Microwave Pyrolysis for Yaojie Oil Shale

Yonghui Song¹, Jianmei Zhe¹, Xinzhe Lan¹, Jimmy Jia², Rick Sherritt², Xicheng Zhao¹, Wenzhi Shang³

¹ School of Metallurgical Engineering, Xi’an University of Architecture & Technology, Research Center of Metallurgical Engineering & Technology of Shaanxi Province ² PROCOM Consultants Ltd., ³Shenmu Shanjiang Coal Chemical Co.

Abstract

Yaojie oil shale is a coalmine by-product and contains high organic content. The Fischer Assay oil yield of Yaojie oil shale varies from 6.15 to 25.73 wt. % with an average of 12.67 wt. %. The Fischer Assay gas yield of Yaojie oil shale varies from 2.91 to 6.20 wt. % with an average of 4.70 wt. %. There is great economic and environmental interest in utilizing Yaojie oil shale to produce oil. Microwave pyrolysis technology has been investigated for processing Yaojie oil shale in this study, which focuses on the temperature characteristics, and the influence of microwave power on the composition and yield of semi-coke, shale oil and gas. The experimental results showed that the pyrolysis temperature inside the retort can reach as high as 800°C within a few minutes. Microwave power ranging from 180W to 800W has been applied in this study, which measured oil yield and composition, and gas yield and composition at different power levels. The maximum concentration of 55% of H₂ + CH₄ + CO was reached at 480W of microwave power. Gas yield increases steadily with increase of microwave power applied and gas yield of 10% was achieved at 480W. Oil yield increases gradually with increased power application and maximum oil yield of 13.8% is achieved with 480W power application and then oil yield decreases gradually with the power increase above 480W. This change appears to result from oil cracking reactions. With the increase of microwave power, the yield of semi-coke decreased steadily.

1. Introduction

Oil shale is a sedimentary rock containing organic matter which cracks and forms oil and gas at elevated temperature due to pyrolysis reactions. Oil shale is an alternative oil and gas resource and a replacement energy source for coal, oil and natural gas, as well as other non-renewable fossil energy sources. As the international oil price has stayed high in recent years, oil shale has been regarded as an alternative source of fuel oil.

It has been almost one hundred years since simply heating up oil shale produced the first drop of shale oil. Current shale oil production technology includes gas heat carrier, solid heat carrier and electrical heating processes. Hot gas is used as a heat resource in gas heat carrier technology; a hot solid or ash is used as the heat source in solid heat carrier processes and electrical heating processes use electricity as the major heat source. Microwave heating is a newer heating method that places materials in an electromagnetic field (Wall et al. 1979). Compared with conventional pyrolysis technology, the microwave heating method has demonstrated advantages such as high heating rate, uniform heating inside oil shale particles, and lower temperature gradients. Therefore, microwave heating has been used in coal (Lan et al., 2010; Song et al., 2011), minerals (Peng and Liu, 1997), sludge (Menédez et al., 2004), biomass (Appleton et al., 2005) and waste plastic (Hussain et al., 2010) and other pyrolysis processes.

Fundamental research has revealed the effectiveness of microwave power application
to pyrolysis reactions. Bradhurst and Worn-ner (1996) revealed that the role of micro-wave energy is effective in crushed oil shale and can improve the yield and increase the value of shale oil. The shale oil product from microwave pyrolysis contains a high proportions of hydrocarbons and lower levels of sulfur and nitrogen. K. El Harfi et al. (2000) and other authors have shown that oil derived from oil shale using microwave pyrolysis exhibits higher quality, less polar material and smaller amounts of sulfur and nitrogen, compared with the oil derived from conventional pyrolysis processes.

Zhu Zhi-Rong (2001) reported a qualitative analysis of central Chinese oil shale using gas chromatography-mass spectrometry (GC-MS) and found there were a total of 269 components with individual mass fraction greater than 0.02%, in which about 79% of all species accounted for are hydrocarbons (alkanes, alkenes and cycloalkanes making up a total of 52%); the other species belong to a variety of sulfur, nitrogen and oxygen compounds. Wang Jia-Ning (1992) carried out a separation operation by using a semi-automatic high performance thin layer chromatography instrument to split an shale oil sample into six different species groups and then conducted a qualitative and quantitative analysis on the composition of each species group by using GC-MS. He concluded that about 40% of shale oil consisted of alkanes (mostly alkanes, with lower cyclo-alkane content, mainly as alkyl cyclo-hexane), whereas the relative content of n-alkanes increases as the distil-late temperature increases.

It was reported that the shale oil derived from Maoming oil shale using conventional pyrolysis contains even more chemical compounds. Guo Shuhua (1995) has carried out analysis for Maoming shale oil distillate (<350°C) using GC-MS, which identified a total of 574 compounds including 272 miscellaneous atomic compounds, 221 aromatic compounds and 81 aliphatic hydro-carbon compounds.

A microwave pyrolysis study on Australian oil shale showed that shale oil produced by the microwave power heating method contained increased amounts of the lighter fractions (kerosene fraction increased by 53.3%, distillate by 26.1%, light gas oil by 10%), and correspondingly smaller amounts of the heavy fractions (heavy gas oil reduced by 33%, nonvolatiles reduced by 81.8%) (Bradhurst and Worner, 1996). This result indicates there are some advantages to using microwave power to produce high quality shale oil over conventional py-rolysis technology.

Previous research showed shale oil quality, yields and the effectiveness of microwave power on oil shale pyrolysis varied significantly for Maoming, Moroccan and Australian oil shale samples. Therefore, this study was carried out to investigate the impact of microwave power on 1) yields of pyrolysis products; 2) composition of pyrolysis products.

2 Experimental Procedures

2.1 Oil Shale Sample Preparation

Yaojie oil shale is a by-product of Yaojie coalmine. An oil shale sample was collected from Yaojie coalmine and then crushed and screened to prepare oil shale with a particle size of 5~12mm. Yaojie oil shale is characterized as high volatile and low ash (Han, 1996) and its Proximate analysis and Ultimate analysis results are shown in Table 1.

2.2 Experimental Apparatus

A bench top experimental apparatus was designed and set up in the laboratory to carry out microwave pyrolysis experiments. The experimental device consists of a microwave power generator, oil/gas cooling and collection system and on-line instrumentation as shown in Figure 1. The microwave power generator is modified from a commercial model microwave oven (Galanz G80F23CSL-A9). The microwave power generator is capable of producing electromagnetic radiation (microwaves) with power range of 0 ~ 1600W at a fixed frequency of 2450MHz. 50g of Yaojie oil shale sample is put into a 100ml quartz reactor and sealed properly. The quartz reactor is then put into the microwave power gen-
erator device. The microwave power generator is set up and then turned on for 30 minutes; oil and gas generated from the quartz reactor pass through the cooling bath and U-tube cooler. Oil is condensed and collected in the cooling system for analysis using GC-MS, whereas retort gas is kept flowing through an on-line GC (Gas Board – 3100P). After 30 minutes, spent shale in the quartz reactor is cooled down and then prepared for Proximate and Ultimate analyses.

3. Results and Discussion

3.1 Impact of Microwave Power on Yield of Pyrolysis Products

Table 2 and Figure 2 show the yields of shale oil, retort gas and spent shale at different microwave power levels and the impact of microwave power on pyrolysis products. The yield of spent shale decreases steadily whereas the yield of retort gas increased gradually with increased microwave power applied as expected. This increase is due to the greater extent of pyrolysis that occurs and more volatile constituents being driven out from shale as a result of increased temperature and heat applied to oil shale. With lower microwave power applied, it requires longer irradiation times to reach pyrolysis reaction temperatures. With 160W microwave power applied, the yield of spent shale is more than 99%, due to the oil shale temperature not reaching the desired pyrolysis temperature within 30 minutes. The weight loss is contributed only by moisture evaporation.

With higher microwave power applied, the oil shale temperature can reach pyrolysis temperature within a few minutes. This enables the volatiles inside the oil shale to escape from oil shale particles faster. With further increase of microwave power, still higher temperature than the pyrolysis temperature can be reached within a couple of minutes. Shale oil could precipitate inside oil shale due to the limited diffusion rate.
analyzed and the result of proximate and ultimate analyses of spent shale under different microwave power levels is shown in Table 3. The result showed that the remaining carbon content (or char) in spent shale increased gradually and volatile matter content in spent shale decreased slightly with the increase of microwave power applied, as expected. When much higher temperature than pyrolysis temperature is reached with higher microwave power applied, shale oil is more likely to be cracked and more char or carbon will be formed and stay inside the spent shale.

However, the results showed that content of C, H, N, S and other elements in spent shale do not vary very much with the different microwave power applied and indicated that the impact of microwave power does not imply a great impact on content of C, H, N, S elements in spent shale.

3.3 Impact of Microwave Power on Retort Gas

Retort gas composition changes with different microwave power applied and the impact of microwave power on the retort gas composition is shown in Figure 3. The retort gas concentration is close to zero with

<table>
<thead>
<tr>
<th>Power/W</th>
<th>Product yield / % (mass)</th>
<th>Semi-coke</th>
<th>Oil</th>
<th>Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>160</td>
<td>99.4</td>
<td>0</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>320</td>
<td>84.6</td>
<td>8.5</td>
<td>6.6</td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>77.2</td>
<td>13.3</td>
<td>9.2</td>
<td></td>
</tr>
<tr>
<td>480</td>
<td>76.2</td>
<td>13.5</td>
<td>10.0</td>
<td></td>
</tr>
<tr>
<td>640</td>
<td>74.4</td>
<td>11.7</td>
<td>13.6</td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>72.3</td>
<td>12.0</td>
<td>15.0</td>
<td></td>
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</table>

Figure 2: Impact of microwave power on pyrolysis product
microwave power of 160W applied. This is because the temperature of oil shale is far below pyrolysis temperature and there is no or negligible pyrolysis reaction occurring within 30 minutes of microwave power application.

Figure 3 shows that the concentration of all gas components - CO$_2$, CO, CH$_4$, H$_2$, C$_n$H$_m$ - increase significantly due to pyrolysis reaction occurring as the microwave power increases from 160W up to 320W. With further increase of microwave power until 800W, concentration of CO exhibited gradual increase all the way to 800W; concentration of CH$_4$ and C$_n$H$_m$ exhibited stable concentration with minimal decrease all the way to 800W; concentration of H$_2$ gradually increases until 480W and then decreases very slightly with further increase of microwave power; while the concentration of CO$_2$ exhibited an increase up to 400W and then decreased slightly before leveling out to 800W.

Kerogen is the main organic matter contained in oil shale and contains many COOH compounds. Kerogen started to prolapse and produce CO$_2$ at temperature of 200˚C (Hayashi et al., 1994) whereas thermal

<table>
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<tr>
<th>Table 3: Proximate and ultimate analyses of spent shale under different microwave power</th>
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<tr>
<td><strong>Power/W</strong></td>
</tr>
<tr>
<td>M$_{ad}$</td>
</tr>
<tr>
<td>------------------</td>
</tr>
<tr>
<td>160</td>
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<td>320</td>
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<td>640</td>
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<td>800</td>
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**Figure 3**: Impact of microwave power on retort gas
decomposition of the inorganic component of some carbonate compounds will produce more CO₂ with higher temperature of oil shale. H₂ is mainly produced from post-condensation thermal decomposition reactions in which the less aromatic compounds form into more aromatic compounds and hydrogen is released. CH₄ is mainly produced by the degradation of larger molecular structures, decomposition of alkyl groups, hydrocarbon condensation and polymerization, and hydrogenation of volatile material. Thus the variation of microwave power applied will impact the concentration of CH₄ due to the influence on reaction kinetics of temperature variation resulting from power variation. Production of CH₄ is expected to increase with the increase of microwave power application, whereas the slight decline in the concentration of CH₄ was noticed in this experiment at microwave power levels over 480W. This pattern may be caused by rapid increase in production of H₂ and CO, which contributed a significant increase in retort gas volume. The rapidly increased retort gas lead to relatively lower concentrations of CH₄. However, the total concentration of CH₄, H₂ and CO in retort gas increases with the increase of power applied.

The CO is mainly derived from (Hu, et al., 2006):
1. the carbonyl decomposition reaction occurring above 400 °C;
2. ether bond breaking reactions occurring above 700 °C;
3. decomposition reactions of oxygen-containing heterocyclic hydrocarbon above 500 °C.

Therefore, production of CO increases gradually with the increase of microwave power applied.

Shale oil produced with 480W, 640W and 800W microwave power were analyzed using GC-MS and the results are shown in Figure 4. There are 62, 52 and 50 kinds of compounds identified for oil samples derived with 480W, 640W and 800W power applied respectively.

Qualitative and quantitative shale oil composition analysis is summarized and shown in Table 4. Paraffinic, aromatic and olefinic compounds were the main products in shale oil and counted for 70% or more of total weight of the shale oil. Shale oil samples at all three power levels also contain small quantities of the group of phenolic compounds, which accounted for 2 - 6.15% of the total weight of shale oil. The concentration paraffinic and olefinic compounds increased gradually with the increase of power applied whereas the concentration of aromatic compounds decreased with increased power applied. This effect might be caused by thermal cracking reactions occurring at elevated temperature.

4 Conclusions

This study has revealed the major impacts of microwave power on the yields of pyrolysis product and on the composition of pyrolysis products, and can be summarized as follows:

1. With increased power applied, yields of spent shale decreased gradually and yields of retort gas increased gradually, whereas the yield of oil increased, reached a maximum at 480W power applied, then declined.

<table>
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<th>Table 4: Oil composition analysis at various power levels</th>
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<tbody>
<tr>
<td>Power /W</td>
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<tr>
<td>480</td>
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<tr>
<td>640</td>
</tr>
<tr>
<td>800</td>
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2. The impact of microwave power does not imply a large impact on content of C, H, N, S in spent shale. However, the remaining carbon content (or char) increased gradually, whereas volatile matter content decreased slightly with
the increase of microwave power applied.

3. Concentration of each gas component varies with the increase of power applied, however, the total concentration of CH₄, H₂ and CO in retort gas increased with the increase of power applied.

4. The concentration of paraffinic and olefinic compounds increased gradually with increase in applied power, whereas the concentration of aromatic compounds decreased with increased of power applied.

References Cited


Han, D., ed. China Coal Petrology. 1996, China Mining University.


