Characterization and reduction behavior of carbon-infiltrated goethite ore by impregnation of tar recovered from coke oven gas

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Abstract. The Iron/Steel industry is currently facing serious problem due to excessively dependent on metallurgical coke, which is produced a large amount of CO₂ emission and it was limited source in Indonesia. Coke-free iron-making is one of the efficient method to reduce the amount of cokes. Carbon-infiltrated iron ores were prepared by impregnation process from coaltar solution and goethite ore at 500°C and 600°C to promote direct reduction in iron making. These variables were systematically characterized by XRD and SEM/EDX. Pore distribution and BET surface area were determined by N₂ adsorption-desorption measurement. The XRD signals attributed to Fe₂O₃ in the goethite ore were completely disappeared and replaced by signals attributed to Fe₃O₄ after impregnation process. Cross-sectional analyses of composite particles prepared using both temperatures showed that tar-derived carbonaceous materials have completely either impregnated or vapor infiltrated into the mesoporous in pyrolyzed goethite ore. Carbon-infiltrated goethite ore showed a higher reduction degree than conventional coke. It is confirmed that high reactivity of carbon-infiltrated iron ores is due to close contact between the goethite ore and carbon in its nanoporous interior facilitated the fast reduction.

1. Introduction
The worldwide iron and steel consumption has been highly considered as a barometer of the economic growth and prosperity indicator of each country. In the case of developing countries like Indonesia, the combination of a large population and a low level of steel consumption per capita would force the increasing of steel consumption in this country to construct the infrastructures such as ports, bridges and industrial equipment [1], [2]. However, the ironmaking industry facing serious problem due to excessively dependent on metallurgical coke, which is produced from high-grade bituminous coal and it's limited source in Indonesia. The increase of steel production would force high demand for coking coal which in turn increasing their price in the market [3], [4]. Other than that, the high consumption rate of coking coal produces a large amount of CO₂ emission. Thus, there is a demand to develop iron-making materials showing rapid reduction reactivity to reduced CO₂ emission and energy consumption in the blast furnace [5].

Recently, the authors have developed to use alternative materials that have the low-rank quality that have the low-rank quality to increase the value of materials and reduce production costs. Coal tar-based liquid is a by-product during the pyrolysis process in the production of metallurgical cokes in a cokes oven unit. Coal tar has not yet
been utilized and often causes the process failed because of its condensation even though it has contained high amounts of carbon and energy. In line with this, Goethite ore, FeOOH (total Fe < 60 mass%) is still available abundantly but the utilization of these ores in the ironmaking industry is limited due to a large amount of energy is required to dehydrate the ore because of the high content of combined water (CW). Nonetheless, the nano-porous materials can be produced after the dehydration process nanopores which can be used as valuable reaction sites are produced within the ore [6].

In this regard, coke-free-iron-making has been approached as one of the efficient methods to reduce the amount of cokes by using these materials. The main concept of these projects is to make composites of the iron ore and carbon in close contact with each other to improve the reactivity [7]. In previous work, Chemical Vapor Infiltration (CVI) has been studied as a catalyst for the decomposition of tar vapor from coal using various of low-grade ore [8]–[11]. It has been reported that tar carbon infiltrated and deposited within the pores of iron ore and increased the carbon content by approximately 3-5 wt% dry after the decomposition reaction of tar. However, the amount of deposited carbon in the composite is too low, meaning that it is not possible to complete reduction to iron metal.

For this reason, Mochizuki et al have conducted research by mixing iron ore and coaltar with a ratio from 0 to 4 then heating it to a temperature up to 500 °C and this method is defined as impregnation method [5], [12]. High carbon contents up to 50 mass % in limonite ore are attainable using this method. It is important to determine the optimum temperatures for pyrolysis of carbonized iron ore to obtain maximum carbon deposition. High-temperature pyrolysis generated large amounts of volatile matter (tar and gases), which caused high tar decomposition and produced larger deposited carbon and gases. Nevertheless, at certain temperatures, tar tends to decompose as a volatile gas and carbon are not deposited in the pores of the iron ore [10]. However, this research was only carried out at a temperature of 500 °C and the degree of reduction was not measured.

Therefore, the objectives of this research are to study the effect of the temperature in an impregnation process using Indonesian coaltar and examine the characterization of these materials. In addition, the value of the reduction degree will also be measured as a parameter to calculate the amount of oxygen oxidized to obtain purer iron from the ore. The reactivity of the reduction of the carbon-infiltrated iron ore and the mixture of iron goethite and a conventional metallurgical coke were performed as a comparison. Data comparison from these experiments is expected to reveal carbon content and thermogravimetric pattern, which determine the reduction reactivity.

2. Materials and Methods

2.1. Samples
A low-rank iron ore from Sebuku, Kalimantan Selatan, consists of 3.55-4.0 mm particles was used in this study. Based on X-ray diffraction (XRD), the iron form in the Robe-River was determined as goethite (α-FeOOH). The composition of the Robe-River was Fe, 58; Si, 2.71; Al, 0.92; and Ca, 0.32. The ore contains a large amount (9.32 mass %) of CW. Different amounts of CW affect the dehydration process which creates a porous material for carbon deposition. Initially, raw material was crushed and sieved to obtain samples with similar particle sizes, ranging from 0.95 to 2 mm fragments. Goethite ore was therefore dehydrated by heating it to 350 °C at a rate of 5 °C/min, and it was held at that temperature for 2 h in an air atmosphere to remove the CW and create a porous material. The dehydration process was evaluated based on the Brunauer–Emmett–Teller (BET) method to determine changes in BET surface area and the pore size distribution of ores after the experiments.

2.2. Preparation of Carbon-Infiltrated Iron Ore
Figure 1. illustrates the impregnation apparatus. Coke oven gas (COG) tar recovered from a commercial coke oven was used as the carbon source. Tar solution (40 mL) was placed into a stainless steel tube and 10 g of the calcined goethite ores was added. The goethite ores with the tar solution were then heated at 10 °C/min up to 500 °C and 600 °C for 2 h under an N₂ flow in order to obtain the composites.
2.3. Characterization of Carbon-Infiltrated Iron Ore

All of the samples both before and after impregnation methods was characterized by XRD analysis to identify the type of iron form. XRD measurements were performed using a benchtop X-ray diffractometer (Rigaku Miniflex600) with Mn-filtered monochromatized Cu Kα radiation generated at 40 kV and 15 mA. The samples were crushed and loaded it into a glass holder, and the XRD patterns were collected for 2θ over the range of 20 - 80° at 2°/min in steps of 0.01°.

The cross sectional and elemental analysis were performed using a scanning electron microscopy (SEM) instrument equipped with an energy-dispersive X-ray spectroscopy (EDS) (JEOL, JSM-6510LA) probe operated at 15 eV and an acceleration of 3 nA. The purposes of this method was to identify carbonaceous materials deposited in the prepared carbon-infiltrated goethite ore.

The specific surface area and the pore volume were measured using N₂ adsorption analysis (Quantachrome, NOVA 2000). The values then were estimated using the BET and BJH methods to identify the effect of heating treatment. The samples were first dried at 108 °C under vacuum for 1 h in a glass cell, and then high-purity N₂ (>99.9999%) gas was adsorbed/desorbed in liquid nitrogen of −196 °C. The analysis was repeated to ensure that the results could be reproduced.

2.4. Reduction Test

The reduction reaction of the carbon-infiltrated goethite ore was examined with a thermogravimetric analyzer (TGA) to analyze the weight change ratio during the heating process. The composites was heated until the reduction reaction was complete at heating rates of 20 °C/min in an N₂ atmosphere. Meanwhile, metallurgical coke was mixed well with dehydrated iron ore and examined with the TGA and was used as a comparison of carbon-infiltrated iron ores. This mixture was heated until the completion of reduction at the same operation condition. All of the samples was heated at temperature range of 30 °C until 1200 °C.
3. Results and Discussions
The schematic process diagram from this experiment was illustrated in Figure 2. The final purpose of these steps is to reducing carbon-infiltrated goethite ore into metallic iron following the oxidation/reduction reaction.

**Figure 2.** The schematic diagram of iron making using impregnation methods

Tar decomposition and carbon deposition required a large surface area and pore volume as a reaction site and carbon storage. During heating-up, CW from the original ore, $\alpha$-FeOOH was decomposed and evaporated into Fe$_2$O$_3$ and H$_2$O described in Figure 3.

**Figure 3.** Effect of dehydration on the removal of the hydroxide (OH) group

It was confirmed that the CW of the natural goethite is significantly removed from the ore at 330 °C. The formation of ~4 nm nanopores of FeOOH begins from 230 °C and the nanopores still exist after calcination until 800 °C. The optimal temperature for goethite ore calcination was 230–400 °C because heating at higher temperatures will decrease their specific surface areas drastically [13]. So, the temperature of 350 °C was sufficiently effective to remove the CW and create a porous material. The remaining site of CW was vacant and enhanced pore volume.
Figure 4. Changes in pore size distribution (a) and $S_{BET}$ (b) of Carbon-Infiltrated Iron Ore

Figure 4 presents changes in the pore size distribution and $S_{BET}$ of goethite for each heating process. $S_{BET}$ for dehydrated goethite ore is significantly increased compared to natural goethite ore which showed that CW had been evaporated thus expanding the pores formed. Inversely, the decrease of $S_{BET}$ occurs in carbon-infiltrated goethite ore. In addition, the pore size distributions of these ores indicate that carbon-infiltrated goethite ore possessed fewer nanopores than the dehydrated goethite ore. Nanosized pores were observed in the dehydrated goethite ore but almost no pore size peaks were observed for the composites. Types of a mesoporous structure are existent in goethite ore ($<4$ nm and $>4$ nm). The peak intensity of calcined goethite ore is higher than the natural ore. The pores volume increased after the decomposition reaction of goethite ore. This pore size is a suitable size for carbon deposited into the pores because of the specific tar to infiltrated. Approximately 2 nm tar molecules [i.e., low molecular compositions such as kata-type 2-3 ring aromatic compounds (molecular size: approximately 1.0-3.0 nm)] are loaded into ~4 nm pores [12]. Carbon is well deposited into the pores shown by the intensity of the peak attributed to the ~4 nm pores decreased to zero after the impregnation process. Therefore, the pore size distribution was the dominant parameter rather than the surface area in determining the amount of deposited carbon within the iron ore. These results strongly proved that carbon was successfully penetrated and deposited within the ore.

In order to strengthen the argument, Figure 5 shows the cross-sectional SEM-EDX images of the carbon-infiltrated goethite ores compared to dehydrated ore. The surface of dehydrated ore particles is coarser than the surface of the composites due to a several hundred micrometer thick carbon layer formed on the surface of the composites. Small carbon was detected on the natural ore but a larger amount of carbon was deposited inside both composites. The carbon content of the composites conduct at 500 °C (36.17 mass % average) is greater than the composite conduct at 500 °C (mass 24.58% average). Tar thermal cracking occur during heating treatment to decomposed it into gases, deposited carbon and lighter hydrocarbons due to the high component activity over the surface of porous iron ore through (1).

$$\text{Tar} \rightarrow \text{Tar} \rightarrow \text{H}_2 + \text{CO} + \text{CO}_2 + \text{CH}_4 + \text{other light hydrocarbons} + C \quad (1)$$
Figure 5. Cross-sectional SEM-EDS images of (a) dehydrated iron ore and carbon-infiltrated iron ore (b) at 500 °C; (c) at 600 °C.

Nanoscale contact between metal oxides with tar affects decreasing the activation energy by weakening the C-C bonds and preventing the formation of stable chemical structures in hydrocarbons thereby increasing the rate of degradation of complex hydrocarbons during the tar decomposition process [14]. Tar carbon deposition within the porous ore was predominant in the temperature range 400–600 °C rather than the formation of gas products. At temperatures above 600 °C, tar decomposition generated gas products rather than depositing carbon [11]. There is a reason this research was conducted at 600 °C as a maximum temperature.

In order to clarify the iron formation, Figure 6. shows the results of XRD analysis for each carbon-infiltrated iron ore at different tar decomposition temperatures. It can be clearly seen that the XRD signals attributed to hematite (Fe₂O₃) in the goethite ore were completely disappeared and replaced by...
signals attributed to magnetite (Fe₃O₄) after the impregnation process. The results indicated that direct reduction (from carbon deposited) and indirect reduction (gas product) of hematite ore to magnetite occurred simultaneously during the decomposition process.

Figure 6. Dependence of XRD patterns of the carbon-infiltrated goethite ore (a) at 500 °C and (b) at 600 °C.

Thermogravimetric analysis was performed to describe the reaction mechanism of carbon-infiltrated goethite ore compared to metallurgical coke by identifying the weight changes ratio to temperature rise at the same heating rate. It is known from Figure 7. that the weight change ratio of composites decreases drastically at some point temperature but no significant weight changes in the case of goethite ore mixed with coke. It means that the reactivity of carbon-infiltrated iron ore was much higher than that in metallurgical coke. In the case of composites, more carbon produced from composites at 500 °C affects higher reactivity (lower reduction temperatures) compared to composites at 600 °C. Hosokai et al were explained that there are two reasons to cause it. Firstly, the high nanoscale contact area between the ore with carbon. Secondly, the distribution of functional groups that contain O and other heteroatoms that affects the reactivity of carbon [15]. There is 3 region of reduction reaction from the composites describe in Table 1.

| Temperature | Process |
|-------------|---------|
| 0 – 450 °C  | re-evaporation and carbonization of coke tar |
| 450 - 700 °C| reduction reaction of the ore |
|             | \(Fe₃O₄(s) + C(s) \rightarrow 3FeO(s) + CO(g)\) (2) |
|             | \(Fe₃O₄(s) + CO(g) \rightarrow 3FeO(s) + CO_2(g)\) (3) |
|             | \(C(s) + CO_2(g) \rightarrow CO(g)\) (4) |
| >700 °C     | reduction reaction of the ore |
|             | \(FeO(s) + C(s) \rightarrow Fe(s) + CO(g)\) (5) |
|             | \(FeO(s) + CO(g) \rightarrow Fe(s) + CO_2(g)\) (6) |
Figure 7. Temperature dependence of the weight change ratio in thermogravimetric analysis.

In order to clarify the results, XRD analysis was performed to determine the phase change of the ores after the reduction test. In line with the reaction step, the final results of both composites were detected as wustite (FeO) and metallic iron (Fe). The peak intensity of carbon-infiltrated goethite ore at 500 °C is more intense than the other one because of its high content of carbon for the excess reactant in the reduction reaction. More amorphous carbon produced in a composite made at 500 °C resultant more high reduction degree.

4. Conclusion
Calcination of goethite ore causes the ore to have a nanoporous structure so that carbon can easily be deposited into the pores during tar decomposition resulting in a reactive composite. The amount of carbon deposited in the porous iron ore is an important parameter to obtain the optimum reduction degree. A comparison was made between the carbon-infiltrated iron ore produced at a different temperature to understand the key factors in carbon deposition. A composite made at 500 °C is more reactive than composite at 600 °C because of more carbon deposited, producing a higher reduction degree. However, both shows a satisfying result for direct reduction. The reduction of carbon-infiltrated goethite ore takes place at relatively low temperature compared with the mixture of goethite ore and metallurgical coke. This is because extensive nano-order contact between goethite ore wall and amorphous carbon making it more effective for direct iron making.

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