Effect of Fe-modified ZSM-5 catalyst during microwave assisted pyrolysis of Mengdong lignite for the oil production

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Abstract. Microwave catalytic pyrolysis of Mengdong lignite by Fe-modified ZSM-5 catalysts was studied. The effects of pyrolysis method and the ZSM-5 molecular sieves loading different amounts of Fe₂O₃ on the total tar yield were investigated. The results show that the microwave heating technology could effectively improve the yield of lignite pyrolysis tar; In the conventional pyrolysis, the total yield of raw coal pyrolysis oil was 2.19%. When the Fe₂O₃ loading was 5%, the catalyst had the best effect with the yield of 3.56%, and the increase rate was 62.56%; Under microwave condition, the pyrolysis oil yield of raw coal is 6.43%. When the Fe₂O₃ loading increased from 0 to 10%, the total yield of tar increased from 7.02% to 9.47%. When the Fe₂O₃ loading was 10%, the catalyst had the best effect with the increase rate of 62.56%.

1. Introduction
Microwave heating is widely used in various industries due to its advantages of fast heating speed, energy saving, selective heating, and environmental protection. In recent years, many researchers have been keen to use microwave as a heating source to study the pyrolysis of biomass, solid waste, fossil fuels, etc[1-3]. Uslu et al.[4] studied the temperature rise of coal in the microwave field, and found that the absorbing materials such as Fe₃O₄ and SiC are beneficial to the rapid heating of coal in the microwave field, and the pyrolysis temperature can be raised to above 1000℃ in 3 minutes. Xinzhe Lan et al. investigated the effect of particle size on the quality and yield of low-metamorphic coal microwave pyrolysis products. The study showed that under microwave heating conditions, the temperature of low-metamorphism coal could rise to 750℃ after heating for about 10 minutes; Compared with conventional pyrolysis, the yield of pyrolysis tar obtained by microwave pyrolysis was 4% higher, which is 12%; And the content of CO, H₂ and CH₄ in pyrolysis gas also increased.

Microwave and catalyst have the promotion effect on lignite pyrolysis, and the total yield of tar and the light degree of tar are higher than that of ordinary pyrolysis[5-7]. However, there are few studies on the catalytic pyrolysis of lignite in the microwave field. According to the characteristics of microwave heating, the catalyst for microwave field can be designed to pyrolyze lignite, in order to obtain more tar and lighter components. Zeolite molecular sieve is a mesoporous material with uniform pore size distribution, which can allow organic macromolecules to enter and undergo a series of reactions such as cracking, cycleization and isomerization under the action of acidic sites[8]. Considering its large specific surface area, it is conducive to the thermal cracking reaction. In this paper, ZSM-5 molecular sieve is
selected as the carrier with the chemical formula of $0.7\text{CaO} \cdot 0.3\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2.0\text{SiO}_2 \cdot 4.5\text{H}_2\text{O}$ and the ratio of silicon to aluminum is 2. And $\text{Fe}_2\text{O}_3$ was loaded by sedimentation method, trying to catalytically crack the primary pyrolysis product entering its pore structure, the effects of the different amounts load of $\text{Fe}_2\text{O}_3$ on the total tar yield was studied.

2. Materials and methods

2.1. Preparation of coal sample
In this paper, Mengdong brown coal was taken as the research object, and the raw coal was pulverized and sieved to select coal samples with a diameter of 40 mesh to 60 mesh. Then the selected coal samples were placed in a vacuum drying oven, after drying for 12h at 80℃, they were sealed for storage.

2.2. Preparation of catalyst
The $\text{Fe}_2\text{O}_3@\text{ZSM-5}$ catalyst was prepared by deposition and sedimentation method. The specific operation steps were as follows: firstly, the ZSM-5 molecular sieve was calcinated at 400℃ for 4 h under the air atmosphere, in order to remove impurities in the hole; and then using a sample pulverizer ground the molecular sieve to a particle size of <0.15 mm. Weighing 10.00g molecular sieve in the conical flask, and weigh the corresponding mass of $\text{Fe(NO}_3)_3 \cdot 9\text{H}_2\text{O}$ according to the $\text{Fe}_2\text{O}_3$ loading of 1%, 5%, 10% and 15% adding into the conical flask, while adding a certain amount of CO ($\text{NH}_2$)$_2$ as a precipitant, and finally adding 100 ml of deionized water, after fully stirring for 30 minutes under 40℃ water bath, it was heated to 90℃ and kept for 6 h, when the turbid liquid was cooled to room temperature, it was suction filtered and washed. The obtained solid was dried in a vacuum oven for 8 h at a temperature of 80℃ and then calcinated at 875℃ for 4 h, after cooling, it was taken out and placed in a sealed bag for storage.

2.3. Microwave catalytic pyrolysis experiment
This experiment was carried out in a modified Galanz P70D20TL-D4 microwave oven with the resonant cavity size of 220×200×180mm, the magnetron model of M24FB-610A, and the rated output power of 700W. A certain amount of coal sample and catalyst were weighed and mixed mechanically at a mass ratio of 5:2. The mixed samples were numbered according to Table 1. In each pyrolysis experiment, 35g samples were accurately weighed and placed in a quartz reactor. The upper part of the sample was covered with quartz wool with a diameter of 40mm and a thickness of 20mm. The purpose was to prevent the coal powder from entering the subsequent pipeline along with the pyrolysis airflow and causing the pipeline to be blocked. Control the $\text{N}_2$ flow rate to 250ml/min before the experiment, after purifying for 10 minutes, adjust the flow rate to 25ml/min, start the microwave oven, set the microwave output power to 700w. Successively condensed in three stages by ice water, the pyrolysis pyrolysis product entered the acetone washing system, and then entered the drying tower. The tar attached to the outlet end of the reactor and the condenser was washed with acetone into the round bottom flask, and the water in the tar was absorbed by anhydrous sodium sulfate, and then the acetone was distilled off by a rotary evaporation method at 65℃ in a water bath. After that, the tar was dried at 30℃ in the dry box to constant weight and weighed to obtain the quality of tar. The total pyrolysis time was 15 minutes.

| Table 1. catalyst name and sample number. |
|------------------------------------------|
| catalyst     | Fe$_2$O$_3$ load (mass fraction) | Sample number |
|---------------|---------------------------------|----------------|
| 0%Fe$_2$O$_3$@ZSM-5 | 0  | 1#  |
| 1%Fe$_2$O$_3$@ZSM-5 | 1% | 2#  |
| 5%Fe$_2$O$_3$@ZSM-5 | 5% | 3#  |
| 10%Fe$_2$O$_3$@ZSM-5 | 10% | 4# |
| 15%Fe$_2$O$_3$@ZSM-5 | 15% | 5#  |
2.4. Conventional catalytic pyrolysis experiment
In order to compare with microwave catalytic pyrolysis, catalytic pyrolysis experiments under conventional heating conditions were carried out in a tube furnace. 35g coal samples were weighed into a quartz reactor, then placed in a vertical tube furnace heated to 600°C in advance, and the rest of the operations were the same as microwave catalytic pyrolysis.

3. Results and discussion

3.1. Characterization of the catalysts

3.1.1. SEM analysis
Figure 1 is a scanning electron micrograph of the catalyst. Most ZSM-5 molecular sieves after milling were spherical with different sizes. After loading Fe2O3, due to the interaction between the metal oxide and the carrier, adhesion between the spherical particles occurs.

3.1.2. XRD analysis
Figure 2 shows the XRD patterns of Fe2O3@ZSM-5 catalysts with different loadings. As can be seen from the figure, the characteristic peak of ZSM-5 molecular sieve gradually weakens as the load increases from 1% to 15%. And a similar phenomenon is observed in the experiment of Shuping Zhang et al.[9, 10], which may be due to the interaction between Fe2O3 and ZSM-5 molecular sieve carrier, leading to the decrease of the latter's crystallinity. At the same time, it was also observed that 10% Fe2O3@ZSM-5 and 15% Fe2O3@ZSM-5 have a relatively broad peak in the range of 25°-30°, which is also one of the evidences of the decrease in crystallinity. It should be noted that after loading Fe2O3, no corresponding characteristic peaks were observed in the XRD patterns, indicating that Fe2O3 was uniformly loaded on the catalyst surface and did not aggregate to form detectable crystals.

3.2. analysis of microwave catalytic pyrolysis oil

3.2.1. Tar yield analysis
Figure 3 shows the effect of ZSM-5 molecular sieve catalyst with different mass of Fe2O3 on the microwave pyrolysis results of lignite. The pyrolysis process of Fe2O3 with load of 0, 1wt%, 5wt%, 10wt% and 15wt% was studied respectively in the experiment. The results show that the tar yield reaches the maximum 9.47wt% when the ZSM-5 molecular sieve catalyst with a loading of 10wt% was added. While under the same conditions, the yield of microwave pyrolysis tar was only 6.43wt% without the addition of catalyst, the relative increase of 47.29%. Therefore, the composite catalyst can
Effectively improve the yield of lignite microwave pyrolysis tar.

### 3.2.2. Coal sample weight loss analysis

Table 2 shows the weight loss of the samples before and after pyrolysis and the temperature at the end of the pyrolysis experiment. As can be seen from the table, the final temperature of samples increased after adding catalysts, indicating that the addition of the catalyst improved the apparent dielectric loss factor of samples, enhanced the material's wave absorption ability, and improved the efficiency of converting electromagnetic energy into internal energy. When the Fe$_2$O$_3$ load was 15%, the pyrolysis temperature could reach 695.9$^\circ$C. The weight loss rate of the sample was up to 59.16%, and the corresponding catalyst was 10% Fe$_2$O$_3$@ZSM5. Meanwhile, the tar yield is up to 9.47%.

| Coal sample | Final temperature $^\circ$C | Weight loss ratio/\% |
|-------------|-----------------------------|---------------------|
| 1#          | 644.9                       | 55.7                |
| 2#          | 673.0                       | 51.5                |
| 3#          | 672.0                       | 57.9                |
| 4#          | 694.9                       | 59.2                |
| 5#          | 695.9                       | 55.8                |

### 3.3. Analysis of conventional catalytic pyrolysis tar yield

Figure 4 shows the effect of ZSM-5 molecular sieve catalyst with different Fe$_2$O$_3$ mass on the conventional pyrolysis of lignite. The pyrolysis process of Fe$_2$O$_3$ with load of 0, 1wt%, 5wt%, 10wt% and 15wt% was studied respectively in the experiment. The results showed that when the ZSM-5 molecular sieve catalyst with a loading of 5wt% was added, the tar yield reached the maximum of 3.56wt%, while under the same conditions, the yield of conventional pyrolysis tar was only 2.19wt% without the addition of catalyst, the relative increase of 62.56%. Therefore, the composite catalyst could effectively improve the yield of lignite pyrolysis tar.

### 3.4. Comparison between conventional catalytic pyrolysis and microwave catalytic pyrolysis

Fe$_2$O$_3$@ZSM-5 series catalysts have different effects on pyrolysis oil production under two heating modes. Under the conventional heating condition, all the catalysts increased the yield of tar to some extent, and the effect was best when the Fe$_2$O$_3$ loading was 5%. Under the condition of microwave heating, all the catalysts also increased the yield of tar to some extent, but when the Fe$_2$O$_3$ loading was 10%, the tar yield was the highest. Speculated that the cause of this difference is that under conventional heating, the catalytic effect mainly depends on the mesoporous structure of the zeolite.
molecular sieve and the active site, and catalytic cracking of the lignite primary depolymerization product, however too strong acidity can lead to rapid carbon catalyst deactivation, the Fe₂O₃ loading can effectively improve the molecular sieve acidity [11], but it also reduces the specific surface area of the catalyst. If the load exceeds a certain limit, the mesoporous structure of the zeolite molecular sieve is blocked and the catalytic effect is reduced. In the process of microwave heating, in addition to the above catalytic effects, the catalyst also plays the role of a microwave absorber, producing special "active sites" such as "hot spots" and "microplasma", which are related to the loading of Fe₂O₃, and the experiment shows that the effect is best when the load amount is 10%.

4. Conclusion
This paper mainly discusses the effects of heating method and different amounts of Fe₂O₃ loaded on ZSM-5 molecular sieve on microwave assisted pyrolysis of Mengdong lignite for the oil production. The yield of microwave pyrolysis tar of lignite was about 6.43wt%. Compared with the conventional pyrolysis results under the same conditions, the yield of lignite pyrolysis tar was relatively increased by 193.61%, which proved that microwave heating technology could effectively improve the yield of lignite pyrolysis tar. According to the XRD characterization of the catalyst, Fe₂O₃ does not form crystals which can be detected on the surface of the catalyst, and the load was relatively uniform, with the increase of Fe₂O₃ load, the crystallinity of the catalyst decreased. Moreover, the addition of the catalyst increased the dielectric loss factor of the material, accelerated the microwave pyrolysis process, and improved the yield of tar, which had the best effect when the Fe₂O₃ loading is 10%, the total yield of tar is up to 9.47%, and the tar yield is relatively increased by 47.29%, therefore, Fe/ZSM-5 molecular sieve catalyst can promote the effective improvement of lignite microwave pyrolysis tar yield.

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