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Optimum temperatures for carbon deposition during integrated coal pyrolysis−tar decomposition over low-grade iron ore for ironmaking applications

Rochim B. Cahyono[a,b], *Naoto Yasuda*[a], *Takahiro Nomura*[a], *Tomohiro Akiyama*[a,*]

[a] Center for Advanced Research of Energy Conversion Materials, Hokkaido University, North 13 West 8, Kita-ku, Sapporo 060-8628, Japan

[b] Department of Chemical Engineering, Gadjah Mada University, JI. Grafika 2, Bulaksumur, Yogyakarta 55281, Indonesia

*CORRESPONDING AUTHOR

Tel: +81 11 706 6842; Fax: +81 11 726 0731

E-mail: takiyama@eng.hokudai.ac.jp

ABSTRACT

Carbon deposited within low-grade iron ore, which was produced using an integrated process of coal pyrolysis and tar decomposition, showed high reactivity as a reducing agent. Coal pyrolysis and tar decomposition were both highly sensitive to temperature and exhibited contrasting behaviours during carbon deposition. In these experiments, the optimum temperatures for pyrolysis and tar decomposition were determined to obtain maximum carbon deposition within porous iron ore. High-temperature pyrolysis generated large amounts of volatile matter (tar and gases), which caused high tar decomposition and produced large amounts of deposited carbon and gases. The deposited carbon was the major product of tar decomposition at lower temperatures (400–600 °C), whereas mainly gases were produced at higher temperatures (700–800 °C), because of gasification of carbon. However, sintering started at 800 °C, and it significantly diminished the BET surface area and pore size distribution. The highest amount of deposited carbon was obtained at a pyrolysis temperature of 800 °C and a tar decomposition temperature of 600 °C. Hamersley ore gave higher amounts of deposited carbon than Robe-river ore because of its large pore size less than 4 nm, which was suitable for carbon deposition. The pore size distribution was a more important factor than the surface area in the carbon deposition process. Based on these results, the proposed system could achieve maximum carbon deposition in porous iron ore and solve problems related to reducing agents, tar materials, and the use of expensive raw materials in the ironmaking industry.

KEYWORDS: tar decomposition; optimum temperature; carbon deposition; innovative ironmaking

1. Introduction

The iron and steel industry is highly dependent on metallurgical coke, which is produced from high-grade bituminous coal, and has crucial roles as an energy source, reducing agent, and maintaining bed permeability in blast furnace operation [1,2]. A pyrolysis process is used to convert high-grade coal to coke, tar, and gas in a coke oven unit. The main product, coke, is transported to the top of the blast furnace and used as a reducing agent; tar vapor and gases are the by-products and contain high amounts of carbon and energy. The tar material is mainly composed of condensable organic materials and may cause operational problems such as pipe plugging, condensation, and tar aerosol formation [3,4]. High rates of consumption and a shortage of high-grade coal has forced researchers to explore several innovative methods to substitute the conventional reducing agents. Srivastava et al. used woody biomass as a reducing agent by combining it with magnetite ore to produce pellets. This material successfully produced pig iron by high-temperature (1475 °C) reduction [5]. Other researchers have used carbon sources such as steelmaking wastes, tar sludge, and oil from steel-rolling mills to fabricate briquettes of materials as replacements for conventional reducing agents [6]. A hydrothermal method using an autoclave (0.1 MPa) has been used to improve the properties of low-grade sub-bituminous coal, which can be used as coking coal [7]. The treatment can greatly increase the strength and reactivity of sub-bituminous coal. Non-coking coal is upgraded to metallurgical coke by blending with biomass materials such as bagasse pitch, coconut shell, coconut waste, molasses, and sawdust [8]. In addition, carbon deposition within porous low-grade iron which is produced through integrated coal pyrolysis–tar decomposition shows excellent activity in reduction reactions. The tar material obtained as a by-product of pyrolysis decomposes into gases and carbon over porous iron ore. Simultaneously, the carbon infiltrates the carbon infiltrates and

deposited within iron ore to produce a carbon–iron composite ore. The reduction reaction of this product starts at a lower temperature, 750 °C, than in the case of a conventional mixture (magnetite and coke), 1200 °C [9]. Nanoscale contact of iron ore and carbon enhances the contact area and promotes high reactivity. This system can also be used to upgrade steelmaking slag as a supplementary fuel in sintering and blast furnace operations [10,11]. Based on the facts above, integrated coal pyrolysis–tar decomposition over low-grade iron ore is a promising candidate for resolving not only problems related to reducing agents, but also tar-related problems. Catalytic tar decomposition can improve the gas quality and increase the overall pyrolysis efficiency [12].

Integrated coal pyrolysis–tar decomposition is a two-stage process involving pyrolysis in the upstream part and tar decomposition over porous low-grade ore in the downstream part. It is well known that pyrolysis and tar decomposition are highly dependent on temperature. In the pyrolysis process, the thermal cracking of coal at elevated temperatures produces large amounts of volatile matter, which is the raw material for tar decomposition. The large amount of raw material from the pyrolysis enhances tar conversion in the decomposition process to produce deposited carbon and gases [13]. In contrast, a high-activity tar component at elevated temperatures promotes gas production rather than carbon deposition within a porous ore [14]. Coal pyrolysis and tar decomposition therefore show opposite behaviors in carbon deposition within porous ores. Specific temperature conditions for each process should be determined to obtain maximum carbon deposition in low-grade iron ore. The objective of this study was to obtain the optimum temperatures for both the pyrolysis and tar decomposition processes for high carbon deposition within porous ores. The processes over two different low-grade iron ores with

different contents of combined water (CW) were also evaluated to understand the main factors in the carbon deposition process.

2. Materials and experimental methods

2.1 Materials

A lignite coal from Australia was used as the carbon source in this study. The proximate and ultimate analyses are shown in Table 1. The small amount of fixed carbon compared with that of volatile matter indicated a low-grade coal. The raw coal was crushed and sieved to a granular size of approximately 250–500 μm.

Table 1. Proximate and ultimate analyses of coal raw materials

Sample	Proximate analysis [mass%, air-dried basis]			Ultimate analysis [mass%, dry basis]				
	[a]FC	Volatile	Ash	C	H	N	O[b]	S
Lignite coal	47.2	50.9	1.9	68.5	5.0	0.6	25.6	0.3

[a]FC: fixed carbon. [b]Calculated by difference.

Two kinds of low-grade iron ore, Robe-river (R) and Hamersley (H), were used to evaluate carbon deposition from the tar decomposition process. The main properties of these ores are shown in Table 2. The utilization of these ores in the ironmaking industry is limited due to small amounts of total iron and high content of CW. Different amounts of CW affect the dehydration process which creates a porous material for carbon deposition. Both ores were crushed and sieved to obtain samples with similar particle sizes, ranging from 0.95 to 2 mm.

Table 2. Properties of ore samples

	PS[a] [mm]	TFe[b] [mass%]	CW[c] [mass%]	SA[d] [m^2/g]
Robe-river (R) ore	0.95–2	57.20	7.60	17.15
Hamersley (H) ore	0.95–2	58.22	8.62	23.20

[a]PS: particle size; [b]TFe: total iron; [c]CW: combined water; [d]SA: Brunauer–Emmett–Teller surface area.

The two ores were prepared using a dehydration process to remove the CW and create a porous material. Thermogravimetric experiments showed that the CW started to decompose at 350 °C and completely dissipated at 450 °C [15]. The ores were therefore dehydrated at 450 °C at a heating rate of 3°C/min and a holding time of 1 h in an air atmosphere. The dehydration process was evaluated based on changes in the Brunauer–Emmett–Teller (BET) surface area and the pore size distribution after the experiments, determined by the BET method using an Autosorb 6AG (Quantachrome Instruments).

2.2 Tar decomposition and carbon deposition

The integrated coal pyrolysis–tar decomposition experiments were carried out using apparatus similar to that described elsewhere by Cahyono et al. [11] and Rozhan et al. [10]. The experimental procedure was modified slightly to adapt the temperature control. The electrical furnace was equipped with six thermocouples and a temperature controller at the top, middle, and bottom. The pyrolysis and tar decomposition temperature were precisely controlled and monitored by the top and bottom controllers, respectively. The temperature of the middle controller was fixed at the average of the top and bottom temperatures. Experiments were performed at atmospheric pressure with a total N_2 flow of 250 mL/min. Coal was continuously added to the reactor, using a bowl feeder, at a rate of 0.1 g/min for 40 min after the temperature of each controller became stable at 400–800 °C. Pyrolysis occurred rapidly inside the reactor and produced char, tar vapor, and gases. The char product was collected using a thimble filter (SUS

404 mesh) while the tar vapour and gases flowed and contacted the iron ore bed for the tar decomposition and carbon deposition processes. The final gas product and remaining tar vapor were removed from the bottom of the reactor. Separation of the tar vapor and gases was performed using a cold trap, which was maintained at -73 °C by adding liquid N_2. A gas chromatography (GC) analyzer (GC 2014, Shimadzu), which was equipped with a flame ionization detector, was used to detect CO, CO_2, and light hydrocarbon gases. In addition, the amount of H_2 in the gas product was analyzed using a GC (GC 323, Hitachi) with a thermal conductivity detector. X-ray diffraction (XRD) analysis (Miniflex, Rigaku) was used to observe changes in the ore structures, and changes in the BET surface areas and pore size distributions were evaluated using an Autosorb 6AG instrument (Quantachrome Instruments). The carbon content in the iron ore (i.e., carbon deposition) was measured using an elemental analyzer (MT-6, CHN Corder). We used the experimental results to evaluate the tar decomposition and carbon deposition to determine the optimum temperature for each process.

In order to obtain the optimum temperature of the pyrolysis process, we examined different temperatures (500–800 °C), with a constant temperature for tar decomposition (600 °C). Subsequently, the optimum pyrolysis was used to find the optimum of tar decomposition by examination different temperatures (400-800^{o}C). A comparison of two different iron ores was performed under the optimum conditions for both the pyrolysis and tar decomposition temperatures.

3. Result and discussion

3.1 Effect of pyrolysis temperature

Fig. 1 shows the effect of pyrolysis temperature on the product distribution of integrated coal pyrolysis–tar decomposition over low-grade iron H ore. When the temperature of tar decomposition process and other experimental parameters were kept constant, the amount of deposited carbon within the iron ore was affected mainly by the volatile matter (tar and gases) produced by coal pyrolysis. Tar decomposition occurred over the porous iron ore, and produced gases and deposited carbon through reaction (1).

$$\text{Tar} \rightarrow H_2 + CO + CO_2 + CH_4 + \text{other light hydrocarbons} + C \quad (1)$$

A high pyrolysis temperature decreased the amount of tar and increased carbon deposition in the ore as a result of the tar decomposition process shown in Fig. 1. Gas production was also enhanced at high temperatures because of thermal cracking of the coal and tar decomposition. A large amount of tar promoted high conversion of tar material in the decomposition process to produce gases and deposited carbon. High carbon deposition was achieved when a large amount of tar was generated from the pyrolysis process. High-temperature pyrolysis, which produced large amounts of tar, was therefore suitable for the carbon deposition process.

As well as tar carbon deposition in the porous iron ore, the integrated coal pyrolysis–tar decomposition also produced several gases such as CO, CO_2, H_2, CH_4, and other light hydrocarbon. Fig. 2 shows the effect of pyrolysis temperature on the gas composition and lower heating value. It can be seen that all gas components were enhanced at elevated temperatures, as a result of thermal cracking of coal and decomposition of the tar component. Thermal cracking, decarboxylation, and depolymerization of carbonaceous materials are promoted at high temperatures [16]. In addition, the high activities of tar components at elevated temperatures

increased tar conversion and made decomposition to the gas phase easier. It was also found that H_2 production at 800 °C increased rapidly compared with CO production. Gas reforming began to occur and enhanced H_2 and CO production [17]. Based on the gas reforming stoichiometry, the mole of H_2 was higher than CO in the gas reforming products. High contents of H_2 and CO at elevated temperatures also increased the heating value of the gas product. A high pyrolysis temperature therefore produced not only high carbon deposition but also increased the heating value of the gas products.

3.2 Effect of tar decomposition temperature

Based on the results of the pyrolysis experiments, tar decomposition was performed at the highest pyrolysis temperature, which generated the largest amount of deposited carbon. Fig. 3 shows the effect of decomposition temperature on the tar product distribution over H ore at a constant pyrolysis temperature of 800 °C. The amount of unreacted tar decreased at elevated temperatures, indicating high conversion of tar components during the decomposition process. High activity of the tar component over the surface of the porous iron ore promoted decomposition to produce gases, deposited carbon, and lighter hydrocarbons. Metal oxides prevent the formation of stable chemical structures in hydrocarbons and speed up hydrocarbon degradation by weakening the C–C bonds, decreasing the activation energy for the complex tar decomposition process [18]. The products of tar decomposition altered with tar decomposition temperature (400–800 °C). Tar carbon deposition within the porous ore, rather than formation of gas products, was predominant in the temperature range 400–600 °C. At temperatures above 600 °C, tar decomposition generated gas products rather than depositing carbon. At temperatures above 600°C, tar decomposition generated gas products rather than depositing carbon. Based on the gibbs free energy, ΔG^0, the gasification of carbon and direct reduction of iron ore through

reaction (2) and (3) would be started at 698 and 651°C, respectively [19,20]. Therefore, direct reduction of iron ore and gasification of the deposited carbon took place and enhanced carbon conversion to gas products. This means that the rate of carbon deposition from tar decomposition was smaller than the rate of carbon consumption by reaction (2) and (3). The maximum carbon deposition in the porous ore was achieved at a tar decomposition temperature of 600°C. The optimum conditions of integrated coal pyrolysis–tar decomposition for producing deposited carbon in porous iron were therefore pyrolysis at 800°C and tar decomposition at 600°C.

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

$$C + CO_2(g) \leftrightarrow 2CO(g) \quad (3)$$

The phase diagrams in Fig. 4a show the effect of tar decomposition temperature on the iron–wustite–magnetite system for H ore. This figure explains the indirect reduction of CO through reactions (4)–(6).

$$3Fe_2O_3(s) + CO(g) \leftrightarrow 2Fe_3O_4(s) + CO_2(g); \ \Delta H^o = -52.86 kJ/mol \quad (4)$$

$$Fe_3O_4(s) + CO(g) \leftrightarrow 3FeO(s) + CO_2(g); \ \Delta H^o = 36.25 kJ/mol \quad (5)$$

$$FeO(s) + CO(g) \leftrightarrow Fe(s) + CO_2(g); \ \Delta H^o = -17.31 kJ/mol \quad (6)$$

The pyrolysis process occurred at a constant temperature and resulted in similar tar and gas products, but indirect reduction of CO generated different products. The reaction rate of iron ore reduction was higher at high temperatures, and was sufficient to produce FeO in tar decomposition at 800 °C [21]. High-temperature tar decomposition therefore resulted in a large degree of reduction, as indicated by the generation of FeO, because of the high reduction reaction.

In order to clarify the reduction degree, XRD analysis was performed for the products at different tar decomposition temperatures, as shown in Fig. 4b. It can be clearly seen that all Fe_2O_3 was changed into Fe_3O_4 as a result of indirect reduction by pyrolysis gases. Indirect

reduction occurred simultaneously with tar decomposition and carbon deposition. This result agreed with the phase diagram, which showed that FeO was found at elevated tar decomposition temperatures because of a large amount of indirect reduction. Tar decomposition at elevated temperatures therefore produced small amounts of deposited tar carbon in the porous iron ore, but a high degree of reduction.

Fig. 5 shows the changes in pore size distribution and BET surface area of H ore after tar decomposition at different temperatures. Simultaneously with tar decomposition, carbon infiltrated and was deposited in the porous iron ore, resulting in reduction in both the pore size distribution and the BET surface area. Interestingly, the carbon was only deposited in pores of size less than 4 nm because of the specific tar component. The carbon content of the porous ore was proportional to the decreases in pore size distribution and BET surface area, except in the case of tar decomposition at 800 °C. The carbon content of the iron ore at 800 °C was the smallest, but the decreases in pore size distribution and BET surface were higher than those under other temperature conditions. During the tar decomposition process, the iron bed was heated and kept at a constant temperature of 800 °C, which was sufficiently high to promote sintering of the iron ore. The melting point of the iron ore (Fe_2O_3) was 1460°C [20]. During sintering, the pores in the iron ore joined up, resulting in a dense material. This phenomenon significantly decreased the BET surface area and pore size distribution and resulted in the lowest carbon deposition. Thus, the tar decomposition process should be performed below 800 °C to produce high carbon deposition and avoid sintering.

3.3 Effect of amount of CW in iron ore

The results described above show that the optimum conditions for producing high carbon deposition were pyrolysis at 800 °C and tar decomposition at 600 °C. Another iron ore, the R ore,

with a different CW content, was subjected to similar conditions for comparison. Fig. 6 shows the effect of different iron ores on the amount of deposited carbon and the total gas volume under the optimum temperature conditions. Using a similar tar component from coal pyrolysis, the H ore generated a larger carbon content but a smaller gas volume than the R ore. This indicated that the H ore had higher selectivity for carbon deposition during tar decomposition than the R ore. Decomposition of the tar component produced gases and deposited carbon in the porous ore, and the selectivity of the iron ore was established from the ratio of these products. Generally, several factors influence the selectivity of a solid catalyst, such as surface structure, composition, surface mobility, and charge transport [22].

In order to investigate the factors related to the selectivity of the tar decomposition process in detail, BET analysis was performed over both H and R ores, as shown in Fig. 7. Dehydration of CW at 450 °C enhanced the surface area of the iron ore and created a porous ore. The surface areas of both the H and R ores after the dehydration and tar decomposition processes were similar. The surface area therefore could not explain the selectivities and different carbon contents. Different results were obtained for the pore size distributions after dehydration of CW. The H ore had larger numbers of micropores than the R ore, in particular pores of size 4 nm, although dehydration was performed under similar conditions. The tar carbon was deposited in the iron ore in pores of size less than 4 nm [11]. These results clearly show that differences among the carbon contents were caused by the number of micropores after the dehydration 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.

Fig. 8 shows the gas compositions and reduction degrees for integrated coal pyrolysis–tar decompositions, using different iron ores, under the optimum temperature conditions. As

explained in the previous section, indirect reduction of the iron ore by pyrolysis gases occurred simultaneously with tar decomposition and carbon deposition. The reduction degree was estimated using the following equation:

$$\text{Reduction degree}(\%) = \frac{\text{Oxygen generated from ores}}{\text{Total removable oxygen}} \times 100\% \quad (7)$$

The H ore gave a higher reduction degree than the R ore. Based on the indirect reduction in reactions (4)–(6), a higher reduction degree represented large consumption of a reducing agent, CO, to produce CO_2. The gas composition shown in Fig. 7 confirmed this phenomenon, because the amount of CO gas in the H ore was smaller than that in the R ore, because of high CO consumption in the indirect reaction. The H ore therefore produced larger amounts of deposited carbon in the porous ore and a higher reduction degree, but a smaller total volume and energy of gas products.

4. Conclusions

Integrated coal pyrolysis–tar decomposition over low-grade iron ore was highly dependent on the temperature. The optimum temperature was determined to obtain the maximum carbon deposition in the porous iron ore. A comparison was made between the two low-grade iron ores to understand the key factors in carbon deposition. The main results can be summarized as follows.

1. Pyrolysis at the highest temperature produced a large amount of deposited carbon and a clean gas product with extra heating value. Thermal cracking of the coal component increased at high temperatures and produced large amounts of gas and tar for the decomposition process.

2. Deposited carbon, rather than gas products, was predominantly produced at lower temperatures (400–600 °C), and the opposite behavior was observed in tar decomposition at higher temperatures (700–800 °C). The gasification of carbon at higher temperatures decreased the amount of carbon deposited within the porous ore. In addition, tar decomposition at 800 °C resulted in the largest indirect reduction, and generated FeO as a result of the high rate of reduction reaction. However, the tar decomposition process should be performed below 800 °C as sintering started at this temperature. The highest carbon deposition was obtained at a pyrolysis temperature of 800 °C and a tar decomposition temperature of 600 °C.
3. H ore gave higher carbon deposition but a lower amount of gaseous products compared with R ore, as a result of the formation of larger pores during the dehydration process. The pore size distribution was a more important factor than the BET surface area in the carbon deposition process. The H ore showed a higher reduction degree during tar decomposition, indicated by the small amounts of CO and H_2 in the gas products.

Based on these results, the proposed system could generate maximum carbon content, solving problems related to reducing agents and tar materials, and avoiding the use of expensive high-grade iron ores.

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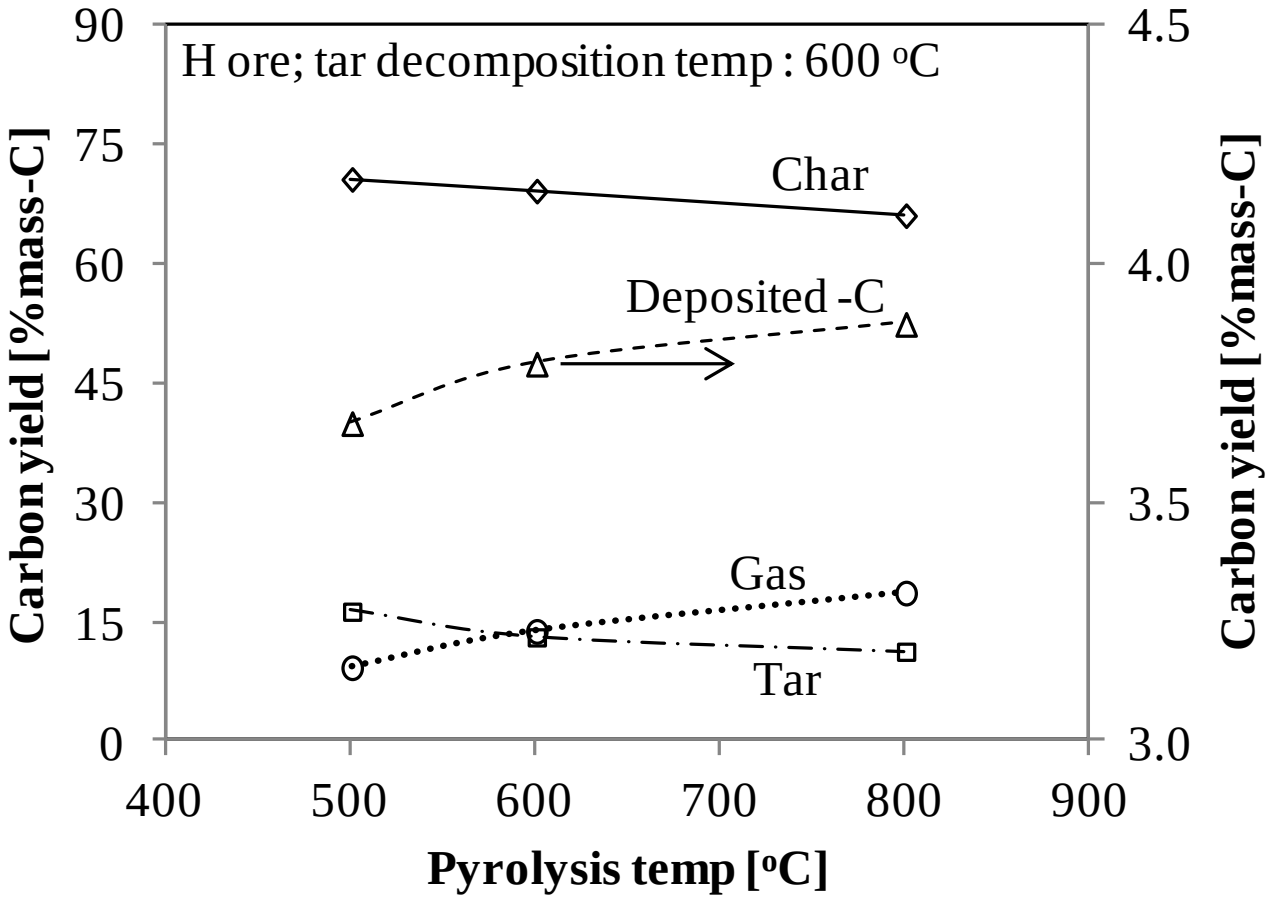


Fig. 1. Product distributions of integrated coal pyrolysis–tar decomposition over Hamersley (H) iron ore at different pyrolysis temperatures showed that tar decomposition occurred at elevated temperatures to produce small amounts of tar components and high amounts of deposited carbon.

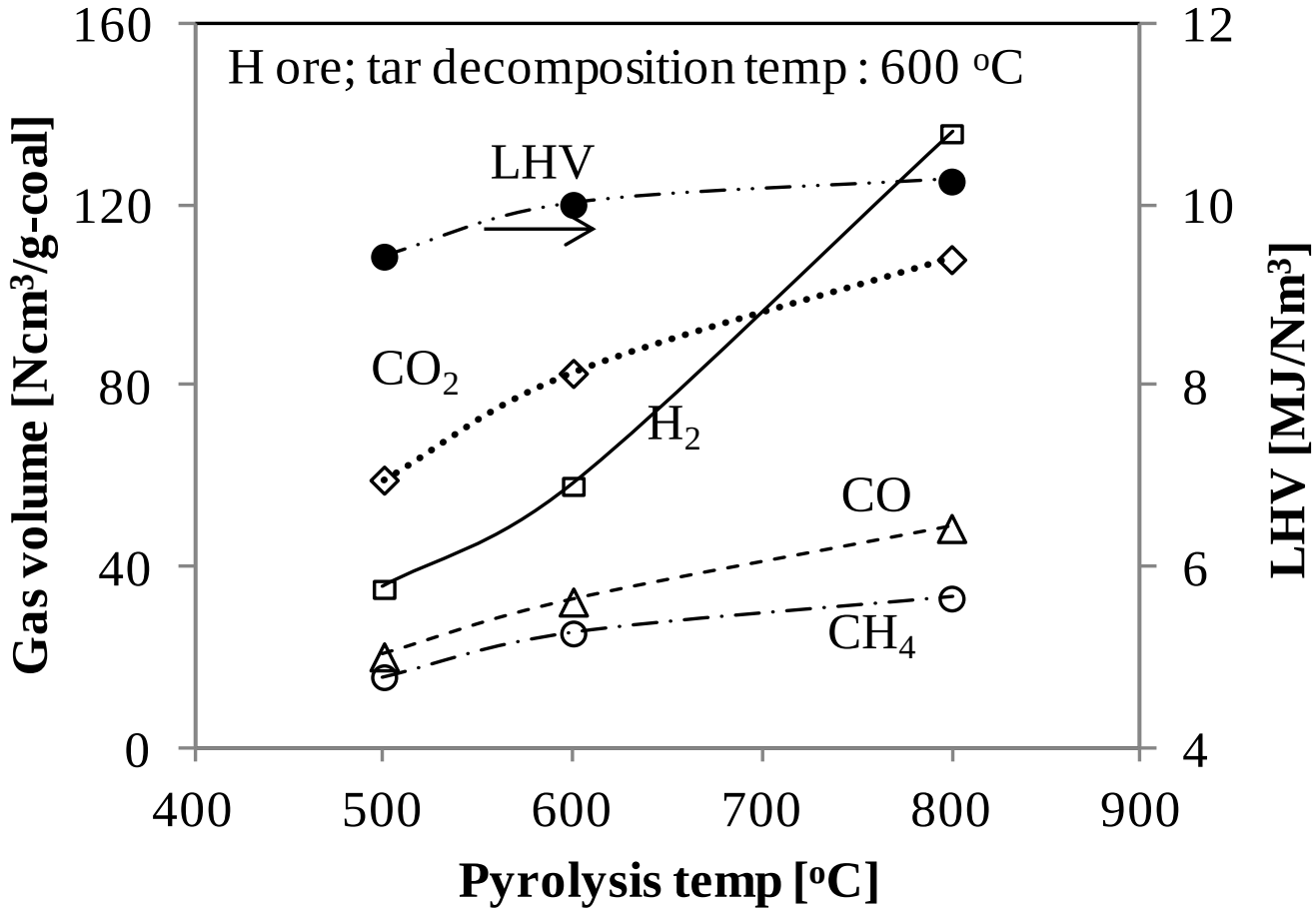


Fig. 2. Effect of pyrolysis temperature on gas composition and lower heating value (LHV) of integrated coal pyrolysis–tar decomposition over Hamersley iron ore; each gas volume increased at elevated temperature as a result of thermal cracking of coal and tar components.

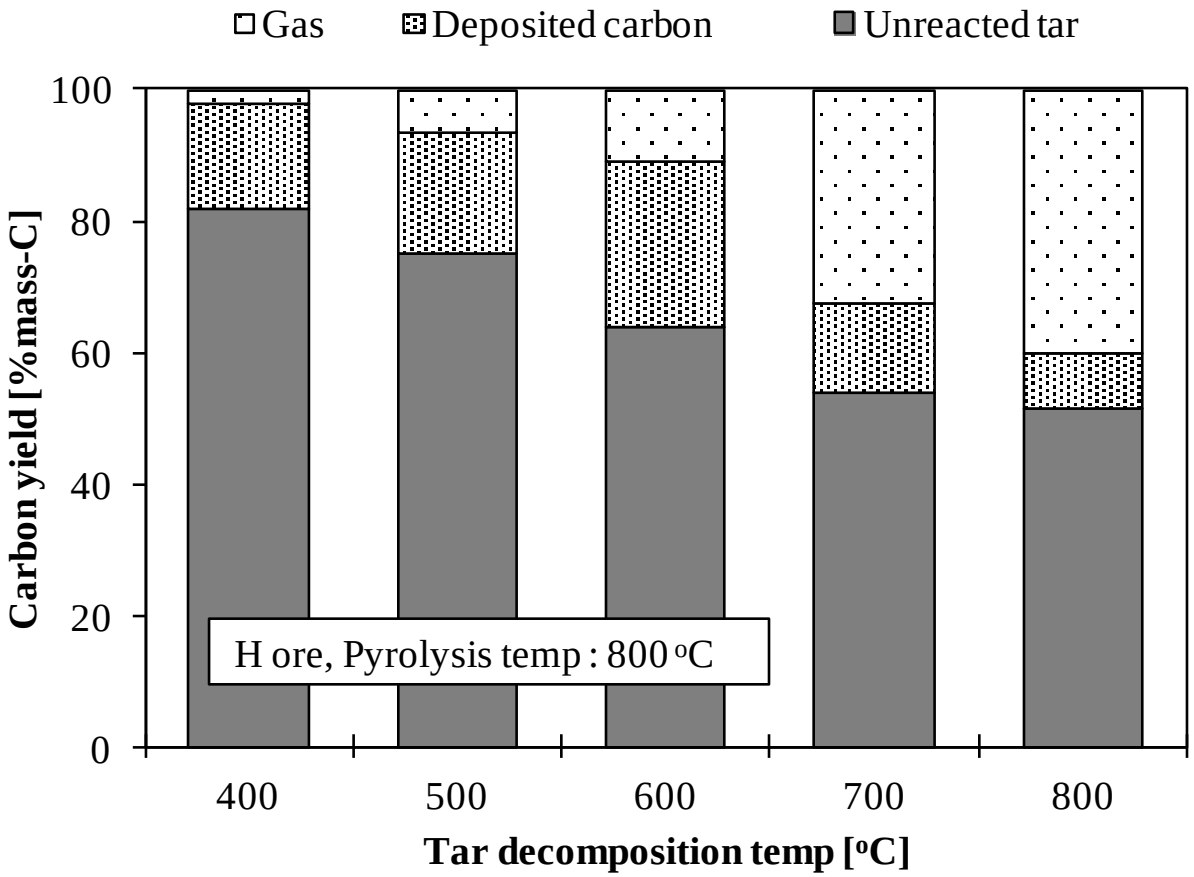


Fig. 3. Effect of tar decomposition temperature on tar product distribution; the tar decomposition over Hamersley ore showed that the highest carbon deposition was attained at 600°C, whereas thermal cracking was predominant to produce gases at higher temperatures (>600°C)

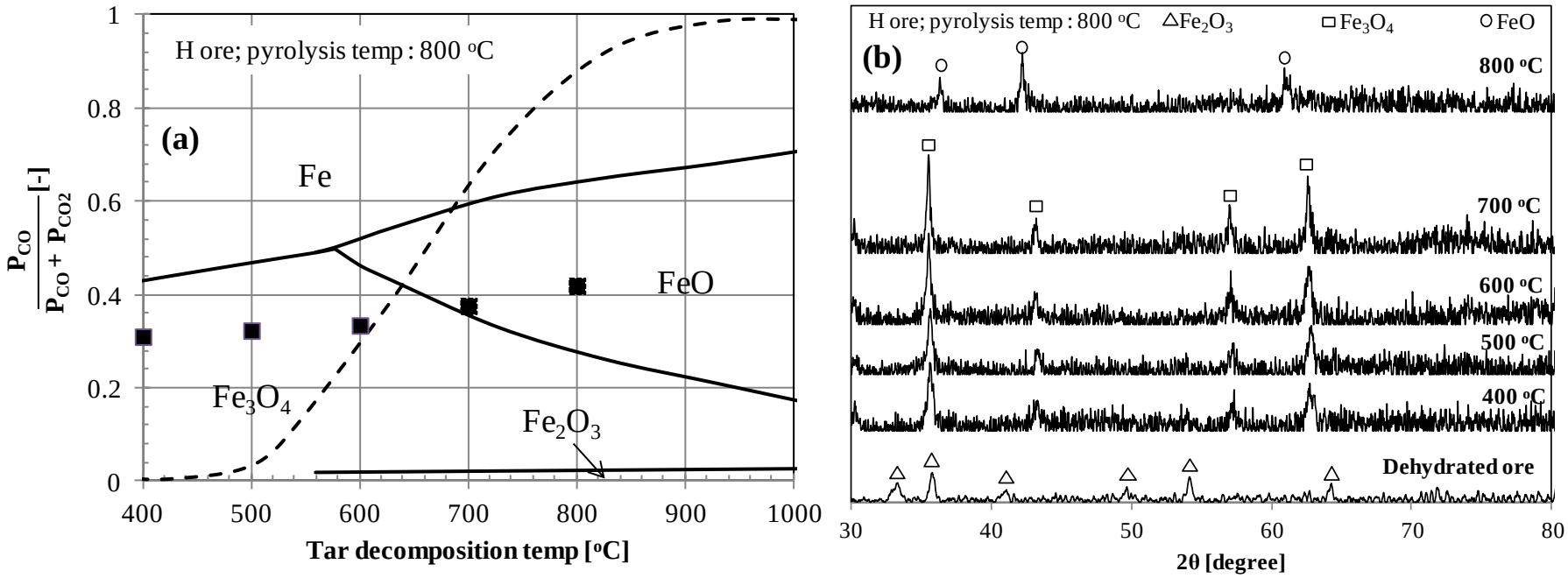


Fig. 4. (a) Phase diagrams for iron–wüstite–magnetite systems showed that a high temperature of tar decomposition resulted in a large reduction degree due to high amount of CO and faster reduction rate. (b) X-ray diffraction (XRD) patterns of iron ore after tar decomposition at different temperatures showed that FeO can be found at 800°C; this was consistent with the phase diagram.

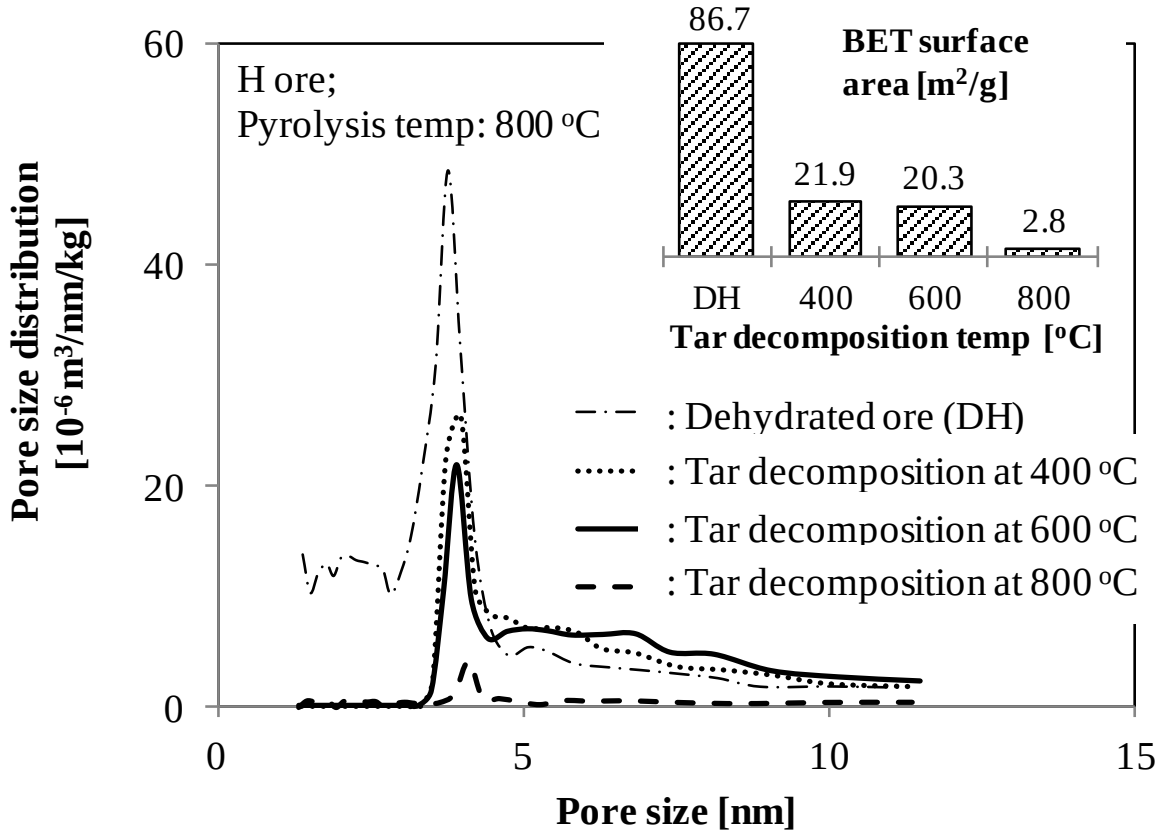


Fig. 5. Changes in pore size distributions and Brunauer–Emmett–Teller (BET) surface areas of Hamersley ore after tar decomposition at different carbonization temperatures showed that the BET surface area and pore size distribution at 800 °C decreased significantly when the amount of deposited carbon was smallest, indicating that sintering started to occur.

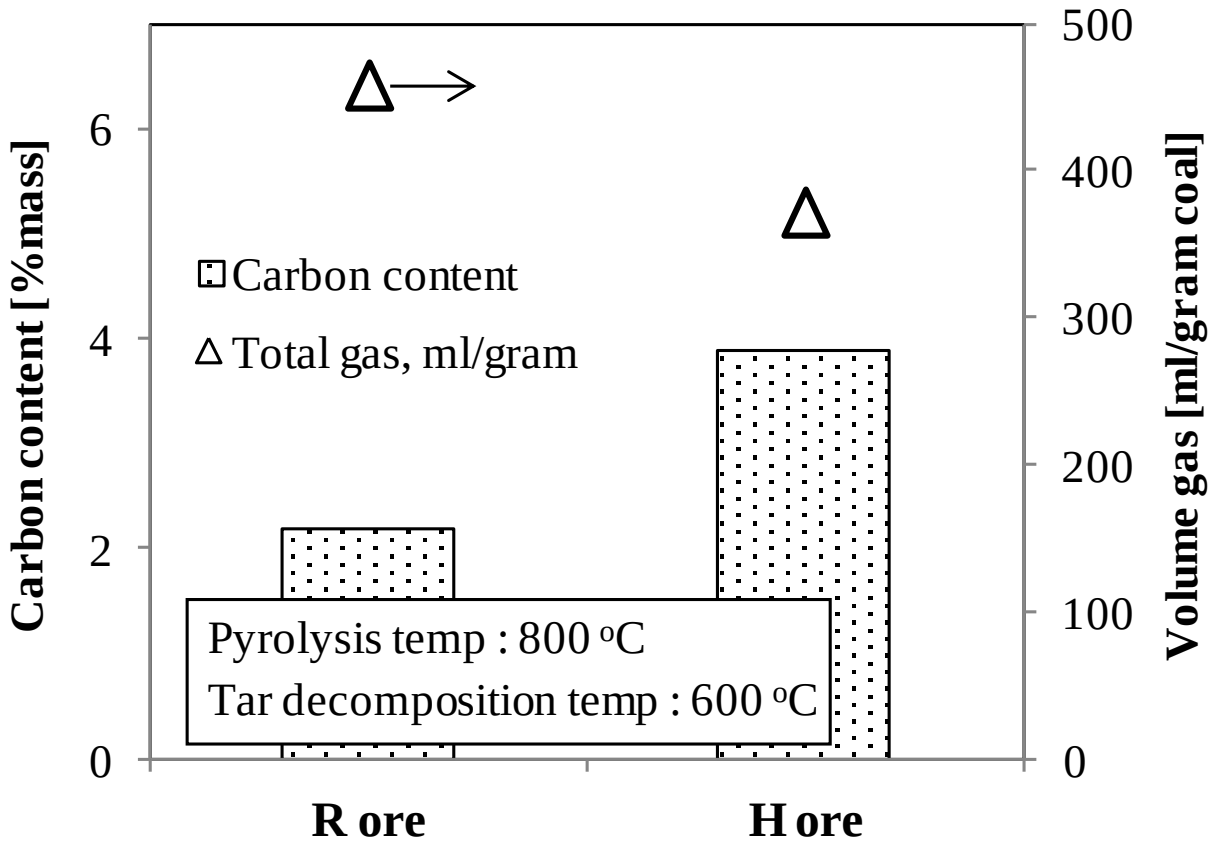


Fig. 6. Effect of different iron ores on deposited carbon and total gas volume showed that Hamersley (H) ore gave higher carbon deposition but a lower total gas volume compared with Robe-river (R) ore.

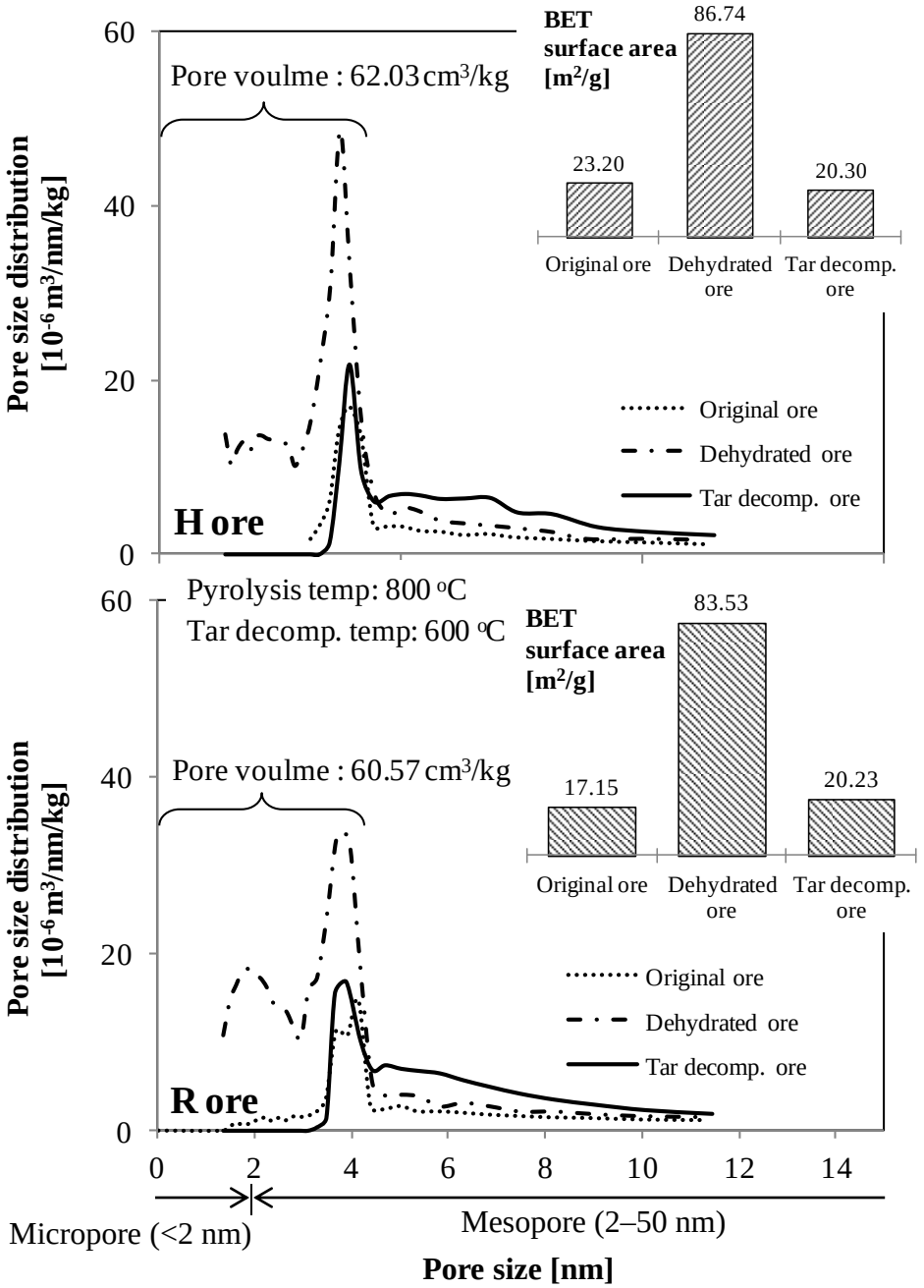


Fig. 7. Changes in Brunauer–Emmett–Teller (BET) surface areas and pore size distributions of two different iron ores [Hamersley (H) and Robe-river (R)] showed that larger carbon deposition in the R ore was the result of larger micropores, which were created during dehydration.

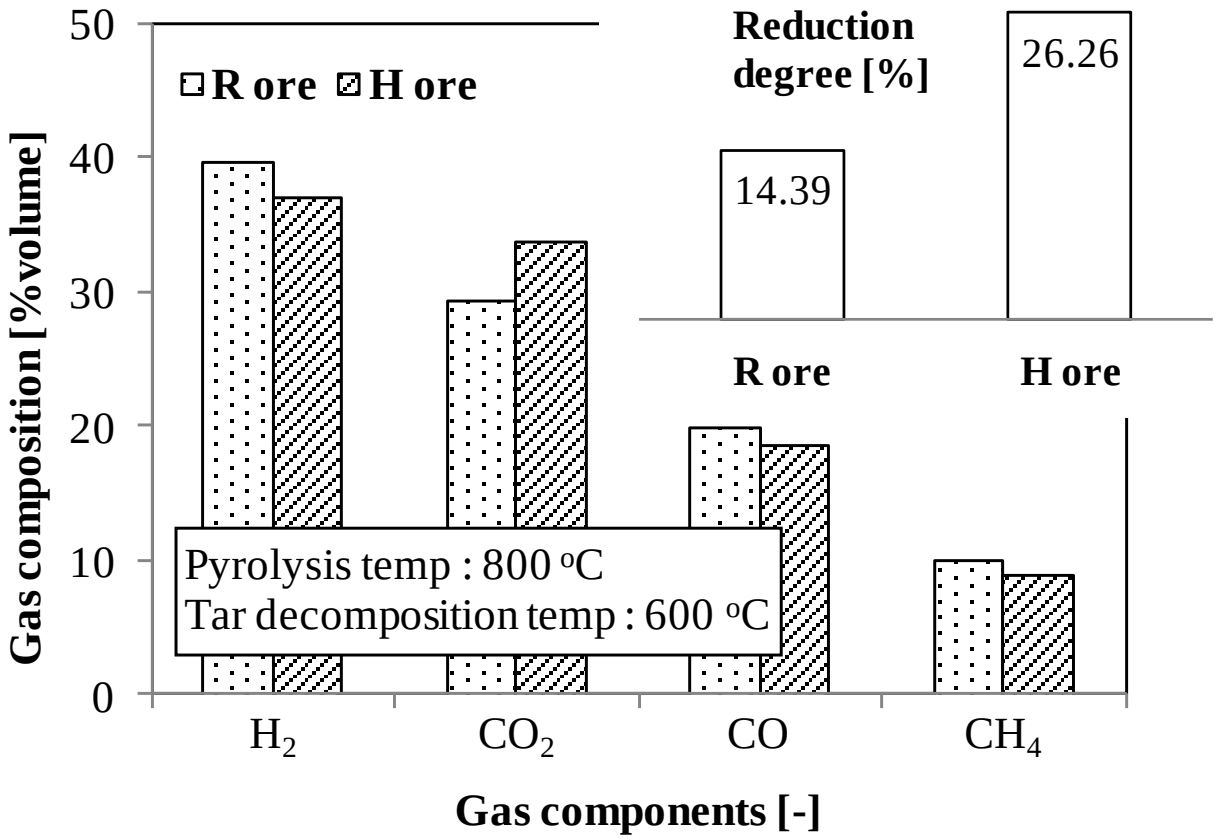


Fig. 8. Reduction degree of iron ore and gas composition of integrated coal pyrolysis–tar decomposition with various iron ores [Hamersley (H) and Robe-river (R)] showed that H ore produced smaller mounts of H_2 and CO, but gave higher reduction degrees, as a result of large consumption of these gases in indirect reduction.