Microwave-Assisted Pyrolysis of Low-Rank Coal with K$_2$CO$_3$, CaCl$_2$, and FeSO$_4$ Catalysts

Yanjun Zhang, Gang Chen, Liping Wang, Kaiyong Tuo, and Shuqin Liu*

**ABSTRACT:** Combined with the advantages of microwave pyrolysis and catalytic pyrolysis, the microwave pyrolysis experiment of low-rank coal under the synergism of catalyst was carried out. The dielectric response of coal samples and metal compound catalysts to microwave was analyzed quantitatively. The microwave pyrolysis behavior and product distribution of low-rank coal were studied. The effects of microwave heating and catalyst properties on the properties of pyrolysis products were analyzed in depth. Results show that the heating effect of dielectric loss and ionic conduction loss of metal compound catalysts could further promote the rapid temperature rise of coal samples. The catalysts could effectively improve the product distribution and properties in the process of microwave pyrolysis of low-rank coal. Compared with the control group, the output of syngas (H$_2$ + CO) increases by a maximum of 1.72 times, and the content of asphaltene in tar reduces by a maximum of 0.66 times. The introduction of K$_2$CO$_3$ and CaCl$_2$ is conducive to the formation of a more developed pore structure and the increase of the specific surface area of semicoke. The co-action of the developed pore structure of semicoke and properties of residual catalysts could significantly improve the CO$_2$ gasification activity of semicoke.

1. **INTRODUCTION**

Microwave heating technology has the advantages of clean, environment friendliness, safety, and unique heat and mass transfer. It is expected to be more convenient to realize the staged conversion of low-rank coal and improve the utilization efficiency and environmental and economic benefit of coal.

Zhang et al. studied oil production from microwave-assisted pyrolysis of a low-rank American brown coal, and results showed that microwave-assisted pyrolysis may be a more suitable technology for obtaining oil from brown coals than electrical heating pyrolysis. Williams et al. indicated that via microwave-assisted pyrolysis, noncoking coals could potentially be used to produce high-quality cokes, potentially expanding the raw material options for metallurgical coke production. Reddy et al. studied the pyrolysis of three coking coals and a noncoking high-ash Indian coal via microwave-assisted heating, and results showed that microwave pyrolysis was a suitable process to produce polyaromatic tar along with high-quality gases and char. High selectivity of polyaromatics in microwave pyrolysis tar was due to the generation of localized hotspots, which lead to excessive cracking of primary pyrolysis vapors. Hydrogen and methane were the major components in the gaseous fraction. Coal chars were rich in carbon (>80 wt %) with high energy content (29 MJ/kg).

Dielectric properties of materials determine the feasibility and economic benefits of microwave heating. At ambient temperature, the dielectric properties of coal itself are generally poor, so it is necessary to add strong microwave-absorbing materials to take full advantage of rapid microwave pyrolysis. Liu et al. studied the microwave pyrolysis characteristics of Ulanqab lignite promoted by the absorber, which showed that the dielectric properties of lignite itself were poor, but the microwave heating rate of lignite increased by 2–3 times and the pyrolysis efficiency increased significantly after adding strong microwave absorbers. Mushtaq et al. studied the effect of coconut shell activated carbon (CAC) as a microwave absorber on coal microwave pyrolysis. In the process of microwave pyrolysis of coal without CAC, the temperature of the coal seam was far lower than the surface temperature, and no pyrolysis took place. After adding CAC evenly, the pyrolysis efficiency of the coal samples was significantly improved under optimal conditions, and the yields of coal tar, pyrolysis gas, and semicoke were 18.59, 19.42, and 61.99%, respectively. The pyrolysis gas could be used as gas fuel because of the high
content of H$_2$. Rajasekhar et al.\textsuperscript{15} studied the microwave co-
pyrolysis of high-ash Indonesian coal and rice husk with
graphite as a microwave absorber, and results showed that the
tar component and calorific value changed significantly, H$_2$ was
a major fraction of the pyrolysis gases, and the addition of rice
husk promoted the evolution of CO.

However, rapid microwave pyrolysis cannot completely
avoid the problems in the coal pyrolysis process. For example,
it is difficult to collect tar, and it is difficult to remove dust in
high-temperature gas and tar, which affects the stable operation
of the subsequent oil–gas separation unit. The content of
heavy components in product oil is high,\textsuperscript{16,17} which increases
the hydrogen consumption in the later stage of hydrogenation
and light-weight process. In the process of coal pyrolysis,
adding catalysts could control the product distribution and
realize direct transformation of pyrolysis products.\textsuperscript{18–20} Metal
compounds, such as alkali metal K, alkaline earth metal Ca,
and transition metal Fe, have attracted much attention in the
catalytic pyrolysis process because of their advantages of
low price, simple preparation, and good catalytic effect. Tuo et
al.\textsuperscript{21} studied the effects of different metal compounds on the
composition of pyrolysis tar. The results showed that K and Fe
compounds can effectively reduce the content of polycyclic
aromatic hydrocarbons (PAHs) above three rings and promote
the lightness of tar products. Therefore, choosing strong
microwave-absorbing materials as catalysts can not only ensure
the high efficiency of microwave heating but also realize the
depth cracking of tar, increase the gas yield, improve the
semicoke quality, and tune the product distribution.

Herein, combining the advantages of microwave pyrolysis
and catalytic pyrolysis, the catalytic microwave pyrolysis
experiment of low-rank coal was carried out. The dielectric
properties of three metal compound catalysts (K$_2$CO$_3$, CaCl$_2$,
and FeSO$_4$) and the coal samples were investigated. The
microwave heating characteristics of coal were studied. The
distribution and properties of the products were analyzed in
depth. An important goal is to obtain the catalytic microwave
pyrolysis characteristics of low-rank coal. The obtained results
provide a theoretical reference for optimizing product
properties and tuning product distribution.

2. EXPERIMENTS SECTION

2.1. Raw Coal and Catalyst. The coal sample was taken
from Huayin coal mine (Shanxi Province, China). The particle
size of the coal sample was less than 6 mm after crushing and
screening. The properties’ analysis of coal is shown in Table 1.
K$_2$CO$_3$, CaCl$_2$, and FeSO$_4$ are used as catalysts, and their
purity is higher than 99, 96, and 98%, respectively.

2.2. Dielectric Properties’ Measurements. In this
article, coaxial probe method was used to test the dielectric
constant of the materials, and the testing system is shown in
Figure 1. The sample was crushed and ground to below 200
meshes before testing. The sample was put into a cylinder
(diameter 25 mm, height 30 mm) and pressed under 16 MPa.
The cylinder was placed in a poly(tetrafluoroethylene) (PTFE)
sleeve with a wall thickness of 10 mm and a base thickness of
20 mm. Then, the vector network analyzer (E5071C, Keysight
Technologies) was switched on for preheating, parameter
adjustment, and calibration.

During the measurements, the end of the coaxial probe in
the vector network analyzer was fully contacted with the
upper-end face of the cylinder, and complex relative
permittivity of the material was measured at normal temper-
ature.

2.3. Microwave Pyrolysis Experiments. The experimental
system of microwave pyrolysis is shown in Figure 2, with a
microwave frequency of 2450 ± 50 MHz and nonpulse
continuous microwave heating.

The incipient wetness impregnation method was used to
introduce various metal compound catalysts to coal particles
equably and steadily. Before the experiment, 50 g of Huayin
coal was immersed in 100 ml of K$_2$CO$_3$, CaCl$_2$, or FeSO$_4$
deionized aqueous solution, followed by stirring for 24 h.
The resulting mixtures were dried in the vacuum oven at 105 °C for
12 h, and the coal samples with a catalyst loading of 5 wt % (K,
Ca, or Fe element to dry coal basis) were obtained. Different
catalyst samples were placed in a quartz boat, and microwave
pyrolysis experiments were carried out in order. Then, a
microwave pyrolysis experiment of Huayin coal without a
catalyst was done as the contrast group. According to Figure 2,
the experimental system was connected to a 99.7% pure flow of
N$_2$ as a carrier gas to ensure an oxygen-free environment.
According to the previous work, the microwave power was
selected as 800 W, and the microwave radiation time was set to
30 min. The liquid and gas products were collected by
condensing bottles and collecting pockets. After the experi-

Table 1. Properties’ Analysis of Coal

| Proximate analysis (wt %) | Ultimate analysis (wt %) | Petrographic analysis (vol %) |
|--------------------------|--------------------------|-----------------------------|
| $M_{ad}$ | $A_d$ | $V_{daf}$ | $C_{daf}$ | $H_{daf}$ | $N_{daf}$ | $O_{daf}$ | $S_d$ | Vitrinite | Inertinite | Exinite | $R_{max}$ (%) |
| 3.66 | 15.56 | 38.17 | 79.9 | 4.75 | 0.94 | 13.73 | 1.28 | 60.8 | 35.5 | 3.7 | 0.39 |

Figure 1. Testing system of dielectric properties.

Figure 2. Microwave pyrolysis system: (1) N$_2$ cylinder, (2) rotameter,
(3) microwave oven, (4) quartz reactor, (5) asbestos cover, (6)
thermocouple, (7) cooling bottle, (8) wet-type flow meter, (9) gas
pocket, and (10) gas chromatograph.

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ment was completed, the furnace chamber was cooled to ambient temperature, and the semicoke product was collected and weighed. The gas volume was calculated from the difference between the two flow meters in Figure 2, while the gas yield was calculated from the gas volume and the gas composition determined by gas chromatography. Trichloromethane was used to wash the quartz reactor and all of the pipes of the condensing system to colorless, the cleaned tar solution was combined with the tar in the condensing system, and tar products were obtained after filtration and dehydration. The experiments were nonconsecutively repeated three times to determine the uncertainty in product yields. The standard deviations of product yields with respect to the average values were within 3%.  

2.4. Product Property Analysis. A gas chromatograph (GC-2014C, Shimadzu, Japan) was applied to analyze the gas components. The chromatographic columns were Porpark-N and MS-13x. The carrier gas was Ar with a flow rate of 60 mL/min, the temperatures of the column oven and TCD detector were 50 and 100 °C, the hot filament current was 60 mA, and the analysis time was 13 min. The instrument was calibrated with a standard gas sample based on the external standard method, and then the sample was tested. Pyrolysis gas was composed of a variety of combustible gases, and its calorific value was calculated as follows

\[
Q_{\text{all}} = \sum Q_i V_i / 100
\]  

As indicated in eq 1, \( Q_{\text{all}} \) is the calorific value per unit volume of gas (MJ/m³); \( Q_i \) is the unit volume calorific value of each component in gas (MJ/m³); and \( V_i \) is the volume fraction of each component (vol %). The calorific value per unit volume of each component in the gas is shown in Table 2.

| gas composition | calorific value per unit volume (MJ/m³) |
|-----------------|----------------------------------------|
| \( \text{H}_2 \) | 10.81                                   |
| \( \text{CH}_4 \) | 35.79                                   |
| CO              | 12.56                                   |
| \( \text{C}_6\text{H}_n \) | 71.20                                   |

The group composition of tar was determined by the chromatography column method, as shown in Figure 3. Asphaltene was obtained from \( \text{n} \)-hexane insoluble components by chloroform leaching. The \( \text{n} \)-hexane soluble components were added into the silica gel alumina chromatography column and then saturates, aromatics, and resins were leached out by dichloromethane and \( \text{n} \)-hexane mixed solvent (2:1), chloroform, and anhydrous ethanol, respectively. The content of each component was obtained after the solvent was evaporated.

A pore structure analyzer (SI 4, Quadrasorb) was applied to measure pore volume and specific surface area of the semicoke with \( \text{N}_2 \) as the adsorption medium. Adsorption isotherms of semicoke were measured at 77.35 K and relative pressure of \( 10^{-6} \)–1. Then, specific surface area and pore structure parameters of the sample could be obtained by calculation.

Gasification activity is an important quantity index of gasification feedstock. The \( \text{CO}_2 \) gasification activity experiment of semicoke was carried out on a TG-DTA/DSC thermal analyzer. About 8 mg of semicoke sample was put into a crucible and flattened, and the furnace was raised to the gasification temperature at a heating rate of 30 °C/min in a \( \text{N}_2 \) atmosphere. After the constant temperature was kept for 3 min, the \( \text{CO}_2 \) atmosphere was switched, and the \( \text{CO}_2 \) flow rate was 60 mL/min. The gasification time was 30 min. The weight loss curve of semicoke was automatically collected during gasification. The fixed carbon conversion of semicoke during gasification was calculated by isothermal thermogravimetry, as shown in eq 2.

\[
x = \frac{\Delta W}{W_0(1 - A_{\text{ad}} - A_{\text{fl}} - V_{\text{ad}})}
\]  

As indicated by eq 2, \( x \) is the carbon conversion (%). \( \Delta W \) is the weight loss of semicoke in the gasification reaction (mg). \( W_0 \) is the initial mass of semicoke (mg). \( A_{\text{ad}} \) is the moisture content of semicoke (%). \( A_{\text{fl}} \) is the ash content of semicoke (%). \( V_{\text{ad}} \) is the volatile content of semicoke (%).

3. RESULTS AND DISCUSSION

3.1. Dielectric Properties of Coal and Catalysts. Dielectric properties of materials determine the feasibility and economic benefits of microwave heating11,12 and their ability to attenuate microwave energy, which can be represented by complex relative permittivity, penetration depth, and average power density of dielectric loss,6,11,22–26 as shown in eqs 3, 4, and 5, and 6, respectively.

\[
\varepsilon = \varepsilon' - i\varepsilon''
\]  

\[
d_p = \frac{\lambda}{2\pi\sqrt{2\varepsilon'}} \left\{ 1 + \frac{1}{\sqrt{1 + \left( \frac{\varepsilon'}{\varepsilon} \right)^2}} \right\}
\]  

\[
\Psi_d(z) = \frac{\omega}{c} \sqrt{\frac{4\varepsilon'' \sigma_0 e^{-2\alpha z}}{\sqrt{\varepsilon''^2 + \varepsilon''^2} - 2 + 2(\sqrt{\varepsilon''^2 + \varepsilon''^2} + \varepsilon') + 1}}
\]  

\[
\alpha = \frac{\omega}{c} \sqrt{\frac{2 - 2\sqrt{\varepsilon''^2 + \varepsilon''^2} - \varepsilon')}{2}}
\]  

As indicated by eq 3, \( \varepsilon \) is the complex relative permittivity, which consists of \( \varepsilon' \) and \( \varepsilon'' \). \( \varepsilon' \) is the real part, which reflects the ability of the dielectric material to store electric field energy due to polarization. \( \varepsilon'' \) is the imaginary part, which indicates the loss of electric field energy in the dielectric material. As indicated by eq 4, the penetration depth \( d_p \) is the distance that the microwave penetrates, where the microwave power decays to \( 1/e \) of the surface value, reflecting the attenuation speed when the microwave propagates in the dielectric material. As indicated by eq 5, the average power density of dielectric loss \( \Psi_d \) represents the microwave energy absorbed per unit volume.
in unit time in the dielectric material (z coordinate), which reflects the absorption of microwave energy in different spatial positions in the dielectric material. It is one of the embodiments of the selectivity of microwave heating. As indicated by eq 5, δ0, α, ε, and ω are the average energy current density, attenuation coefficient, vacuum light speed, and microwave angular frequency of the electromagnetic wave, respectively. Complex relative permittivity, penetration depth, and average power density of dielectric loss all provide theoretical methods for quantitative analysis of the dielectric response process of the coal to microwave and the energy attenuation intensity of microwave propagation in the coal. Under the conditions of normal temperature and a microwave frequency of 2450 MHz, the dielectric response parameters of Huayin coal and catalysts to microwave are obtained through the dielectric properties' test and formula calculation, as shown in Table 3.

| Sample          | e'−iε'' | d₀ (cm) | P̅₀ (W/m²) |
|-----------------|----------|--------|------------|
| Huayin coal     | 2.6649−0.0260i | 122.31 | 0.2838   |
| K₂CO₃           | 4.9571−0.1527i | 28.43  | 1.11S₀   |
| FeSO₄           | 14.2305−4.4429i | 1.68  | 14.24S₀  |
| CaCl₂           | 11.7936−3.3752i | 2.00  | 12.61S₀  |

"Microwave incident depth z = dₚ = P̅₀/ε₀: average energy current density of the microwave oven.

The order of e', ε'', and P̅₀ (z = dₚ) is the same, which is FeSO₄ > CaCl₂ > K₂CO₃ > coal sample. The order of dₚ is opposite to the above order. These results show that the ability of FeSO₄ to store microwave energy and produce dielectric loss, attenuation speed, and intensity of microwave in it are the largest, followed by CaCl₂ and K₂CO₃. The dielectric properties of Huayin coal are relatively weak and far weaker than those of the three catalysts. In conclusion, FeSO₄, CaCl₂, and K₂CO₃ have a strong dielectric response to microwave and could quickly convert microwave energy into heat energy. Therefore, the three catalysts could be used as microwave absorbers to promote coal pyrolysis.

3.2. Effect of Catalysts on the Characteristics of Microwave Heating. Microwave heating characteristics and the relationship between the average heating rate and the average power density of dielectric loss of the Huayin coal with the synergism of K₂CO₃, CaCl₂, FeSO₄, and without catalyst (the control group) are shown in Figure 4.

As shown in Figure 4a, the heating rate of the coal samples without catalyst (the control group) is significantly slower. The temperature rise trend is gentle due to the evaporation of water and the absorption of a large amount of heat at 100−200 °C. Then, the heating rate increases rapidly after water evaporation, which is due to the structure change of semicoke, i.e., significant enhancement of dielectric property resulting in a dielectric response enhancement of semicoke to microwave. The heating rate of coal samples increases significantly under the synergism of each catalyst. The catalysts could promote the rapid temperature rise of Huayin coal in the microwave field, especially at the initial temperature rise stage below 200 °C, and there is no heating rate flat and slow period. This is because K₂CO₃, CaCl₂, and FeSO₄ have good dielectric properties, and their dielectric response to microwave is much higher than that of Huayin coal, which could quickly convert microwave energy into heat energy and make the temperature of coal samples to rise rapidly. Besides, K₂CO₃, CaCl₂, and FeSO₄ were added by the impregnation method, which was equivalent to the introduction of metal ions such as K⁺, Ca²⁺, and Fe³⁺ in the coal samples. The ions would migrate and move rapidly and repeatedly with the high-frequency alternating electromagnetic field in the microwave field. The ion migration would induce a current, generate the dielectric loss, and transform microwave energy into heat energy, as shown in Figure 5. Therefore, the heating effect of dielectric loss and ionic conduction loss of K₂CO₃, CaCl₂, and FeSO₄ could promote the rapid temperature rise of coal samples.

As shown in Figure 4b, the changing trend of the average heating rate of coal samples and P̅₀ (z = dₚ) of the Huayin coal under the synergism of catalysts (2450 MHz, 800 W).
dielectric loss effect of ion conduction would be weakened. Under the comprehensive effect, the heating rate of coal samples under the synergism of FeSO₄ is reduced. Through the comparison, it could be concluded that the catalysts could effectively promote the fast heating of coal in the microwave field, which is conducive to take full advantage of fast microwave heating.

### 3.3. Effect of Catalyst on the Product Distribution

The effect of different catalysts on the product distribution of microwave pyrolysis of coal samples is shown in Figure 6.

Under the synergism of K₂CO₃ and FeSO₄, the yield of semicoke, tar, and pyrolysis water is significantly reduced. At the same time, gas production is significantly increased, which is 1.34 and 1.35 times more than that without a catalyst. Under the synergism of CaCl₂, the distribution of pyrolysis products is similar to that without a catalyst. It can be concluded that K₂CO₃ and FeSO₄ can not only ensure the high efficiency of microwave heating but also realize the deep cracking of tar, increase the gas yield, and tune the product distribution. However, CaCl₂ has no obvious effect on the product distribution.

### 3.4. Effect of Catalyst on the Composition of Pyrolysis Gas

The output of each component of pyrolysis gas is shown in Figure 7, and the calorific value of gas is shown in Table 4.

As shown in Figure 7, under the synergism of K₂CO₃ and FeSO₄, the output of each component of gas is in the order of H₂ > CH₄ > CO > C₂H₄ > CO₂ > C₂H₆ with the largest content of H₂ and CH₄. The output of CO increases significantly under the synergism of K₂CO₃ and FeSO₄. It has been reported in the literature³¹ that carbon in coal char released CO through reaction with K₂CO₃ during pyrolysis, and the higher the temperature was, the stronger the fluidity of K₂CO₃ was, and at the same time, the higher the catalytic activity was. The iron ion in FeSO₄ formed a highly active surface complex with the oxygen atom of the oxygen-containing functional group in coal, promoting decomposition of the oxygen-containing functional group³² and releasing more CO. Compared with the control group, under the synergism of K₂CO₃ and FeSO₄, the output of syngas (H₂ + CO) increases by 1.72 and 1.40 times, respectively.

As shown in Table 4, the calorific value of the gas produced under the synergism of K₂CO₃ and FeSO₄ is significantly reduced. This is due to a significant increase in the content of syngas with low calorific value. At the same time, the hydrocarbon content of C₁−C₂ with high calorific value is 15.19 and 18.75 vol %, respectively, which is far lower than that without a catalyst (32.01 vol %). The calorific value of gas increases under the synergism of CaCl₂ because the content of H₂ with low calorific value is 56.86 vol %, lower than that without a catalyst (59.33 vol %), and the hydrocarbon content of C₁−C₂ is 39.20 vol %, higher than that without a catalyst.

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**Table 4. Calorific Value of Gas**

| catalyst     | K₂CO₃ | CaCl₂ | FeSO₄ | no catalyst |
|--------------|-------|-------|-------|-------------|
| caloric value (MJ/(N m³)) | 14.95 | 23.57 | 15.04 | 21.87       |

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3.5. Effect of Catalyst on the Properties of Tar. The relative content of the group composition of tar produced under the synergism of catalysts is shown in Figure 8.

![Figure 8. Relative content of four components of tar.](image)

As shown in Figure 8, asphaltene and resins are the main components of tar, among which asphaltene content is the highest. Under the synergism of FeSO₄, the content of asphaltene decreases significantly, and the content of resins and saturates increases significantly, indicating that FeSO₄ is favorable for pyrolysis of the Huayin coal to produce resins and saturates. Under the synergism of FeSO₄, the content of asphaltene and saturates decreases obviously, while the content of resins and aromatics increases, indicating that FeSO₄ is favorable for pyrolysis of the Huayin coal to produce resins and aromatics. A significant decrease of asphaltene shows that K₂CO₃ and FeSO₄ could effectively promote the deep cracking of heavy components in tar, which benefits conversion of tar to the light fraction. It is consistent with the analysis of the decrease of tar yield and the increase of gas yield. However, under the synergism of CaCl₂, the content of each component in tar has little change, indicating that CaCl₂ has little effect on the group composition of tar.

The ultimate analysis of tar produced under the synergism of different catalysts is shown in Table 5. Under the synergism of K₂CO₃, the hydrogen content and H/C ratio in tar increase obviously while the sulfur and oxygen content decrease. It implies that the tar is significantly lighter, and the removal rate of heteroatoms like oxygen and sulfur is high under the synergism of K₂CO₃, which is consistent with the analysis of the increase of saturate content in the group composition of tar. H/C ratio in tar increases to a certain extent and the content of sulfur and oxygen decreases under the synergism of CaCl₂ and FeSO₄, indicating that CaCl₂ and FeSO₄ are also conducive to tar lightening and heteroatom removal. Besides, K₂CO₃ and FeSO₄ significantly reduce the oxygen content in tar, which is consistent with the analysis of CO and CO₂ in gas products.

3.6. Effect of Catalyst on the Properties of Semicoke.

3.6.1. Proximate Analysis, Ultimate Analysis, and Calorific Value of Semicoke. According to the test results, proximate analysis, ultimate analysis, and calorific value of the semicoke after deducting the influence of catalysts are shown in Table 6. Among them, the decomposition reaction of FeSO₄ at a high temperature (above 800 °C) would occur as follows: 2FeSO₄ → Fe₂O₃ + SO₂ + SO₃ so the quality of Fe₂O₃ would be calculated by FeSO₄ and then be deducted.

As shown in Table 6, the water content of semicoke decreases (CaCl₂ is prone to deliquesce and absorb water, i.e., CaCl₂ + 6H₂O ⇌ CaCl₂·6H₂O resulting in higher water content), the ash content increases, the fixed carbon decreases, and the volatile content changes little under the synergism of each catalyst. The carbon content is very high, up to 95 wt %, and the content of other elements is less than 2 wt %. The calorific value of semicoke produced under the synergism of K₂CO₃ and FeSO₄ decreases slightly. The deliquesence of CaCl₂ results in a significant decrease of the calorific value.

3.6.2. Pore Structure of Semicoke. The N₂ adsorption–desorption isotherms of semicoke are shown in Figure 9. The isotherms of semicoke produced under the synergism of K₂CO₃, CaCl₂, and no catalyst are all reverse-S shape. According to physisorption isotherm classification,33,34 they belong to type-II isotherm. The initial half of the curve rises slowly and is convex upward, which indicates that micropore filling mainly occurs in the low-relative-pressure range. The subsequent half of the curve rises rapidly, indicating that there are mesopores and macropores in the semicoke. When the relative pressure is high, volume filling of macropores occurs due to capillary condensation, so it demonstrates that the semicoke contains micropores, mesopores, and macropores at the same time. The adsorption isotherm of semicoke produced under the synergism of FeSO₄ is inclined to the x-axis in the low-relative-pressure range, which belongs to the type-III adsorption isotherm. The adsorption capacity in low pressure (P/P₀ < 0.1) and medium pressure (0.3 < P/P₀ < 0.8) is very small, and the adsorption capacity in high pressure increases rapidly, indicating that macropores are dominant in the semicoke. Through the hysteresis loops in the isotherms, it

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Table 5. Ultimate Analysis of Tar

| catalyst    | C (%) | N (%) | H (%) | S (%) | O (%) | H/C | O/C |
|-------------|-------|-------|-------|-------|-------|-----|-----|
| K₂CO₃       | 82.53 | 1.03  | 7.85  | 0.10  | 8.49  | 1.14| 0.08|
| CaCl₂       | 83.21 | 1.16  | 5.95  | 0.35  | 9.33  | 0.86| 0.08|
| FeSO₄       | 84.35 | 1.19  | 5.57  | 0.42  | 8.48  | 0.80| 0.08|
| No catalyst | 83.86 | 1.00  | 5.26  | 0.54  | 9.34  | 0.75| 0.08|

Table 6. Proximate Analysis, Ultimate Analysis, and Calorific Value of Semicoke

| catalyst    | Mdaf | Ad (%) | Vdaf | FCdaf | Cdaf | Hdaf | Ndaf | Odaf | Sdaf | Qb,ad (MJ/kg) |
|-------------|------|--------|------|-------|------|------|------|------|------|--------------|
| K₂CO₃       | 0.47 | 23.48  | 4.56 | 73.03 | 95.14| 1.53 | 1.91 | 0.07 | 1.04 | 29.17        |
| CaCl₂       | 2.11 | 23.15  | 4.25 | 73.58 | 95.70| 1.26 | 1.53 | 0.07 | 1.11 | 28.84        |
| FeSO₄       | 0.47 | 23.07  | 4.30 | 73.63 | 94.98| 1.82 | 1.28 | 0.09 | 1.41 | 29.71        |
| no catalyst | 1.09 | 22.36  | 4.42 | 74.21 | 95.55| 1.26 | 1.69 | 0.04 | 1.14 | 30.02        |
could be speculated that the slit pores in semicoke produced under the synergism of K$_2$CO$_3$, CaCl$_2$, and no catalyst are formed by the accumulation of sheet particles, while for FeSO$_4$, the slit pores are produced by the layered structure.

According to the N$_2$ adsorption–desorption isotherms, pore size distributions in the mesopore and macropore range are calculated by the Barrett–Joyner–Halenda (BJH) method, as shown in Figure 10. The accumulated pore volume of semicoke produced under the synergism of K$_2$CO$_3$ and CaCl$_2$, increases rapidly in the pore size range of 2–10 nm, changes little in the range of 10–30 nm, and increases again in the range of 30–300 nm, indicating that the mesopores of 2–10 and 30–50 nm and macropores of 50–300 nm in the semicoke contribute a lot to the pore volume. It could be seen from the pore size distribution curves that the proportion of pores at 2–10 nm is the largest. The accumulated pore volume
of the semicoke produced under the synergism of FeSO₄ changes little in the pore size range of 2−10 nm and increases rapidly in the range above 10 nm, indicating that the pores with a size above 10 nm contribute a lot to the pore volume. It could be seen from the pore size distribution curves that the proportion of small mesopores of 3−4 nm and large mesopores above 12 nm is large. The accumulated pore volume of semicoke produced without catalyst increases rapidly in the pore size range of 2−10 nm and above 30 nm, indicating that the mesopores of 2−10 nm and meso-/macropores above 30 nm contribute a lot to the pore volume of semicoke. According to the pore size distribution curves, the proportion of mesopores with a size above 10 nm in semicoke is the largest.

According to the N₂ adsorption−desorption isotherms, specific surface area of semicoke is calculated by the Brunauer−Emmett−Teller (BET) method and pore volume and average pore diameter of semicoke are calculated by the BJH method. The corresponding pore structure parameters are shown in Table 7.

Table 7. Pore Structure Parameters of Semicoke

| catalyst     | S_{BET} (m²/g) | V_{2−300 nm} (×10⁻² cm³/g) | D_{ave} (nm) |
|--------------|----------------|-----------------------------|--------------|
| K₂CO₃        | 27.67          | 3.69                        | 6.35         |
| CaCl₂        | 31.82          | 4.34                        | 7.77         |
| FeSO₄        | 5.52           | 3.99                        | 30.92        |
| no catalyst  | 11.13          | 1.87                        | 8.01         |

As shown in Table 7, the order of accumulated pore volume of semicoke is CaCl₂ > FeSO₄ > K₂CO₃ > no catalyst, the order of specific surface area is CaCl₂ > K₂CO₃ > no catalyst > FeSO₄, and the order of average pore size is FeSO₄ > no catalyst > CaCl₂ > K₂CO₃. The specific surface area of semicoke produced under the synergism of FeSO₄ is much smaller than that of CaCl₂, K₂CO₃, and no catalyst. The reason may be that the macropore proportion of the semicoke produced under the synergism of FeSO₄ is very high. According to the hysteresis loop in the N₂ adsorption−desorption isotherm (Figure 9c), the pores of the semicoke produced under the synergism of FeSO₄ is mainly the slit pores between the lamellar structure, which is similar to the “disordered structure”.35 The irregular arrangement of the lamellae and the large pores lead to the small difference of the total pore volume and the very small specific surface area of the semicoke, but the average pore diameter is very large. As shown in Figure 11, there are many small cracks on the semicoke produced under the synergism of K₂CO₃. The layered structure similar to a “corrosion structure” appears in the semicoke produced under the synergism of CaCl₂. There are a lot of obvious layered structures in semicoke produced under the synergism of FeSO₄.

According to the above analysis, compared with the pore structure parameters of semicoke produced under the action of no catalyst, the addition of K₂CO₃ and CaCl₂ is conducive to the formation of more developed pore structures and the increase of specific surface area of semicoke under microwave pyrolysis. At the same time, the addition of FeSO₄ is more conducive to the production of larger pores in semicoke.

3.6.3 CO₂ Gasification Reactivity of Semicoke. The CO₂ gasification activity of semicoke produced under the synergism of different catalysts is shown in Figure 12. With the rising temperature, the reaction activity of semicoke increases continuously. Compared with the control group, the CO₂ gasification activity of semicoke produced under the synergism of three catalysts is significantly improved. The carbon conversion of semicoke produced under the synergism of K₂CO₃ is the highest, followed by CaCl₂ and FeSO₄, which is consistent with the analysis of pore structure. It indicates that the original pore structure of the semicoke has a great influence on its reaction activity. However, the pore structure of semicoke produced under the synergism of FeSO₄ is not as rich as that of the control group, and the carbon conversion is significantly higher than that of the control group, indicating...
that the residual catalyst still plays an important role in the CO₂ gasification activity of semicoke. The residual catalyst can increase the reactivity sites of semicoke and then enhance the gasification activity.

When the temperature is above 850 °C, the carbon conversion of semicoke produced under the synergism of K₂CO₃ begins to increase rapidly, which is significantly higher than that of CaCl₂ and FeSO₄. The carbon conversion curve of semicoke produced under the synergism of CaCl₂ gradually approaches that of FeSO₄. It indicates that with the increase of gasification temperature, the effect of the properties of the residual catalyst on the gasification activity of semicoke is enhanced. According to the previous reports in the literature,³¹,³⁶⁻³⁹ K⁺ has good migration fluidity, and the higher the temperature is, the better the fluidity is. With the increase of gasification temperature, K⁺ completely melts (K₂CO₃ melting point is 891 °C) and begins to migrate, covering the surface of semicoke better, contacting to it fully, and then improving the reaction activity. The mechanism of K₂CO₃ catalyzing C→CO₂ can be explained by oxygen transfer theory, which is expressed as follows

\[
\begin{align*}
K_2CO_3 + 2C & \rightarrow 2K + 3CO \\
2K + 2nC & \rightarrow 2C_nK \\
2C_nK + CO_2 & \rightarrow (2C_nK)OCO \rightarrow (2nC)K_2O + CO \\
(2nC)K_2O + CO_2 & \rightarrow (2nC)K_2CO_3 \rightarrow 2nC + K_2CO_3
\end{align*}
\]

Therefore, the higher the temperature is, the better the migration fluidity of K₂CO₃ is, and the fuller the contact is, as well as the higher the catalytic efficiency is. Calcium and iron ions could increase the active sites on the surface of semicoke. However, the catalytic effect of CaCl₂ is not as good as that of K₂CO₃ because of the poor migration fluidity of CaCl₂. The melting point of FeSO₄ is relatively low, and it may transform into FeOOH, Fe₂O₃, and Fe₃O₄ in the microwave pyrolysis process. These substances are then further transformed into ultrafine iron compounds,²⁸⁻⁵⁰,⁴⁰,⁴¹ which have a higher melting point, leading to worse migration fluidity and less contact with semicoke than FeSO₄, so the CO₂ gasification activity is poor.

In sum, the co-action of the developed pore structure of semicoke and properties of residual catalysts could significantly improve the CO₂ gasification activity of semicoke. After introducing three metal compound catalysts, the efficiency of microwave pyrolysis of low-rank coal is improved, and the distribution and properties of the products are optimized, while the effect of K₂CO₃ is the best.

4. CONCLUSIONS

(1) The heating effect of dielectric loss and ionic conduction loss of metal compound catalysts could further promote the rapid temperature rise of coal samples. Compared with the control group, under the synergism of K₂CO₃ and FeSO₄, the output of gaseous products increases by 1.39 and 1.31 times, respectively, among which the output of syngas (H₂ + CO) increases by 1.72 and 1.40 times, respectively. K₂CO₃ and FeSO₄ could effectively promote asphaltene decomposition in tar, reducing by 0.66 and 0.83 times, respectively, which benefits tar conversion to a light fraction.

(2) Compared with the control group, the introduction of K₂CO₃ and CaCl₂ is conducive to the formation of a more developed pore structure and the increase of the specific surface area of semicoke under microwave pyrolysis. The order of the CO₂ gasification activity of the semicoke is K₂CO₃ > CaCl₂ > FeSO₄ > no catalyst. The co-action of the developed pore structure of semicoke and properties of residual catalysts could significantly improve the CO₂ gasification activity of semicoke. Finally, it can be concluded that the catalytic microwave pyrolysis of low-rank coal can not only ensure a high efficiency of microwave heating but also promote the lightness of tar and obtain high-quality gas and semicoke.

■ AUTHOR INFORMATION

**Corresponding Author**
Shuqin Liu – School of Chemical and Environmental Engineering, China University of Mining and Technology (Beijing), Beijing 100083, China; orcid.org/0000-0002-2831-6600; Email: 13910526026@163.com

**Authors**
Yanjun Zhang – School of Chemical and Environmental Engineering, China University of Mining and Technology (Beijing), Beijing 100083, China; Shanghai Research Institute, National Engineering Laboratory for Direct Coal Liquefaction, China Shenhua Coal to Liquid and Chemical Co., Ltd., Shanghai 201108, China

Gang Chen – Shanxi High Carbon Energy Low Carbon Utilization Research and Design Institute Co., Ltd., Taiyuan 030006, China

Liping Wang – Shanxi High Carbon Energy Low Carbon Utilization Research and Design Institute Co., Ltd., Taiyuan 030006, China

Kaiyong Tuo – School of Chemical and Environmental Engineering, China University of Mining and Technology (Beijing), Beijing 100083, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c01400

**Notes**
The authors declare no competing financial interest.

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