Reduction of Iron Ore/Empty Fruit Bunch Char Briquette Composite

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Utilization of Malaysian low grade iron ore is an attractive option of domestic iron resource; however, extra energy consumption is required and thus contributes to greenhouse gases. In this study, incorporation of low grade iron ore deposits with oil palm waste as substitution of coke was studied. Briquette composites of iron ore and char derived from oil palm empty fruit bunch (EFB) pyrolysis were produced with minute amount of distilled water. Reduction processes were carried out at 873 K to 1 173 K under argon atmosphere in an electric furnace for briquette composites with different mass ratio of ore/char. For kinetic analysis, briquette with 8:2 ore/char ratio was used and reduction was carried out by varying the residence time. The percentage of reduction was estimated by oxygen removal and considering the weight loss. The structural and chemical changes of raw materials and briquettes were characterized using XRD, TG/DTA, and XRF. The results indicate that increasing in temperature, time and EFB char content in the briquette will increase the percentage of reduction. XRD and XRF results show that the original iron oxide hydrate has been transformed into partial wustite by several stages and the iron content increased up to 62.7 wt% for 6:4 ore/char ratio briquette. Kinetic results suggest that reduction of iron is controlled by gasification of carbon and the activation energy is 43.21 kJ. EFB char appears to be a promising energy source for replacing part of coal consumption in iron making, and reducing CO₂ emission.

KEY WORDS: empty fruit bunch char; iron ore; briquette; reduction; kinetics; gasification.

1. Introduction

In blast furnace method of iron making requires coke as a reductant, and since coking coal is not available in many countries, non-blast furnace technology becomes a significant alternative. Direct reduction, a process of directly reducing the iron ore in solid form by reducing gases either H₂ or CO or mixture of both is an example.1–14) This process is more productive since coal can be used directly with iron in the form of pellet or lump. Regardless of the two different methods, iron and steel making are known as industries that consumed the largest energy for many decades.

In addition to high energy consumption and scarcity of coking coal, the iron and steel industries are facing new challenges in the form of depleting high grade iron ore or hematite in the near future.15–18) Utilization of low grade iron ore is an attractive alternative for iron resource especially for countries that have abundant deposits of low grade iron ore and these countries’ demand on cast iron and steel is increasing annually. Malaysia is a good example since iron ores mined in Malaysia are considered as low grade because the ores are composed of high combined water and low iron (Fe) content between 56–58%.19) In order to expand iron production up to 3.2 Mt, Malaysian steel producers planned to invest about $1.5 billion in 2010 by importing high-grade iron ore from Bahrain, Mexico, Chile and Brazil to produce quality iron and steel products.19) Thus, the exploitation of low grade iron ore using conventional methods is necessary in spite of importing the high grade one but it contributes to greenhouse gas emission since high amount of coal is needed, which corresponds to high energy consumption. The use of coal which is a non-renewable fuel as energy source for iron and steel industries, causes increasing carbon dioxide emission and over ash accumulation as a result of its combustion and gasification.20–25)

As the largest industry that consumed energy which is approximately 10%–15% of annual industrial energy requirement, iron producers require to find alternative of energy source other than coal to make use of low grade iron ore.26) Replacing coal with the abundant renewable energy resources such as biomass waste from agro-industry is a good option to reduce coal consumption and promote green technology. Biomass waste from the palm oil industry is well known as a renewable and carbon neutral source which contains less harmful elements such as sulfur, phosphorus and others.26) In order to support the World’s efforts to overcome energy crisis and global challenges, renewable energy has been the main issue of the 10th Malaysia Plan (2011–2015) and Third Outline Perspective Plan for 2001–2010 (OPP3).27) Malaysia produced approximately 17.7 Mt of palm oil on 4.5 million hectares of land in 2008 and ranked as the second largest producer of palm oil in the World Growth Oil Green Development campaign in 2009.27,28) The
oil palm biomass consists of fiber, trunk, empty fruit bunch (EFB), shell, frond and palm oil mill effluent (POME). Empty fruit bunch’s production of about 16 Mt annually portrays that Malaysia should utilize the EFB efficiently, otherwise Malaysia will face an energy scarcity in 2100.20) Furthermore, reduction of CO$_2$ emission by 25 139 tons per year using waste from palm oil empty fruit bunch (POEFB) had been reported by United Nations Framework Convention on Climate Change, UNFCCC in 2006.20) However, the use of biomass either as fuel or energy source generates incomplete combustion as well as huge amount of very fine particles of biomass char or bio-char which poses disposal and environmental problems. Instead of using EFB directly, char derived from rapid pyrolysis of EFB containing carbon and other reactive materials can be a promising reductant source for iron making through direct reduction process.

EFB char contains carbon that has potential to be used as solid reductant and produce intermediate CO gas as reducing agent during reduction when it is mixed with iron ore. Moreover, bio-char also contains less harmful elements such as alumina and silica, but has more iron, potassium and phosphorus, and it does not contain toxic metals like in the case of coal ash.26,29,30) Although there are some researchers that have conducted detailed study in converting the EFB char into value added products such as organic fertilizer, biodiesel and cement replacement material for concrete making, none of them used it as energy fuel or reductant source.31,32) Hence, incorporation of Malaysian domestic low grade iron ore with bio-char in iron-making is promising in replacing coal, reducing CO$_2$ emission and indirectly solving the problems of waste disposal. In this paper, domestic low grade iron ore was mixed with EFB char derived from pyrolysis and compacted into briquette form. The influences of residence time, reduction temperature, and mass ratio of ore to char on iron content in the product were studied. Furthermore, the rate determining step of reduction was probed by kinetic analysis and comparing the experimental and calculated data. Carbon consumption on utility of EFB char was also analyzed by comparing with the carbon from coke used in industrial application.

2. Experimental

2.1. Sample Preparation

Malaysian iron ore was taken from Chini, in Pahang state while oil palm empty fruit bunch (EFB) from local palm oil mill. Both materials were oven dried for 24 hours to remove moisture. The ore was crushed and ground to particle size below 100 $\mu$m. Char derived from EFB was prepared by pyrolysis of the EFB at 973 K in an electric tube furnace. The char then was crushed to minimize the particle size for optimum binding during mixing process.

Briquette with dimension of 13 mm in diameter and 5 mm height was prepared from mixing iron ore and char at 9:1, 8:2, 7:3 and 6:4 ore to char mass ratio with minute amount of distilled water as binder using a uniaxial compaction machine at pressure of 47 MPa. The briquette was dried at 383 K for 2 hours to dry-off any remaining water. The raw materials and sample produced were characterized using X-ray diffraction (XRD), X-ray fluorescence spectrometer (XRF) and thermo gravimetric-differential thermal analysis (TG-DTA), CHNS analyzer and TGA.

2.2. Reduction Test

Figure 1 schematically represents the experimental apparatus for reduction in an electric tube furnace. The briquette’s weight before reduction was recorded before it is enclosed with glass fiber in the quartz tube of the furnace. Subsequently, heat was supplied to the sample at a rate of 283 K/min which was kept under an inert atmosphere by blowing argon gas at flow rate of 5 mL/min. A thermocouple was put inside the quartz tube, nearest to the sample as possible and the actual temperature at the sample was detected by a thermocouple. The reduction temperatures were varied from 873 K to 1 173 K at 100 K increment while 30 to 180 minutes residence times were implemented at each temperature run. Samples in the furnace were allowed to cool to room temperature under continuous argon flow to avoid re-oxidation. The weight of samples after reduction was measured.

3. Results and Discussion

3.1. Characteristics of Iron Ore and EFB Char

Table 1 shows the elemental composition of iron. The predominant element in the ore is Fe, accounting to 58.1 wt% of the ore which is followed by other elements such as Ti, Al, Si, Cl, V, Mn, Ca and S that are considered as impurities. Table 2 represents the ultimate and proximate analyses for EFB char. EFB char composed of high amount of carbon by ultimate analysis (70.57 wt%) and 62.69 wt% of fixed carbon from proximate analysis. The ultimate analysis also indicated the presence of 26.14 wt% oxygen as well as insignificant amount of hydrogen, nitrogen and sulfur in EFB char. The proximate analysis of EFB char also revealed significant presence of volatile matter: 15.32 wt%, ash: 15.81 wt% and moisture: 6.18 wt%.

Figure 2 illustrates the TG-DTA patterns of the iron ore. At temperature range between 513 K to 613 K the maximum weight loss is caused by decomposition of goethite (FeO(OH)$_x$) releasing up to 3.75 wt%, accompanied by an endothermic peak at 546 K in the DTA curve. This peak occurs due to the endothermic reaction caused by the heat required for heating iron ore that depends on the amount of
goethite present in the sample. The higher amount of goethite in the ore leads to higher heat to remove the combined water, which then generates a sharp endothermic peak at temperature range where goethite decomposed.

### 3.2. Effect of Temperature and Char Content

Figure 3 illustrates the XRD patterns of briquettes at various temperatures. The patterns show that the major iron minerals in the untreated ore are hematite (Fe₂O₃) as well as goethite (Fe₂O₃·H₂O). Silicate minerals present are identified as quartz (SiO₂) and kaolinite (Al₂Si₂O₅(OH)₄), and both are considered as gangue minerals of iron ore. 8,15,16) The peaks corresponding to magnetite and wustite become more apparent with increasing temperature. The kaolinite peaks disappear when temperature reaches 873 K and the intensity of quartz peaks become diminished as temperature increases. It is observed that by heating the sample at 873 K, the ore is completely reduced to hematite. As temperature increases to 973 K, the magnetite peaks appear and the ore is successfully transformed into magnetite at 1 073 K. It is observed that at 1 173 K the iron ore is partially reduced to wustite since magnetite peaks are still present at this temperature. The results indicated that increasing of reduction temperature causes more carbon-rich in char volatilizes and react with oxygen to form CO as reducing agent and promote reduction process.16

Table 3 shows the estimation of oxygen removal according to stage of reduction. It is observed that the total theoretical removal of oxygen is 36.12%. Meanwhile, about 19.6% oxygen was removed in experiment since the ore is partially reduced to wustite at 1 073 K. Figure 4 demonstrates a graph of sample’s weight loss versus temperature for each char content in briquette. There appears to be a similarity between estimated and experimental values of weight loss with respect to the stage of reduction. It is apparent that the stage of iron ore reduction follows reduction mechanism which corresponds to Eqs. (2) – (4). Besides, reduction temperature and char content show similar influence on the weight loss of sample, in which increasing of both parameters slightly increase the weight loss of briquette up to 41% for 40 wt% of char content at 1 173 K of reduction temperature. The weight loss, in general, is not only caused by removal of oxygen from the original iron ore but also due to char’s volatilization and removal of high combined water, simultaneously.

Figure 5 demonstrates the percentage reduction versus char content within the 873–1 173 K temperature range which was calculated according to Eq. (1) below:

\[ f = W_{r} - (W_{cw} + W_{a}) \]  

\[ \text{Eq. (1)} \]

where \( f \) denotes percentage reduction (%); \( W_{r} \) is weight loss of sample (%); \( W_{cw} \) is weight loss of combined water (%) and \( W_{a} \) is weight loss of char’s volatilization (%).

The values of weight loss of sample are depicted from Fig. 4, while weight loss of combined water which corresponds to decomposition of goethite is obtained from the
TG curve. Goethite is known as iron oxide hydrate or a combination of iron oxide with water and its molecular formula is inferred in Eq. (2).\textsuperscript{15,16} As for char, the weight loss is calculated from the weight change of char before and after been heated at each temperature for several times until a constant weight loss is obtained. The constant weight loss is considered as weight loss corresponding to volatilization of char, where specifically the amount of carbon in char that volatilize upon heating at each temperature, since different heating temperatures will result in different weight loss of char’s volatilization. By considering the weight loss of combined water in ore and volatilization of char in briquette, the actual amount of oxygen removal could be calculated and referred as percentage reduction.

The percentage reduction is shown in Fig. 5. Apparently, increasing temperature and char content in briquette cause a gradual enhancement on percentage reduction as supported by Eq. (1). This is reasonable with regard to the basic principles of thermodynamics and kinetics that predict the diffusion or kinetic energy of particles become higher at high temperatures. Besides, more carbon was supplied due to increasing char content. Since the oxygen was removed through reaction between ore and carbon particles in char, higher char content generates more CO reducing gas and promotes indirect reduction. Therefore, different temperatures and char content consequently affect the amount of CO produced and oxygen removed from the ore.

The reduction process of the ore is started with the decomposition of goethite into hematite by releasing combined water. The hematite then reduced into magnetite and wustite following Eqs. (2) until (4). The Eq. (5) is the gasification reaction which attributed to Boudouard reaction:

\[
\begin{align*}
2\text{FeO(OH)} & \rightarrow \text{Fe}_2\text{O}_3 + \text{H}_2\text{O} \quad \text{(2)} \\
3\text{Fe}_2\text{O}_3 + \text{C} & \rightarrow 2\text{Fe}_3\text{O}_4 + \text{CO} \quad \text{(3)} \\
\text{Fe}_3\text{O}_4 + \text{CO} & \rightarrow 3\text{FeO} + \text{CO}_2 \quad \text{(4)} \\
\text{CO}_2 + \text{C} & \rightarrow 2\text{CO} \quad \text{(5)}
\end{align*}
\]

Figure 6 depicts the XRD patterns of composites after reduction at 1 073 K for different compositions. In addition to temperature dependence, it is apparent that increment of EFB char by 10% per run also affects the reduction process, as evident from the peaks of magnetite and wustite that start to appear and become more prominent as the amount of EFB char increases. On the other hand, the hematite peaks diminished and goethite peaks disappear as char content reaches 20 wt%, in which the iron ore is successfully transformed into magnetite. Addition of 30 wt% of EFB char in briquette contributes to more carbon supply which then acts as reductant and produces more intermediate CO gas and promotes the reduction process. At 40 wt% EFB char, the ore is apparently reduced to wustite as more wustite peaks are observed compared to 7:3 compositions.\textsuperscript{8,15,16}

Based on Boudouard equilibrium phase diagram, as CO content and temperature increase, the iron oxide becomes easier to be reduced.\textsuperscript{8} Hence, it is expected that higher carbon content produces more intermediate CO gas during the reduction process which then increases the reducibility of briquette. Based on XRD patterns in Figs. 3 and 6, it is evident that the iron ore is only partially reduced to wustite at 1 173 K and 40 wt% of EFB char or 1 073 K and 30 wt% of EFB char is added to the briquettes.

Table 4 shows the elemental composition of samples for two different ratios which were analyzed using XRF. It is apparent that the Fe content increases from 58.1 wt% to 62.7 wt% for 6:4 ratios of briquette sample while the total Fe
content for 9:1 ratio briquette increases by approximately 2% from the original Fe content in the iron ore. This is due to the enhancing of intermediate CO reducing gas generated from increasing carbon content that is in direct contact with iron ore, which then acts as a reducing agent or energy source and allows reduction process to proceed indirectly. Despite of solid-solid reaction between ore and carbon particles in char, the iron ore is considered to be reduced indirectly by CO since solid-gas reaction proceeds at a higher rate than solid-solid reaction. The oxygen was removed by CO and then generates CO2 as a by product. Removal of oxygen, subsequently, contributes to increasing of iron content since the original ore was transform from goethite into partial wustite. It could be seen that the impurities still remain in the briquette since the iron ore is not completely reduced to iron but only into partial wustite although the Fe content increases.

3.3. Kinetics Analysis

The mechanism of reduction of iron oxides by solid carbon is shown in Eqs. (3)–(4) and assumed to be direct reduction since carbon in solid form is considered to be in direct contact with the iron ore. Moreover, in this study the iron ore is mixed with EFB char where both particles are directly in contact with each other. From Eq. (3), the carbon monoxide (CO) is initially produced by a reaction of carbon with oxygen from the oxides as it is in contact with the carbonaceous materials (char). Then, the reduction of iron oxides by carbon is assumed to proceed indirectly via the gaseous intermediate, CO and CO2, as revealed in Eq. (4) because solid-solid reaction is much slower compared to gas-solid reaction. The carbon dioxide will react with carbon to reform carbon monoxide and then allows the reduction to continue due to restoration of the reducing potential of the gas phase which is expressed in Eq. (5) of the Boudouard equilibrium phase diagram.

Figure 7 shows the fractional reduction plot against the residence time of reduction for a number of kinetic models that need to be considered in identifying which model fits the experimental values and becomes the rate determining step. By comparing the fractional reduction plots in Figs. 7 and 8, the model \(-\ln (1-f) = kT\) which corresponds to chemical reaction due to gasification of carbon closely follows the graphical representation of the experimental data. As gasification of carbon favors and proceeds at appreciable rates at high temperature, and that carbon gasification rate is slowest at low temperature, the overall reduction rate is controlled by this rate determining step. The values of \(-\ln (1-f)\) at different temperatures against residence time are shown in Fig. 9.

Figure 9 depicts the relation between \(-\ln (1-f)\) and time for briquette. The slope of the linear relationship from this figure gives the measure of reduction rate constant (K) at a given time. Figure 10 shows an Arrhenius plot of \(\ln (K)\) against the inverse of temperature. The activation energy (E) of the reduction reaction is determined to be 43.21 kJ/mol. The activation energy is the slope of the plot in which the negative sign is neglected, multiplies with universal gas constant (R). Fundamentally, the activation energy value is known as an index that indicates the ease or difficulty of reaction process and the minimum energy which particle must possess for reaction to take place at a certain temper-
The activation energy using EFB char is quite low compared to value of activation energy for coal which is in the range of 116–335 kJ/mol.1–14 This indicates that the reduction of briquette starts at low temperature and the extent of reduction of reaction in case of EFB ash is high. Other than that, it was reported that low values of activation energy could be due to catalytic effect of iron and alkaline compound on the rate of carbon gasification reaction.1–14

The rate determining step can be inferred from calculating the mathematical kinetic model for iron oxide reduction according to Eq. (6), and comparing the result with experimental kinetics data. A simple mathematical model is developed to predict the rate determining step by assuming that reduction follows unreacted core model for a cylindrical briquette in accordance with Eqs. (2) and (3). The Eq. (6) represents the prediction or theoretical calculation of fractional reduction which is referred as reduction follows unreacted core model for a cylindrical briquette in accordance with Eqs. (2) and (3). Industrially, in order to produce one ton of pig iron using blast furnace, approximately 1.75 tons of iron ore and 0.75 ton of coke are required which produces 3.4. Reduction of Carbon Dioxide Emission

Carbon consumption was analyzed by calculating and comparing the mass and mole of carbon, carbon monoxide and carbon dioxide produced from coke and biomass char, according to Eqs. (2) and (3). Industrially, in order to produce one ton of pig iron using blast furnace, approximately 1.75 tons of iron ore and 0.75 ton of coke are required which in turn releases about 2 tons of CO2.3 Since XRD patterns show that the briquette samples are only partially reduced to wustite, the total oxygen removal is only considered up to 10.22% (Table 3), which is the summation of oxygen removal of 3.33% and 6.89% for stage 1 and stage 2, respectively. The oxygen removal for partially reduced wustite is 10.22% (Table 3), which is the summation of oxygen removed from the reduction follows the Bouduard reaction.

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The experimental value of the total mass of carbon where EFB char is used as reductant is 0.296 ton/ton pig iron (Table 5). This result shows that the amount of carbon in EFB char can replace about 39.52% C (mass ratio of carbon in EFB char/carbon using coke in industrial blast furnace) to produce partial wustite through reduction process. Furthermore, the total CO2 emission released using EFB char is 1.0868 ton/ton pig iron which is lesser than CO2 dis-

![Fig. 10. Temperature dependence of rate constant for gasification of carbon.](image)

![Fig. 11. Comparison between measured data (dot line) and prediction (straight line).](image)

### Table 5. Experimental result of total CO2 and C produced using EFB char.

<table>
<thead>
<tr>
<th>Classification</th>
<th>Source of reductant</th>
<th>Chemical reaction equations</th>
<th>Mass of Total mass CO2 (tonne)</th>
<th>Mass of Total mass C (tonne)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental EFB char</td>
<td>3Fe2O3 + C → 2FeO2 + CO</td>
<td>FeO2 + CO → 3FeO + CO2</td>
<td>1.0868</td>
<td>0.296</td>
</tr>
</tbody>
</table>

\[
F = \frac{2A_t (C_0 - C^*)}{3W_0 \left( \frac{1}{k} \left( 1 + \frac{1}{K} \right) \right)} \quad \text{........................ (7)}
\]

However, the \( D_e \) value is assumed to be negligible since the diffusion model in Fig. 8 opposes the experimental data, and thus Eq. (7) is obtained where negative sign of \( F \) is also neglected. The value of \( C_b \) is calculated from Eqs. (2) and (3) by mole’s formula \((n = \text{mass/molar mass})\) as referred to mass ratio of briquette used for kinetic analysis. The difference of CO concentration produced from Eq. (2) and CO concentration consumed in Eq. (3) gives the value for \( C_b \), where it is assumed that CO gas which has not been consumed will be released to the bulk. Meanwhile, \( C^*_b \) is acquired from the Bouduard phase diagram for different temperatures according to phase detected by XRD analysis since the reduction follows the Bouduard reaction.

![Fig. 11. Comparison between measured data (dot line) and prediction (straight line).](image)
charged in case of coke which released approximately 2 tons/ton pig iron.1) These results signify that utilization of EFB char could lower the CO₂ greenhouse gas emission in iron-steel industry, and become a good potential material to substitute coke as energy and reductant source in iron-steel industry.

4. Conclusions

The reduction of local Chini iron ore using char derived from EFB was investigated. Results revealed that both temperature and residence time were significant factors in the reduction of briquette composite. The percentage reduction of briquette was controlled by gasification of carbon where the activation energy is 43.21 kJ/mol. The carbon consumption indicated that reduction of iron ore using EFB char is almost similar to amount of carbon as coke and discharged CO₂ compared to coke.

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