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AGRICULTURAL WASTE AS IRON REDUCTANT FOR PRODUCING METALLIC IRON IN STEELMAKING

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ABSTRACT

Agricultural waste can be an interesting possibility to be applied as reducing agent instead of coal-based used in steelmaking which is considered to be one of the largest energy intensive sector. As a result of enormous amount of wastes generated by agricultural sectors, numerous research on application of waste as energy source have been conducted. Utilisation of these wastes as valuable materials could provide solution to environmental problems. This present study investigated the reduction of iron oxide with agricultural waste from palm shells in a horizontal tube furnace. Composite pellets of iron oxide (96.0 % Fe_2O_3) with palm char in three different proportions were rapidly heated up to 1550 °C under argon gas flow. The reduced sample after reaction time, 30 minutes was examined using a Scanning Electron Microscope (SEM) equipped with Energy Dispersive Spectroscopy (EDS) and measured for degree of reduction. The results indicated that iron oxide which composed primarily Fe_2O_3 can be effectively reduced by palm shells as reductant where a significant improvement in the degree of reduction. The initial hematite powder could successfully reduced to metallic iron after a complete reduction process. This finding indicates that carbon from palm shells could be used as reductant in steelmaking processes.

Keywords: agricultural waste, iron oxide, reduction.

INTRODUCTION

The growth and development of iron and steel industry is a reflection of global economy. Steel plays an essential role to modern life as ubiquitous material and towards a sustainable future. Currently, the amount of steel manufactured and used were estimated to approximately 1.6 billion tonnes per year and was expected to keep growing every year (World Steel Association, 2014).

At present, wastes from agricultural activities have created a significant disposal problem. In Malaysia, palm shells are generated in large quantities annually, thus affecting the environment. In this research, utilization of palm shells as a potential alternative carbon source in steelmaking could be considered. The use of palm shells offer a significant advantage as agricultural waste is considered as a carbon neutral which means no carbon dioxide emission is released to the environment due to fixed carbon utilized will have the same value as photosynthesis process for the growth of plant (Strezov, 2006). Therefore, greenhouse gas footprint and energy consumption can be reduced effectively by the steel production.

Apart from being a primary agricultural waste in Malaysia and abundantly found, palm shells have been selected in this research due to its possibility in substituting coal/coke in steelmaking. One of the main problems hindering the coke source is the need of continuous supply of high quality coking coke in steel production which is considered as limited reserves. The challenges facing the steelmaking industry drives researches to seek for other solution of alternative reductants.

Previous researchers have been done on the effective utilization of biomass. Earlier research has identified that biomass alone could be utilized as a reducing agent (Srivastava *et al*., 2013). It has been reported that the utilisation of wood as charcoal has shown a positive end result in replacing metallurgy coke in steelmaking (Matsumura *et al*., 2008), (Matsuda *et al*., 2006), (Gupta *et al*., 2007). Carbonaceous reductants such as coal, coke and plastics have been previously reported as alternative reducing agents (Dankwah *et al*., 2011), (Ueda *et al*., 2009), (Zaharia *et al*., 2009).

This present study involves application of activated carbon derived from palm shells in order to enrich the carbon content in the precursor and develop porosity to enhance iron reduction process (Hidayu *et al*., 2013). Recently, the pyrolysis method for precursors with high carbon content including coal and biomass becomes an upward trend due to the forces in reducing carbon dioxide emission encountered by steel production sector (Griessacher *et al*., 2012). Hence, activated carbon is largely used in research and industry. High carbon content of palm shells proved that it has a good potential for the production of activated carbon. Furthermore, the contents of carbon and hydrogen available in palm shells could leads to faster rate of reduction as obtained when high density polyethylene (HDPE) and rubber tyre waste were used as reductant (Dankwah *et al*., 2011).

This study evaluate the possibility of agricultural waste in ironmaking by using palm shell. To promote an effective use of agricultural waste from palm shells char as carbon source and reducing agent in steelmaking, the reduction reaction in this present research was investigated at high temperature. This raw material can be a promising

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carbon and energy sources for reduction to occur instead of coal/coke as well as acheive a sustainable steelmaking. By applying palm shells as alternative reductant of iron oxide, negative environmental problems of landfills especially disposal problem can be minimized and can provides solution to reduce greenhouse gases.

METHODOLOGY

Sample preparations

The palm shells generated from oil palm mill provided by The Malaysian Palm Oil Board (MPOB) were applied in this study as carbonaceous material. Prior to the experiment, the palm shells were firstly dried at room temperature to reduce moisture content. The carbonaceous material was then prepared by crushing using a crusher machine and sieving into uniform particle size (< 250µm). The ultimate and chemical analysis for raw palm shells and palm shells char in wt % are presented in Table-1 and Table-2.

Table-1. Ultimate analysis for carbonaceous materials.

Composition (wt %)	Carbon	Hydrogen	Nitrogen
Palm shells	45.67	5.86	0.37
Palm shells char	59.35	2.98	0.30

Table-2. Ash analysis of palm shells and char used for this research.

Composition (wt %)	Palm shells	Palm shells char
Fe_2O_3	62.55	66.40
SiO_2	22.00	20.20
Al_2O_3	6.00	7.50
K_2O	3.23	2.88
CaO	2.09	1.16
MnO	0.17	0.14
TiO_2	0.34	0.45
Other oxides	3.62	1.27

The raw palm shells were converted into char by devolatilization at 450 ºC with a heating rate of 10 ˚C/min in nitrogen, N_2 atmosphere for two hours. From Table-1, it indicates that the carbon content can be rises after pyrolysis.Then, the palm char was grinded to fine powder by using a ring mill. Iron oxide (hematite) powder (96.0 wt % of Fe_2O_3) with red in color was used in this research. Table-3 shows chemical composition of iron oxide used in this research.

Table-3. Composition of iron oxide powder.

	Fe_2O_3	SiO_2	CaO	MnO
Composition (wt %)	96.0	0.40	0.02	0.02

Preparation of composite pellet

Palm shells char and iron oxide were mixed and weighed to a required weight in three different ratios. The selected weight ratios of carbonaceous material to iron oxide were labeled as A (30:70), B (40:60) and C (50:50). These selected ratios will determine the optimum parameter for final reduction product. Mixture of constituent powder was milled thoroughly using a ball mill machine at 200 rpm for 1 hour. After the raw materials were mixed, the samples were compacted in a die by applying load of 8 tonnes by using a hydraulic pressing machine to produce cylindrical composite pellets of ~20 mm diameter (Figure-1).

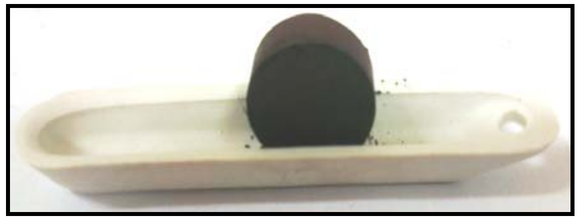

Figure-1. Composite pellet.

Reduction reaction of pellet

Reduction of iron oxide, Fe_2O_3 was done in a horizontal tube furnace at 1550˚C under inert temperature (1 L/min of Argon). After the furnace being preheated to the desired temperature, the sample was rapidly inserted and heated for the reduction process for 30 minutes. Subsequently, the reacted sample was quenched by rapidly withdrawn from hot zone and moved to cold zone of the furnace. Particles of metallic iron which was possible to be identified visually and its residues were removed for further analysis (Dankwah *et al*., 2011). The microstructure of reduced samples as a result of high temperature reaction were examined using a Jeol Scanning Electron Microscope (SEM) with a 20 kV accelerating voltage and EDS to determine the elements of composite pellets after reduction.

RESULTS AND DISCUSSION

Degree of reduction of composite pellet

For reduction of iron oxides by carbon, the degree of reduction was calculated from the weight loss of sample. The initial and final weights of pellets were noted to determine the weight loss after a constant reaction time, 30 minutes. Degree of reduction for composite pellet was presented in Figure-2.

The reduction degree for sample A, B and C are 24.2 %, 32.4 % and 33.5 % respectively. The results show that the degree of reduction increased as the content of carbon increased. The same gradual increase trend was obtained by other researcher when used composite pellets composed of low grade iron ore and palm kernel shell (PKS) and found that the higher amount of carbonaceous material will leads to higher reduction (Abd. Rashid *et al*., 2014). Porous structure of palm shells char as a result from pyrolysis could be a key factor that influenced the r eaction.

The net rate of reduction is expected to be controlled by the rate of gasification of agricultural waste and reducing gases during reduction reaction. According to Ueki *et al*., the presence of reducing gases such as carbon monoxide (CO) and hydrogen (H_2) at high temperature could influence the degree of reduction by promoting diffusion through composite pellet (Ueki *et al*., 2013). The carbon monoxide gas is generated from the carbon in the palm shells char which produced by pyrolysis process (Hanrot *et al*., 2009). Basically, agricultural waste or lignocelullosic material can be converted into hydrocarbon and its hydrogen content will influence the reduction process.

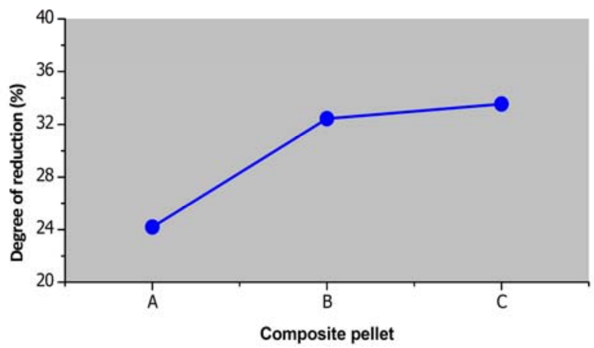

Figure-2. Degree of reduction calculated by the difference of weight loss of sample resulted from the reduction reaction at 1550 ˚C. Noted that composite pellet A (30:70), B (40:60) and C (50:50).

For instance, the increase amount of carbonaceous material in composite pellet is corresponding to devolatization of volatile matter in agricultural waste to give maximum reaction rate for the stage of carbon gasification and CO gas reduction. Hence, the total weight loss will also increased (Zou *et al*., 2013).

From Figure-2, it can be concluded that the highest degree of reduction is performed by composite pellet C, followed by B and finally A. For composite pellet A, the low carbon content is insufficient in producing CO gas and becomes a limited factor that leads to slower reduction. In this case, the degree of reduction can be greatly enhanced by increasing the weight ratio of carbon by addition of palm char. For composite pellet B and C, there are sufficient amount of carbon as reducing agent in the composite pellet, thus reduction reaction can proceed completely. Therefore, the effect of weight ratio on the reduction reaction is contributed by carbon content and a closer contact between carbon and oxide particles in the composite pellet (Zou *et al*., 2013).

In direct reduction process, carbon will react directly with hematite (Fe_2O_3), then converted to magnetite (Fe_3O_4), wustite (FeO) and further reduced to metallic iron (Fe). CO and CO_2 gases are generated by the reduction reaction of iron oxide with carbonaceous materials. The analysis of reduction showed that the reduction steps process occurred simultaneously.

$$Fe_2O_3(s) + 3C(s) \rightarrow 2Fe(s) + 3CO(g) \quad (1)$$

Thermodynamic reactions for the direct reduction of iron oxide by CO gas can be divided as following:

$$3Fe_2O_3(s) + CO(g) \rightarrow 2Fe_3O_4(s) + CO_2(g) \quad (2)$$

$$Fe_3O_4(s) + CO(g) \rightarrow 3FeO(s) + CO_2(g) \quad (3)$$

$$FeO(s) + CO(g) \rightarrow Fe(s) + CO_2(g) \quad (4)$$

It was expected that at high temperature reaction, carbon will be converted into CO which could play as reducing agent for its further reduction as the atmosphere becomes reductive. Apart from the above reactions, there are possibility to form other reaction known as Boudouard reaction at high temperature:

$$C(s) + CO_2(g) \rightarrow 2CO(g) \quad (5)$$

From equations (1) to (5), it could be elucidated that the hematite to magnetite reduction was completed within 30 minutes of reaction and this was followed by further reduction of the magnetite to wustite and finally iron (Huang *et al*., 2012).

Production of metallic iron

Figure-3 shows the reduced iron resulted from reduction reaction of composite pellet at 1550 ˚C for 30 minutes while Figure-4 presents the images and dimension of metallic iron which are removed from the crucible by using a magnetic screwdriver. The reduced metals of metallic iron have spherical shape with various sizes rang from 5 mm to 25 mm that formed by diffusion of small particles and gradually formed a bigger particle. The spherical shape produced indicated that the metal was formed from a molten state (Dankwah *et al*., 2011). Presence of many types of oxides in palm shells was expected to consequently enhance the reduction reaction of iron oxide to metallic iron.

From Figure-4, it is obvious that there is tendency to the particle to form a bigger lump of metallic iron. However, the particles could not coagulate into one due to the excess amount of carbon content in the composite pellets for the weight ratios selected. This was done deliberately to ensure enough amount of carbonaceous material is available to complete the reaction.

In other words, high content of carbon is desirable for the reduction process to reach completion which suggests overall reaction depends on the amount of carbonaceous reductants. The similar observation was also reported where the increase in metallization and an improved metal separation were observed after reduction of slag with carbonaceous material e.g. polymer addition in the pellets (Dankwah *et al*., 2011).

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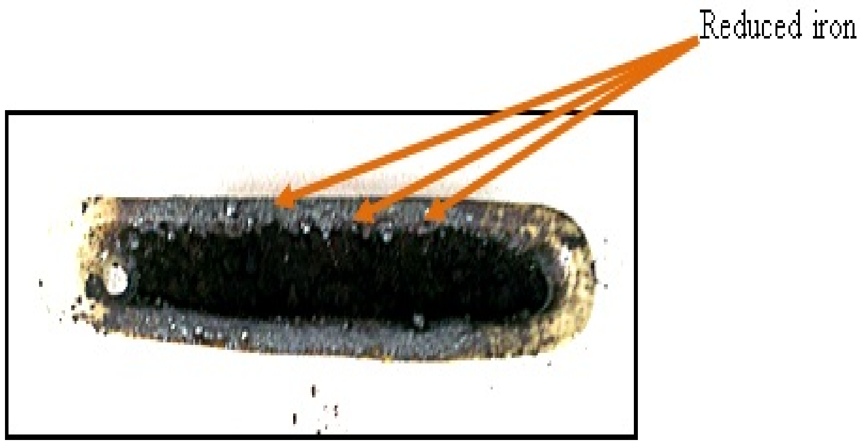

Figure-3. Images of spherical particles of reduced iron after reduction.

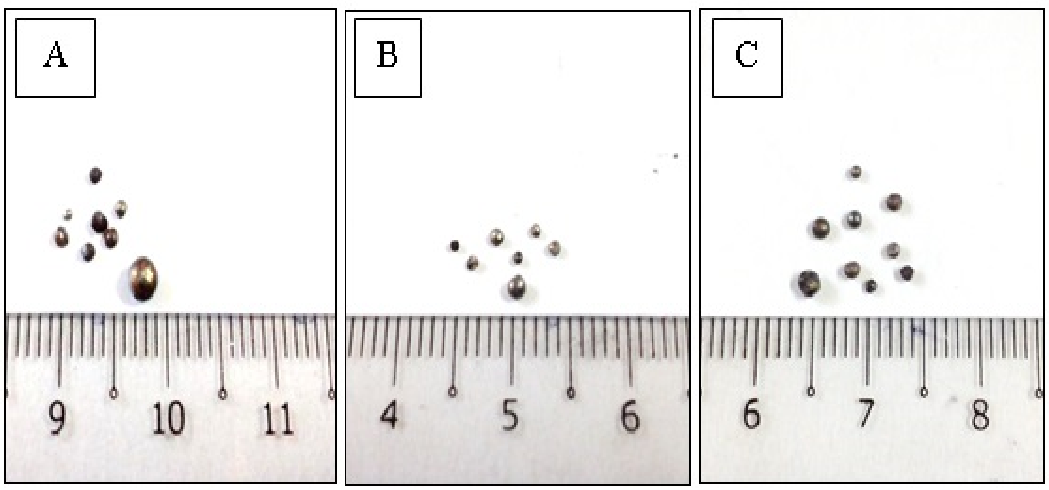

Figure-4. The metallic iron produced after reduction reaction at 1550 ˚C for composite pellet A (30:70), B (40:60) and C (50:50).

Observation on reaction's product (Metallic iron)

Figure-5 shows the scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS) analysis on reduced metal obtained through the reduction of composite pellet at temperature of 1550 ˚C. SEM analysis was done on metallic iron taken at 100x magnification. Rough texture on the surface of reduced metal can be observed from the figure and qualitative analysis on three different proportion of samples were analyzed. EDS spectra revealed that the present of iron (Fe) is the predominant element in the reduced metal, demonstrated by the highest intensity of Fe peaks. This showed that the reduction step was completed after 30 minutes of reaction due to the reduction of the iron oxide with palm shells. The main elements exist in metallic iron are iron (Fe), carbon (C), oxygen (O), silicon (Si) and aluminium (Al).

The EDS analysis of sample A after reduction showed the presence of iron, Fe (69.86 wt %) as major composition with small amount of C, O and Si. For reduced sample B and C, analysis with EDS concludes that the reducing product are mainly composed of Fe (77.07 wt % and 70.65 wt % respectively) with small percentage of other elements. The gradual decrease of oxygen from the initial oxygen content means iron oxides has been successfully reduced to metallic iron by carbon. Oxygen is probably comes from the minerals oxide in palm shells. Meanwhile, the rises amount of carbon in the EDS peak from A (6.53 wt %), B (11.29 wt %) to C (18.32 wt %) has suggested that the metallic iron is scattered in the form of small granule with the remaining palm char as reducing agent (Zuo *et al*., 2013).

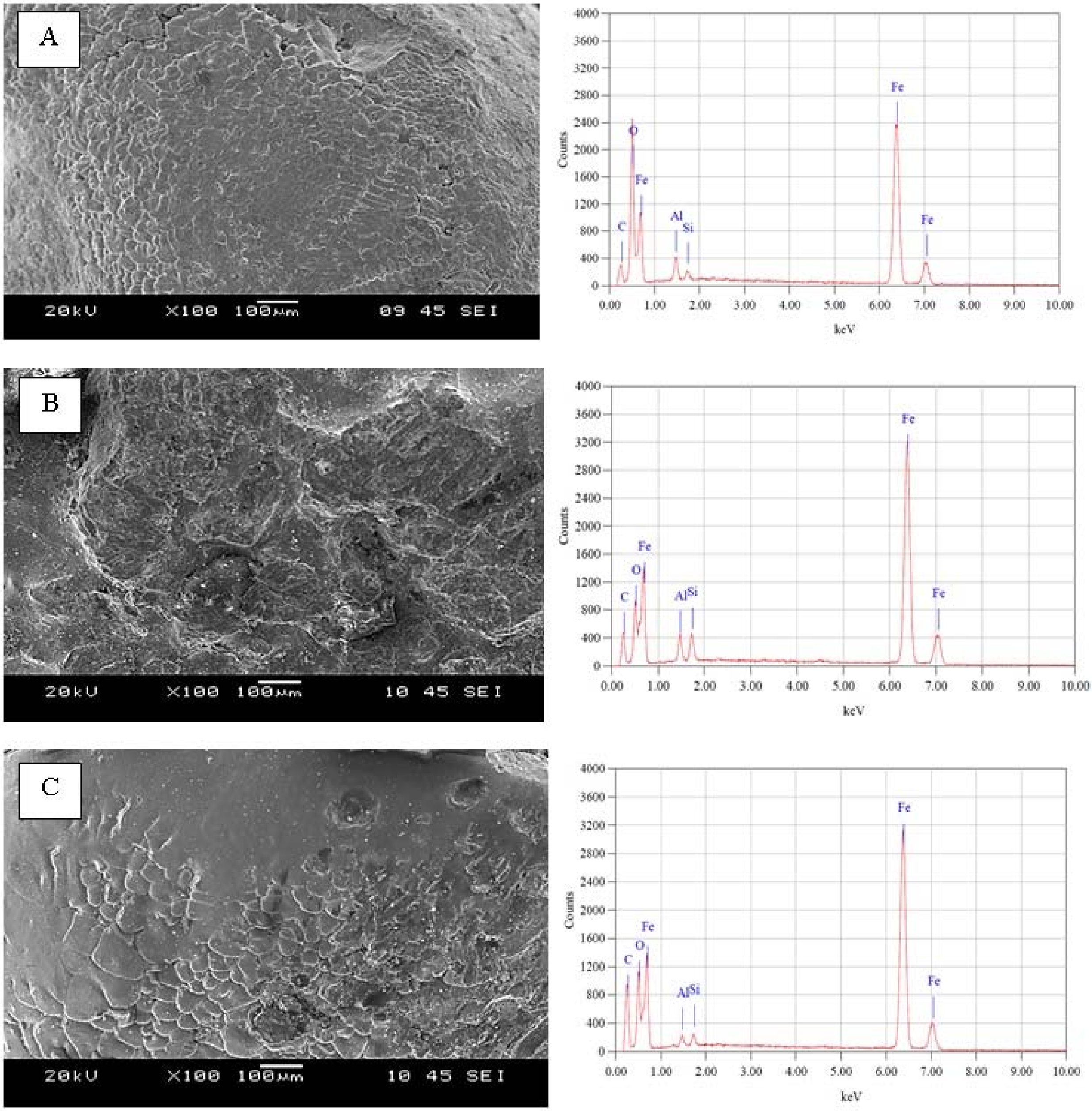

Figure-5. SEM/EDS of reduced iron after reduction process at 1550 ˚C for composite pellets. A (30:60), B (40:60) and C (50:50).

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CONCLUSIONS

An investigation has been conducted on possibility of recycled palm shells as reducing agents for steelmaking applications. The following findings were obtained from this study:

- Palm shells could be used effectively as reducing agent where a significant improvement in degree of reduction was observed. The degree of reduction was raised by increasing the carbon content in the composite pellet which leads to more metallic iron produced.
- From SEM/EDS result, it can be confirmed that the composite pellet can be reduced successfully to metallic iron by palm shells after a complete reduction when the reaction is conducted at 1550 °C.

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