BIOMASS IRONMAKING USING GOETHITE ORE AND PINE TREE[1]

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Abstract

In this study, in order to reduce our dependence on fossil fuels in ironmaking, we experimentally examined the possibility of developing a new ironmaking method that employs low-grade iron ore and woody biomass for promoting the direct reduction, FeO + C = Fe + CO, in which dehydrated, porous limonite iron ore was filled with carbon deposited from the biomass tar. In our experiments, three types of iron ores containing different amounts of combined water (CW: 1.6, 3.8, 9.0 mass%) were first dehydrated at 450 °C to be make them porous and then heated with pine tree biomass at 500 to 600°C in order to gasify the biomass and deposit the resulting tar vapor within/on the porous ores. The dehydration treatment made the iron ores porous by removing CW and significantly increase their BET specific surface areas and porosities. The use of the limonite ore containing 9 mass% CW drastically increased the BET area from 13 to 74 m2/g. In the second treatment of biomass gasification and deposition of tar vapor, the biomass was changed into char, tar vapor, and reducing gas, the tar vapor (volatile matter) was decomposed and carbonized within the porous ores. Interestingly, the ores caught tar effectively, not only on the surface but also inside their pores. Here, the ores with the nanosized pores served as catalysts for tar carbonization with gas generation. Simultaneously, the ores were partially reduced to magnetite by the reducing gas. The ores containing carbonized material were easily reduced to iron by only heating until 900 °C in a nitrogen atmosphere, this was due to the direct contact of carbon and iron oxide within the ores, called direct reduction. In conclusion, the dehydrated limonite iron ore was most effective for solving the problem of tar generation in biomass gasification and the product filled with carbonized material from tar can be a promising raw material for ironmaking. The results suggest an innovative ironmaking method with large reduction of carbon-dioxide emission using low-grade iron ore and woody biomass

Key words: Ironmaking; Biomass; Direct reduction; Goethite; Pine tree

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1 INTRODUCTION

Effective use of low-grade limonite iron ore such as Australian goethite in ironmaking is necessary to achieve cost reduction and solve the problem of resource shortage.[1] However, its use in sinter and pellet plants is thermally disadvantageous because it requires additional dehydration energy due to the presence of combined water (CW). In contrast, the dehydration of ore is physically interesting for the production of porous materials; cracks are initiated and propagated by the combined water that is released during the dehydration, producing many nanopores within the ore.[2] As a result, the porous structure of goethite is controllable by the dehydration of CW. Dehydrated goethite can be a catalyst, although it has not yet been practically used in ironmaking.

It is well known that woody biomass is attractive alternative fuel as a solution of the global-warming problem. We can easily produce reducing gas and char from the pyrolysis of biomass; however, the biomass pyrolysis poses a serious problem: the sticky tar that is produced as a byproduct causes operational difficulties such as the contamination the inner wall of a reactor and blockages in pipes. In order to avoid this problem, energy-consuming, high-temperature operation over 800°C is generally necessary. Therefore, for effective use of biomass, it is necessary to develop technology of biomass gasification at low temperature without tar generation. Recently, it has been reported that porous material such as □-Al2O3 and active carbon are quite effective for eliminating tar in the biomass pyrolysis process.[3] In this process, tar is carbonized within pores, together with hydrogen generation. The operating temperature of this process is 500°C to 600°C, it is not required to heat up the reactor, and the porous material behaves as a catalyst to decompose the tar.

From the two facts mentioned above, dehydrated goethite ore can be used as a catalyst for eliminating the tar produced in biomass gasification process; however, to the best of our knowledge, no study has ever been published on this matter. Therefore, the purpose of this study is to evaluate the possibility of using biomass for ironmaking by using dehydrated goethite ore and biomass tar. In this study, we examine the following aspects: (1) the effect of dehydration on the pore structure of iron ore, (2) the relationship between the carbon deposited within the ore and the combined water of the ore, and (3) the carbothermic reduction of the ore with deposited carbon. The results obtained will provide a hint for optimizing the operating conditions for biomass ironmaking with drastic reduction of carbon dioxide emission.

2 EXPERIMENTAL PROCEDURE

2.1 Dehydration of Ores

Table 1 lists the three iron ores used in the present experiments; the ores were selected so that they contained different amounts of combined water: the R ore, a type of limonite ore, had the largest content of combined water, namely, 9.02 mass%; in contrast, the C ore was high-grade hematite ore with only 1.59 mass% of combined water. The sample of all these ores were sieved to obtain particles ranging from 355 to 500 micro meter in size, and their pore structures were identified by BET and porosimeter.

Table 1 Three sample ores used in the experiments.

Sample ore	Particle size [μ m]	C.W. [%]	T. Fe [%]	R.O. [%]	BET [m^2/g]	Average Pore Size [nm]	Porosity [%]
R ore	355~500	9.02	57.2	24.58	13.13	5.14	16.7
H ore	355~500	3.79	56.9	24.45	4.05	5.45	6.3
C ore	355~500	1.59	67.6	29.05	1.93	7.39	6.8

C.W.: Combined water, R.O.: Removable oxygen, BET: BET surface area, Porosity: Analyzed from pores having a size of <300 nm.

Next, the sample ores were dehydrated by heating them to 450 °C at a rate of 3.5 K/min in air. These heating conditions were determined from the fact that combined water of goethite, gibbsite, and kaolinite decomposes at 330 °C.[4] This heat treatment makes the sample ores porous due to the removal of the combined water. In order to confirm this effect, the sample ores were heated and their pore structure, BET surface area, average pore volume, and pore size distribution, were measured before and after the experiment.

2.2 Tar Carbonization

In general, biomass pyrolysis generates reducing gas, char, and tar the tar vapor generated at high temperature condenses at room temperature. In order to prevent the tar generation, the dehydrated sample ores were placed in a biomass pyrolyzer. A pine tree was used as biomass; before use, it was washed by water and pulverized. Table 2 gives the elemental compositions and particle sizes of the biomass used. Figure 1 shows the experimental apparatus used for this treatment.[5] In this figure, the system shown on the left side consisted of two parts; the pyrolyzer and coker for tar carbonization are shown on the right side. The reactor was made of quartz; the thimble filter of the pyrolyzer; of an SUS 304 mesh. Local temperatures in the furnace were monitored by five thermocouples to maintain the desired temperatures of 600 °C and 500 °C at the pyrolyzer and coker, respectively. Nitrogen gas was flowed into the screw feeder and the reactor at the flow rates of 600 and 200 ml/min (STP), respectively.

Table 2 Elemental compositions of biomass used (pine tree).

Composition [mass%]		Size [μm]
C/H/O	49.83/6.18/43.99	710~1190

A pulverized pine tree was packed in the screw feeder and charged into the reactor at a charging rate of 0.07 g/min. The tree charged was first pyrolyzed within the thimble filter to produce gas, tar vapor, and char. Then, gas and tar vapor were introduced into the packed beds of the dehydrated sample ores placed in the coker in a nitrogen atmosphere. The tar vapor from the coker was collected by a cold trap that was filled with glass beads of 40-mm diameter and cooled in an acetone bath at a temperature of –73 °C.

Table 3 gives the experimental conditions for tar carbonization. The pyrolyzer temperature of 600 °C was determined from the fact that tar is generated in a temperature range from 450 °C to 700 °C. The height of the packed bed of ores was constant at 10 mm, in which the mass of ores was approximately 3.0 g. Here, the contact time was 0.37 s, calculated from the N2 flow rate of 800 ml/s (STP) and the coker diameter of 2.0 mm. The temperature of the cold trap was sufficiently low for collecting tar, but not carbon dioxide. Table 4 gives the compositions of the gas produced in the pyrolyzer under these experimental conditions.

After the experiments, the tar was recovered in the cold trap by injecting acetone, and the composition of the tar dissolved in acetone was analyzed by using capillary gas chromatography (GC). The tar that did not dissolve in acetone was recovered by injecting tetrahydrofuran (THF) and its weight was measured after removing THF by a rotary evaporator at 40 °C. The pore structure and composition of the carbon deposited on the sample ores were analyzed after the experiments.

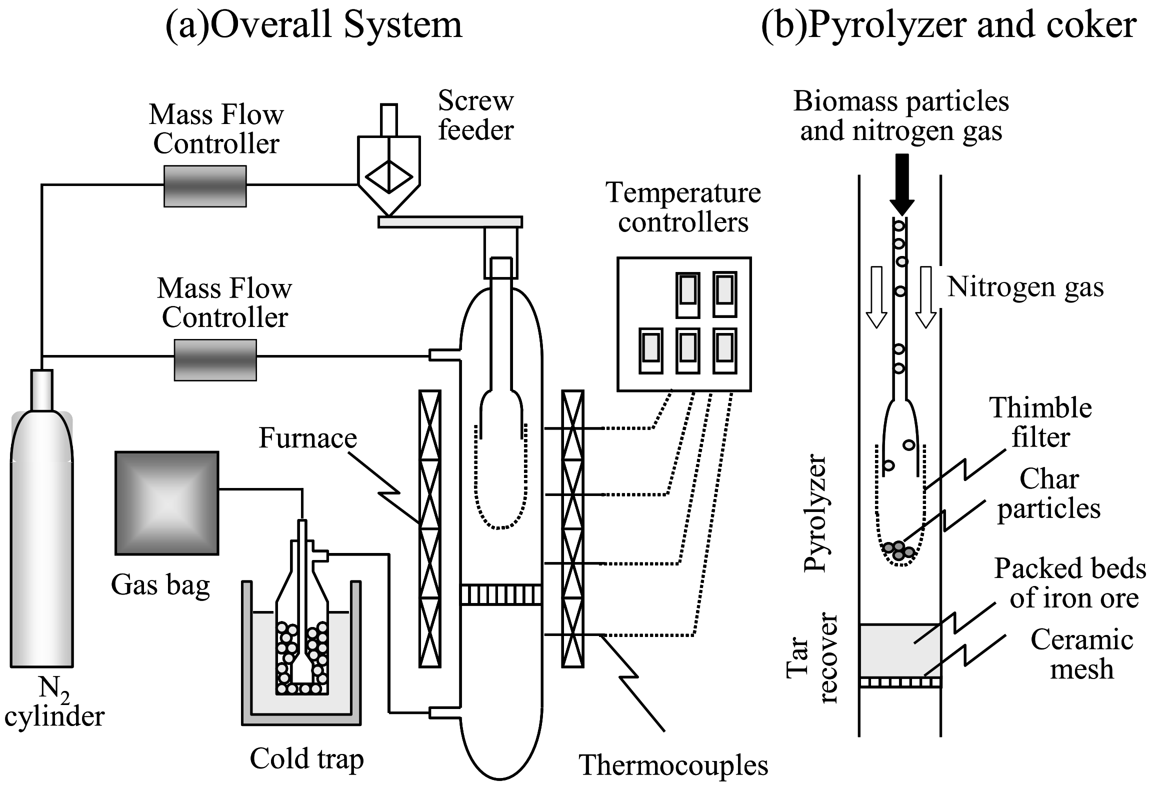


Fig. 1 Experimental apparatus for the pyrolysis of woody biomass and tar deposition.

Table 3 Experimental conditions for tar carbonization.

Exp. time	Charging rate	Pyrolyzer temp.	Coker temp.	Height of ore bed	N2 flow rate	Cold-trap temp.
40 [min]	0.07 [g/min]	600 [°C]	500 [°C]	10 [mm]	800 [ml/min]	–73 [°C]

Table 4 Gas compositions of pyrolyzed biomass.

Gas	CO	CH4	CO2	C2H4	C2H6	C3H6	C3H4	C3H8	C2H4O	H2	Total
Comp	1.54	12.74	20.99	1.81	0.97	0.93	0.18	0.15	1.82	8.88	100.00

2.3 Direct Reduction of Iron Ore by Carbonized Tar

The effect of direct reduction of iron ore by carbonized tar was examined: 3.0 g of the sample ores that were subjected to the experiment were heated to 900 oC at a heating rate of 15 oC/min and kept in a nitrogen atmosphere for 2 h. Then, the sample ores were allowed to cool; thereafter, their structures were characterized by

XRD and the reduction ratios were estimated by the following equation under the four assumptions that follow it:

$$Reduction \quad ratio\,[\%] = \frac{Oxygen \quad generated \quad from \quad ores}{oxygen\ removed} \times 100$$

(1) Carbonized tar is completely gasified through various reactions,

(2) All mass changes of the sample ores during the heating treatment are due to oxygen generation from ore and gasification of carbonized tar,

(3) Composition of the sample ores before the heating treatment is magnetite

(4) Tar composition is C:H:O = 100:61.8:6.8 in molar ratio.

3 RESULTS AND DISCUSSION

Figure 2 shows the changes in the BET specific surface area and average pore size of the original, dehydrated, and tar-carbonized R, H, and C sample ores. The results indicate that the dehydration of combined water created nanosized pores, within which tar was carbonized. The sample of the R ore with the largest amount of combined water exhibited the largest changes in the pore structure after dehydration and tar carbonization: The dehydration significantly increased the BET surface area of the R ore from 13.13 to 74.90 m^2/g, whereas it only slightly increased the average pore of this ore. On the contrary, the tar carbonization decreased the BET surface area of the R ore from 74.9 to 17.27 m^2/g, while it increased the average pore size of this ore.

Figure 3 shows the pore size distribution of the original, dehydrated, and tar-carbonized R, H, and C sample ores. Note that the average pore size of each sample ore decreased by dehydration and increased by tar deposition. Interestingly, by dehydration, the average pore size of the R ore was increased by less than 4 nm, which was lost by the subsequent tar deposition.

Figure 4 shows the tar amount of the sample ores after tar carbonization. According to chemical analysis, the composition of the carbonized tar was C100H61.8O6.8. As a result, the largest amount of tar was deposited in the R ore, namely, 4.0%. Figure 5 shows the schematic diagrams of the dehydration and tar carbonization processes for the R ore. During dehydration, the movement of the combined water created nanopores; during subsequent tar carbonization, tar vapor entered the nanopores and carbonized within them.

Figures 6, 7, and 8 show the XRD patterns of the R, H, and C ores, respectively: (a) after dehydration of combined water, (b) after tar carbonization, and (c) after heating at 900 °C. After the dehydration, all ores were hematite and were reduced to magnetite by the subsequent tar deposition and carbonization. The gas produced by the biomass pyrolysis contained reducing gases namely, carbon monoxide and hydrogen. The peaks of iron and FeO were found in the samples even after the direct heating in the nitrogen atmosphere due to the reduction of ore by the deposited carbon.

Table 5 gives the reduction ratio of the ores in which tar was carbonized. The results show that the R ore exhibited the maximum reduction ratio of 46%. The value of reduction ratio will depend on the carbon deposited within the iron pores. In the heating treatment, the R ore exhibited the largest changes in the reduction ratio.

Table 5 Reduction ratio of three carbonized-tar-containing ores after heating at 900 °C

	Carbon content after tar carbonization.[mass%]	Reduction ratio of ores after heating at 900 °C.[%]
R ore	4.04	45.79
H ore	1.72	33.13
C ore	1.11	20.76

Figure 9 shows the biomass utilization potential of several selected countries, together with energy requirement of Japanese steelmaking in 2007. *Forest land(FL)* is annual growth rate of the biomass in each country and *Fuel wood(FW)* is practically consumed biomass per year at the present. Obviously, Japan, although having not a small FL, has still very small FW. This is due to difficulty in collecting them at reasonable price according to several feasibility reports. Philippines has too large FW now; The consumption rate of biomass is larger than the growth rate of biomass. This implies we will use up all of the biomass in this country in the future. In contrast, it looks like Australia, Malaysia and Indonesia have still enough biomass to use instead of fossil fuel. In particular, Australia has advantage in doing *Biomass Tar Ironmaking* proposed in this paper from the fact that most of limonite ore such as goethite comes from east Australia which is forest land. Remember that this method of biomass tar ironmaking is kill-two-birds-with-one-stone solution by the combination of tar unavoidably generated in the gasification of biomass and low-grade iron ore of goethite with combined water.

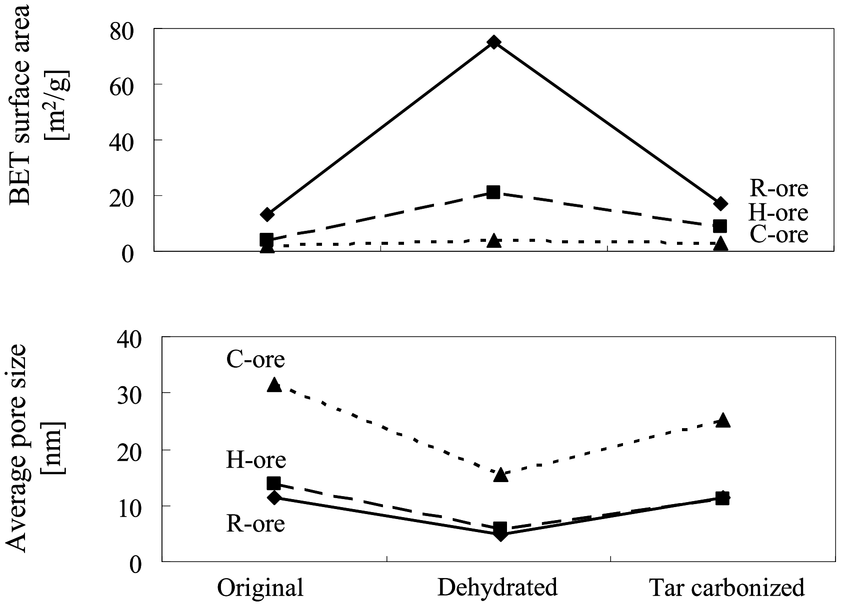


Fig. 2 Changes in BET surface area and average pore size of three ore samples; original, dehydrated ore and tar-carbonized ore.

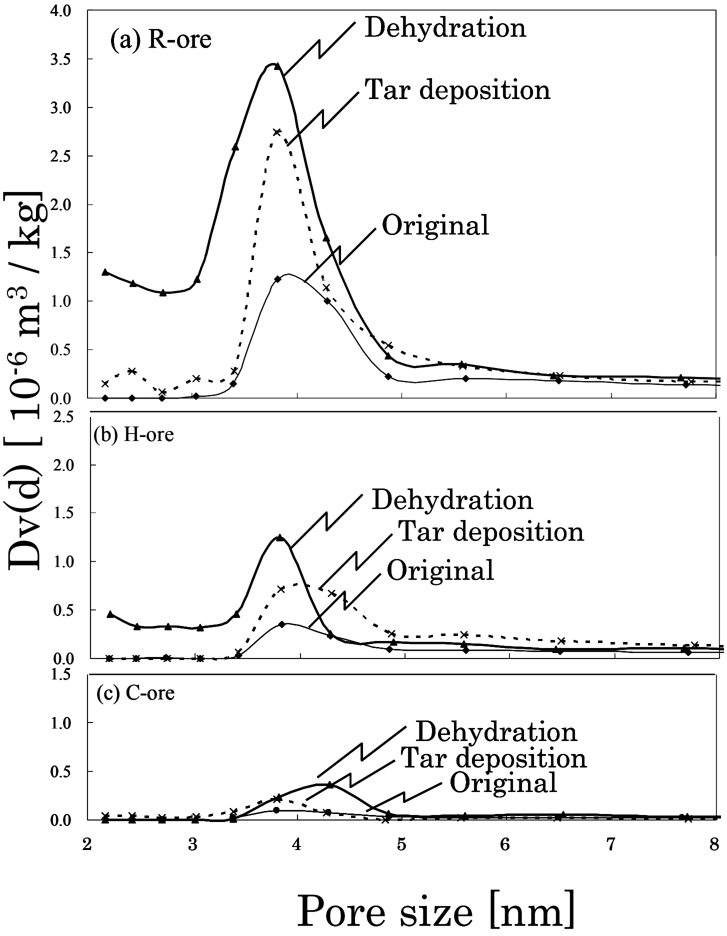


Fig. 3 Changes in pore size distribution of three samples; original, dehydrated ore and tar deposited ore.

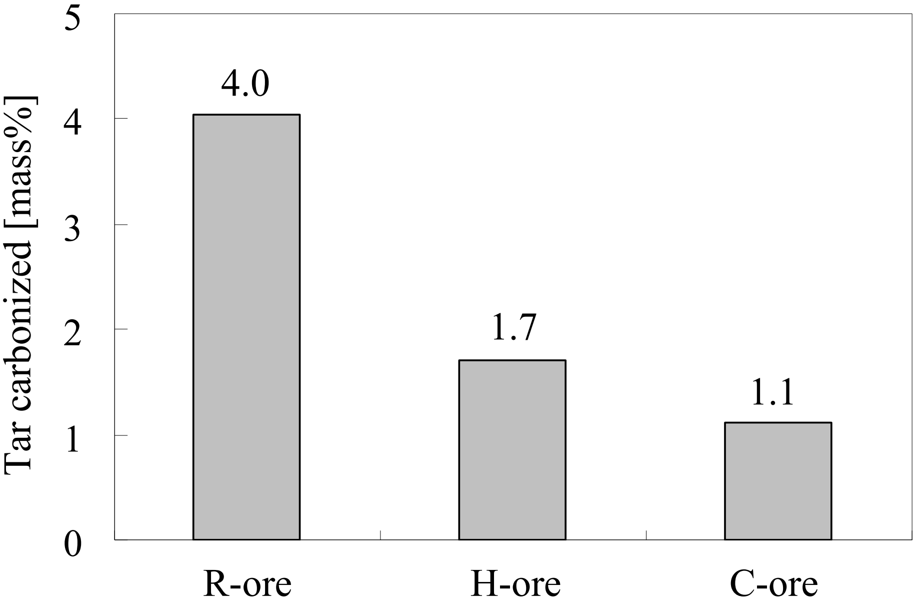
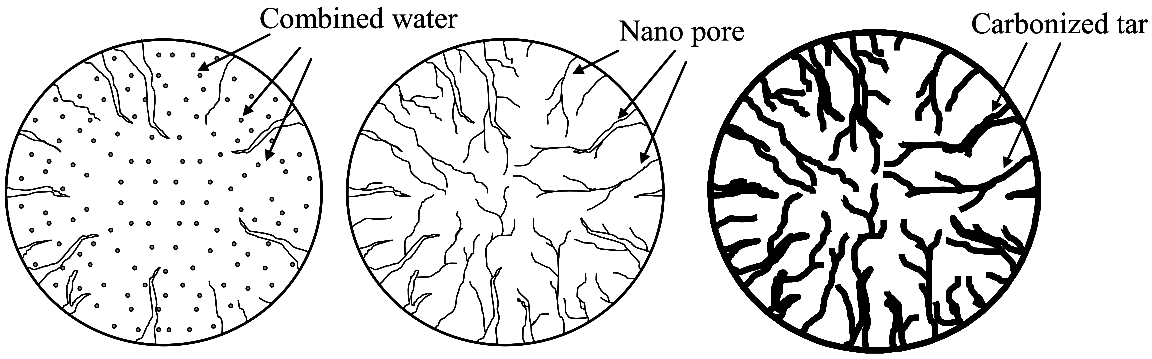
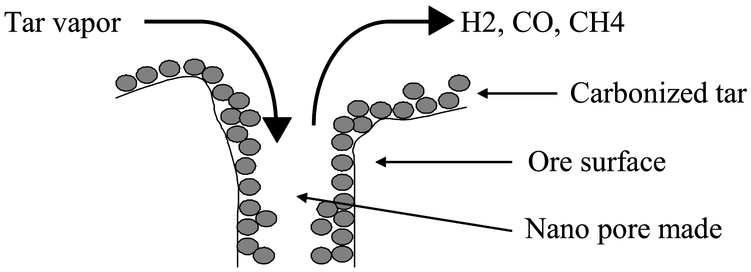


Fig. 4 Degree of tar deposited within the three samples on the mass basis of dehydrated ore, in which waste pine tree was charged into the pyrolyzer heated at 600 °C in the chainging ratio of 0.07 g/min for 40 min and tar was recovered by the sample of 3.0 g.



(a) Original (b) After dehydration (c) After tar-carbonization



(d) Tar carbonized in nanopore.

Fig.5 Schematic diagrams of dehydration and tar carbonization process.

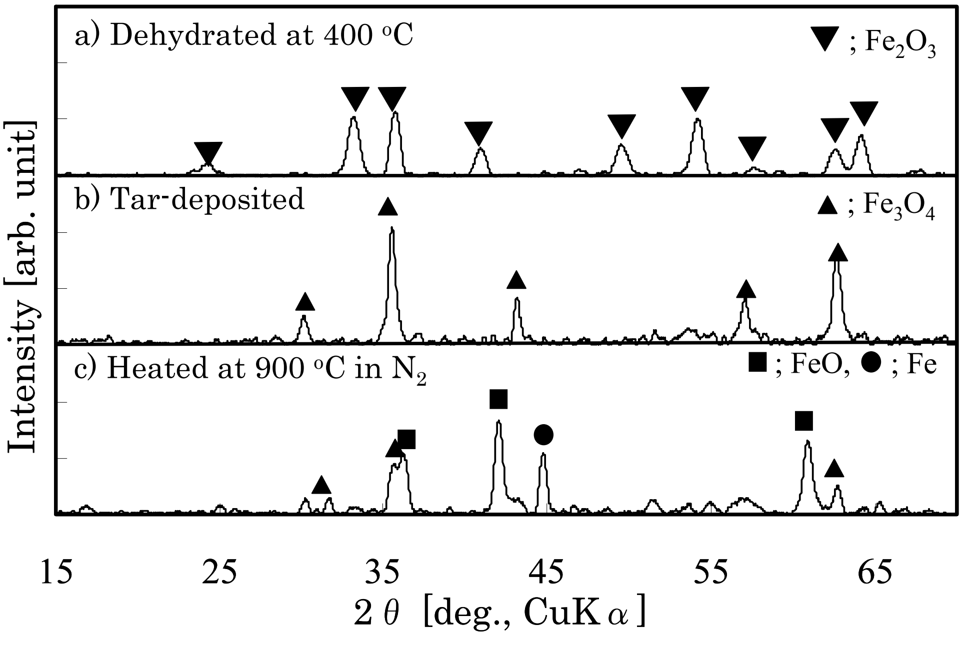


Fig. 6 XRD patterns of the R ore; a) Dehydrated ore at 450 °C, b) Tar-deposited ore and c) Heated ore upto 900 °C at nitrogen atmosphere.

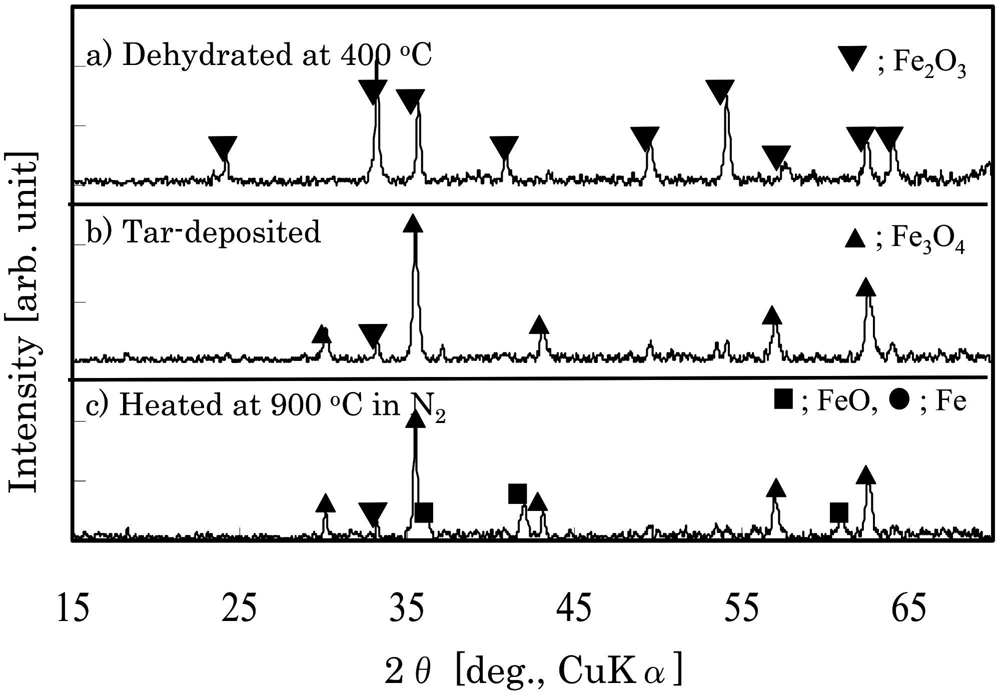


Fig. 7 XRD patterns of the H ore; a) Dehydrated ore at 450 °C, b) Tar-deposited ore and c) Heated ore upto 900 °C at nitrogen atmosphere.

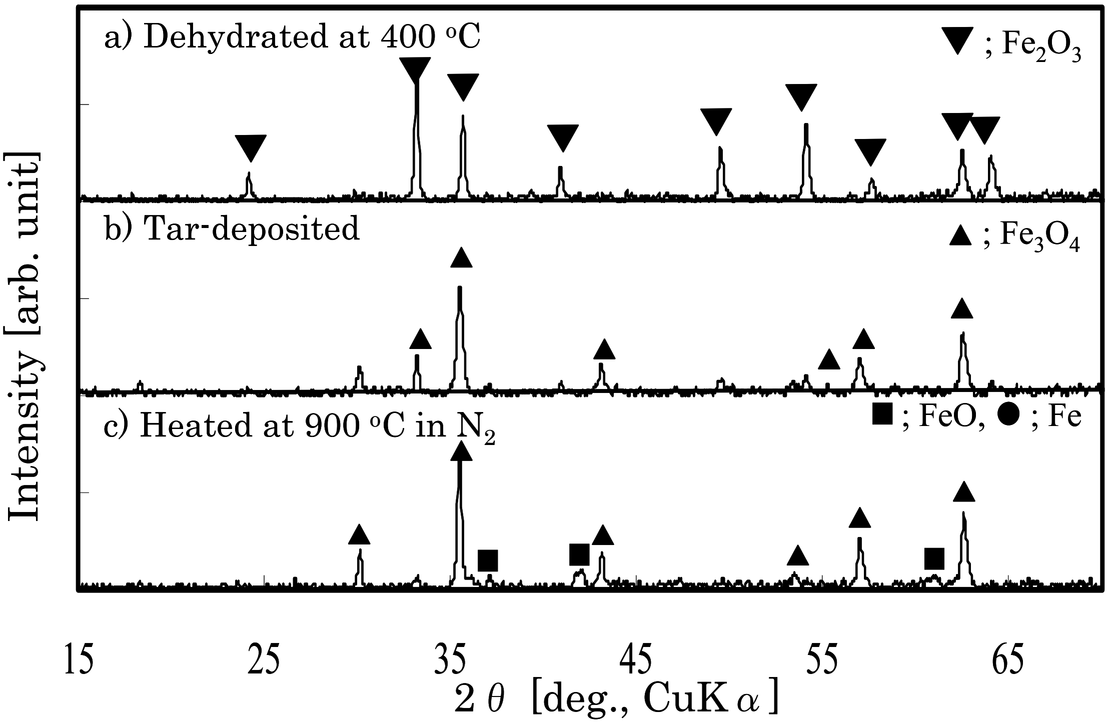


Fig. 8 XRD patterns of the C ore; a) Dehydrated ore at 450 oC, b) Tar-deposited ore and c) Heated ore upto 900 oC at nitrogen atmosphere.

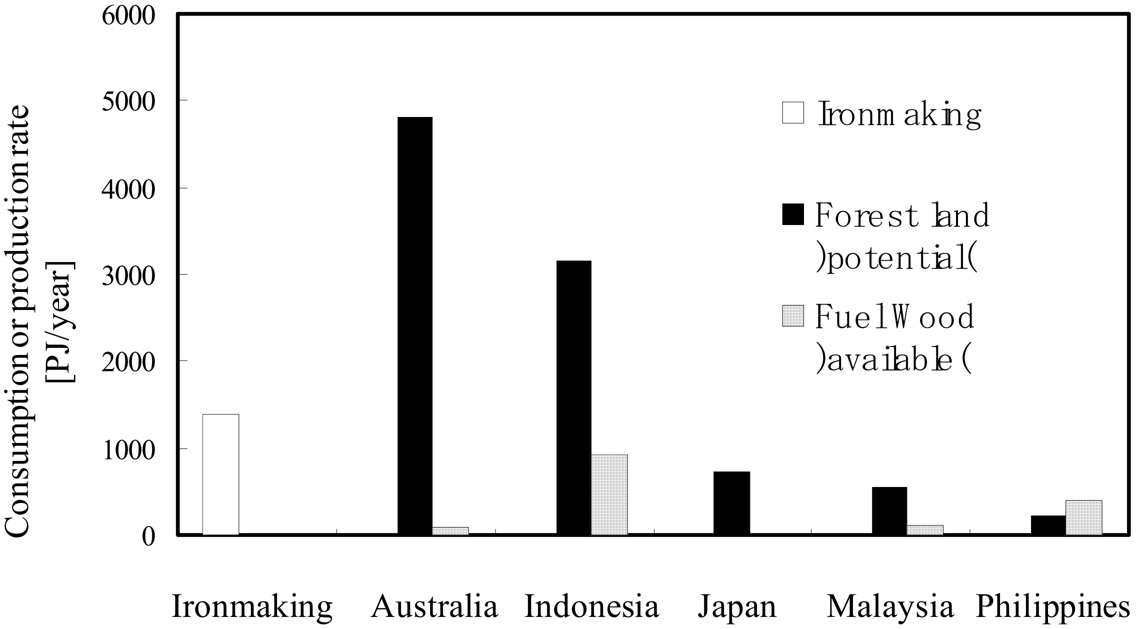


Fig. 9 Potential of biomass energy in southeast Asia and Australia, together with energy requirement of steelmaking in Japan.

4 CONCLUSIONS

Three ores containing different amounts of combined water were dehydrated at 450 °C; subsequently, they were placed next to the pyrolyzer of pine-tree biomass that was heated at 600 °C and were then heated up to 900 °C in an N2 atmosphere. The following conclusions were drawn:

1) The dehydration rendered the ore very porous due to the decomposition of the combined water. The ore containing the largest amount of the combined water had the largest porosity, the largest BET area, and the smallest pore-size.

2) Tar vapor from the pyrolysis of pine-tree biomass was successfully carbonized within/on the dehydrated ore. The amounts of deposited carbon were 1.1 and 4 mass% in the ores with 1.6 and 9.0 mass% of CW, respectively. The ore obtained was also prereduced from hematite to magnetite due to the pyrolysis gas.

3) The ore heated was reduced to iron even in the nitrogen atmosphere, due to direct reduction ($Fe_xO + C \rightarrow xFe + CO$) by the carbon deposited. This is attractive for saving energy by increasing the reduction rate and lowering the equilibrium temperature of FeO-Fe in an ironmaking reactor such as a blast furnace. The results reveal the possibility of developing a new ironmaking technology by the simultaneous use of goethite and woody biomass.

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