Effect of using Palm Char and Coke as a Reductant in Production of Ferrosilicon

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Abstract. This research focused on the synthesis of ferrosilicon alloy by coke and palm char as a reductant. Raw materials which were iron ore, silica sand, coke and palm char mixed and compacted into pellets. The pellets were reduced at temperature of 1300°C using horizontal tube furnace with nitrogen gas flow. The pellets after reduction process were characterized by X-ray fluorescence (XRF), X-ray diffraction (XRD), Scanning electron microscope equipped with energy dispersive spectra (SEM/EDS). The results from XRD analysis indicated that the formation of FeSi, Fe3Si and SiC phases were appeared at 1300°C for both reductants. The brighter phases were observed in SEM/EDS mapping analysis represents as iron and silicon. The EDX analysis showed the high amount silica developed for coke compared to palm char due to high content of silica and carbon. The results found that palm char as carbon reductant has the potential to produce ferrosilicon and silica carbide in sustainable way.

1 Introduction

Ferrosilicon (FeSi) and silicon carbide (SiC) production processes are all carbothermic reduction processes, where carbon materials are used as reductant to produce the ferroalloys. For ferroalloy and silicon producers, the carbon materials used in the process have a large effect on the total cost, energy consumption, and stability of the operation and, ultimately, on the quality of the final product [1]. There is hence a continual quest for the optimal carbon material available. The determination of the industry to reduce carbon dioxide emissions has directed people’s attention even more toward carbon materials. For many producers, the main carbon material is using metallurgical coke that produced from coal. However, the possibility of using alternative reductants such as charcoal from palm shell waste is becoming increasingly popular. Hence, the aim of this study is to investigate the effect of using different carbon reductants in ferrosilicon synthesis where coke as carbon-based material and compare it to renewable carbon material like palm char.

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It is well known that, biochar, a coal-like material obtained by slow pyrolysis of biomass, can be used as a renewable reductant and may partly or fully replace fossil agents [2-4]. Biochar pellets were investigated as renewable reducing agents in substitution of coal and coke in the silicon/ferrosilicon and iron making production, where a high reactivity, good mechanical properties and low feedstock costs are appreciated [5-8]. In the silicon and ferrosilicon production, the silicon monoxide (SiO) reactivity is considered. Compared to fossil fuel, biochar has higher reactivity [9]. Previous researched by Liu, et al. reported approximately 20% waste carbon material (woodchips) of the total carbonaceous reductants (petroleum coke and coal) was applied to a submerged arc furnace to identify better carbonaceous reductants for the silicon production process. The results indicated that the silicon yield reached a maximum value of 0.945 higher than other reductants [10]. The low ash and high carbon content of macadamia shell waste showed as an attractive carbon source for synthesising high purity SiC and Si3N4 nanopowders in the size range 20-80 nm and 40-100 nm respectively [11].

The most important role of carbonaceous material in ferrosilicon/silicon synthesis is to react with the SiO gas to produce SiC [12]. The reactivity of conventional reduction material like coke/coal is directly correlated to the material properties and leads to high silicon (Si) recovery and economical with good furnace operation. A number of studies investigated the effect of coke and coal properties in the production of high Si alloys focusing on the SiO reactivity [13, 14]. Farzana et. al. found that the initial volatiles generation from bakelite as renewable reductant accelerated the rate of silica reduction compared to coke, particularly the formation of silicon carbide (SiC) through gas phase reduction reactions of silica (SiO2) [14]. However, higher crystallinity of graphite compares to coke facilitated the faster carbon dissolution into iron. This solute carbon increased the rate of ferrosilicon alloy formations were detected by XRD [15]. A complete reduction of silica and alumina (Al2O3) was observed in the Fe2O3-SiO2-C system, along with the formation of phases of FeSi and SiC at temperature of 1550 °C were found in XRD pattern and SEM respectively [16].

Even the number of studies on using graphite, plastic waste from bakelite and charcoal/macadamia shell as renewable reductant is increasing by year, it is crucial to investigate the effect of palm char as renewable reductant in ferrosilicon synthesis considering the reduction capability, reactivity and environment impact. Thus, in this paper, the influence of using different carbon reductants is established and investigated. This study has led to a sustainable alternative solution by transforming agricultural waste into a reducing material for ferrosilicon synthesis.

2 Experimental Procedures

2.1 Preparing palm char via pyrolysis technique

Palm shell used as a raw material which act as reductant in ferrosilicon process was collected from Palm Oil Mill Pahang. The palm shell is crushed and ground by jaw crusher to attain particle size of less than 1 mm. The palm char is prepared via pyrolysis technique by using a horizontal tube furnace with injection of nitrogen gas (flow rate of 0.1 L/min) at temperature 450°C for 2 hours to produce palm char.

2.2 Sample preparations and characterizations

Iron ore as an iron oxides (Fe2O3) sources was collected from Kulim Kedah while coke as carbon control from Southern Steel Sdn Bhd, Penang. Silica sand was used as the main sources of SiO2 for ferrosilicon synthesis. All raw materials were crushed and sieved to get
fine particles less than 63μm in powder form. Next, the palm char, iron ore, coke and silica sand are added into a ball milling machine using the mass ratio of SiO$_2$:C (coke):Fe$_2$O$_3$ and SiO$_2$:C (palm char):Fe$_2$O$_3$ which were 0.5:0.7:0.3 and 0.3:1.0:0.2, respectively based on reducible carbon and oxygen ratio calculation [19]. The speed of ball milling is set to 400 rpm for 2 hours to complete the mixing process homogeneously. The mixture is transformed into pellets by adding distilled water. Then, the pellets are dried in an oven for 12 hours at 90˚C.

The proximate and ultimate analysis of coke and palm char was conducted using CHONS elemental analyzer and the results are presented in Tables 1 and 2. The chemical composition for all materials used in ferrosilicon synthesis were detected by using XRF and presented in Table 3.

**Table 1.** Ultimate analysis for carbonaceous materials.

|          | Carbon | Hydrogen | Nitrogen | Sulfur | Oxygen |
|----------|--------|----------|----------|--------|--------|
| Coke     | 83.36  | 1.14     | 0.39     | 0.30   | 14.82  |
| Palm char| 59.35  | 2.98     | 0.30     | -      | 37.37  |

**Table 2.** Proximate analysis for carbonaceous materials.

|          | Moisture | Ash | Volatile matter | Fixed carbon |
|----------|----------|-----|-----------------|--------------|
| Coke     | 2.4      | 8.0 | 6.5             | 83.1         |
| Palm char| 6.2      | 5.9 | 6.6             | 81.3         |

**Table 3.** XRF analysis for all materials used in ferrosilicon synthesis.

| Composition [wt. %] | Coke     | Palm char | Silica | Iron ore |
|---------------------|----------|-----------|--------|----------|
| SiO$_2$             | 43.36    | 26.80     | 53.9   | 16.4     |
| Fe$_2$O$_3$         | 9.60     | 52.87     | 5.3    | 53.9     |
| Al$_2$O$_3$         | 30.51    | nd        | 16.4   | 5.3      |
| TiO$_2$             | 7.07     | 0.44      | nd     | nd       |
| P$_2$O$_5$          | 0.60     | 0.66      | nd     | nd       |
| MnO                 | 0.30     | 0.64      | 9.69   | 0.25     |
| CaO                 | 4.1      | 3.43      | 3.7    | 4.80     |
| K$_2$O              | 0.70     | 9.75      | nd     | 1.32     |
| SO$_3$              | 0.73     | nd        | nd     | 9.69     |
| Other oxides        | 3.03     | 6.05      | 11.01  | 8.34     |
|                     | *nd (not detected) |           |        |          |

**2.3 Ferrosilicon synthesis**

Horizontal tube furnace was used in the ferrosilicon synthesis process. The experimental setup was explained in previous works [4]. Once the temperature was set at 1300˚C, then the pellets were placed in a ceramic crucible and pushed in the hot zone of the tube for 1 hour of reaction. The nitrogen gas was supplied at a rate of 0.1 L/min with the heating rate of 10 ºC/min.
2.4 Phases and Microstructures Transformation Analysis

The phases transformation of the reduced ferrosilicon was identified using XRD (Bruker D2 Phaser M32002) with CuKα beam radiation. The scanning range, 2θ was set from 20º to 90º with a step size 0.02º at rate of 0.1s/step. The XRD pattern analysis was then analysed using X’pert High Score Plus software to identify the phases present in the samples and referred to Inorganic Crystal Structure Database (ICSD)[16]. While the changes of microstructure were observed using SEM/EDS (JSM6460LA) operating at an accelerating voltage of 10 kV.

3 Results and discussion

Fig. 1 shows the XRD patterns of the reduced pellets (coke and palm char) at 1300 ºC. SiO2 was the main reaction product for both reductants showed that the reaction is not fully reduced due to low temperature. It was found that SiO2 will fully reduce to SiC at above temperature of 1300 ºC [20]. Fe3Si was detected at angle of 45° for both carbon reductants, which indicated that reduction of iron oxide was quicker than silica [21]. Iron oxide reduction followed reaction in Eq. 1 and the Boudouard reaction (Eq. 2):

\[
\begin{align*}
\text{Fe}_2\text{O}_3(s) + 3\text{C}(s) & \rightarrow 2\text{Fe}(l) + 3\text{CO}(g) \quad (1) \\
\text{C}(s) + \text{CO}_2(g) & \rightarrow 2\text{CO}(g) \quad (2)
\end{align*}
\]

The generated CO from iron oxide reduction facilitated gas phase reduction of silica through intermediate phase of SiO (Eqs. 3 and 4).

\[
\begin{align*}
\text{SiO}_2(s) + \text{CO}(g) & \rightarrow \text{SiO}(g) + \text{CO}_2(g) \quad (3) \\
\text{SiO}_2(s) + \text{C}(s) & \rightarrow \text{Si}(l) + \text{CO}(g) \quad (4) \\
\text{SiO}_2(g) + 3\text{C}(s) & \rightarrow \text{SiC}(s) + 2\text{CO}(g) \quad (5)
\end{align*}
\]

At higher temperatures (1300 ºC), the reduction of silica takes place by carbon. The silica is completely volatile and it gets vaporized significantly during high temperature reaction [22]. The reaction between silica in sand and carbonaceous material initiates at the contact point between SiO2 and C. Once both SiO and CO are formed, the reactions proceed at the surfaces of both carbon and silica particles via gas phases. Some amount of SiO will be used in the system, and the remainder of the SiO will escape in the gas phase. Thus, some silicon loss could be attributed to the SiO gas escaping from the system prior to its conversion to SiC [14]. Some reduced silica in the form of silicon, dissolved into the molten iron, while the rest of the silica reduced to SiC.

SiC formation also started to occur below 1400ºC through a solid-state reaction of silica and carbon (Eq. 5) [23]. SiC peaks were detected at angles of 35.7º and 60º for both reductants. When iron and silicon are formed due to inter-diffusion during solidification, a number of iron silicides like Fe3Si and FeSi can be formed [24]. Therefore, more silica is reduced and formation of SiC phase and transformation of Fe3Si to FeSi was evident where FeSi phase was found in both reductants (Fig. 1 (a) and (b)).
Fig. 1. XRD pattern for ferrosilicon synthesis using different reductants (a) coke and (b) palm char at 1300 °C.

Fig. 2 shows the SEM images with EDS mapping scan of the synthesized ferrosilicon alloy by using both coke and palm char as carbon reductant. The darker phase represents the higher concentration of carbon, the brighter phase remarks as silicon and iron were found in both reductants. Coke showed higher concentration of silicon (41.14 wt. %) compared to palm char, while palm char contained higher iron concentration with amount of 30.99 wt.% (Table 4). Higher carbon content (Table 1 and 4) of coke facilitated the faster carbon dissolution into iron from coke compared to palm char derived carbon. This solute carbon, because of higher carbon pickup by iron from coke, increased the alloy formation [15]. Therefore, predominantly Fe₃Si, FeSi along with SiC peaks were detected in XRD analysis (Fig. 1 (a)) was in a good agreement with SEM/EDS mapping analysis (Fig. 2 (a)) showed better silica reduction by coke compared to palm char (Fig. 2 (b) and Table 4). However, by considering the product formation (FeSi and SiC) and environmental aspects, palm char and generally agricultural waste could be considered as an alternative reductant in the ferrosilicon/silicon industry.
Fig. 2. SEM/EDS mapping for ferrosilicon synthesis using different reductants (a) coke and (b) palm char at 1300 °C.

Table 4. SEM/EDS mapping with elemental analysis for ferrosilicon synthesis using different reductants.

| Element (wt. %) | Coke  | Palm char |
|-----------------|-------|-----------|
| Carbon          | 56.79 | 51.78     |
| Iron            | 2.06  | 30.99     |
| Silicon         | 41.14 | 17.23     |

Conclusions

XRD analysis confirmed that Fe$_2$Si, FeSi and SiC phases were developed during ferrosilicon synthesis at 1300 °C using coke and palm char as reductants. The brighter phase was observed as iron and silicon in SEM analysis. Coke showed better silica production due to high silica and carbon content in the sample compared to palm char. In conclusion, waste carbon material from agricultural industry can be successfully used for silicon production and will help build a foundation for future steps with new carbonaceous reductants in the silicon production process.

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