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# Utilization of Empty Fruit Bunch Derived Vapor for Carbon Deposition within Iron Ores

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**Abstract.** Metallurgical coke is the main source of fuel and reducing agent for iron and steel industry. Empty fruit bunch (EFB) biomass which is abundantly available in Malaysia could be utilized as a source of energy as well as reducing agent in iron making process. This research presents carbon infiltration within low-grade iron ore via chemical vapor infiltration (CVI) method from EFB pyrolysis vapor. Low-grade iron ore was first heated to remove the combined water (CW) that consequently created pore network within the iron ore. These pores would act as sites for carbon infiltration in the iron ore. The EFB treatment on iron ore has been carried out at different temperatures and the effect of pyrolysis temperature on the carbon infiltration has been investigated. The Brunauer−Emmet−Teller (BET) and Barrett−Joyner−Halenda (BJH) methods have been performed to analyze pore surface and pore volumes of the iron ore. Pore surface and pore volume decreased as the temperature increased indicated that more carbon has been deposited. Using X-ray diffraction (XRD) analysis, it was shown that the low-grade iron ore has been transformed into iron (Fe). The infiltrated carbon from the EFB pyrolysis vapor in the pore surface iron ore is proven to be able to be utilized as source of energy and reducing agent to partially replace metallurgical coke in the blast furnace in order to reduce emission of harmful gas.

## Introduction

Iron and steel are important materials in this modern era as they are widely used in various industrial sector. The sustainability of iron and steel industry is essential as it highly influences the economic growth of the country [1]. Therefore, the upgrading of low-grade iron ore to enable it to be used as a feedstock in blast furnace for iron making is necessary. In comparison to high-grade iron ores, low-grade iron ores are not suitable to be used as a feedstock in the blast furnace due to its relatively high combined water (CW) content that requires extra energy to reduce it to hematite form. Metallurgical coke is very important in iron and steel industry as the source of energy and as the reducing agent in iron making process in blast furnace [2]. However, the usage of metallurgical coke produces harmful gas that could lead to deterioration of the environment. On the other hand, empty fruit bunch (EFB) is one of the biomass materials that is abundantly available in Malaysia that shows promising prospect for the energy sources in iron making process. However, it is not efficient to use it directly in blast furnace due to its high moisture content, that would influence its behavior during heating treatment and would adversely affect the efficiency of iron production. In order to address this issue, thermochemical treatment could be used to utilize the EFB via pyrolysis process, in which it would yield gas, char and tar vapor [3][4]. The gaseous products are to be put into contact with iron ores, in order to get them to infiltrate into the pores of the iron ores via the mechanism of chemical vapor infiltration (CVI). The porous structure of iron ore shows promising features for tar vapor decomposition and carbon storage sites [5]. The products of this process in which the carbon infiltrated within the low-grade iron ore could be utilized both as fuel and reducing agent for iron making process in blast furnace. The purpose of this study is to investigate the carbon deposition within low-grade iron ore via CVI method using EFB pyrolysis vapor. This study analyzes the effect of EFB pyrolysis temperature on carbon infiltration and examines the carbon deposited in the pore surface of iron ore. The objective of the research is to study the effect of the temperature on the chemical vapor infiltration process and how this will affect the phase transformation of low-grade iron ore. The previous research on the CVI process of the biomass and iron ore proved that the deposited carbon can be utilized as source of energy and reducing agent in iron making process. This research presents the research gap of the study of the local biomass such as empty fruit bunch to be utilized in the CVI process by analyzing the reactivity of the EFB derived carbon by using Raman spectroscopy analysis.

## Materials and Method

The raw materials used in this study are empty fruit bunch (EFB), collected at Malaysian Palm Oil Board (MPOB), Bangi and low-grade iron ore, collected from Pahang. The EFB sample was dried at 105°C for 24 hours to remove the moisture content. The iron ore was crushed into particles smaller than 1 cm and dried at 105°C to remove moisture content. The iron ore was heated at 400°C for 3 hours at a heating rate of 10°C/min. This is to remove CW content from the iron. This CW removal left voids within the iron ore thus creating pore networks inside the iron ore. This porous structure of iron ore shows promising features for tar decomposition and carbon storage sites [6].

$$2FeO(OH) \rightarrow Fe_2O_3 + H_2O \quad (1)$$

Biomass treatment was conducted on the dehydrated low-grade iron ore by using pyrolysis and gasification method. The temperatures for each experiment conducted were varied from 500°C, 700°C, 800°C, 900°C and 1000°C. This process was conducted at a heating rate of 30°C/min and was held for three hours. Argon gas was flown into the chamber at a rate of 10mm/min in order to create an inert atmosphere with an absence of air. The specific surface area and pore size distribution of the iron ore were analyzed by the Brunauer−Emmet−Teller (BET) and Barrett−Joyner−Halenda (BJH) method, respectively. X-ray diffraction (XRD) method was used to analyze the composition change of iron ore after CVI process. Raman spectroscopy analysis was performed to analyze the amorphicity of the deposited carbon by calculating the $sp^3$ fraction of the deposited carbon.

## Results and Discussion

The weights before and after the treatment of iron ore with the EFB were recorded and the weight loss of each sample was measured. Table 1 below shows the weight loss of each sample. Fig. 1 shows the weight loss percentage of each samples. The iron ore samples after EFB pyrolysis and gasification treatment experienced weight loss. The percentage of the weight loss increased as the temperature increased. This is due to the reduction process of iron that occurred simultaneously with the infiltration of carbon. There are two types of reduction process that could possibly occur which are direct reduction and indirect reduction process. Direct reduction process is the process of reducing iron oxides directly into iron with carbon. Meanwhile, indirect reduction process is process of reducing iron oxide into iron in the presence of CO gas [7]. The justification of these two types of reduction process to occur are the presence of CO gas from pyrolysis process will acts reducing agent for indirect reduction to occur, meanwhile, the presence of carbon particle that infiltrate during CVI process act as reducing agent that prompt direct reduction process to occur. The Eq. 2 until Eq. 4 below shows the indirect reduction process that shows the phase transformation of iron ore and the temperature of each process to occur can be related in Fig. 3 of the XRD analysis.

Table 1: Weight loss of the iron ore after carbon infiltration process

| Temperature [°C] | Weight before treatment [g] | Weight after treatment [g] | Weight loss percentage [%] |
|---|---|---|---|
| 500 | 50 | 49.7 | 0.6 |
| 700 | 50 | 48.0 | 4.0 |
| 800 | 50 | 47.3 | 5.4 |
| 900 | 50 | 46.5 | 7.0 |
| 1000 | 50 | 43.3 | 13.4 |

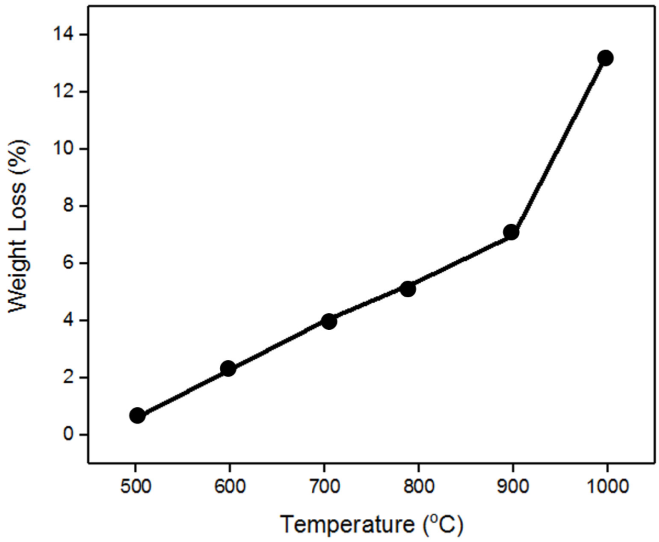



Fig. 1: Weight loss percentage of iron ore after CVI process

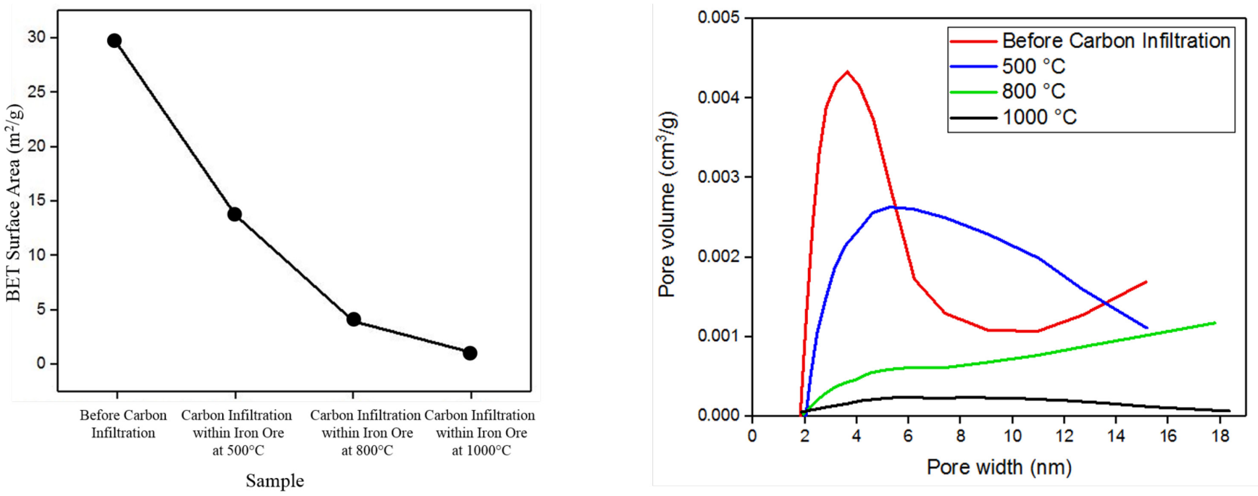
Hematite to Magnetite: $3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$ (2)

Magnetite to Wustite: $Fe_3O_4 + CO \rightarrow 3FeO + CO_2$ (3)

Wustite to Iron: $FeO + CO \rightarrow Fe + CO_2$ (4)

At infiltration temperature of 1000 °C, the weight loss of the iron ore has showed different trend from the other temperature of infiltration. This is because at 1000 °C, the iron ore has experienced direct reduction and this direct reduction reaction produces CO gas as product. Although indirect reduction does not favor to take place at higher temperature, but if the CO gas is high enough, the indirect reduction can still occur. The combination amount of CO gas from pyrolysis process at 1000 °C would yield the highest amount of CO composition of about 35%, and the CO gas produced from the direct reduction reaction will push the indirect reduction to occur [8]. The combination of direct and indirect reduction that occurred has increased the rate of reduction thus making the weight loss of iron ore after infiltration of carbon at temperature of 1000 °C becomes more significant.

Fig. 2a and 2b show the results for BET and BJH analysis. The surface area and pore volume distribution before the deposition of carbon and after treatment have been analyzed and it can be seen that both surface area and pore volume decreased as the deposition temperature increased. The presence of pores after dehydration process acts as catalyst for the deposition of carbon on pore surface of iron ore [9]. This deposited carbon had infiltrated and deposited within the pores thus decreasing the surface area and pore volumes of the iron ore.




a) b)

Fig. 2: BET and BJH analysis

The plots obtained from the BET and BJH results confirmed that the tar vapor decomposition from the empty fruit bunch (EFB) pyrolysis has caused infiltration of carbon within the porous structure of iron ore. The yields from the EFB pyrolysis are the biogas, tar vapor and biochar. The tar vapor will further decompose, and this process is known as secondary decomposition by EFB pyrolysis treatment that would yield solid carbon particle and biogas. Therefore, as carbon is the only solid particles that would yield from the pyrolysis process that could infiltrate into pores of the iron ore, it confirms that carbon had infiltrated into the pores of iron ore as the surface area and pore volume of the iron ore decreased. Even though the initial surface area and pore volume of the raw iron ore before CVI process is low, there is still carbon particle that manage to infiltrate into the pore network of iron ore. This has been proven through BET/BJH analysis for iron ore that undergoes CVI process in which it shows that pores have been filled. The mechanism of the carbon infiltration into the pore structure of iron ore from the EFB pyrolysis product is that the tar vapor comes into contact with the wall of the iron ore pores, it acts as a catalyst for the decomposition of the tar vapor to occur. The decomposition of the tar vapor would yield solid carbon, and biogas in the form of $CO_2$, CO, $H_2$, $CH_4$ and other hydrocarbon gases. The solid carbon from the decomposition would infiltrate and deposit on the pore surface of iron ore and the biogas would leave the pores.

X-ray diffraction (XRD) analysis had been performed to characterize the iron ore after the EFB pyrolysis and gasification to analyze the transformation that had occurred due to the reduction process of the iron ore after the carbon infiltration. The result for XRD analysis is as illustrated in the Fig. 3. The transformation of hematite into magnetite, wustite and metallic iron can be observed. This might be due to the presence of CO gas and solid carbon particles that act as reducing agent as discussed earlier. As the temperature of infiltration increased, the peak of metallic iron, Fe could be observed, that indicates that there is a possibility that the direct reduction process has occurred. By theoretical calculation, the minimum and maximum amounts of carbon for direct reduction process to occur are 2.45% and 4.79%, respectively [10].

$$\text{Maximum C needed: } Fe_2O_3 + 3C \rightarrow 2Fe + 3CO \quad (5)$$

$$\text{Minimum C needed: } Fe_2O_3 + \frac{3}{2}C \rightarrow Fe + \frac{3}{2}CO_2 \quad (6)$$

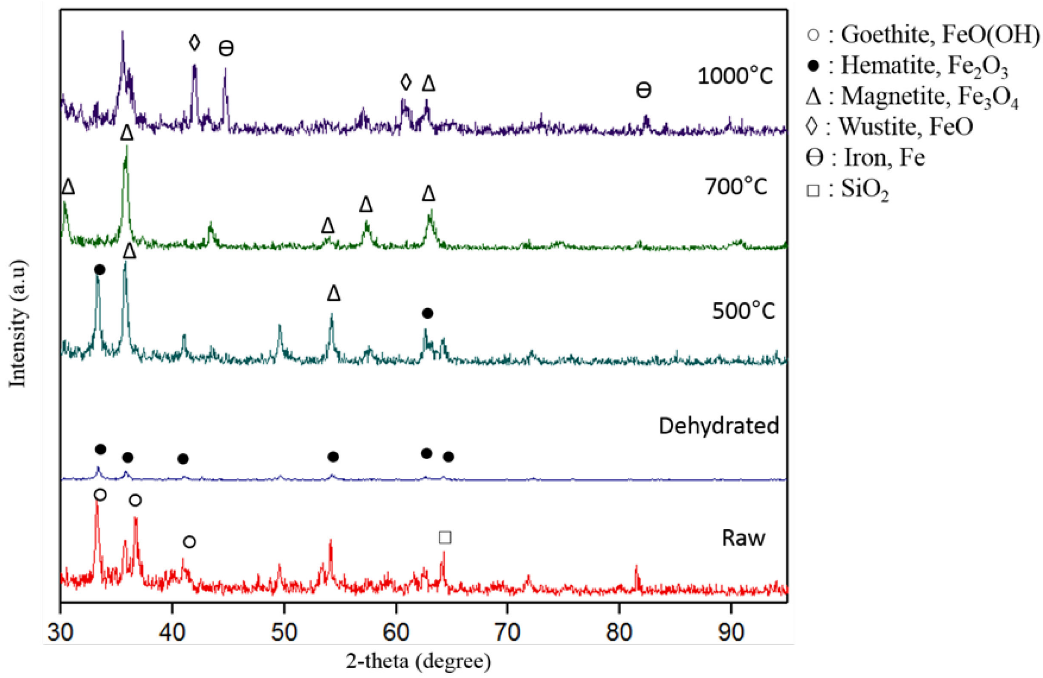



Fig. 3: XRD analysis of raw iron ore, dehydrated iron ore and carbon infiltrated iron ore at 500 °C, 700 °C and 1000 °C

As it has been shown in the XRD patterns, the iron ore has experienced reduction process after the infiltration of carbon into the pore of iron ore took place. For raw sample of iron ore, the three most prominent peaks are goethite and the other mineral peaks shown in the XRD are not significant in this project. There were two types of reduction mechanism that was experienced by the iron ore after carbon infiltration process, and those were the direct and indirect reduction reactions. Indirect reduction is the reduction process by using the CO gas as the reducing agent that been produced from the pyrolysis process. Meanwhile, direct reduction is the reduction process using solid carbon as the reducing agent. The indirect reduction is an exothermic reaction in which it is more favorable to occur at lower temperature. On the other hand, direct reduction is an endothermic reaction that is more favorable to occur at higher temperatures [8]. It is worth noting that, the pyrolysis process done at 500 °C to 1000 °C would yield the CO gas of only around 8% to 35% [3, 11, 12]. This might not be sufficient to transform all the hematite into iron. This is proved that by the XRD pattern at 500 °C, that there was only transformation of hematite into magnetite was observed and there were hematite that was left without being reduced. The direct reduction only occurs at higher temperatures due to its nature as endothermic reactions usually takes place at temperatures higher than 1100 °C, however the Kashiwaya et al., (2004) reported that the strong contact between the carbon particles and the iron ore could remarkably reduce the starting temperature for the direct reduction reaction to occur. The nature of nanoscale contact between the infiltrated carbon and the iron ore has reduced the starting temperature for direct reduction reaction to occur at 750 °C compared to at 1100 °C for conventional mixing of coke and iron ore [13]. This is being confirmed further by the XRD analysis in which the iron peaks appeared for samples produced at carbon infiltration temperature of 1000 °C.

Raman spectroscopy analysis as illustrated in Fig. 4 was carried out to analyze the amorphous structure of the carbon [14]. This can be calculated by using G peak position of the Raman spectra, $\omega_G$ and the intensity ratio of ($I_D/I_G$). The formula to calculate the $sp^3$ fraction [15, 16] is as shown below.

$$sp^3 \text{ fraction} = 0.24 - 48.9\,(\omega_G - 1580) \times 10^{-4} \tag{7}$$

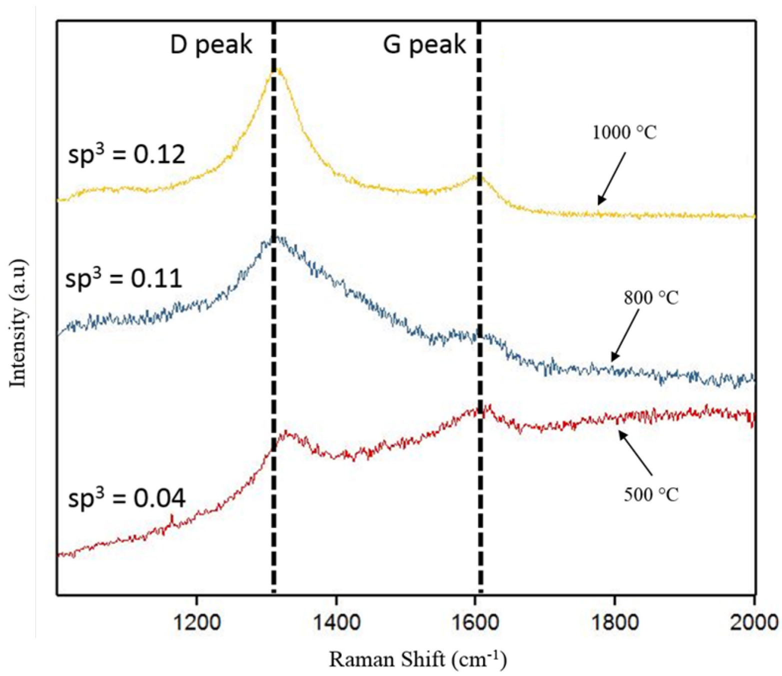



Fig. 4: Raman spectra of infiltrated carbon at temperature of 500 °C, 800 °C and 1000 °C

The $sp^3$ fraction of the infiltrated carbon shows an increasing pattern as the temperature for infiltration increased. The higher $sp^3$ fraction shows that the infiltrated carbon was more disordered and amorphous. This amorphous structure of the infiltrated carbon reflects the reactivity of the carbon during direct reduction process in which the higher $sp^3$ shows the most reactivity. The amorphous nature and nanoscale contact of the infiltrated carbon with iron ore contributed iron reduction temperature in which the reduction started at 750 °C compared to conventional methods at 1100 °C [13].

## Conclusion

Throughout this research, the effects of temperature on infiltration of carbon into iron ore were characterized using BET and BJH methods to analyze the surface area and pore volume distribution that showed decrease of the surface area and pore volume as temperature increased. The XRD analysis indicates that hematite phase of iron ore has been reduced to magnetite, wustite and metallic iron due to the presence of CO gas and carbon as reducing agent. Raman spectroscopy shows the $sp^3$ fraction of the deposited carbon in which carbon deposit at 1000°C. The objective of the research was to study the effect of the temperature on the CVI process and how this would affect the phase transformation of low-grade iron ore have been achieved. It can be concluded that temperature has a significant impact on CVI and pyrolysis process in which affects the outcome of the phase transformation of the low-grade iron ore, in which it shows that as the temperature of CVI process increases, the degree of reduction reaction also increases.

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