Reduction—Magnetic Separation of Pickling Sludge by Biomass Pyrolysis Reducing Gas

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ABSTRACT: The neutralization process of carbon steel pickling wastewater produces a large amount of steel hydrochloric acid pickling sludge (SHPS), and improper treatment of this sludge poses a serious threat to the environment. Considering that SHPS contains a large amount of iron oxide and given the huge demand for iron concentrate in China’s ironmaking industry, refining iron oxide in SHPS into iron concentrate will have great environmental and economic benefits. This paper proposes a new method that uses biomass (corn cob) to replace conventional coal-based reductants for the recovery of iron components in SHPS to simultaneously utilize two kinds of solid waste resources. Factors that affect the iron recovery rate and iron grade of SHPS, such as the reaction temperature, corn cob dosage, residence time, and magnetic field strength, were studied using a fixed bed and a magnetic separator. These studies were combined with thermodynamic analysis, thermogravimetric analysis, X-ray diffraction, inductively coupled plasma—mass spectrometry, gas chromatography, etc. The results showed that when the reaction temperature was 680°C, the corn cob dosage was 5%, the residence time was 20 min, and the magnetic field strength was 200 mT, the recovery rate of iron reached 91.83%, and the iron grade of the recovered products was 67.72%, meeting the level I requirements in GB/T 32545-2016. Based on this result, a process involving SHPS reduction roasting with corn cob pyrolysis reducing gas—magnetic separation was established to recover iron from SHPS. This process not only effectively utilizes the iron oxide in SHPS by converting it into iron concentrate powder for the ironmaking industry but also proves that the pyrolysis gas of corn cob has good reduction ability.

1. INTRODUCTION

Carbon steel is a widely used and versatile material. During carbon steel production and processing, an oxide layer is formed, and this oxide layer reduces the corrosion resistance of steel. At present, the most common surface treatment for carbon steel strips is pickling, which uses hydrochloric acid to remove the oxide layer. This method produces a large amount of pickling wastewater, which is highly acidic and contains large amounts of heavy metal ions and chloride. Therefore, the wastewater must be treated before being discharged. Lime or caustic soda neutralization is recognized as one of the most effective heavy metal wastewater disposal methods for some small- and medium-sized carbon steel surface treatment plants, but it produces a large amount of heavy metal-containing steel hydrochloric acid pickling sludge (SHPS), which contains chloride. According to statistical reports, the annual output of SHPS in China in recent years has exceeded 500,000 tons.1 SHPS exhibits leaching toxicity, pollutes soil and water, can cause chromosomal aberrations in plants, and causes potential harm to human health.2–4 In China, as per the National List of Hazardous Waste (2021 version),5 SHPS is hazardous waste, so it is urgently necessary to develop treatment, management, and disposal technologies for SHPS.

The conventional approach for treating SHPS is landfilling, which often follows stabilization/solidification. Increasingly stringent environmental and landfill regulations coupled with the increasing costs of raw materials make it imperative to find a feasible method of recycling and treating SHPS to replace the traditional landfill method. Some theoretical and experimental studies have been performed on utilizing SHPS resources. The utilization methods studied include making bricks6,7 and glass ceramics,8 preparing P-doped polyferric chloride coagulants,9 and preparing spinel ferrite.10 However, when SHPS is used for building materials such as bricks or ceramics, the amount of SHPS added is limited and the metals in SHPS still exist in the
building materials; these materials have not been effectively utilized as resources and involve a risk of leaching into the environment under specific environmental conditions. The process of preparing iron-based coagulants takes a long time. The market demand for the production of ferrite is very limited.

However, SHPS is an inevitable product in the carbon steel industry and contains a large amount of Fe₂O₃. Effectively utilizing the Fe contained in SHPS in the modern ironmaking industry is a highly attractive strategy to solve the problems related to the depletion of high-grade iron ores. The traditional method to improve the iron grade of an iron ore is to reduce weakly magnetic Fe₂O₃ to strongly magnetic Fe₃O₄ with a coal-based reducing agent and then separate the strongly magnetic Fe₃O₄ and nonmagnetic components in the roasted material by magnetic separation. However, coal-based reductants usually need a high reduction temperature, so some researchers have used alternatives, such as biomass, to replace coal-based reducing agents.

Biomass not only has good reducing agent characteristics but also has the advantages of a large number of resources, low price, and renewability. To date, there have been some relevant studies on reducing iron oxide with biomass instead of coal-based reducing agents. For example, Rath et al. explored the application of biomass briquette that was produced from unused vegetative remnants as an alternative reductant for the reduction of iron ore is to reduce weakly magnetic Fe₂O₃ to strongly magnetic Fe₃O₄ with a coal-based reducing agent and then separate the strongly magnetic Fe₃O₄ and nonmagnetic components in the roasted material by magnetic separation. However, coal-based reductants usually need a high reduction temperature, so some researchers have used alternatives, such as biomass, to replace coal-based reducing agents.

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appropriate experimental conditions. Considering the above-mentioned facts, the present study aims to explore the possibility of the application of biomass (corncob) in the reduction roasting of a Chinese SHPS sample containing Fe₂O₃ to recover iron from SHPS; the goal of this recovery process is to effectively utilize SHPS as a resource and alleviate the supply shortage of iron concentrate powder, as well as to establish a new bioreductant (corncob) that will function as an alternative to coal in the future and broaden the resource utilization channels of the corncob. First, the characteristics (including appearance, chemical composition, elemental and industrial analysis, scanning electron microscopy (SEM) microstructure, X-ray diffraction (XRD) crystal phase, and thermogravimetric (TG) properties) of SHPS and corncob were analyzed. Then, the pyrolysis characteristics of the corncob were studied to clarify the temperature range and concentration of reducing gas emitted by corncob pyrolysis. Furthermore, the Gibbs free energy of the reaction of reducing components such as CO, H₂, CH₄, and C with Fe₂O₃ in SHPS at different reaction temperatures was studied by thermodynamic calculations. Finally, the effects of the reaction temperature, corncob addition amount, residence time, and magnetic separation intensity on the Fe recovery ratio and Fe grade in SHPS were studied using a fixed bed and magnetic separation tube. This research provides a new idea for the recovery and utilization of SHPS and corncob.

2. MATERIALS AND METHODS

2.1. Preparation of SHPS and Corncob Samples. The SHPS sample was supplied by a steel surface processing plant (Tianjin City, China). The corncob sample was collected from a farm in a suburb of Tianjin City. The SHPS powder and corncob were crushed into fine particles and sieved such that only particles less than 150 μm in diameter were utilized. Figure 1 presents photographs of the SHPS and corncob samples.

2.2. Characterization Techniques. Different integrated instrumental characterization studies were carried out for the reductant (corncob), SHPS sample, and roasted and magnetic separation products. The O, N, and H contents in the ultimate analysis of the samples were analyzed by an American Leco ONH863 analyzer, while C and S were analyzed by an American Leco CS844 analyzer. The proximate analysis of the samples was carried out on an American Leco TGA801 industrial analyzer. The elemental content (except chlorine) of the samples was tested using an Agilent ICP–MS 7700 instrument. The chlorine content in the powder samples was analyzed using an ARL AdvantX Intellipower TM3600 X-ray fluorescence spectrometer (Thermo Fisher). X-ray diffraction (XRD) patterns of the samples were obtained with a Rigaku D/Max 2500 (Japan) X-ray diffractometer utilizing a Cu Kα radiation source to determine the crystalline phases. Scanning electron microscopy (SEM) images were recorded by a Zeiss Sigma 300 (Germany) scanning electron microscope to observe the morphology.

TG analysis was carried out using a synchronous STA 8000 thermal analyzer (PerkinElmer). To preheat the reaction system and evacuate the air in the reaction chamber, the circulating water pump was opened before the beginning of the experiment, and 100 mL/min argon was injected at the same time. When the system temperature was stable and the carrier gas pressure was constant at 2 MPa, approximately 8–10 mg of dried experimental sample was placed in a prefired ceramic crucible. The heating rate for TG analysis was 15 °C/min, and the final temperature was 950 °C.

2.3. Experimental Methods: Pyrolysis—Reduction Roasting and Magnetic Separation. All reduction roasting experiments were conducted in an electric furnace. Figure 2 shows a schematic diagram of the experimental device during pyrolysis—reduction roasting. A total of 10 g of an SHPS sample was thoroughly mixed with the desired amount of the corncob and stored in a quartz tube. Before each test, high-purity N₂ with a flow rate of 40 mL/min was injected into the quartz tube to maintain an inert atmosphere for the reactions. After roasting for the required time, the samples were removed and cooled with N₂. The roasted mass was ground to a −150 μm size and subjected to magnetic separation using a low-intensity magnetic separator with a magnetic field intensity of 0–400 mT. The strongly magnetic and nonmagnetic fractions were collected separately, dried, and analyzed for total iron (Fe(T)) content, and the iron recovery rate was calculated. The strongly magnetic fraction was regarded as the product. The experimental process flow is presented in Figure 3.

In the pyrolysis experiment of the corncob without SHPS, after the pyrolysis reaction was completed and the sample had cooled to room temperature, the coke product was collected and weighed. The pyrolysis tar was collected with dichloromethane and then distilled through a rotary evaporator, and the masses of bio-oil and water were calculated. The gas products were collected in an air bag, and then the volume fractions of the main small-molecule reducing gases were analyzed by gas chromatography (Shimizu GC112a).

The product yield of corncob pyrolysis was calculated as follows
and Fe (char, tar, water, and feedstock, respectively. As shown in Table 2, the C content in the corncob reached 43.62%, and the content of H was 5.98%, while the proximate analysis showed that the volatile content reached 76.16%; therefore, corncob has the potential to produce volatile reducing gas by pyrolysis to reduce iron oxide in SHPS.

Figure 4 shows the results of SEM analysis of the external characteristics of the corncob and sludge. The microstructure of the corncob shown in Figure 4a consists of long strips embedded with pores, and this structure is conducive to the release of volatile compounds during pyrolysis. As shown in Figure 4b, SHPS has a microscopic structure consisting of bright and fluffy irregular spheres and dark and very small irregular particles, and the structure of the sludge is complicated.

To determine the phases in the SHPS sample, an XRD analysis was performed, as shown in Figure 5. In addition, Figure 5 shows that Fe in SHPS generally exists in the form of a trivalent iron oxide, which is weakly magnetic and cannot easily be recycled. Furthermore, the diffraction peak in the diffraction pattern of SHPS is complex, which means that this material is difficult to recycle without treatment.

3. RESULTS AND DISCUSSION

3.1. Thermogravimetric Analysis and Pyrolysis Characteristics of the Corncob. Figure 6 shows the TG-derivative thermogravimetry (DTG) curves of the high-temperature behavior of the SHPS and corncob samples. A mass loss of approximately 15.09% was observed for SHPS in the temperature range of 100–900°C. The weight loss at 50–150 °C was mainly caused by the desorption of physically adsorbed water and adsorbed gas, and the weight loss at 200–400°C was mainly caused by the dehydroxylation of a small amount of aqueous minerals, such as goethite (formula 6), in SHPS. The weight loss at 260–950 °C was mainly caused by the thermal decomposition of a small amount of organic matter and calcium carbonate in SHPS. When the temperature was 100–260 °C, the mass reduction rate of corncob remained basically unchanged; there was basically no thermal decomposition reaction at this stage, and the composition of the corncob remained basically unchanged. When the pyrolysis temperature was greater than 260 °C, the TG curve began to decline rapidly, indicating that volatile compounds were released. There was a second trough in the DTG curve near 290 °C, and the release rate of volatiles reached the maximum at this point. The TG curve shows that the weight loss of the corncob was very small after 500 °C, indicating that the pyrolysis reaction tends to become stable when the pyrolysis temperature of the corncob exceeds 500 °C. The residual mass of the corncob decreased from 94.84 to 22.68% in the range of 260–500 °C, which was attributed to the complex composition of the corncob. A corncob contains cellulose and

![Figure 3. Flowchart of SHPS reduction.](image)

\[ Y_1 = \frac{m_1}{m} \times 100\% \]  
\[ Y_2 = \frac{m_2}{m} \times 100\% \]  
\[ Y_3 = \frac{m_3}{m} \times 100\% \]  
\[ Y_4 = 100 - Y_1 - Y_2 - Y_3 \]

where \( Y_1, Y_2, Y_3, \) and \( Y_4 \) are the yields of pyrolysis char, tar, water, and gas, respectively, and \( m_1, m_2, m_3, \) and \( m \) are the masses of the char, tar, water, and feedstock, respectively.

2.4. Statistical Design. The recovery rates of Fe in the strongly magnetic concentrates were calculated according to mass balance. The formula used to calculate the recovery rate is as follows:

\[ \text{recovery rate} = \frac{M_1 \times \omega_2}{M_1 \times \omega_1} \times 100\% \]

Note: \( M_1 \) — quantity of strongly magnetic concentrate, g; \( \omega_1 \) — grade of iron in concentrate, %; \( M_2 \) — quantity of the raw material, g; and \( \omega_2 \) — grade of iron in the raw material, %.

2.5. Analysis of SHPS and Corncob Characteristics. The chemical composition of the SHPS sample is shown in Table 1. As shown in Table 1, SHPS contains large amounts of Ca, Cl, and Fe (~30%), and Fe is one of the main raw materials in the iron and steel industry, can be well separated, and has a great recovery value.

The ultimate and proximate analyses of the corncob and SHPS are presented in Table 2. The results of the ultimate analysis presented in Table 2 show that the C content of SHPS was 2.38%; this C mainly comes from the organic acid mist inhibitor that was added to prevent HCl gas from escaping during the steel pickling process. The relatively low content of C indicates that it is difficult for SHPS to burn. The H content was only 1.94%, which indicates that there are few hydrogen-rich aliphatic side chains in SHPS and that SHPS has a low calorific value. The moisture content in SHPS was 13.38%, the ash content was 77.14%, and the volatile content was 4.65%. The high ash content further indicates that SHPS has a low calorific value during combustion and a low organic matter content. As shown in Table 2, the C content in the corncob reached 43.62%, and the content of H was 5.98%, while the proximate analysis showed that the volatile content reached 76.16%; therefore, corncob has the potential to produce volatile reducing gas by pyrolysis to reduce iron oxide in SHPS.

![Figure 4. SEM analysis of the external characteristics of the corncob and sludge.](image)

![Figure 5. XRD analysis of the SHPS sample.](image)

![Figure 6. TG-derivative thermogravimetry (DTG) curves of SHPS and corncob samples.](image)

| Chemical Composition (%) | SHPS |
|--------------------------|------|
| Fe          | 29.80|
| Zn          | 0.02 |
| Mn          | 0.29 |
| Ca          | 11.11|
| Na          | 3.38 |
| K           | 0.005|
| Mg          | 0.19 |
| Si          | 4.78 |
| Al          | 0.21 |
| Cl          | 12.13|
| P           | 0.01 |
| S           | 0.02 |
hemicellulose, which are connected by weak bonds. In this temperature range, the bonds in the corncob were easily broken, generating a large amount of volatiles and resulting in a significant decrease in weight.22 The temperature range of 300–325 °C mainly involved the decomposition of hemicellulose and a small amount of lignin, and at 340–375 °C, the degradation of cellulose predominated.23 After the experiment, the mass fraction of residual carbon was 22.48%. Additionally, the corncob had a higher mass loss than SHPS because the corncob contains a higher content of volatile matter, as shown in Table 2.

The corncob (10 g) was dried and sieved to 150 μm and the temperature was increased to 300, 400, 500, 600, 700, 800, and 900 °C in a tubular pyrolysis furnace, as shown in Figure 2, at a heating rate of 15 °C/min. Gas samples were collected in a collection bag at intervals of 100 °C from 300 to 900 °C, and the gas composition was analyzed by gas chromatography. After being maintained at the desired temperature for 40 min, the residue was removed and cooled to room temperature. The distribution of the pyrolysis products obtained is shown in Table 3, and Figure 7a shows the change trends for the four pyrolysis
Table 3. Dependence of Corncob Product Yields on Pyrolysis Temperature

| temperature (°C) | char (wt %) | gas (wt %) | oil (wt %) | water (wt %) |
|------------------|-------------|------------|------------|--------------|
| 300              | 31          | 33         | 15         | 21           |
| 400              | 30          | 34         | 16         | 20           |
| 500              | 27          | 35         | 22         | 16           |
| 600              | 25          | 37         | 23         | 15           |
| 700              | 26          | 41         | 16         | 17           |
| 800              | 24          | 42         | 14         | 20           |
| 900              | 22          | 43         | 13         | 22           |

Figure 7. Yield of corncob pyrolysis products at different pyrolysis temperatures (a) and volume fractions of small-molecule reducing gases in corncob pyrolysis gas (b).

The volume fraction of the main small-molecule reducing gases at different pyrolysis temperatures is shown in Table 4, and can be explained by the fact that the gaseous yield is higher during the transition from 600 to 900 °C than for other temperature intervals, as shown in Figure 7a.

Table 4. Volume Proportions of Small-Molecule Reducing Gases Produced by the Corncob at Different Pyrolysis Temperatures

| temperature (°C) | CO (vol %) | H₂ (vol %) | CH₄ (vol %) |
|------------------|------------|------------|-------------|
| 300              | 6.89       | 1.84       | 0.41        |
| 400              | 7.92       | 2.91       | 0.56        |
| 500              | 8.54       | 3.96       | 0.62        |
| 600              | 10.43      | 4.48       | 0.71        |
| 700              | 22.01      | 7.78       | 0.83        |
| 800              | 24.32      | 9.95       | 1.12        |
| 900              | 26.51      | 10.05      | 2.69        |

Figure 7b shows the corresponding change trends. As shown in Figure 7b and Table 4, the yield of small-molecule reducing gases increased with increasing temperature, especially above 600 °C. CH₄ in the pyrolysis gas mainly comes from the cracking of aliphatic side chains. CO mainly originates from the decomposition of oxygen-containing functional groups, and the yield of CO was higher than that of H₂ and CH₄, which indicated that the corncob contained a relatively high content of oxygen. The gas from corncob pyrolysis originates not only from the primary pyrolysis process but also from the secondary thermal cracking of volatile compounds. These pyrolysis reducing gases provide reducing agents for the medium- and low-temperature reduction of iron oxide in SHPS.

3.2. Thermodynamic Analysis. To investigate the ability of reducing gases in corncob pyrolysis gas to reduce iron oxide in SHPS, the change law of the Gibbs free energy for the reaction between the gas components and SHPS at different reduction temperatures was calculated by thermodynamic analysis. After the sample is dried, Fe is mainly present as an oxide. Therefore, the thermodynamic analysis in this paper mainly examines the reaction of Fe₂O₃ with multiple reducing substances. When the pyrolysis temperature is 600 °C, the main reducing components in corncob pyrolysis gas are approximately 4.48 vol % H₂, 0.71 vol % CH₄, and 10.34 vol % CO. According to the relevant species of reactants and products, the possible chemical reaction between pyrolysis gas and Fe₂O₃ is shown in eqs 7–18. As a comparative study, this paper also calculates the reduction thermodynamic data for coal series reductants. When using a coal series reductant, the main reduction medium is fixed carbon; the main reduction reaction is shown in eqs 19–22. According to the thermodynamic calculation method (listed in eqs 7–22; the calculation formula of ΔrGθ m(°C) is ΔrGθ m(°C) = ΔrHθ m(298.15 K) − TΔrSθ m(298.15 K), where ΔrHθ m(298.15 K) and ΔrSθ m(298.15 K) are based on Schedule 1 (i.e., thermodynamic data for selected substances) from “Inorganic Chemistry” (5th edition) compiled by the Department of Inorganic Chemistry of Dalian University of Technology), the standard reaction Gibbs free energy change (ΔrGm, kJ/mol) of each reaction varies with temperature, as shown in Figure 8. Thermodynamically, ΔrGm > 0 means that a chemical reaction cannot occur; on the contrary, when ΔrGm < 0, the reaction will spontaneously occur, and the more negative the ΔrGm value is, the more easily the reaction takes place.
Figure 8. Change in standard reaction Gibbs free energy against temperature for the reaction of iron oxides with H₂ (a), CO (b), CH₄ (c), and C (d).

3Fe₂O₃(s) + H₂(g) = 2Fe₃O₄(s) + H₂O(g), ΔᵣGᵣ° = −15 547 − 74.40T, J/mol

Fe₃O₄(s) + CO(g) = 3FeO(s) + CO₂(g), ΔᵣGᵣ° = 23 940 − 73.62T, J/mol

FeO(s) + CO(g) = Fe(s) + CO₂(g), ΔᵣGᵣ° = 23 430 − 16.16T, J/mol

Fe₂O₃(s) + CO₂(g) = 3FeO(s) + CO₂(g), ΔᵣGᵣ° = 35 550 − 30.40T, J/mol

CH₄(g) + 12Fe₂O₃ = 8Fe₃O₅ + CO₂(g) + 2H₂O(g), ΔᵣGᵣ° = −167 906 − 521.27T, J/mol

4Fe₃O₄(s) + CH₄(g) = 12FeO(s) + CO₂(g) + 2H₂O(g), ΔᵣGᵣ° = 477 307 − 534.60T, J/mol

ΔᵣGᵣ° values were calculated from expressions of the form ΔᵣGᵣ° = ΔᵣGᵣ°₀ − R T ln (P/PT₀) for each temperature value at the pressure P = 1 bar. The ΔᵣGᵣ°₀ values were obtained from the literature. The reaction Gibbs free energy change is calculated from ΔᵣGᵣ° = ΔᵣGᵣ°₀ − R T ln (P/PT₀).
4FeO + CH₄(g) = 4Fe + CO₂(g) + 2H₂O(g), \( \Delta G_m^0 \)
= 261 012 − 276.24T, J/mol  
(17)  
Fe₂O₄ + CH₄(g) = 3Fe + CO₂(g) + 2H₂O(g), \( \Delta G_m^0 \)
= 315 085 − 340.83T, J/mol  
(18)  
3Fe₂O₃(s) + C(s)  
= 2Fe₂O₃(s) + CO(g), \( \Delta G_m^0 \)  
= 132 028 − 220.85T, J/mol  
(19)  
Fe₃O₄(s) + C(s) = 3FeO(s) + CO(g), \( \Delta G_m^0 \)  
= 209 379 − 224.18T, J/mol  
(20)  
FeO(s) + C(s) = Fe(s) + CO(g), \( \Delta G_m^0 \)
= 155 305 − 159.59T, J/mol  
(21)  
Fe₃O₄(s) + 2C(s)  
= 3Fe(s) + 2CO₂(g), \( \Delta G_m^0 \)
= 330 359 − 351.836T, J/mol  
(22)  

As shown in Figure 8, when the temperature is in the range of 273.00−1400.00 K, the standard reaction Gibbs free energies of eqs 7, 11, and 15 are always negative (\( \Delta G_m^0 < 0 \)), indicating that Fe₂O₃ in SHPS is easily reduced to Fe₂O₃ by H₂, CO, and CH₄. The standard Gibbs free energies of eqs 7, 11, and 15 decrease as the temperature increases, which means that increased temperature can promote the reduction magnetization of Fe₂O₃. The Gibbs free energy of eq 19 is generally positive (\( \Delta G_m^0 > 0 \)) below 600 K, which indicates that the reduction of Fe₂O₃ by carbon-based reductants requires a higher reduction temperature than does the reduction of Fe₂O₃ by reducing gas. This is consistent with the research results of Sohn and Freehan, which confirmed that compared to reduction by reducing gas, reduction by carbon was negligible at and below 900 °C. However, when the temperature exceeded 1000 K, weakly magnetic FeO was produced, and the recovery rate of the product was reduced. Therefore, to ensure that the reduction product is strongly magnetic, the reaction temperature should theoretically be below 1000 K. The composition of SHPS is complex, the biomass pyrolysis reduction process may be affected by various factors, and the theoretical analysis may differ from the actual reaction, so we need to comprehensively investigate the influencing factors of the reduction–magnetic separation process.

3.3. Effect of Pyrolysis Temperature on the Recovery Index. The mass ratio of SHPS to corn cob was 96:4%, the final pyrolysis temperature was 400−800 °C, and the residence time after the final temperature was reached was 10 min. The solid pyrolysis residue of SHPS was magnetically separated with a 250 mT magnetic field intensity in a magnetic separator. The effect of pyrolysis temperature on the Fe recovery rate and Fe grade of the concentrate is shown in Figure 9.

Figure 9 shows that the reduction temperature had a strong influence on the iron grade and recovery ratio. When the temperature was 680 °C, the reduced iron grade and recovery ratio were the highest and reached 67.31 and 92.42%, respectively. When the reduction temperature was lower than 680 °C, the Fe grade and recovery ratio increased gradually with increasing reaction temperature. With increasing reaction temperature, the volatile content of small-molecule reducing gas produced by corn cob pyrolysis also increased after volatile decomposition; thus, the conversion rate of Fe₂O₃ to Fe₃O₄ was accelerated. This is consistent with the phenomenon in Figure 6b, which shows that when the temperature increased to 260−600 °C, two large weight loss peaks of corn cob appeared, indicating that the main reducing gases were released. According to the thermodynamic analysis (Figure 8), the Gibbs free energy of the reaction of CO, H₂, and CH₄ with Fe₂O₃ decreases significantly with increasing temperature, which is conducive to the reduction of Fe₂O₃ to Fe₃O₄. When the temperature exceeded 680 °C, on the one hand, too high a temperature causes SHPS to experience local sintering, and the reducing atmosphere cannot fully contact Fe₂O₃ in SHPS, which reduces the reduction rate of SHPS; on the other hand, according to the thermodynamic analysis (Figure 8), the Gibbs free energy of the reaction between CO, H₂, and Fe₂O₄ is less than 0 at 600 and 700 °C, indicating that the higher content of reducing gases such as CO and H₂ from corn cob pyrolysis can deeply reduce part of the SHPS into weakly magnetic wustite (FeO), reducing the Fe grade and recovery rate of SHPS. In addition, when the temperature is too high, Fe₂O₃ may react with Na₂O and CaO to form 2CaO·Fe₂O₃ and Na₂O·Fe₂O₃ which will also reduce the grade and recovery ratio of iron. In addition, if the temperature is too high, the reduction roasted material is sintered, and the reduction conditions deteriorate. Therefore, the roasting temperature should be maintained at approximately 680 °C.

3.4. Effect of Biomass Addition on the Recovery Index. Further experiments were performed to investigate the effect of the biomass addition amount on SHPS Fe₂O₃ reduction and recovery. Corn cob dosages of 1, 2, 3, 4, 5, 6, and 7 wt % were used in reduction experiments at 680 °C for 10 min. The magnetic field strength was 250 mT. Figure 10 shows variation in the recovery index with the corn cob addition amount.

As shown in Figure 10, the Fe recovery rate and grade were greatly affected by the amount of biomass added. As the amount of the corn cob increased, the reduced iron grade and recovery ratio showed a trend of first increasing and then decreasing. When the addition ratio was less than 5 wt %, the iron oxide in the sludge could not be fully reduced, and the recovery rate was

![Figure 9. Effect of pyrolysis temperature on the recovery index.](https://doi.org/10.1021/acsomega.2c01122)
low. When 5 wt % corncob was added, the grade and recovery rate of the product increased significantly, reaching 67.39 and 92.68%, respectively, and the magnetic separation index was better. With a further increase in corncob addition, the grade and recovery rate began to decrease, which may be due to a large amount of reducing volatiles being produced by excessive corncob quantities, leading to overreduction; as a result, weakly magnetic wustite (FeO) formed, which reduced the magnetic separation recovery. In addition, pickling sludge contains a large amount of alkali metals, which easily reduce the ash melting temperature of corncob and lead to agglomeration.15 When the amount of corncob is large, the impurities in the product increase,15 and the Fe grade decreases. Therefore, the appropriate amount of corncob was 5 wt %.

3.5. Effect of Residence Time on the Recovery Index.

The amount of the corncob used was 5 wt %, and the particle size was less than 150 μm; at 680 °C, the particle size of SHPS was less than 150 μm, and the magnetic field strength was 250 mT. The magnetization effect of SHPS in the 5−35 min time range is shown in Figure 11. As shown in Figure 11, the residence time had a great influence on the SHPS magnetization effect; SHPS magnetization increased more obviously with increasing residence time. Before a residence time of 20 min, the total Fe grade and recovery rate increased significantly. After 20 min, the Fe grade decreased significantly, and the recovery showed a gradual downward trend. Therefore, when the temperature reaches 680 °C, the appropriate residence time should be set to 20 min.

3.6. Effect of the Magnetic Field Strength on the Recovery Index.

The influence of magnetic field intensity on the recovery index is shown in Figure 12 under the following conditions: 5 wt % corncob, at 680 °C for 20 min, and a roasted product particle size of less than 150 μm. With increasing magnetic field intensity, the change trends of the iron grade and recovery rate were opposite. When the magnetic field intensity increased from 150 to 300 mT, the recovery rate nearly linearly increased from 87.83 to 92.93%, while the iron grade of the product decreased from 67.95 to 67.26%. When the magnetic field intensity is too low, the recovery rate is low.36 When the magnetic field intensity is too high, some weak magnetic substances may be adsorbed, and some undissociated impurities can be trapped, resulting in an increase in the recovery rate and a decrease in the Fe grade of the recovered products. When the magnetic field intensity was 200 mT, the Fe grade and recovery rate were 67.72 and 91.83%, respectively. Choosing the appropriate magnetic field intensity can not only realize the recovery of magnetic materials but also save energy. In this paper, 200 mT was selected as the magnetic field intensity for magnetic separation of the reduction product.

In summary, the optimized conditions were a reaction temperature of 680 °C, a corncob dosage of 5%, a N2 atmosphere, a residence time of 20 min, a roasted product particle size of less than 150 μm, and a magnetic field strength of 200 mT. Under these conditions, the recovery rate of Fe reached 91.83%, and the grade of Fe reached 67.72%.

3.7. Characterization of the Products Obtained under the Optimum Conditions.

The XRD spectrum of the recovered product from the optimized conditions is shown in Figure 13. Compared with the original SHPS (Figure 5), almost all of the Fe2O3 peaks in the roasted material disappeared, and Fe3O4 peaks appeared instead. The impurities in the magnetic
concentrate product are significantly reduced, and the main component is \( \text{Fe}_3\text{O}_4 \). The tailings mainly consisted of non-magnetic components, such as \( \text{CaCO}_3 \), \( \text{SiO}_2 \), and \( \text{Al}_2\text{O}_3 \).

Figure 14 shows photos of the roasted material, concentrate, and tailings. Figure 14 shows that after reduction roasting of SHPS is performed, the color of the product is notably different from the red color of the SHPS raw material. The roasted material and concentrate are black, while the tailings are light gray.

Table 5 shows the main components of the concentrate product; the total content of Fe in the product reached 67.72%. Compared with the values in Table 1, the content of Cl in the concentrate decreased from 12.13 to 0.39% after roasting-magnetic separation, and the contents of Na, Ca, and K also decreased significantly because these three elements in SHPS mostly combined with Cl to form water-soluble chlorides. Most of these chlorides were dissolved in an aqueous solution during wet magnetic separation, and only a small amount remained in the concentrate. The filtrate produced by wet magnetic separation is mainly saline liquid containing soluble chloride salt, and this part of the filtrate should be recycled after water treatment, such as pretreatment—microfiltration—reverse osmosis—evaporative crystallization.

Table 6 shows the classification of the magnetite concentrated in GB/t 32545-2016. In addition to the magnetic separation concentrate obtained under the selected experimental conditions reached the level I requirements in GB/T 32545-2016. In addition to the magnetic separation concentrate having the potential to be used as a raw material for ironmaking, magnetic separation tailings can be used to solidify metal ions by the sintering method to prepare permeable bricks and comprehensively utilize waste.

4. CONCLUSIONS

Based on the test results and related analysis, the following conclusions can be drawn:

1. When the pyrolysis temperature is 600 °C, the main reducing components in corn cob pyrolysis gas are approximately 4.48 vol % \( \text{H}_2 \), 0.71 vol % \( \text{CH}_4 \), and 10.34 vol % \( \text{CO} \). According to the thermodynamic analysis, the pyrolysis gas produced by the pyrolysis of corn cob at medium and low temperatures has the potential to reduce \( \text{Fe}_3\text{O}_2 \) to \( \text{Fe}_3\text{O}_4 \) in SHPS.

2. When the reaction temperature is lower than 680 °C, the addition amount of corn cob is less than 5%, and the residence time is less than 20 min, the Fe recovery from SHPS increases with increases in these three factors. When the reaction temperature exceeds 680 °C, the addition amount of the corn cob is higher than 5%, and the residence time exceeds 20 min, the thorough reduction of SHPS is promoted, and the Fe recovery rate is reduced. With an increase in the magnetic field intensity, the changes in the Fe grade and recovery rate of the product exhibit the opposite trend. In addition, 200 mT is the appropriate magnetic field strength for magnetic separation of the reduction roasted SHPS material. The recovery rate of Fe in SHPS is mainly affected by the temperature, corn cob addition ratio, residence time, and magnetic field strength.

3. Under the optimized conditions (i.e., a reaction temperature of 680 °C, a corn cob dosage of 5%, a residence time of 20 min, a roasted product particle size of less than 150 \( \mu \text{m} \), and a magnetic field strength of 200 mT), the recovery rate of Fe reached 91.83%, and the grade of Fe
reached 67.72%, which met the level I requirements in GB/T 32545-2016. Through the verification provided by this experiment, the reducing gas produced by the pyrolysis of corncob can effectively reduce iron oxide in SHPS, allowing this iron oxide to be used as a resource.

Table 5. Main Element Contents of the Products after Wet Magnetic Separation (wt %)

| project  | TFe  | SiO₂  | Al₂O₃ | P   | S   | K₂O + Na₂O | Cl  | Ca  |
|---------|------|-------|-------|-----|-----|-------------|-----|-----|
| concentrate | 67.72 | 1.29 | 0.11 | 0.03 | 0.01 | 0.01 | 0.39 | 1.41 |
| tailings   | 8.13  | 32.37 | 1.58 | 0.03 | 0.01 | 0.13 | 0.32 | 22.91 |

Table 6. Classification of the Magnetite Concentrate Grade

| grade   | TFe   | SiO₂   | Al₂O₃   | P   | S   | moisture | granularity |
|---------|-------|--------|---------|-----|-----|----------|-------------|
| level 1 | ≥67.0 | ≤6.0   | ≤0.8    | ≤0.05 | ≤0.08 | ≤10.0    | ≥0.075 mm: ≥60 |
| level 2 | 65.0 to <67.0 | ≤7.0   | ≤1.0    | ≤0.10 | ≤0.12 |          |             |
| level 3 | 63.0 to <65.0 | ≤9.0   | ≤1.2    | ≤0.10 | ≤0.20 |          |             |
| level 4 | 61.0 to <63.0 | ≤11.0  | ≤1.2    | ≤0.10 | ≤0.20 |          |             |
| level 5 | 59.0 to <61.0 | ≤15.0  | ≤1.5    | ≤0.10 | ≤0.50 |          |             |

*Note: the moisture index is for reference.*

Figure 14. Photos of the roasted material (a), concentrate (b), and tailings (c).

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**Notes**

The authors declare no competing financial interest.

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