Study on the microwave catalytic pyrolysis characteristics and energy consumption analysis of oil shale

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Abstract. In order to explore the high-efficient utilization of oil shale, the effects of different microwave powers and different kinds of catalysts (metal oxides and metal salts) on the temperature characteristics and product yield towards the oil shale are investigated by microwave catalytic pyrolysis. The results show that the effect of microwave power on the heating and pyrolysis rates of oil shale is significant, and the maximum output of shale oil is 5.1\% when the microwave power is 1500W; CaO has a certain effect on the temperature rise of oil shale, and MgO and CuO have a certain degree of inhibition, but the addition of three kinds of metal oxidation is beneficial to increase the shale oil production; From the perspective of unit power consumption and gas production, the catalytic effect order of three kinds of metal oxides is MgO> CaO> CuO; The addition of three kinds of metal salts is favorable for the increase of pyrolysis temperature of oil shale, after adding 5\% ZnCl\textsubscript{2}, the unit power consumption of shale oil and pyrolysis gas increases by 62.60\% and 81.96\% respectively. After adding 5\% NaH\textsubscript{2}PO\textsubscript{3}, the unit power consumption of shale oil increases by 64.64\%, and reduces by 9.56\% by adding 5\% MgCl\textsubscript{2}.

1. Introduction
With the increasing tension in oil and gas resources and the rising of international oil prices, unconventional energy development and utilization have also been taken seriously. Oil shale is recognized as having the potential for alternative fossil fuels because of its rich reserves, ease development and utilization \cite{1}. Oil shale is a high-ash sedimentary rock containing combustible organic matter, which belongs to unconventional energy and oil content of which is generally higher than fossil fuels by approximately 3.5\% \cite{2}. At present, the utilization of oil shale is mainly adopting the traditional heating method-----dry distillation technology, but this way exists the shortcomings of long-time consuming and low oil
production\cite{3}. Microwave pyrolysis is a kind of new heating method, compared with conventional pyrolysis technology, this new method has the advantages of faster pyrolysis speed, higher efficiency, more uniform pyrolysis and easier control\cite{4}. Therefore, this technology received great attention by many scholars for oil shale pyrolysis.

In this paper, the microwave reactors were used to study the effects of different microwave powers, metal oxides and metal salts on the pyrolysis characteristics of oil shale and the yield of three-phase products. And the absolute productivity of oil shale microwave pyrolysis was studied by combining the energy consumption and energy output evaluation method. The results can provide theoretical guidance for the exploitation of oil shale by microwave.

2. Experimental facilities and methodology

2.1. Sample preparation

The oil shale used in the experiment is from the kiln and the basin in Gansu. The industrial analysis and elemental analysis of oil shale are shown in Table 1. The experimental microwave absorbers were metal oxides (CaO, CuO and MgO) and metal salts (MgCl$_2$, ZnCl$_2$ and NaH$_2$PO$_3$). Before the start of the experiment, the activated carbon is dried at 105°C for 24 hours thermostatically. For coherent comparison, the reactants (dry basis) and the microwave absorptions used for each experiment were 30 g and 5%, respectively.

\begin{table}[h]
\centering
\begin{tabular}{lcccccccc}
\hline
Sample & Elemental analysis (wt %) & Industry analysis (wt %) & Low calorific value (MJ/kg) \\
\hline
 & C & H & O & N & S & V & A & FC & Q$\text{net,ar}$ \\
Oil & 15.68 & 2.3 & ----- & 0.57 & 0.63 & 26.97 & 72.13 & 0.90 & 5.56 \\
shale & & & & & & & & & \\
\hline
\end{tabular}
\caption{Elemental analysis, proximate analysis and low calorific value of oil shale}
\end{table}

2.2. Experimental facilities

The experimental device of microwave system is shown in Figure 1. Experiment device mainly consists of microwave generation and control system, temperature measurement system, material reaction system, pyrolysis products collection system and data acquisition system.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{image1.png}
\caption{The reactor of experimental device}
\end{figure}

3. Results and discussion

3.1. Effect of Different Microwave Power on of Oil Shale Pyrolysis

The sample weight for each pyrolysis experiment was 30 g, and three microwave powers were selected (750 W, 1500 W and 2250 W). The curves for temperature vs pyrolysis time of the oil shale at different microwave powers measured by thermocouple is shown in Fig. 2 (a). The percentage distributions of the oil shale pyrolysis products at different microwave powers is shown in Fig. 2 (b).

![Figure 2(a): The impact of different microwave powers different on the temperature rise](image1)

![Figure 2(b): Percentage of product at microwave power](image2)

It can be seen from Fig. 2 (a) that the oil shale temperature increased gradually when the pyrolysis time prolonged. At the beginning, the oil shale was heated up quickly, when the temperature reached its maximum there was no significant change observed. This could be ascribed that the amount of heat generated by the pyrolysis gas was close to the heat (generated by the microwave) absorbed by material \(^5\). With the increase of microwave power, the material reached the maximum temperature with less time, and the final temperature of the material was also higher, which may be due to the greater microwave power, which made the microwave field interaction among water molecules become faster, and it accelerated the pyrolysis of the material\(^6\).

As can be seen from Table 2, with the increase of microwave power, the average heating rate and the maximum heating rate were increased. This is mainly because when the microwave power is small, the oil shale involved in pyrolysis is less, resulting in a small heating rate. And with the increasing microwave power, microwave energy absorbed by oil shale increases, the intensity of molecular motion also increased\(^7\). And the impact of microwave power on the heating rate is very obvious, indicating that by controlling the microwave power can be very good to achieve the purpose of controlling the temperature in practice.

As can be seen from Fig. 2 (b), when the microwave power is 1500W, the oil production reaches its maximum value of 5.1%; when the microwave power is 750W, the amount of residue becomes the largest, reaching 83.73%. With the increase of microwave, the amount of gas produced decreases first
and then increases, and the oil production increases first and then decreases. When the microwave power is 1500W, due to the larger power, oil shale pyrolysis is nearly more completed, resulting in a large number of shale oil and pyrolysis gas. While the microwave power of 2250W, the polymerization reaction and cracking reaction occurred in the material competed with each other\cite{8}, during this period, the cracking reaction rate is greater than the polymerization reaction rate, t severe secondary decomposition reaction occurred, shale oil production rate is smaller than the shale oil decomposition rate, making the oil production decreased.

| Microwave power | Average heating rate (°C/s) | Maximum heating rate (°C/s) |
|-----------------|-----------------------------|----------------------------|
| 750W            | 0.378                       | 1.41                       |
| 1500W           | 0.538                       | 4.031                      |
| 2250W           | 0.703                       | 5.031                      |

In summary, 1500W is the best power for oil shale pyrolysis, its highest oil production is 5.1%, so in the experiment 1500W is selected as the pyrolysis power.

3.2. Effect of Different Metal Oxide on Pyrolysis of Oil Shale

The microwave power, the reactants (dry basis) and the microwave absorption (CuO, MgO and CaO) used for each experiment were 1500W, 30g and 5%, respectively. The pyrolysis temperature curves of the oil shale measured by thermocouple is shown in Fig. 3 (a). The percentage distribution of the oil shale pyrolysis products at different microwave power is shown in Fig. 3 (b).

![Figure 3(a). The impact of different metal oxides different on the temperature rise](image-url)
It can be seen from Fig. 3 (a) that the curves of the samples with MgO and CuO were very close to each other. After 413s, the temperature was always lower than pure oil shale, and the final pyrolysis temperatures of which were lower than the pure oil shale by 132.8°C and 88.8°C, respectively. This could be resulted from that MgO and CuO have no significant effect on the chemical reaction within the material and it increased the mass transfer and heat transfer during pyrolysis. After adding calcium oxide, the temperature rise of the sample is very close to that of pure oil shale, and the final temperature is only 26.4°C higher than that of pure oil shale. Because CaO is a weak-absorbing material that absorbs a small amount of microwave while increasing the heat transfer resistance of the specimen.

It can be seen from Fig. 3 (b) that the amount of residue after adding CuO, MgO and CaO were 4.16%, 4.53% and 1.00%, respectively, which were lower than that of pure oil shale, and the shale oil production with these three additions were 2.00%, 3.80% and 2.83%, respectively, which were higher than pure oil shale. Studies have shown that CuO, MgO and CaO and other alkaline earth metal oxides have the catalytic effect, contributing to shale oil pyrolysis, which may be the reason for the decline in residue. The gas production of the sample adding CuO and MgO were 2.16% and 0.73% higher than that of pure oil shale, but which was reduced by 1.84% when adding CaO. This may be due to the reaction of CO_2 and CaO to produce CaCO_3, resulting in a decrease in gas production.

From the unit power consumption of the three-phase product shown in Fig. 3 (c), it can be seen that the unit power consumption of shale oil and pyrolysis gas increases with the addition of metal oxide. The unit power consumption of the pyrolysis residue of the samples with MgO and CaO increased and the unit power consumption of the pyrolysis residue of the CuO sample was decreased. From the perspective of unit power consumption and gas production, it can be seen that the catalytic effect of the three kinds of metal oxides is MgO> CaO> CuO.
3.3. Effect of Different Metal Salt on Pyrolysis of Oil Shale

The microwave power, reactants (dry basis) and the microwave absorption (MgCl$_2$, ZnCl$_2$, and NaH$_2$PO$_3$) used for each experiment were 1500W, 30 g and 5%, respectively. The pyrolysis temperature curves of the oil shale measured by thermocouple is shown in Fig. 4 (a). The percentage distribution of the oil shale pyrolysis products at different microwave power is shown in Fig. 4 (b). It can be seen from Fig. 4 (a) that the reaction rate of the material was accelerated after adding three kinds of metal salts, and the final temperatures of MgCl$_2$ and NaH$_2$PO$_3$ were 29.1% and 26.6% higher than that of pure oil shale respectively. The four temperature rising curves have a rapid warming range, and the reason for the rapid warming range is that the residue formed after pyrolysis of oil shale presents good microwave-absorbing ability \cite{9}, which can promote the pyrolysis reaction of the sample. After adding the three metal salts, the time to enter the rapid warming range is in advance, which may be resulted from the addition of the metal salt so that the time of the residue formation in advance.

Fig.4 (b) shows that the three-phase production percentages of sample with addition of MgCl$_2$, ZnCl$_2$ and NaH$_2$PO$_3$, the amount of residue decreased by 5.28%, 2.08% and 1.88%. This suggests that the addition of metal salts promote the pyrolysis of oil shale. The shale oil production of samples with MgCl$_2$ and ZnCl$_2$ decreased by 1.53% and 3.07%, while the gas production increased by 6.76% and 1.76% respectively. This is because of the addition of MgCl$_2$ and ZnCl$_2$ that promote the secondary pyrolysis of shale oil, resulting in an increase in pyrolysis gas production and a decrease in shale oil production\cite{10}. After adding NaH$_2$PO$_3$, shale oil production increased by 2.97% and pyrolysis gas decreased by 1.14%. This shows that NaH$_2$PO$_3$ is conducive to the production of shale oil.
Figure 4(a). The impact of different metal salts on the temperature rise

Figure 4(b). Percentage of product under different metal salts

Table 4. The impact of different metal salts on the power consumption

| sample       | Power (W) | Time (h) | Power consumption (kWh) |
|--------------|-----------|----------|-------------------------|
| No catalyst  | 1500      | 0.304    | 0.681                   |
| MgCl₂        | 1500      | 0.253    | 0.566                   |
| ZnCl₂        | 1500      | 0.195    | 0.437                   |
| NaH₂PO₃      | 1500      | 0.273    | 0.611                   |
Figure 4(c). The impact of different metal salts on the mass of products of unit power consumption

It can be seen from Table 4 that after adding MgCl₂, ZnCl₂ and NaH₂PO₃, the electricity consumption decreased by 16.89%, 35.83% and 10.28%, respectively. It can be seen from Fig. 4 (c) that the addition of three kinds of metal salts can significantly improve the unit power consumption of pyrolysis residue and pyrolysıs gas. After adding ZnCl₂ and NaH₂PO₃, the unit power consumption of shale oil increased and the unit power consumption of MgCl₂ sample was decreased. The unit power consumption analysis shows that the catalytic effect order of three kinds of metal salts was ZnCl₂>MgCl₂>NaH₂PO₃.

Compared with the addition of metal oxide and metal salt in 3.2 and 3.3, the catalytic effect of metal salt is generally better than that of metal oxide. The best catalytic effect is MgCl₂.

4. Conclusion
The greater the microwave power, the higher the average heating rate and the pyrolysis temperature of the oil shale. When the pyrolysis power is 1500W, the shale oil production reaches the maximum value of 5.1%.

After adding 5% CaO, the final temperature of the sample increased slightly, while with the addition of MgO and CuO, the pyrolysis temperature decreased by 12.69% and 17.73%, respectively.

The addition of three kinds of metal salts was beneficial to the increase of pyrolysis temperature of oil shale. After adding 5% ZnCl₂, the unit power consumption of shale oil and pyrolysis gas production increased by 62.60% and 81.96% respectively. After adding 5% NaH₂PO₃, the unit power consumption of shale oil increased by 64.64%, while decreased by 9.56% by adding 5% MgCl₂.

The catalytic effect of metal salts is generally better than that of metal oxides, and the MgCl₂ has the best catalytic effect.

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