolysis temperature on occurrence mode of nitrogen in pyrolysis products by rapid pyrolysis experiment towards sewage sludge of Xuzhou in the drop-bed quartz tube reactor. Liu Hongzhen [12] studied pyrolysis characteristics of wheat straws in a microwave field. Based on the preliminary studies, this paper analyzed and characterized low metamorphic coal and tar, gases and semi coke produced by microwave pyrolysis of liquefaction residuals by adopting the chromatograph-mas spectrometer (GC-MS) and gas analyzer in order to explore the affecting rules of microwaves on coal pyrolysis & destructive distillation.
2. Experiment

2.1. Experiment Materials & Equipments
The materials in the experiment are residues directly liquefied from coal supplied by National Institute of Clean-and-low-carbon Energy and Shendong coal. Industrial analysis and element analysis of coal and liquefaction residuals followed GB/T 2001-1991 Analysis and Determination Method in Coking Industry and GB/T 214-2007 Method of Determining Total Sulfur in Coal. Contents of C, H, N, S and Mad, Aad, V_ad are taken as averages of two or three parallel samples. The content of FC_ad is calculated by minusing. The detailed formula is as follows:

Table 1 shows industrial and element analyses on coal and liquefaction residuals.

| raw material         | Industrial analyses | element analyses |
|----------------------|---------------------|------------------|
|                      | Mad     | Aad    | FC_ad  | V_ad   | C_ad   | H_ad   | N_ad   | S_t,ad |
| SDM                  | 4.64    | 7.26   | 54.92  | 33.18  | 70.71  | 4.32   | 0.84   | 0.22   |
| Liquefaction Residue | 0.14    | 17.74  | 48.37  | 33.75  | 75.00  | 4.22   | 0.79   | 2.16   |

2.2. Experiment Method
Under different microwave powers (320 w, 480 w, 640 w, 800 w & 960 w), condensation temperature 0 ℃ and pyrolysis durations (10 min, 20 min, 30 min, 40 min & 50 min), microwave pyrolysis experiments are performed to 50 g of mixture of coal and liquefaction residuals in different proportions (9:1, 8:2, 7:3, 6:4, 5:5) and yields, compositions and properties of the products are detected and analyzed. Industrial and element analyses of coal samples were performed by Shaanxi Energy Institute. Contents of different gases in coal gas were measured with the Gasboard-3100P portable six-component gas analyzer developed by Wuhan Sifang Scientific & Technological Co., Ltd. Constituent analysis of coal tar was done by GCMS-QP2010 Plus gas chromatograph-mass spectrometer of Daojin Company.

3. Results & Discussion

3.1. XRD Analysis of Liquefaction Residuals
Industrial and element analyses on coal and liquefaction residuals show that the residuals are featured with high ash and low moisture. Reason for high ash: Minerals in the coal, including liquefaction catalysts, will concentrate in the residues after organic matters in the coal are liquefied. Reason for high volatile: There are large quantities of heavy oil and asphalting in the residues. Reason for low moisture: The distillation temperature in the solid-liquid separation process of the coal direct liquefaction process is about 425 ℃, so the liquefaction residuals contain less water than the raw coal. Due to use of sulphurous catalysts and promotors in the liquefaction process, the sulphur content of...
the residues is far higher than that of the raw coal. Through analysis on Figure 2 “XRD Diagram of Liquefaction Residuals”, we can see that inorganic components in the liquefaction residuals are mainly $\text{SiO}_2$, $\text{CaCO}_3$ and $\text{Fe}_{1-x}\text{S}$ (pyrrhotite), with contents 32.4%, 42.6% and 24.9% respectively.

![Figure 2 XRD pattern of Liquefaction Residuals](image)

3.2. Analysis on Coal and Liquefaction Residuals Pyrolysis Experiment

Under microwave power 800 W, condensation temperature 0°C and pyrolysis duration 40 min, effects of different proportions of Shendong coal and liquefaction residuals on products yields are investigated. Raw material granularity <1mm. The mixture of coal and liquefaction residuals weighs 50 g. Proportions of coal and liquefaction residuals are 9:1, 8:2, 7:3, 6:4 and 1:1 respectively. Table 2 shows yields of pyrolysis products. From it, we can see that when the proportion of Shendong coal and liquefaction residuals is 6:4, the yield of the pyrolysis oil reaches the maximum value 15.51%. The possible reason for this result is as follows: When the proportion of liquefaction residuals is excessively high, the liquefaction residuals will turn from a solid state into a liquid state in the low temperature section. Large quantities of liquefaction residuals will cover surface gaps of the low metamorphic coal, preventing separation of gases and pyrolysis oils from the coal.

| Table 2 Product Yields (%) in Pyrolysis of Shendong Coal and Liquefaction Residuals in Different Proportions |
|-------------------------------------------------|-------------------------------------------------|---------------------------------|----------------|----------------|
| Product                                        | 9:1                                            | 8:2                                            | 7:3        | 6:4        | 1:1        |
| coal                                           | 83.84                                          | 69.47                                          | 68.44      | 69.63      | 69.60      |
| oil                                            | 7.21                                           | 12.61                                          | 13.21      | 15.51      | 12.21      |
| gas                                            | 8.95                                           | 17.92                                          | 13.35      | 14.86      | 18.19      |

Table 3 shows product yields (%) in pyrolysis of Shendong coal and liquefaction residuals in the proportion of 6:4 under different microwave powers. From it, we can see that when the microwave power for pyrolysis of Shendong coal and liquefaction residuals is 800w, the yield of the pyrolysis oil reaches as high as 15.51%. When the microwave power continues to rise, the amplification of the tar yield slightly decreases. So the optimal microwave power is 800w. Microwave power mainly affects temperature rising rate of the pyrolysis process. The higher the power, the higher the temperature rising rate. Volatiles can be separated out instantly. So the gaseous products have a short retention time in the reactor, leading to low incidences of secondary reactions.
Table 3 Product Yields (%) in Pyrolysis of Shendong Coal and Liquefaction Residuals in the
Proportion of 6:4 under Different Microwave Powers.

| Product | 320  | 480  | 640  | 800  | 960  |
|---------|------|------|------|------|------|
| coal    | 92.51| 90.62| 68.61| 69.63| 67.90|
| oil     | 1.22 | 5.31 | 12.24| 15.51| 15.72|
| gas     | 6.27 | 4.07 | 19.15| 14.86| 16.38|

Under proportion of Shendong coal and liquefaction residuals 6:4, microwave power 800 W, pyrolysis durations 10min, 20min, 30min, 40min & 50min, effects of different microwave pyrolysis durations on products yields are investigated. The experiment result is shown in Table 4.

Table 4 Product Yields (%) of Pyrolysis of Shendong Coal and Liquefaction Residuals in the
Proportion of 6:4 under Different Heating Durations (%)

| Product | Time (min) | 10 | 20 | 30 | 40 | 50 |
|---------|------------|----|----|----|----|----|
| coal    |            | 91.6| 72.01| 68.40| 69.63| 67.90|
| oil     |            | 1.01| 10.61| 12.01| 15.51| 15.32|
| gas     |            | 7.39| 17.38| 19.59| 14.86| 16.78|

From Table 4, we can see that as heating duration increases, the yield of pyrolysis oil gradually increases and the yield of solid coke gradually decreases. When the heating duration is 40min, the yield of pyrolysis oil reaches as high as 15.51%. However, if the microwave pyrolysis duration continues to be prolonged, the increase of the yield of pyrolysis oil is not obvious. So the optimal heating duration is 40min.

4. Conclusion
From the experiment on the mixture of Shendong coal and liquefaction residuals in microwave pyrolysis and in conventional pyrolysis, we can conclude the following: The pyrolysis effect is optimal when the microwave power is 800W and the microwave duration is 40min. When liquefaction residuals account for 40%, the pyrolysis oil yield in microwave pyrolysis of Shendong coal and liquefaction residuals can reach the maximum value 15.51%, which is 2.28% higher than that in conventional pyrolysis. In microwave pyrolysis as compared in conventional pyrolysis, there are more holes with greater diameters, showing that microwave pyrolysis is more adequate.

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