The Correlation between Palm Shell Char Properties and the Production of Metallic Iron in EAF Steelmaking Slag Reduction Reaction

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Abstract. Palm shells wastes generated from oil palm processing are in abundance in landfills every year thereby posing environmental problems. Enormous amount of wastes generated by agro-industry has previously studied as carbon source in steelmaking hence providing solution to environmental problems. This paper studied on the conversion of palm shell waste into carbon material via physical and chemical activation method for metallic iron extraction. Physical char was prepared by pyrolyzed in nitrogen atmosphere at 450ºC while chemical char was impregnated in phosphoric acid before pyrolyzed. Composite pellets of EAF slag (43.18 %Fe2O3) with physical and chemical char were rapidly heated at temperature 1550ºC within 20 minutes under argon flow. All reduced samples were analyzed on the weight loss, degree of reduction, iron recovery and phase analysis using X-ray diffraction (XRD). The results indicated that chemical/slag showed higher weight loss (38.8%) and excellent degree of reduction (29.94%) compared to physical/slag due to higher volatile matter content (9.8%) and larger surface area (562.14m²/g). It was found that the production of metallic iron particles after the reduction process and indicated that chemical char achieved higher iron recovery (15.48%) compared to physical char due to higher total carbon content (60.28%). XRD and Rietveld refinement analysis confirmed that the iron phase was a major component in metallic iron particles for physical/slag and chemical/slag samples. This elucidated that the iron oxides in EAF slag was completely reduced into iron by using palm shell chars as carbon materials. This finding indicates that palm shell chars potentially act as carbon materials in steelmaking applications according to their good characteristics.

1 Introduction

Agricultural wastes could be an alternative carbon sources in steelmaking thereby providing the solution to environmental problems. According to Babich et al., agricultural waste needs to be converted into char before being used in steel production such as pyrolysis [1].

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Hidayu et al. reported that the derivation of waste into char intended to enrich the carbon content in the carbon material and develop porosity to enhance iron oxide process [2]. Char that contained high carbon content, great porosity, lower sulphur and good reducing capacity was a potential carbon reductant in the steelmaking industry [3]. High carbon content in carbonaceous material could lead to faster rate of reduction [4]. When the carbon/slag samples are heated at a certain temperature, the gas-solid reduction process occurred where higher surface area increased the gas molecules diffusivity thus promoting the reduction reaction [5].

The preparation of char involved two crucial processes such as carbonization and activation. Physical activation is the simplest method because it involved only a single step compared to chemical activation with two steps and more expensive however containing good properties that may contribute to the carbon/slag reactivity [6].

Palm shells are among the primary agricultural waste in Malaysia which is increasing steadily over the years [7]. Previously, palm shell char produced by physical activation method used as carbon reductant in reducing the iron oxide has been reviewed by Yunos et al., Zaharia et al. and Najmi et al. indicating that palm shell char had shown better performance in term of iron oxide reduction and off gas generation [8-10]. The reaction between iron oxide in steelmaking slag and carbonaceous materials are as follows: the formation of CO and CO2; the reduction of Fe2O3 to FeO and finally to Fe (metallic iron) as expressed in Eqs (1-4) [3].

\[
\begin{align*}
C(s) + Fe_2O_3(l) & \rightarrow 2FeO(l) + CO(g) \quad (1) \\
C(s) + Fe_2O_3(l) & \rightarrow 4FeO(l) + CO_2(g) \quad (2) \\
C(s) + Fe_2O_3(l) & \rightarrow Fe(l) + CO_2(g) \quad (3) \\
C(s) + 2FeO(l) & \rightarrow 2Fe(l) + CO_2(g) \quad (4)
\end{align*}
\]

At high temperature reaction, the carbon was expected to be converted into CO and CO2 as expressed in Eqs (5 and 6) [11]. Since the CO and CO2 were the primary products of the reactions in Eqs (1-6), therefore the following reactions of Eqs (7) and (8) may also occur where CO has reacted with iron oxide in slags [3, 12].

\[
\begin{align*}
C(s) + \frac{1}{2}O_2(g) & \rightarrow CO(g) \quad (5) \\
C(s) + O_2(g) & \rightarrow CO_2(g) \quad (6) \\
CO(g) + Fe_2O_3 & \rightarrow 2FeO(l) + CO_2(g) \quad (7) \\
CO(g) + FeO(l) & \rightarrow Fe(l) + CO_2(g) \quad (8)
\end{align*}
\]

The palm shell char has beneficial characteristics such as containing high total carbon, lower sulphur content, high volatile matter content and larger specific surface area. Therefore, in the present study, palm shell chars will be prepared by physical and chemical activation method through pyrolysis due to its nature of enriching the carbon content and highly porous with a larger specific surface area that enhances the reduction reaction process [13, 14]. The reduction study was focusing on the potential of the palm shell chars in producing the metallic iron particles from EAF slag.
2 Methodology

2.1 Sample preparations

The palm shell wastes generated from palm oil mill supplied by Felda Palm Industries Sdn Bhd, Pahang were used in this study as carbonaceous material. Prior to the experiment, the palm shells were firstly dried at room temperature and then oven-dried for 24 hours to reduce the moisture content. The palm shell wastes were then crushed into particle size of 2 mm using grinder machine. The carbonaceous material from palm shell wastes was prepared by using physical and chemical activation methods. For physical activation, palm shells was pyrolyzed at 450ºC in electric tube furnace within 2 hours with a heating rate of 10ºC/min in nitrogen atmosphere whereas for chemical activation, the palm shells were impregnated in phosphoric acid (H₃PO₄) first before pyrolyzed at a similar condition as physical activation. The chars from physical and chemical activation then were grinded into fine powder below 63μm using a ring mill to minimize the particle size for optimum binding during mixing process.

2.2 Preparation of composite pellet

The electric arc furnace (EAF) slag provided by Perwaja Steel Sdn. Bhd., Terengganu was used in this study as iron oxide source. The EAF slag was crushed and ground into fine powder for approximately 63 μm. The palm shell chars (physical and chemical char) and EAF slag were weighed and mixed at ratio a 1:3 palm shell chars to EAF slag. The mixture of constituent powder was milled using planetary mill machine at 200 rpm for 1 hour. After mixed, the samples were compacted in a die by applying a load of 78kPa by using uniaxial compact machine to produce cylindrical composite pellets with a dimension of 20 mm in diameter and 5 mm height.

2.3 Reduction reaction of pellet

The reduction of EAF slag was conducted in a horizontal tube furnace at 1550ºC under argon atmosphere with a flow rate of 1L/min (Fig. 1). After the furnace being heated to 1550ºC, the sample was rapidly inserted and heated for the reduction process within 20 minutes. The reacted sample was quenched by rapidly being withdrawn from hot zone into cold zone of the furnace. The metallic iron particles and slag layer was possibly found on the crucible after the reduction process. The metallic iron particles were characterized using X-ray Diffraction (XRD) and Rietveld refinement method to identify and quantify the phase existed in the samples after reduction.

![Fig. 1. Experimental arrangement for reduction reaction study.](image-url)
3 Results and discussion

3.1 Materials characterizations

The ultimate, proximate and specific surface area analyses for raw palm shell and palm shell chars are presented in Table 1. From Table 1, it indicates that the carbon content had risen after the pyrolysis. The specific surface area had also drastically increased after the conversion process from 1.03 to 359.03 m$^2$/g for physical char and to 562.14 m$^2$/g for chemical char. The higher carbon and specific surface area of chemical char compared to physical char was due to the activating agent ($\text{H}_3\text{PO}_4$) which enhanced the development of porous structure and enlarging the existing pores [15]. Fig. 2 demonstrates the pore distribution before and after the activation. Micrograph of raw palm shell showed some pores available with hexagonal structure (Fig. 2 (a)). After 2 hours of activation via pyrolysis, the hexagonal structure disappeared had followed by the development of mesopores and micropores (Fig. 2 (b) physical char and (c) chemical char). Compared to physical activation, chemical activation method showed the development of new pores and widening of existing pores leading to a production of higher specific surface area. $\text{H}_3\text{PO}_4$ appeared to act as acid catalyst to promote the pyrolytic decomposition and reactant in the formation of cross-linked structure [16].

Table 1. Proximate, ultimate and specific surface area analysis of carbon reductants.

| Materials       | Proximate analysis (wt%) | Ultimate analysis (wt%) | Specific surface area (m$^2$/g) |
|-----------------|--------------------------|-------------------------|---------------------------------|
|                 | Fixed carbon             | Volatile matter         | Ash                             | C    | H    | N    |                  |
| Raw palm shell  | 80.3                     | 8.3                     | 3.7                             | 45.67| 5.86 | 0.37 | 1.03             |
| Physical char   | 81.3                     | 6.6                     | 5.9                             | 59.35| 2.98 | 0.30 | 359.03           |
| Chemical char   | 68.5                     | 9.8                     | 12.8                            | 60.28| 1.85 | 0.44 | 562.14           |

Fig. 2. SEM micrograph of (a) raw palm shell, (b) physical char and (c) chemical char.
The elemental analysis of the EAF slag was carried out by X-Ray fluorescence (XRF) as presented in Table 2. The result indicates that the primary component of EAF slag was Fe₂O₃ accounting to 43.18wt% of the slag.

Table 2. Composition of EAF slag.

| Compound  | Fe₂O₃ | CaO   | SiO₂  | Al₂O₃  | MnO  | MgO  | TiO₂ |
|-----------|-------|-------|-------|--------|------|------|------|
| (wt%)     | 43.18 | 27.67 | 16.87 | 5.77   | 2.55 | 2.27 | 0.54 |

3.2 Weight Loss and Degree of Reduction

Table 3 shows the weight loss and the degree of reduction of the physical/slag and chemical/slag samples after the reduction reaction at temperature 1550ºC. The difference in carbonaceous material has influence the weight loss and degree of reduction. The weight loss was calculated by the weight change before and after the reduction while the degree of reduction was obtained from the removal of oxygen content combined with iron in the samples [17, 18]. From the table, the weight loss for physical/slag was 35.2% and for chemical/char was 38.8%. Similar trend was presented by the degree of reduction where the reduction degree of chemical/slag (29.94%) was higher than physical/slag (25.06%). Chemical/slag showed better performance compared to physical slag due to its good characteristics such as higher in volatile matter (9.8 wt%) and having larger specific surface area (562.14 m²/g). Volatile matter presence in chemical char encouraged the gasification thus contributed to reducing gases production therefore improving the degree of reduction. According to Zuo et al., high amount of volatiles were released from the carbon reductant especially agricultural wastes participated in enhancing the iron oxides reduction reaction.

Table 3. Weight loss and degree of reduction of physical/slag and chemical/slag after reduction reaction.

| Samples       | Weight loss (%) | Degree of reduction (%) |
|---------------|-----------------|-------------------------|
| Physical/slag | 35.2            | 25.06                   |
| Chemical/slag | 38.8            | 29.94                   |

3.3 Production of metallic iron

Fig. 3 shows the reduced iron after the reduction reaction at 1550ºC for 20 minus and the metallic iron particles after being removed from the crucible. The reduced metals of metallic iron have spherical shape with various sizes ranging from 1 – 4 mm elucidated formed by diffusion of small particles and gradually formed bigger particles [11, 21]. The metallic iron particles produced were also weighed and the percentage of iron recovery was calculated according to the ratio of iron transferred to metallic iron particles and the initial amount of iron in the slag before reduction [22]. From Table 4, the utilization of chemical char (15.48%) as carbon materials has produced higher iron recovery from EAF slag compared to physical char (15.38%). As expected, the iron recovery of chemical/slag was slightly higher than physical/slag according to an excellent degree of reaction (Table 3).
According to Najmi et al., high amount of carbon content is desired in order to complete the reduction process. It can be clarified that higher total carbon of chemical char (60.28 wt%) has the tendency to form a bigger lump of metallic iron. It was elucidated that besides volatile matter and specific surface area properties, total carbon content of carbonaceous material can influence the reaction process.

Figure 3. Images of metallic iron particles produced after the reduction reaction at 1550ºC for (a) physical/slag and (b) chemical/slag

Table 4. Iron recovery (%) obtained after the reduction of EAF slag by physical and chemical char.

| Samples       | Metallic iron produced (g) | Iron recovery (%) |
|---------------|-----------------------------|-------------------|
| Physical slag | 0.303                       | 15.38             |
| Chemical slag | 0.305                       | 15.48             |

3.4 Qualitative and Quantitative analysis of metallic iron produced

The metallic iron particles produced were characterized by XRD to justify the phase existed and the Rietveld refinement method was performed to quantify the phase as shown in Fig. 4 and Table 5. The refined parameter for the reduced samples included background, phase and profile parameter. In terms of Rietveld refinement, the both physical/slag and chemical/slag has $R_{wp}$ value lower than the recommended valued (12), $R_{wp}$ closed to $R_{exp}$ and the goodness of fit (GOF) value lower than 4. Thus the phase identification and quantification performed are acceptable [23, 24]. From the XRD pattern, two sharp and distinctive peaks corresponding to iron (Fe) appear at position 2θ (45.13º and 65.41º) for physical/slag and (44.91º and 65.66º) for chemical/slag (iron; PDF file: 01-087-0722). The weight percent of iron for physical and chemical slag was found 100wt%. It was indicated that physical and chemical char has successfully reduced the iron oxide from EAF slag into iron suggesting that palm chars can be potentially used as carbon material.

Fig. 4. Observed XRD pattern (black), calculated XRD pattern (red) by Rietveld method and the difference pattern between the observed and calculated pattern (blue) of (a) physical/slag and (b) chemical/slag at temperature 1550ºC.
Table 5. Rietveld quantitative phase of physical/slag and chemical/slag reduced samples.

| Materials        | Iron content (wt%) | $R_{wp}$ (%) | $R_{exp}$ (%) | GOF |
|------------------|--------------------|--------------|---------------|-----|
| Physical/slag    | 100                | 2.71         | 2.98          | 0.83|
| Chemical/slag    | 100                | 2.30         | 2.57          | 0.90|

4 Conclusion

The conversion of palm shell waste using physical and chemical activation method has produced different properties of palm char which was used as carbonaceous material for iron oxide reduction from EAF slag at temperature 1550ºC. Results revealed that the higher volatile matter and larger specific surface area of chemical char has contributed to the higher weight loss and degree of reduction. The formation of metallic iron particles on the crucible after the reduction process can also be observed. It was indicated that higher total carbon content of chemical char has resulted in a higher percentage of iron recovery from EAF slag. XRD pattern and Rietveld refinement analysis has confirmed that the iron phase is dominant in the metallic iron particles for both physical/slag and chemical/slag samples since there was only iron peak existed on the pattern. It was elucidated that the iron oxide contained in EAF slag was completely reduced by physical and chemical char. Thus, it was suggested that palm shell chars can potentially be used as carbon materials for metallic iron extraction where the palm shell prepared via chemical activation method is more effective.

This research has been funded by Fundamental Research Grant Skim (FRGS) (9003-00366). The financial support for this research was also provided by the University Malaysia Perlis and Ministry of Higher Education, Malaysia.

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