Reduction of Magnetite from Copper Smelting Slag using Petro-diesel and Biodiesel

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Experiments were carried out in a slag cleaning electric furnace to reduce magnetite in copper smelting slag using petro-diesel or biodiesel produced from waste cooking oil, and the reduction effects using the two reducing agents were compared. The pyrolysis experiments of petro-diesel and biodiesel were carried out in a fixed bed reactor to study their pyrolysis characteristics and explore the reduction mechanism of magnetite in copper smelting slag. The experimental results showed that the primary crystalline phases in copper smelting slag were magnetite [Fe3O4] and silicate. And the content of fayalite [Fe2SiO4] increased while the magnetite [Fe3O4] decreased after reduction by petro-diesel and biodiesel. In the process of copper smelting slag reduction, the petro-diesel and biodiesel firstly cracked into coke, H2, CO and CH4, and then reacted with the magnetite in the slag. The reduction effect of biodiesel was better than petro-diesel because more reducing gases can be generated through pyrolysis of biodiesel, and its price should be much lower than petro-diesel. Therefore, magnetite reduction in copper smelting slag using biodiesel produced from waste cooking oil should be recognized as an economical and environment-friendly process for waste management and application.

KEY WORDS: copper smelting slag; magnetite reduction; petro-diesel; biodiesel; pyrolysis; waste cooking oil.

1. Introduction

There is more than 80% of copper produced by means of pyrometallurgy all over the world.1) The bath smelting technologies have been widely used in copper pyrometallurgy process with the advantages of high production capacity, low energy consumption, high adaptability to raw materials as well as friendly to environment compared with the traditional technologies and flash smelting technologies.2,3) However, the bath smelting technologies with high oxygen potential can cause the enrichment of magnetite in copper smelting slag, which influences the settling separation of copper droplet due to high viscosity of the molten slag and results in the copper loss in slag. Aiming at the high recovery degree of copper, the depletion method in electronic furnace has been used to reduce the content of copper in slag through the magnetite reduction by reducing agents.

The traditional reducing agents used in the process of copper slag reduction are coal, pure gases and mixed gases with the disadvantages of scarcity and non-renewability. In contrast, approximately over 5 million tons of waste cooking oil is generated in catering industry in China annually, of which 40–60% backflow to dining tables through various improper channels.4,5) The main component of the other cooking waste oil is triglycerides, which can react with methanol to produce fatty acid methyl esters (FAME) and glycerol under the alkali-catalysis, acid-catalysis or enzyme-catalysis. The FAME is what we call biodiesel. Compared with petro-diesel, biodiesel from waste cooking oil has advantages of low carbon, low emission and renewability. The carbon dioxide produced from biodiesel can be recycled by photosynthesis of plants, which can reduce the greenhouse effects from biodiesel.6) Based on the great demand of fuels and reducing agents in the process of metallurgy, the application of biodiesel from waste cooking oil in metallurgical industry is an important way to achieve saving petro-diesel, resource utilization of waste cooking oil and inhibition of the greenhouse effect.

The available information with respect to copper slag reduction by biodiesel from waste oil is scarce. However, several investigations of magnetite reduction or copper slags depletion by other reducing agents have been performed. Zhang, et al. investigated the reduction process of iron oxides by mixed CO–CH4–Ar gas from commercial copper slags.7) The results showed that the magnetite content decreased gradually, while fayalite phase increased during the reduction process. Nagasaka, et al. studied the reduction process of Fe3O4 with hydrogen for copper slag.8) Heo, et al. investigated the effect of CaO addition on iron recovery from copper smelting slags by solid carbon.9) Li, et al. studied the iron recovery efficiency and optimized the technical conditions.10) The experimental
results implied that the iron recovery rate of the copper slag can reach 91.82%, and the extracted iron powder has an iron grade of 96.21%. Maweja, et al. investigated that increasing coal-to-slag ratio to 5 wt.% allowed the recovery of 70–90% for Cu, Co and Zn simultaneously after 30–60 min reduction of the molten slag. The direct reduction of copper slag to antibacterial stainless steel was proposed by Zhang, et al., and it can be obtained that the removal rate of sulfur is 99.64% in reduction of matte in metal. Effects of CaO, reaction temperature and reduction ratio on reduction of copper slag were discussed by Zuo, et al., and experiments of the reduction of copper slag were carried out using biomass.

In current study, experiments were carried out in a slag cleaning electric furnace to compare the reduction performance and economic benefit of the magnetite reduction in copper smelting slag when using petro-diesel and biodiesel. The pyrolysis experiments were carried out in a fixed bed reactor to reveal the mechanism of copper smelting slag reduction using petro-diesel and biodiesel from waste cooking oil.

2. Experimental

2.1. Materials

The mixture of copper matte and slag from Isasmelt furnace was fed into a slag cleaning electric furnace and then layered after settlement in Yunnan COPPER CO., LTD. in China. The chemical compositions of copper smelting slag are shown in Table 1. The petro-diesel was obtained from local petrochemical company and biodiesel was purchased from biodiesel production company, respectively. The ultimate analyses of each oil are shown in Table 2.

2.2. Methods

The copper smelting slag reduction experiments were carried out in a slag cleaning electric furnace as shown in Fig. 1. Six electrodes were settled in the upper zone of the electric furnace. As the reducing agents, petro-diesel or biodiesel was sprayed into the copper smelting slag layer with nitrogen through the spray guns settled in two ends of the electric furnace. Experimental conditions: reduction time 30 min, petro-diesel and biodiesel flow 80 L/h, reduction temperature 1523 K (1250°C). Considering the uneven distribution of magnetite along the vertical orientation of slag layer, three sampling points were set in the upper, middle and lower layers of copper smelting slag, separately. Analyses on samplings were completed before and after reduction. Satmagan135 magnetic analyzer was used to analyze the contents of magnetite in copper smelting slag. X-ray diffraction (Japan Science D/max-R diffractometer) techniques were used to measure phase changes during the reduction, for the further discussion on the reduction effects of magnetite. The morphology was determined using field emission scanning electron microscopy on HITACHI-S3400N scanning electron microscopy.

The pyrolysis experiments were carried out in a pyrolysis system as shown in Fig. 2 to obtain the pyrolysis characteristics of the petro-diesel and biodiesel from waste cooking oil, and explore the copper smelting slag reduction mechanism. The pyrolysis system contained continuous feeding unit, fixed bed reactor, condensation and drying unit as well as gas collection unit. The fixed bed reactor consists of a quartz tube with length of 500 mm and diameter of 30 mm, ceramic fiber cotton fixed bed and stainless steel flanges in the ends of quartz tube. The samples were fed into the reactor continuously with the flow rate of 0.07 mL/min by a peristaltic pump after heating the reactor up to the target temperature. The high purity nitrogen was fed into the pyrolysis system throughout the experiments as the shielding and internal standard gas with the flow rate of 60 mL/min. The pyrolysis gases were collected by gas bag.

Table 1. The chemical composition of copper smelting slag (wt.%).

| Chemical composition | Cu  | Fe  | S   | SiO₂ | Al₂O₃ | MgO  | CaO  |
|----------------------|-----|-----|-----|------|-------|------|------|
| Content              | 10.89 | 33.22 | 4.4 | 24.56 | 4.98  | 4.09 | 6.06 |

Table 2. The ultimate analysis of petro-diesel and biodiesel (wt.%).

| Chemical composition | C   | H   | O   | N   |
|----------------------|-----|-----|-----|-----|
| Petro-diesel         | 85.8 | 13.4 | 0.7 | 0.05 |
| Biodiesel            | 75.7 | 10.5 | 9.6 | 4.1  |

Fig. 1. Schematic diagram of the slag cleaning electric furnace.
after condensing, filtration and drying, and then detected though the gas chromatography (Agilent 7890A). The yield of each pyrolysis gas can be determined as

\[ \text{Yield}_i = \frac{X_i Q_{N_2}}{22400 \times X_{N_2} Q_m} \]  

(1)

Where \( \text{Yield}_i \) - molar yield of gas \( i \), mol/mL; \( X_i \) - volume fraction of gas \( i \), \%; \( X_{N_2} \) - volume fraction of \( N_2 \), \%; \( Q_{N_2} \) - flow rate of \( N_2 \), mL/min; \( Q_m \) - flow rate of sample, mL/min.

The weight of coke produced in the process of pyrolysis was determined by the weight difference of the reactor before and after the experiments. Assuming that the compositions of coke are carbons, the yield of coke can be expressed as

\[ \text{Yield}_{\text{coke}} = \frac{60 \times m_{\text{coke}}}{12 \times t Q_m} \]  

(2)

Where \( \text{Yield}_{\text{coke}} \) - molar yield of coke, mol/mL; \( m_{\text{coke}} \) - weight of coke, g; \( t \) - experiment time, s; \( Q_m \) - flow rate of sample, mL/min.

3. Results and Discussion

3.1. Reduction Experiments by Petro-diesel and Biodiesel

The viscosity of the copper molten slag was largely determined by the magnetite content in slag, which directly influences the settling separation of copper droplet from copper smelting slag. As a result, reducing the magnetite content in slag using reducing agents is an important way to achieve the settling separation of copper droplet from copper molten slag. In this study, the copper molten slag reduction experiments were carried out in a slag cleaning electric furnace to compare the reduction performance to the magnetite in copper smelting slag using petro-diesel or biodiesel from waste cooking oil.

The contents and reduction ratios of magnetite in copper smelting slag before and after reduction by petro-diesel and biodiesel at different sampling points were shown in Figs. 3-5. It is obvious that the magnetite was mainly gathered in the lower layer of copper smelting slag because of its high density. The maximum reduction ratio of magnetite by petro-diesel was 26.15% at upper sampling points, 64.86% at middle sampling points and 62.5% at lower sampling points respectively, while 29.31% at upper, 67.76% at middle and 71.19% at lower by biodiesel from waste cooking oil. The experimental results above indicated that both biodiesel and petro-diesel have good reduction effects as the reducing agents for magnetite reduction in copper smelting slag. Compared with petro-diesel, the reduction effect of biodiesel was more obvious.

Figure 6 shows the XRD pattern of copper smelting slag from lower sampling point for No. 1 before and after reduction by biodiesel. XRD analysis indicated that the primary crystalline phase was magnetite \([\text{Fe}_3\text{O}_4]\) before reduction. And magnetite and fayalite were major crystalline phases after reduction. The fayalite \([\text{Fe}_2\text{SiO}_4]\) produced in the process of copper smelting slag reduction because the magnetite \([\text{Fe}_3\text{O}_4]\) was reduced to ferrous oxide \([\text{FeO}]\) and ferrous oxide \([\text{FeO}]\) combined with \([\text{SiO}_2]\) were transformed into fayalite \([\text{Fe}_2\text{SiO}_4]\).14,15)

The SEM patterns of copper smelting slag from lower sampling point for No. 1 before and after reduction by biodiesel are shown in Fig. 7. The SEM analysis indicated that magnetite had a wide distribution area in SEM patterns before reduction. Then the fayalite phase formed and the magnetite phase areas decreased after reduction. The results of SEM analysis are consistent with the XRD.

3.2. Analysis of Copper Smelting Slag Reduction Process

The primary components of biodiesel are all kinds of fatty acid methyl esters. And the petro-diesel is made up of various kinds of alkanes, alkenes, cycloalkane, aromatic hydrocarbons and polycyclic aromatic hydrocarbons et al. In the process of the copper smelting slag reduction, the petro-
diesel and the biodiesel firstly crack into coke and small molecule gases. Then the pyrolysis products react with the magnetite in the slag. The yields of pyrolysis products from petro-diesel and biodiesel are shown in Figs. 8 and 9. The results indicate that the coke and the small-molecule gases such as H₂, CO increase with temperature increasing because the pyrolysis of macromolecular organics from petro-diesel and biodiesel cracked more complete at higher temperature. And the main products of both reducing agents are coke, H₂, CO and CH₄ when the temperature exceeds 1 473 K (1 200°C). The reaction formula can be expressed as

\[
\text{C}_x\text{H}_y\text{O} \rightarrow \text{C} + \text{H}_2 + \text{CO} + \text{CH}_4 + \cdots \quad (3)
\]

Fig. 3. Comparison of reduction effects of magnetite in copper smelting slag between petro-diesel and biodiesel at the upper sampling points. (Online version in color.)

Fig. 4. Comparison of reduction effects of magnetite in copper smelting slag between petro-diesel and biodiesel at the middle sampling points. (Online version in color.)

Fig. 5. Comparison of reduction effects of magnetite in copper smelting slag between petro-diesel and biodiesel at the lower sampling points. (Online version in color.)
Figure 10 shows the analysis diagram of the molecular structure of the phase transition and material generated during the reduction process for copper slag. It can be seen from the figure that the main pyrolysis products of biodiesel at high temperature, such as hydrogen, carbon monoxide and carbon, would react with magnetite in the copper slag, such as in reactions (4), (5), and (6). The hydrogen gas produced by cracking will react with the magnetite to produce water vapor, which can continue to react with the pyrolysis product carbon and produce hydrogen and carbon monoxide. The product of the reaction could still act as reducing agents to react with the magnetite in the slag. The carbon dioxide produced by the reduction of the magnetite by carbon monoxide could also react with the elemental carbon produced by the pyrolysis of biodiesel to produce carbon monoxide, which could also be a reducing agent. Additionally, the ferrous oxide produced by the reduction reaction combined with silicon dioxide in the slag to generate ferric silicate.16)

From the two-film theory of gas-liquid reaction, the pyrolysis process of petro-diesel and biodiesel was completed in the spray gun. And the stable liquid film and gas film formed between the gases and the molten slag. Then the $\text{Fe}^{3+}$ migrated to the liquid-gas interface through the liquid film while the reducing gases migrated to the interface through the gas film by means of molecular diffusion.17,18) And the reduction reactions occurred in the gas-liquid interface. After the reduction, the $\text{Fe}^{2+}$ diffused to the molten slag and gaseous products diffused to the mixed gas bubble.
Because the rate of the reactions were very fast, the reduction rate-limiting steps were the mass transfer of Fe\(^{3+}\) in the liquid films and the reducing gases diffusion in the gas film.\(^{7,19}\)

\[
\text{Fe}_3\text{O}_4 + \text{C} = 3\text{FeO} + \text{CO} \quad \Delta G = 207510 - 217.62T \quad (4)
\]

\[
\text{Fe}_3\text{O}_4 + \text{CO} = 3\text{FeO} + \text{CO}_2 \quad \Delta G = 35380 - 40.16T \quad (5)
\]
Fe$_3$O$_4$ + H$_2$ = 3FeO + H$_2$O \quad \Delta G = 71,940 - 73.62T \quad ... (6)

The comparison of the products mole yields between petro-diesel and biodiesel from waste cooking oil are shown in Fig. 11. The results indicate that more CO can be produced from biodiesel while more coke and H$_2$ from petro-diesel, and the yield of gases from biodiesel was higher than that from petro-diesel. Biodiesel contains more oxygen, and it is beneficial to produce more CO and improve magnetite reduction. Therefore the effect of oxygen from biodiesel on reduction is very important. Compared to solid reducing agents, the reduction ability of gaseous reducing agents are much better.\textsuperscript{20,21) Therefore, the reduction effect of biodiesel is slightly better than petro-diesel, which conforms to the experimental results above. Considering the low price (Biodiesel: about 0.5 USD/L; diesel: about 1.0 USD/L) and the waste resource recycling of biodiesel and the shortage of fossil fuels, the biodiesel from waste cooking oil is a good alternative to replace the petro-diesel in the reduction process of copper smelting slag.

4. Conclusions

The biodiesel from waste cooking oil is a good alternative to replace petro-diesel in the process of copper smelting slag reduction. The primary crystalline phases in copper smelting slag are magnetite [Fe$_3$O$_4$] and silicate. After reduction using petro-diesel or biodiesel the content of fayalite [Fe$_2$SiO$_4$] increased while the magnetite [Fe$_3$O$_4$] decreased. In the process of copper slag reduction, the petro-diesel and biodiesel firstly cracked into coke, H$_2$, CO and CH$_4$ \textit{et al.} Then the products reacted with the magnetite in copper smelting slag. Compared with petro-diesel, the reduction effect of biodiesel was more obvious, because more reducing gases can be produced from the pyrolysis of the biodiesel, which was more effective for magnetite [Fe$_3$O$_4$] reduction. Therefore, magnetite reduction in copper smelting slag using biodiesel produced from waste cooking oil should be recognized as an economical and environment-friendly process for waste management and application.

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