REDUCTION OF FeO IN EAF STEELMAKING SLAG WITH PALM SHELLS UNDER DIFFERENT ACTIVATION METHODS

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ABSTRACT

Renewable energy for steelmaking production was explored widely by researcher to replace the utilization of coke towards more sustainable steelmaking. By converting agricultural waste (palm shells) into renewable carbonaceous materials in EAF steelmaking has potential to contribute energy conservation and emission reduction. The present study investigates the reduction behaviour of the FeO rich slag by agricultural waste and metallurgical coke for the production of metallic iron through experiments conducted using high temperature horizontal tube furnace. Activated carbon from palm shell was prepared by physical (PAPC) and chemical (CAPC) methods. PAPC was prepared by devolatilized in N_2 atmosphere at 450 °C while CAPC were soaked in H_3PO_4 for one hour before devolatilized. All carbonaceous materials including coke were prepared in powder form mixed with an EAF slag. The composite fine powder was inserted into tube furnace at 1550 °C under Argon gas with a flow rate 0.01L/min for reduction reaction with extended time was twenty minutes. The renewable carbon source from PAPC and CAPC showed more efficient due to improvement in degree of FeO reduction compared to conventional materials. The difference of activation methods used revealed an excellent degree of reduction and metallic iron was produced. A study using palm shell wastes as new reductant in steelmaking industry may open the opportunities to transform the waste into valuable carbon materials.

Keywords: activated carbon, EAF slag, reduction behaviour.

INTRODUCTION

Iron and steel making is an energy intensive industry sector using mainly coal and coke as the heat and carbon sources. This industry gives rise approximately 5 % of the anthropogenic CO_2 emissions in the world (Sahajwalla, 2013), (Yunos, 2011), (Yanjia, 2010), (Ooi, 2008). Accordance to the challenge for CO_2 mitigation, the researcher has been looking for another solution such as capturing and storing the rising CO_2 emissions or explored new resources in order to replace the conventional resources (Danloy, 2009), (Ariyama, 2006).

Currently, renewable resources in steelmaking using rubber tires and plastic wastes were practiced. M. Zaharia *et al*. has studied on slag foaming using a rubber tyres as sustainable carbon sources. She reported that rubber tyres blend with coke is efficient due to improved interaction with EAF slag (Zaharia, 2013). J. Ransford Dankwah has explored the utilization of plastic wastes such HDPE blend coconut shells, PS blend coke and HDPE blend palm nut shells are relevant used as reducing agent for the production of metallic iron from EAF rich slag in steelmaking applications. He revealed that blending of the plastic/biomass has a beneficial effect not only improvement in production of metallic iron but also on the environment through decreasing carbon dioxide emission (Dankwah, 2014), (Dankwah, 2013).

However, fewer researcher investigated on recycled agricultural waste from palm shells as a new carbon materials in steelmaking that would act as reducing agent. The use of palm shell waste for the production of good quality steel was considered according to the abundant amount of palm shell waste (Emmerich, 1996). Currently, Malaysia was producing a huge amount of agricultural waste annually especially from palm oil caused abundances in landfill. Almost 70% of the volume from the processing of fresh fruit brunch (palm oil) is removed in form of empty fruit brunch, palm shells, palm oil mill effluent and etc. Approximately 5.5% from palm oil processing are mostly palm shells waste (Zafar, 2014).

Thus, it is suggested to utilize palm shells as new carbon material in steelmaking. The present study has aimed to convert palm shells into valueable carbon material through different activation methods. Production of activated carbon from palm shells can be carried out by two different methods: chemical and physical activation methods. The preparation of activated carbon involved two processes such carbonization and activation. Physical activation is the most simple method because it involved only single step compared to chemical activation method with two steps and expensive however containing a good properties that may consumed to the performance in the carbon/slag interaction (Montoya, 2012). Moreover, activated carbon from agricultural wastes had advantages that offering an effective and low cost replacement for non-renewable coal (Sugumaran, 2012).

Previous researcher, indicated that, derivation of activated carbon from palm shell wastes has potential due to several characteristics presence with low amount of sulphur and phosphorus content that improved the carbon/slag interactions (Yunos, 2011).

In this present work, the recycled materials from palm shell wastes were activated by physical and chemical methods have a potential on producing metallic iron from EAF slag that function as reductant are investigated. In order to understand the behaviour of recycling materials with EAF slag, the experiments have

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been conducted using EAF slag composite with metallurgical coke, PAPC (physical activation palm char) and CAPC (chemical activation palm char).

EXPERIMENTAL

Sample preparations and characterization

Coke is a conventional carbon material was obtained from the Perwaja Steel Sdn Bhd Kemaman, Terengganu. Palm shells from agricultural waste products of the oil palm industry from Felda Jengka, Pahang was used as a raw material for the formulation of activated carbons. Palm shells were dried at room temperature, then crushed to get the particle size of approximately <63 µm. Activated carbon of palm shells was prepared using two different activation methods; physical and chemical activations.

In physical activation method, approximately 10g of crushed palm shells (PAPC) are devolatilized at a rate of 10 °C/min at temperature 450 °C under nitrogen atmosphere for two hours. In chemical activation method, 10g of crushed palm shells (CAPC) were soaked in 100ml Orthophosphoric acid (H_3PO_4) for one hour. The sample was then placed in a horizontal tube furnace and subjected under nitrogen atmosphere for two hours.

The ultimate analysis of raw palm shell, metallurgical coke, PAPC and CAPC are presented in Table-1. The carbon content of PAPC and CAPC were increasing over than 10wt% after activation in N_2 atmosphere compared to carbon present in the raw palm shell. Carbon content in carbonaceous materials may influence the carbon/EAF slag interaction during the reduction process.

Table-1. Ultimate analysis of carbonaceous materials.

Materials	Carbon (wt.%)	Hydrogen (wt.%)	Nitrogen (wt.%)
Raw palm shell	45.67	5.86	0.37
Metallurgical coke	49.62	0.68	0.44
PAPC	59.35	2.98	0.30
CAPC	60.18	1.85	0.44

Then the powdered samples of the slag, coke, palm shell, PAPC and CAPC were also subjected to XRF analysis to determine the oxides that present in samples as presented in Table-2 and Table-3.

Table-2. Ash analysis of carbonaceous materials used (wt%).

Compound	Coke	Palm Shell	PAPC	CAPC
SiO_2	40.96	21.96	26.8	Nd
Fe_2O_3	20.99	62.57	52.88	8.03
Al_2O_3	20.13	5.97	nd	Nd
TiO_2	1.07	0.34	0.44	0.12
P_2O_5	nd	0.66	0.66	91.00
MnO	0.46	0.17	0.64	0.04
CaO	3.37	2.09	3.43	0.20
K_2O	4.06	3.73	9.75	0.51
SO_3	7.31	nd	nd	nd

Table-3. Slag composition (wt%).

Compound	EAF Slag
MgO	2.27
Al_2O_3	5.77
SiO_2	16.87
CaO	27.67
TiO_2	0.54
MnO	2.55
Fe_2O_3	43.18

Reduction reactions

All the carbonaceous materials were prepared in powder form with a particle size of 63µm. The carbonaceous materials were mixed with an EAF slag powder using planetary mill for 1 hour. The mass of powder composite was fixed at 2.50g and it was comprised of mass ratio 1:4 of carbonaceous materials and EAF slag respectively. The mass ratio was considered to oxygen content in Fe_2O_3 in EAF slag and carbon content in carbonaceous materials to ensure that carbon excess was enough to complete the reaction (Dankwah, 2014).

The powder composite samples were then placed into horizontal tube furnace. Then carbon/slag reaction was carried out at 1550 °C in horizontal tube furnace under Argon gas with flow 0.01L/min. Once the samples pushed into hot zone at (1550 °C), the reduction time was set for 20 minutes to understand reduction behavior.

The reacted carbon/slag samples were carefully pulled out and rapidly quenched into cold zone of the furnace before weighted. Figure-1 shows the schematic diagram representation of experimental arrangement of the experiment.

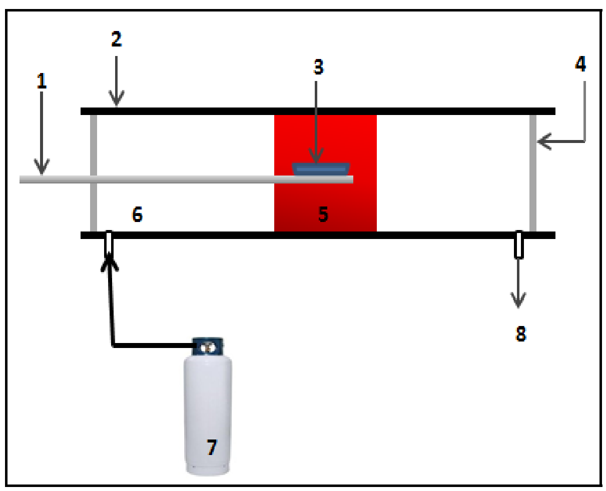

Figure-1. Schematic diagram of the horizontal tube furnace. (1. Sample holder 2. Alumina tube 3. Reaction mixture 4. Quartz window 5. Hot zone 6. Cold zone 7. Argon gas inlet 8. Gas outlet).

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RESULTS AND DISCUSSION

The degree of reduction of carbonaceous materials/slag

Reduction of FeO in EAF slag composite with biomass as carbon materials occurred at temperature 1550 °C under inert argon gas. This reduction phenomenon involved two steps. The step one was occurring when the carbon present in carbonaceous materials reacts directly with Fe_2O_3 rapidly converts to FeO. Then followed by a further reduction from FeO reduce to Fe considered as a slow step accordance with the reaction in equation (1) (Guzzon, 2014).

$$FeO_{(slag)} + C_{(solid)} = Fe_{(metal)} + CO_{(gas)} \tag{1}$$

The reduction process using biomass as carbon material is expected to generate hydrocarbon such CO, CO_2 and H_2O. Previous researchers reported that as the presence of palm shell introduced more complex material that come out with unique structure differ from the conventional materials (Yunos, 2011), (Guzzon, 2014), (Zaharia, 2013), (Dankwah, 2011). The reactions occurring in the slag/carbon interaction are expected to be affected by the presence of an increased level of the hydrocarbon. These hydrocarbon, then further decomposed into carbon and hydrogen. Subsequencely, the chemical reaction occurring in the slag involves the reduction of the iron oxide by hydrogen as equation (2). Thus, the reduction of FeO by carbon and hydrogen leads to derive of CO, CO_2 and H_2O.

$$FeO_{(slag)} + H_{2(gas)} = Fe_{(metal)} + H_2O_{(gas)} \tag{2}$$

After the reduction of FeO, due to the formation of iron and hydrocarbon release during the reduction process, the mass of the composite samples after reduction was changed. The degree of reduction of the composite samples was calculated from the mass of the sample reduced after the carbon/slag interaction process. The result of the degree of reduction for EAF slag with metallurgical coke, PAPC and CAPC attained after 20 minutes are shown in Table-4.

Table-4. The degree of reduction attained after 20 minutes of reduction of FeO in slag with different carbonaceous materials.

Reductant	(CAPC)	(PAPC)	Metallurgical Coke
Degree of reduction (%)	57.21	36.08	22.03

The highest degree of reduction achieved by CAPC that was 57.21%, followed by PAPC and metallurgical coke which are 36.08% and 22.03% respectively. The carbon materials derived from biomass are expected leads the reduction reaction compared to conventional material. This behavior may influence by hydrogen content in palm shells which is 5.86wt% (Table-1). The higher hydrogen content presence in palm shells drives a good characteristic of activated carbon in reduction process. Hydrogen content that presence in the carbonaceous materials will enhance the reactivity between carbon and EAF slag, (Yunos, 2011). Accordance to chemical composition shows in Table-1, the hydrogen content that presence in PAPC (2.98wt%) and CAPC (1.85wt%) are clearly higher than conventional materials, coke (0.68wt%). From the hydrogen content result, PAPC is expected to show a better reduction performance than CAPC. However, the degree of reduction CAPC was resulted higher than PAPC.

It is believe that the high carbon content C also play an important role that affecting in degree of reduction in carbon/slag. V. Sahajwalla *et al.* confirmed that the present of FeO in slag leads to reduction reaction that depending on the reducing agents, carbon content as reducing agent (Sahajwalla, 2013). The activation method of palm shells may influence the carbon content of the PAPC and CAPC after the activation process (pyrolysis). Pyrolysis process may contribute to the increasing of carbon content of palm char. The carbon content determines the calorific value of the fuel as well as the temperature of the flame. The gross properties increase with the increasing carbon content (Yunos, 2012).

Carbon in agricultural wastes is comprised from cellulose, hemicellulose and lignin. Hydrogen produced from condensation of lignin and decomposition of cellulose and hemicellulose during the reaction at high temperature (Yunos, 2011). The CAPC and PAPC are expected to improve the carbon/slag reaction because availability of hydrogen gas and the others hydrocarbon. Thus, the CAPC/slag kinetic advantage might come from its richer hydrogen content in comparison to coke because the reduction reaction in equation (2) is much faster (Zaharia, 2013).

Meanwhile, the degree of reduction of metallurgical coke seems to be lower than PAPC. On the other hand, the composition of the ash also acted as indicator of the reactivity of materials during the reduction. Coke and PAPC are comprised by Fe_2O_3 –K_2O – SO_3 and Fe_2O_3 – SiO_2 – K_2O respectively. Accordance to previous researcher, iron and potassium oxide are known to act as catalyst in the reaction (Yunos, 2011). The higher alkali metals in carbon materials are expected to vaporise faster thus increase the reduction rate. Besides, the presence of sulphur in metallurgical coke also seems to be the reason why the degree of reduction of coke is lowered. During the carbon/slag interaction, sulphur is predicted inhibit the reaction but later would slower the reaction of reduction (Guzzon, 2014).

However, when sample PAPC compared to CAPC, the degree of reduction PAPC much lower due to the different of activation methods that potentially effect the reduction. Palm shells treated with H_3PO_4 showed more efficient in the reduction reaction compared to the untreated palm shell. During the activation process, H_3PO_4 acts as catalyst to promote bond cleavage, hydrolysis,

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dehydration and condensation thus enhance high carbon content in production of CAPC.

Production of metallic iron

The study on production of metallic iron from the Fe reduction phenomena in EAF slag with different powder composite samples was set for 20 minutes at temperature 1550 °C. In the chemical characterization of EAF slag, the presence of iron oxide in EAF slags play an important role that promotes the reaction with the carbon presence in carbonaceous materials that produced the reduced iron and hydrocarbon. Dankwah *et al.* also indicated that at the end product is predominantly metallic iron (reduced iron) and derived gas (CO, CO_2 and H_2). The reduced iron known as metallic iron produced after the reaction was adhered with glassy slag layers.

A clear separation of metallic iron from a glassy slag layer is observed for all carbonaceous reductants as shown in Figure-2(c) (Dankwah, 2012), (Dankwah, 2013), (Dankwah, 2014).

From the Figure-2(c), the composite powder of CAPC and EAF slag composite powder seems like fully melted. The metallic iron formed are predicted due to enough carbon content in the system (Yunos, 2012). However, from the observation on metallurgical coke and PAPC samples, slight amount of composite powder is observed not fully melted can be seen on the crucible's surface as shown in Figure-2(a) and (b) respectively. These phenomena may occurred due to incomplete reduction reaction.

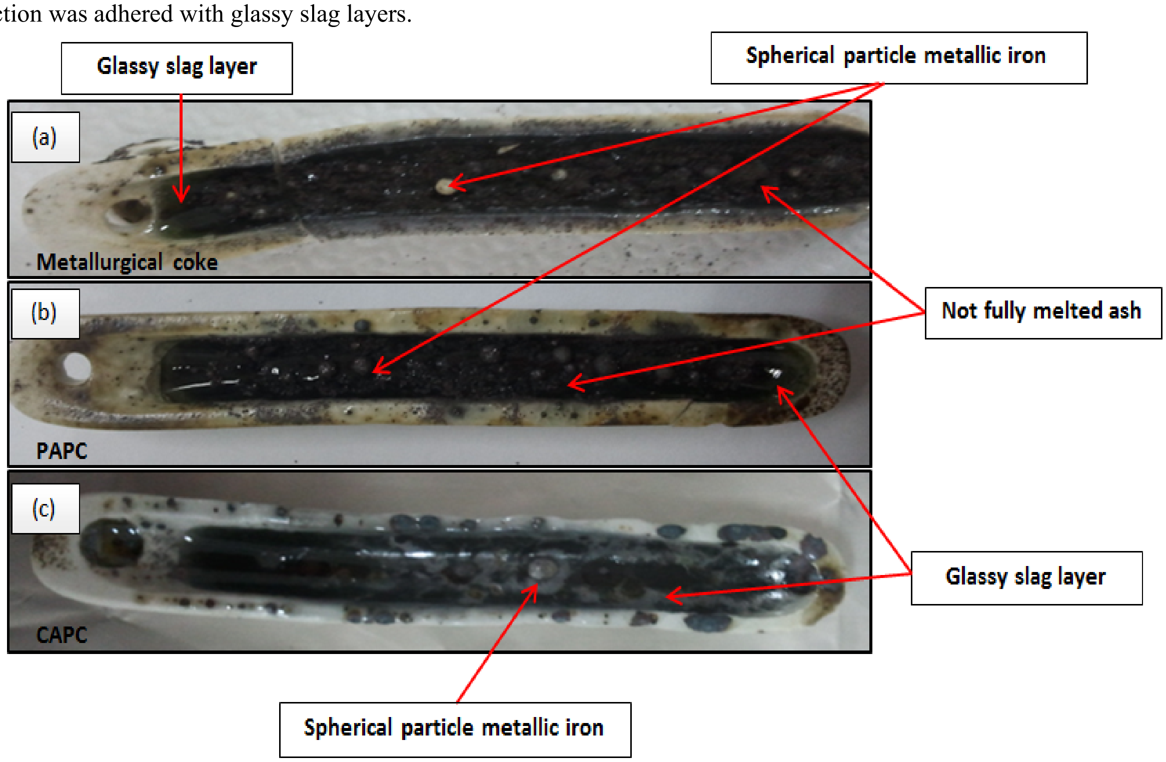

Figure-2. Image of metallic iron and slag layer produced after the reduction reaction of slag by (a) Coke (b) PAPC (c) CAPC.

Particles of reduced iron metal which clearly visible to the naked eye were removed by a magnetic screw driver. The metallic iron produced are spherical particle in shape with different in size were determined and measured as shown in Figure-3. From the figure, the metallic iron formed were separated from melted slag performed different sizes when different activation methods used.

Metallic iron are formed in the size ranges by approximately Coke 3 – 1.5mm, PAPC 2 – 1mm and CAPC 4 – 3mm. As expected, CAPC has the highest size according to an excellent in the reduction reaction in Table-4. Observation on the metallic irons produced by CAPC was clean and smooth surface compared to other carbon material (Dankwah, 2012). Meanwhile, metallic iron produced by Coke are observed slightly bigger than PAPC despite had lower degree of reduction.

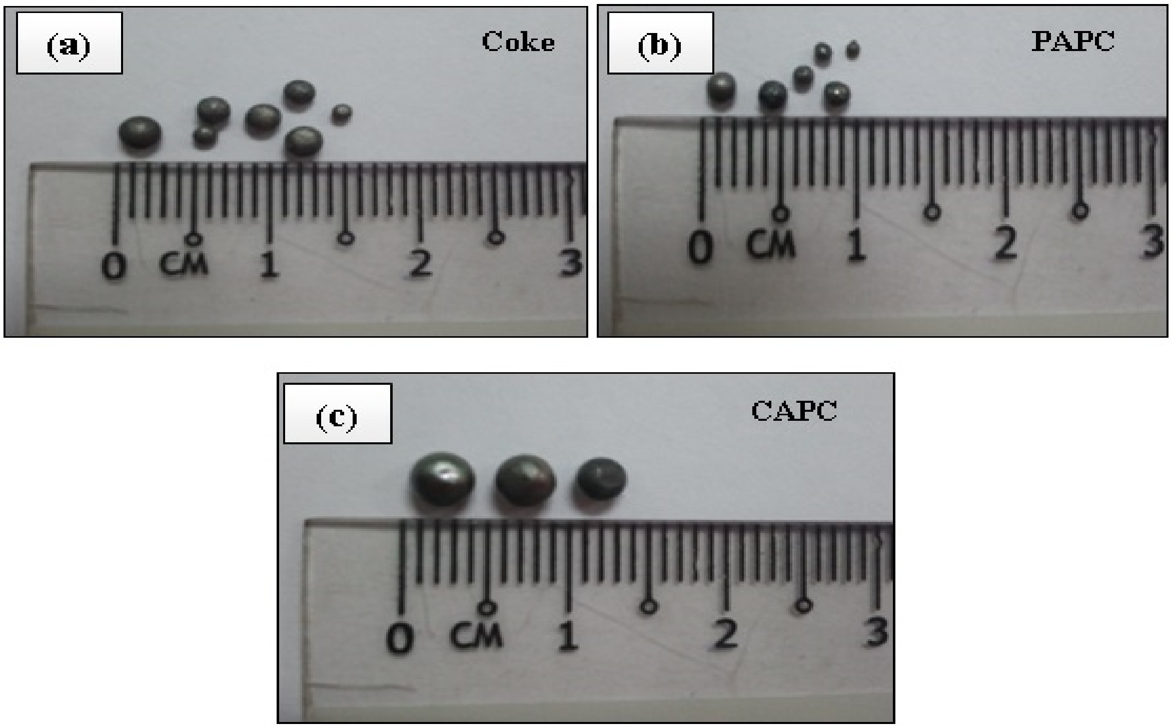

Figure-3. Image of metallic iron produced from the reduction reaction of slag by (a) Coke (b) PAPC (c) CAPC.

Scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS)

Composition analysis of reduced metal (metallic iron) was carried out by Energy Dispersive Spectrometry (EDS) combined with SEM in order to confirm the production of metallic iron particle that produced after carbon/slag interactions. The metallic iron from the reduction reaction of EAF slag by CAPC under 100X magnification is presented in Figure-4. The EDS analyses had revealed that metallic iron showed absolutely high intensity which is 48.86 mass %. CAPC were capable to reduce EAF slag due to high carbon reactivity as shows in Table-1 (Yunos, 2015). The efficiency of CAPC during the reduction reaction process may contribute in producing metallic iron. Yunos *et al*. investigated the growth of the metallic iron initiated with iron oxied on the surface was reduce by the inner surface due to present of carbon as reductant agent.

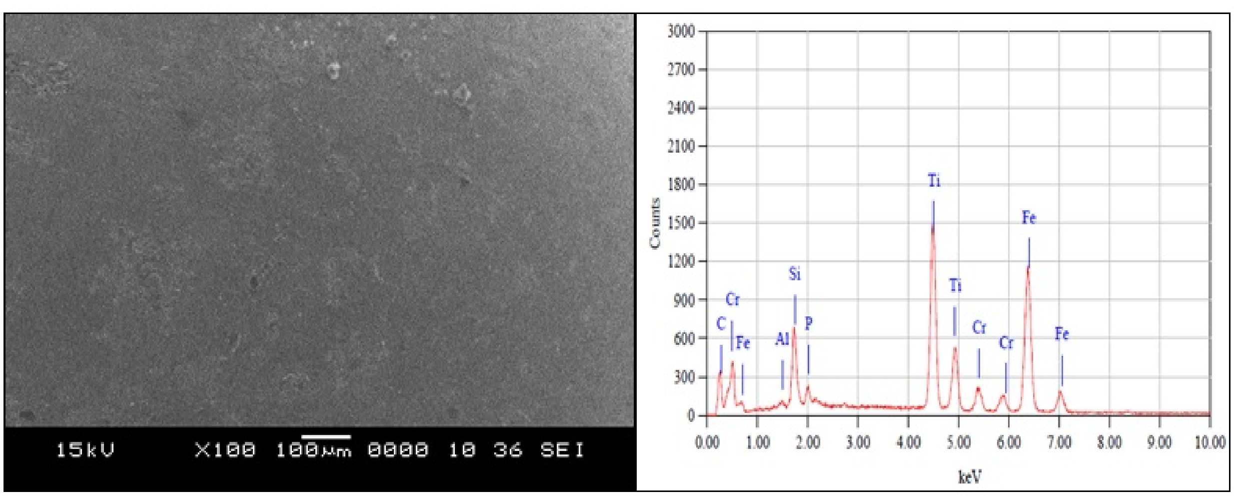

Figure-4. SEM/EDS micrograph of metallic iron produced from the reduction reaction of slag by CAPC under 100X magnification.

CONCLUSIONS

An investigation has been conducted on the possibility of palm shell char as reducing agent in steelmaking using two activation methods. The degree of reduction and the production of metallic iron after 20 minutes of reactions showed an improvement with sample treated with chemical activation due to high hydrogen and carbon content leading higher reduction reaction.

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REFERENCES

[1] Ariyama, T., and M. Sato. (2006). Optimization of Ironmaking Process for Reducing CO_2 Emissions in the Integrated Steel Works. ISIJ International 46, pp.1736-1747.

[2] Dankwah, J. R. (2012). Utilisation Of End-Of-Life Plastics/Rubber Tyres And Their Blends With Metallurgical Coke In Eaf Steelmaking: Reduction Of Iron Oxide. Doctor Of Philosophy, University of New South Wales Faculty of Science, Australia, pp.1-409.

[3] Dankwah, J. R. (2013). Recycling Blends Of Waste Plastics And Biomass As Reducing Agent For The Production Of Metallic Iron From Iron Oxide. International Journal of Engineering Science and Technology (IJEST), 5, pp.1967-1976.

[4] Dankwah, J. R. (2014). Recycling Blends Of HDPE And Coconut Shells As Reducing Agent For The Production Of Metallic Iron From Iron Oxide (Fe2O3). International Journal of Engineering Science and Technology (IJEST), 3(1), pp.40-46.

[5] Dankwah, J. R. (2014). Reduction of FeO in EAF Steelmaking Slag by End-of-Life Polystyrene and It's Blend With Metallurgical Coke. Int. Journal of Engineering Research and Applications, 4(1), pp.274-279.

[6] Dankwah, J. R., Pramod Koshy, Narendra M. Saha-Chaudhury, Paul O'Kane, Catherine Skidmore, David Knights and Veena Sahajwalla. (2011). Reduction of FeO in EAF Steelmaking Slag by Metallurgical Coke and Waste Plastics Blends. ISIJ International, 51, pp.498-507.

[7] Danloy, G., A. Berthelemot and M. Grant. (2009). ULCOS - Pilot Testing of the Low-CO_2 Blast Furnace Process at the Experimental BF in Lulea. Rev. Met. Paris, 1, pp.1-9.

[8] Emmerich, F. G., and C. A. Luengo. (1996). Babassu Charcoal: A Sulfurless Renewable Themo-Reducing Feedstock For Steelmaking. Biomass and Bioenergy, 10(1), pp. 41-44.

[9] Guzzon, M., Veena Sahajwalla, Francesco Memoli and Michele Pustorino. (2014). The Behaviour Of The Secondary Metallurgy Slag Into The EAF. how to create a good foamy slag with the appropriate basicity using a mix of lime and recycled ladle slag as EAF Slag Former. pp.1-12.

[10] Montoya, V. H., Josafat García Servin, and Jose Ivan Bueno Lopez. (2012). Thermal Treatments and Activation Procedures Used in the Preparation of Activated Carbons. Institute Technology of Aguascalientes, pp.19-36.

[11] Ooi, T. C., E. Aries, B. C. R. Ewan, and D. Thompson. (2008). The study of sunflower seed husks as a fuel in the iron ore sintering process. Minerals Engineering, 21, pp.167-177.

[12] Sahajwalla, V., M. Zaharia, I. Mansuri, R. Rajarao, R. Dhunna, F. Nur Yunos, R. Khanna, N. Saha-Chaudhury, P. O'Kane, A. Fontana, C. Skidmore, P. Vielhauer, D. O'Connell and D, Knights. (2013). 2013 AIST Howe Memorial Lecture: The Power of Steelmaking – Harnessing High Temperature Reactions to Transform Waste Into Raw Material Resources. AISTech 2013 Proceedings, pp.1-17.

[13] Sugumaran, P., V. Priya Susan, P. Ravichandran and S. Seshadri. (2012). Production and Characterization of Activated Carbon from Banana Empty Fruit Bunch and Delonix regia Fruit Pod. Sustainable Energy & Environment, 3, pp.125-132.

[14] Yanjia, W., W. Chandler. (2010). The Chinese Non-Ferrous Metals Industry - Energy Use and CO2 Emissions. 38, pp.6475-6486.

[15] Yunos, M., Nur Farhana, Khairel Rafezi Ahmad, Magdalena Zaharia and Veena Sahajwalla. (2011). Combustion of Agricultural Waste and Coke Blends During High Temperature Processes: Effect of Physical, Chemical and Surface Properties. Journal of JSEM, 11, pp.261-266.

[16] Yunos, N. F. D. M. (2012). High Temperature Phenomena Occurring during Reactions of Agricultural Wastes in Electric Arc Furnace Steelmaking: Interactions with Gas and Slag Phases. Doctor of philosophy, University of New South Wales, Australia, pp.1-347.

[17] Yunos, N. F. M., Magdalena Zaharia, Khairel Rafezi Ahmad, Dilip Nath, Masanori Iwase and Veena Sahajwalla. (2011). Structural Transformation of Agricultural Waste/coke Blends and Their Implications During High Temperature Processes. ISIJ International, 51, pp.1185-1193.

[18] Yunos, N. F. M., Magdalena Zaharia, M. Asri Idris, Dilip Nath, Rita Khanna and Veena Sahajwalla. (2011). Recycling Agricultural Waste From Palm Shells During Electric Arc Furnace Steelmaking. Energy & Fuels, 26, pp.278-286.

[19] Yunos, N. F. M., Nor Athirah Aziz, Anis Nadhirah Ismail, Muhammad Asri Idris. (2015). Reduction Behaviour of Iron Ores by Agricultural Waste Chars. Materials Science Forum, 819, pp.31-36.

[20] Zafar, S. (2014). Bioenergy Developments in Malaysia. Retrieved 11 November 2014, from BioEnergy Consult http://www.bioenergyconsult.com/tag/palm-oil-biomass/

[21] Zaharia, M., N. F.M., Yunos and V. Sahajwalla. (2013). Recycled and Renewable materials As Resources for Electric Arc Furnace Steelmaking. Paper presented at the Proceedings of The 22nd Australisian Conference on The Mechanics of Structures and Materials, ACMSM 2012.