Reduction of CO_2 Emissions from Blast Furnace with Carbon Recycling Methane

KAWASHIRI Yuki[*1]   NOUCHI Taihei[*2]   KASHIHARA Yusuke[*3]

Abstract:

In order to reduce of CO_2 emissions from blast furnace, a carbon recycling blast furnace, in which methane synthesized from CO_2 in the blast furnace gas (CN methane) is used again in the blast furnace, was studied. As a result of the evaluation by the Rist diagram, it was shown that CN methane reduced CO_2 emission mainly by the following two functions. (1) To decrease direct reduction by increasing the amount of reducing gas. (2) To supply heat by reacting with oxygen in front of the tuyere. In this study, the carbon recycling blast furnace was found to have the possibility of reducing CO_2 emissions by 30 % or more compared with the conventional blast furnace. It was also found that oxygen blowing and heating gas injection from the shaft upper level were effective for maximizing the amount of CN methane injection.

1. Introduction

The 21st Conference of the Parties to the United Nations Framework Convention on Climate Change (COP21) held in November 2015 adopted the Paris Agreement on emissions of greenhouse gases (GHG), beginning with CO_2[1]. Steel works which mainly use the blast furnace process produce large amounts of steel by consuming coal as a primary energy source. In 2019, the Japanese steel industry emitted 150 million tons of CO_2, or approximately 14 % of the country's total annual CO_2 emissions of 1.1 billion tons (actual results for 2019)[2]. Thus, reducing CO_2 emissions is an urgent challenge for the steel industry as a CO_2 emission-intensive industry. Although various energy-saving tech-

nologies for reducing CO_2 emissions have been developed to date, including burden distribution control techniques and small coke mixed charging, CO_2 emission reduction by operational technologies is approaching its limit [3,4]. With this background, moves to convert energy sources from coal (carbon) to hydrogen which doesn't discharge CO_2 in order to realize a drastic reduction in CO_2 emissions can be seen in Japan and other countries. As examples, a one tuyere hydrogen injection test at ThyssenKrupp's Duisburg No. 9 blast furnace and the COURSE50 project in Japan may be mentioned [5,6]. In recent years, CCU (Carbon dioxide Capture and Utilization) has attracted attention as a method for effectively utilizing CO_2 by producing products using CO_2 captured from the atmosphere or from industrial exhaust gases as a feedstock. Utilizing captured CO_2 to produce products that were originally made from fossil fuels will contribute to low carbonization, and CO_2 will not be emitted while it is fixed in the product. Although CO_2 emissions from manufacturing process are allowed in CCU, there is currently an imbalance between the demand for products that can be produced using CO_2 emitted by the steel industry and the amount of those emissions. For example, Japan imports an average of about 1.7 million tons of methanol each year, but considering the fact that 0.7 tons of methanol can be produced from 1 ton of CO_2, conversion of all the CO_2 emitted by the steel industry to methanol is not realistic, since the supply of methanol would vastly exceed demand.[7]

Therefore, the authors attempted to solve the above-mentioned market problem by reusing a product produced by CCU as a reducing agent in the steel

[*1] Senior Researcher Deputy Manager,
Ironmaking Research Dept.,
Steel Res. Lab.,
JFE Steel

[*2] Dr. Eng.,
Senior Researcher General Manager,
Ironmaking Research Dept.
(currently, Environmental Process Research Dept),
Steel Res. Lab., JFE Steel

[*3] Dr. Eng.,
Senior Researcher Manager,
Ironmaking Research Dept.,
Steel Res. Lab., JFE Steel

industry, in other words, by "carbon recycling" to the steel manufacturing process. It should be noted that this approach has the advantage of not contributing to CO$_2$ emissions, as the carbon that originates from the carbon-recycling reducing agent is repeated recycled in the steel manufacturing process, and is not discharged outside the system. This paper reports on a study aimed at maximizing the reduction of CO$_2$ emissions from the blast furnace process by utilizing carbon recycling technology.

2. Carbon Recycling Technology

Figure 1 shows a conceptual diagram of the blast furnace process using carbon recycling technology.

The coke used in the production of 1 ton of molten pig iron (coke ratio) is reduced by injecting the product synthesized from CO$_2$ (carbon neutral reducing agent) from the tuyeres of the blast furnace in the same manner as pulverized coal, which has long been used in blast furnaces. As the reducing agent synthesized from CO$_2$, methane (CH$_4$) was selected in this study. The technology for synthesizing methane from CO$_2$ and hydrogen, which is called methanation, was discovered by Sabatier at the beginning of the 20$^{\text{th}}$ century[8]. As shown by the chemical reaction equation and heat of reaction expressed by the following Eq. (1), this is an exothermic reaction accompanied by comparatively large heat generation.

$$CO_2 + 4H_2 = CH_4 + 2H_2O + 165 \text{ kJ/mol} \ldots (1)$$

Since 2013, a commercial methanation plant has been in operation using CO$_2$ separated from biogas and hydrogen produced by electrolysis of water by Eto-Gas[9].
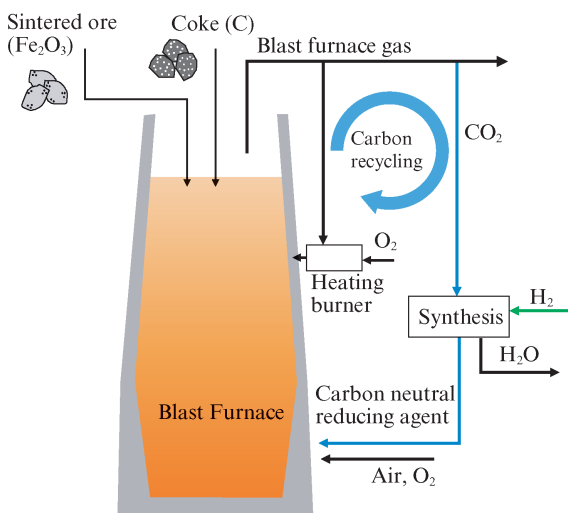
3. Evaluation by Model

3.1 Heat and Mass Balance Model

The potential amount of CO$_2$ emission reduction in a blast furnace process using the carbon recycling technology was studied with a Rist diagram [10,11]. In a Rist diagram, the heat and mass balance is considered by separating the blast furnace into upper and lower parts by the temperature of the thermal reserve zone T$_R$ (temperature at which heat rise and reduction stagnate). A typical example of a Rist diagram is shown in **Fig. 2**, where the horizontal axis shows (O+H$_2$) / (C+H$_2$), the vertical axis shows (O+H$_2$) / Fe and the operational condition of the blast furnace (Rist operating line) is represented by the line RP. Point W shows the reduction equilibrium condition of wustite-Fe at T$_R$, and point P is a point determined from the heat balance in the lower part of the furnace. Actual operation passes through point R, which is separated from point W by some distance. At this time, GR/GW is defined as shaft efficiency and is used as an index of reduction efficiency, which is determined by the reactivity of the raw materials, the burden distribution and other factors. Point Y$_d$ expresses the reduction amount (direct reduction amount) by the apparent C in the coke. The slope of line RP, (C+H$_2$) / Fe, shows the specific reducing gas volume necessary to produce 1 t of molten pig iron. In this study, the CO$_2$ emission reduction rate of the blast furnace using the carbon recycling technology was evaluated on a conventional Rist diagram, considering operational constraints. The CO$_2$ emission of the blast furnace was calculated from the unit consumption of carbon charged to the blast furnace (specific carbon consumption). In calculations of specific carbon consumption, it should be noted that the carbon content

Fig. 1   Schematic of blast furnace process with carbon recycling
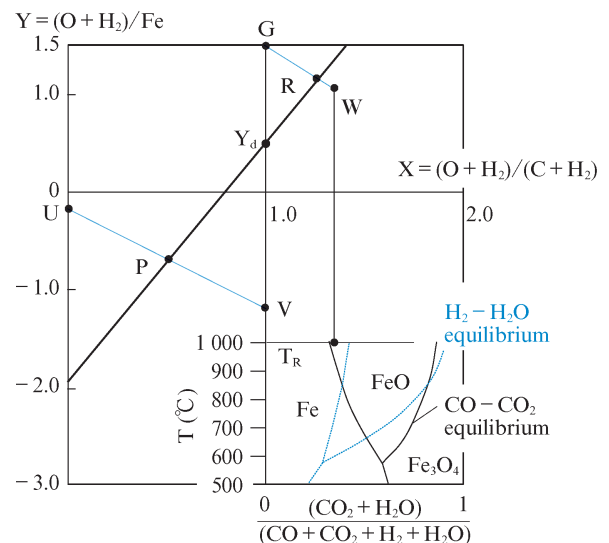

Fig. 2   Rist diagram

of the carbon-neutral reducing agent (CN methane) and the carbon contained in the injected preheating gas (described below) were not counted in the specific carbon consumption because both are recirculated in the system.

3.2 Constraints on Blast Furnace Operation

3.2.1 Theoretical flame temperature in front of tuyere

In a blast furnace, hot blast is blown into the furnace from the tuyeres, and the reducing agent which is injected at the same time and high temperature coke present in front of the tuyere react with the oxygen in the hot blast to produce a reducing gas. The temperature of the reducing gas after this reaction is called the theoretical flame temperature (TFT) in front of the tuyere and is used as a control index in actual operation. If TFT is too high, a large amount of SiO gas will be generated in the raceway, and may cause high Si in the hot metal, scaffolding on the furnace wall and other trouble[12]. On the other hand, if TFT is too low, heat transfer to the molten iron will be insufficient, resulting in a drop in the hot metal temperature. Here, the upper and lower limits of TFT were set at 2 300°C and 2 000°C, respectively, based on actual results. TFT is calculated assuming 100 % of the elements C, H, N and O contained in the hot blast, injected reaction agent and coke react to the form of CO, H_2 and N_2. The temperature of the coke in front of the tuyere was set at 0.75 times TFT following Ramm's equation[13].

3.2.2 Top gas temperature

A low top gas temperature will cause poor blast furnace operation due to problems such as condensation of the moisture in the top gas. Here, the lower limit of the top gas temperature was set at 100°C. One technique for raising the top gas temperature is injection of preheating gas from the upper shaft, which has also been proposed for the oxygen blast furnace[14]. In this study, if the top gas temperature decreases to 100°C or less, preheated gas at a temperature of 1 000°C by partial combustion of the top gas is injected into the furnace from the upper shaft to maintain a top gas temperature of 100°C.

3.2.3 Blast temperature

An upper limit of the oxygen concentration in the blast that passes through the hot stove is set considering the risk to the equipment. Here, the upper limit of the oxygen concentration of the gas passing through the hot stove was set to 29 %. When the oxygen concentration of the blast is raised, the blast temperature was determined assuming mixture of normal tempera-
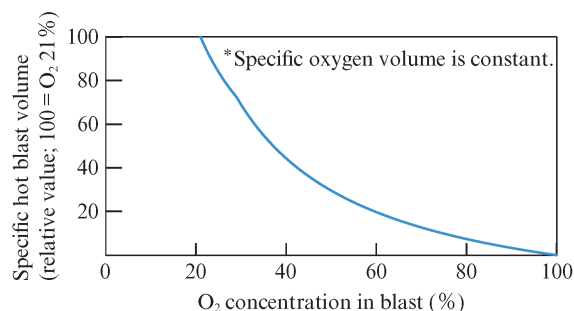

Fig. 3 Relationship between O₂ concentration in blast with specific hot blast volume (relative value)

ture oxygen with the hot blast. **Figure 3** shows the relationship of the O₂ concentration in the hot blast and specific hot blast volume (unit consumption of hot blast) for the case where the specific O₂ volume is constant. The specific hot blast volume decreases when the O₂ concentration in the blast increases.

3.3 Operational Limits of Blast Furnace

3.3.1 Thermal reserve zone temperature and shaft efficiency

In a Rist diagram, the blast furnace is divided into upper and lower parts at the thermal reserve zone, which is determined by the gasification starting temperature of the coke. The reduction equilibrium gas composition is found on the precondition that the temperature of the thermal reserve zone and the wustite-Fe reduction starting temperature are the same, and the reduction equilibrium constraints in blast furnace operation is considered. However, according to Miyashita et al., the heat-flow ratio (ratio of thermal capacity of a solid and thermal capacity of a gas) increases as the O₂ concentration in the blast is increased, heating of the burden in the upper shaft becomes inadequate, and the thermal reserve zone disappears when the O₂ concentration is raised to 35 % or more[15]. This means the reduction equilibrium temperature cannot be determined under high O₂ concentration conditions, and analysis by the Rist diagram is inappropriate. On the other hand, in an experiment with a small-scale blast furnace, Ohno et al. demonstrated an oxygen blast furnace process in which preheating gas was injected in the upper shaft together with the oxygen blast[14]. As a result, a quasi-thermal reserve zone where the temperature stagnates was formed in the vicinity of the preheating gas injection level, and the temperature could be controlled by the temperature and flow rate of the preheating gas. In addition, the ore had been reduced to wustite at the preheating gas injection level. Based on these results, Ohno et al. analyzed the operation of the experimental
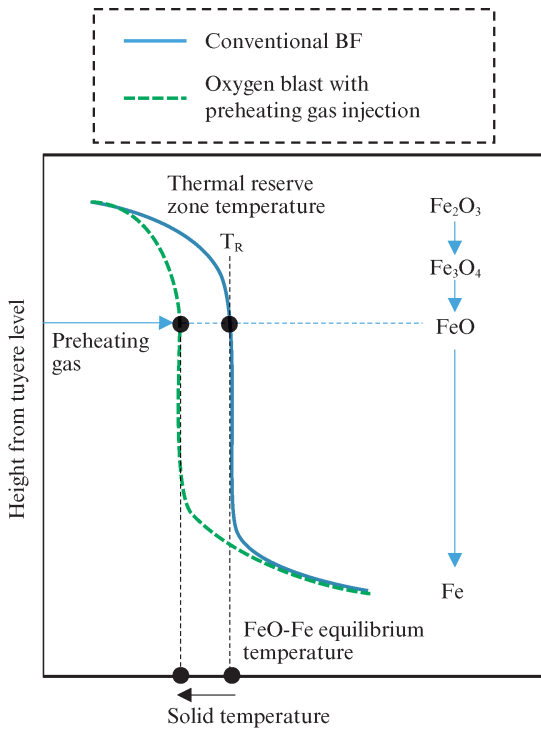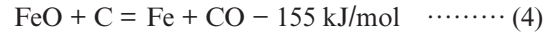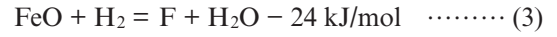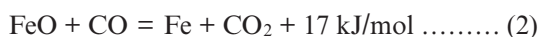
Fig. 4　Themal reserve zone temperature of conventional blast furnace and oxygen blast furnace

blast furnace by a Rist diagram, using the gas temperature at the preheating gas injection level as the temperature of the thermal reserve zone. **Figure 4** shows a conceptual diagram of the thermal reserve zone temperature of a conventional blast furnace and the oxygen blast furnace. The results of this operational analysis confirmed that the shaft efficiency of the oxygen blast furnace process is substantially constant, even though the thermal reserve zone temperature is decreased by approximately 200°C from that of the conventional blast furnace.

Based on this knowledge, in the present study, we assumed that the thermal reserve zone temperature decreases linearly from the blast O_2 concentration of 35 % to 100 %, so that the thermal reserve zone temperature, which is 1 000°C when blowing hot blast decreases to 800°C. In addition, shaft efficiency was assumed to be constant, independent of the blast O_2 concentration, due to preheating gas injection.

3.3.2　Direct reduction ratio

The reduction reaction of ore that occurs in a blast furnace can be broadly divided into three reactions: reduction by CO gas, reduction by H_2 gas and direct reduction by reaction with the apparent C content of the coke. The chemical reaction equations and heat of reaction of these respective reactions are shown in the following Eq. (2) to Eq. (4).

$$FeO + CO = Fe + CO_2 + 17 \text{ kJ/mol} \quad \cdots\cdots\cdots (2)$$

$$FeO + H_2 = F + H_2O - 24 \text{ kJ/mol} \quad \cdots\cdots\cdots (3)$$
$$FeO + C = Fe + CO - 155 \text{ kJ/mol} \quad \cdots\cdots\cdots (4)$$

Because direct reaction is an extremely large endothermic reaction in comparison with the other two reactions, reducing the ratio of direct reduction leads to a decrease in the amount of coke combustion in front of the tuyere, and in turn, a decrease in the CO_2 emission from the blast furnace. Since direct reduction cannot take a negative value, the theoretical lower limit is 0 %. This means the Rist operating line cannot enter the region to the lower right of the coordinate (1, 0).

3.4　Calculation Results

Operation of a blast furnace using the carbon recycling technology was studied with a Rist diagram under the assumptions up to section 3.3. As common conditions, shaft efficiency of 0.9, unit heat loss of 420 MJ/ t-HM and a hot metal and slag temperature of 1 500°C were set. Since pulverized coal is injected from the tuyeres as an injected reducing agent in conventional blast furnaces, a representative pulverized coal ratio of 150 kg/t-HM was assumed. During CN methane injection, pulverized coal was not injected, and the CN methane injection rate was manipulated in the range from 0 to 200 kg/t-HM. When the reducing agent is injected from the tuyeres, TFT decreases for reasons such as an increase in the volume of gas due to gas injection. However, TFT can be increased by increasing the O_2 concentration in the blast, which reduces the energy required to heat nitrogen in the blast. In this study, the O_2 concentration in the blast was manipulated in the range of 25 % to 100 %, and operational parameters which satisfied the heat and mass balance were obtained as calculation results.
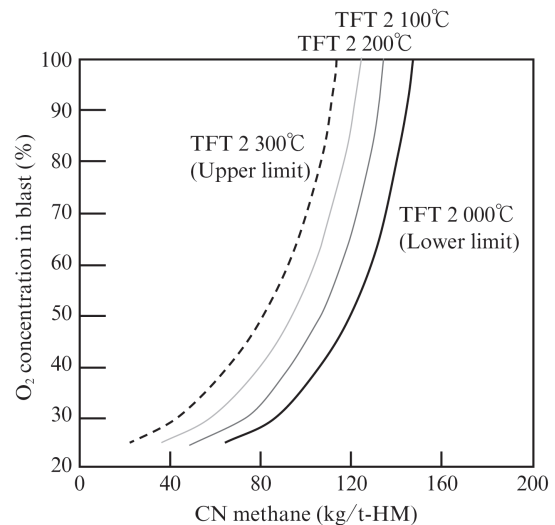

Fig. 5　Change of theoretical flame temperature in front of tuyere (TFT) with O_2 concentration in blast and CN methane injection
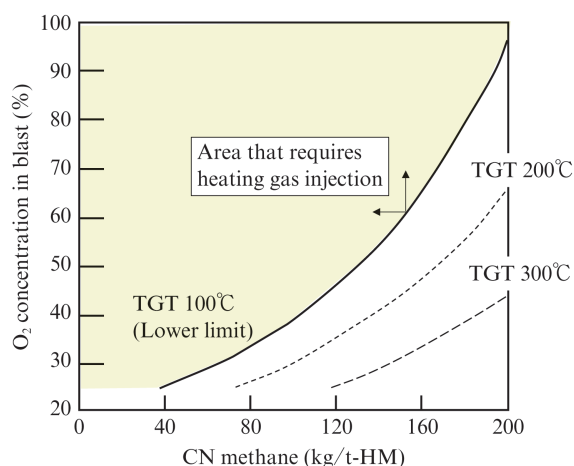
Fig. 6　Change of top gas temperature (TGT) with O_2 concentration in blast and CN methane injection

Fig. 7　Change of specific carbon consumption reduction ratio with O_2 concentration in blast and CN methane injection

Figure 5 shows the change of TFT by manipulation of the CN methane injection ratio and the O_2 concentration in the blast. Although there is an upper limit for injection of CN methane because TFT decreases as the CN methane injection ratio is increased, the CN methane injection volume can be increased by raising TFT by increasing the O_2 concentration in the blast to reduce the energy required to heat nitrogen in the blast.

Similarly, the change in the top gas temperature (TGT) is shown in **Fig. 6**. TGT decreases when the O_2 concentration in the blast is increased. This is due to the increased heat-flow ratio when the amount of nitrogen in the blast is decreased, and in the region where the methane injection ratio is low and the O_2 concentration in the blast is high, TGT decreases to the lower limit of 100°C or less. Therefore, in this region, it is necessary to recover TGT by injection of preheating gas.

Figure 7 shows the change of the specific carbon consumption reduction ratio, together with the permissible range (upper/lower limits) of TFT and the region where injection of preheating gas is necessary. Basically, specific carbon consumption can be reduced significantly by massive injection of CN methane. Therefore, at the same O_2 concentration in the blast, the specific carbon consumption reduction ratio increase as TFT decreases. In addition, preheating gas injection is also necessary in order to reduce specific carbon consumption by 20 % or more. From these results, it was shown that oxygen blowing and preheating gas injection from the upper shaft are effective for maximizing the volume of CN methane injection. Here, it may be noted that the specific carbon consumption reduction rate takes a minimum value with respect to the O_2 concentration in the blast due to the assumptions that the relationship between the O_2 concentration in the blast and the specific hot blast volume (i.e., sensible heat of the hot
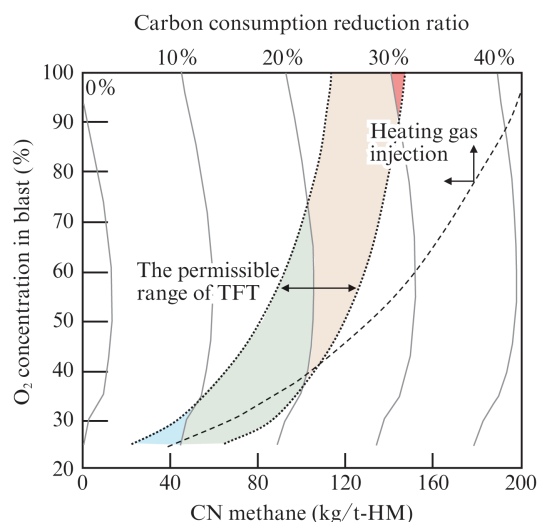
Table 1　Operation condition of conventional blast furnace and carbon recycling blast furnace

	Conventional BF	Carbon recycling BF
Shaft efficiency (—)	0.9	
Heat loss (MJ/t-HM)	420	
Coke rate (kg/t-HM)	354	341
Pulverized coal rate (kg/t-HM)	150	—
CN methane rate (kg/t-HM)	—	145
Blast volume (Nm³/t-HM)	1 014	317
O₂ concentration in blast (%)	24	100
Blast temperature (°C)	1 200	25
Heating gas vol. (Nm³/t-HM)	—	160
Heating gas temperature (°C)	—	1 000
B gas volume (Nm³-dry/t-HM)	1 540	1 030
B gas calorie (MJ/Nm³)	3 400	7 100
Carbon consumption (kg/t-HM)	425	293
CO₂ emissions reduction (%)	—	31
CO reduction ratio (%)	61	61
H₂ reduction ratio (%)	9	35
Direct reduction ratio (%)	30	4

blast) is not linear, and the temperature of the thermal reserve zone decreases as the O_2 concentration in the blast increases.

Table 1 shows the conditions of the carbon recycling blast furnace at the maximum CO_2 emission reduction rate, that is, the conditions of oxygen blowing and CN methane injection to the lower limit of TFT, in comparison with the conditions of the conventional blast furnace. The specific carbon consumption of the carbon recycling blast furnace is 293 kg/t-HM, showing the possibility of reducing specific carbon consumption

by more than 30 % in comparison with the conventional blast furnace.

4. Discussion

4.1 Change of Rist Operating Line

A comparison of the Rist diagrams of the conventional blast furnace and the carbon recycling blast furnace is shown in **Fig. 8**. In the carbon recycling blast furnace, the W point, which is the reduction equilibrium constraint, shifts further to the oxidation gas side due to the decrease in the temperature of the thermal reserve zone. Furthermore, because massive injection of CN methane is possible under the condition of oxygen blowing, the specific reducing gas volume per ton of hot metal increases, and the slope of the corresponding operating line becomes larger. As a result of these changes, the point of intersection between the operating line and the Y axis at X = 1 shifts downward, and the direct reduction amount Y_d decreases greatly
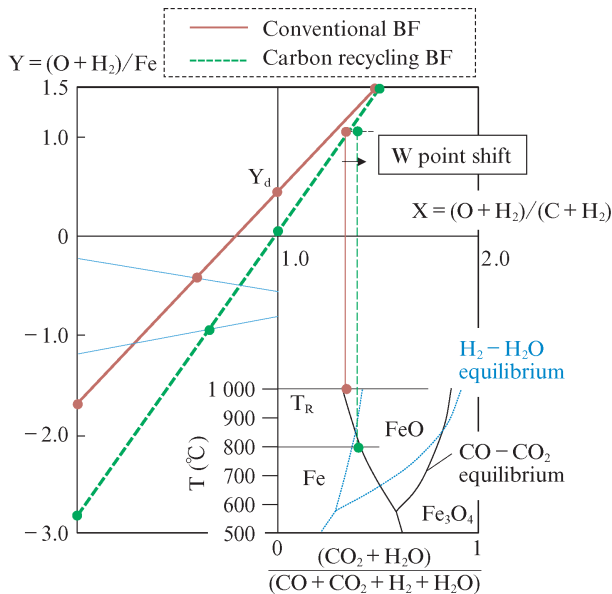
in comparison with the conventional blast furnace.

4.2 Change of Heat Balance

Next, the conventional blast furnace and the carbon recycling blast furnace were compared in terms of the heat balance. **Figure 9** shows the necessary heat (demand) and supplied heat (supply) for production of 1 ton of hot metal by the respective processes. As shown in Table 1, in the carbon recycling blast furnace, the amount of heat necessary for the reduction reaction is small due to the small amount of direct reduction, which is a large endothermic reaction. Therefore, the heat demand for production of 1 ton of hot metal is reduced by approximately 1 000 MJ/t-HM in comparison with the conventional blast furnace process. In addition, the amount of heat supplied by combustion of coke is also reduced because heat is supplied by the reaction of CN methane and oxygen in front of the tuyeres. Because this effect cannot be obtained by blowing hydrogen directly into the blast furnace, this can be considered an advantage of the carbon recycling blast furnace, in which hydrogen is converted to a chemical compound.

4.3 Change of Carbon Consumption Balance

Figure 10 shows the breakdown of the carbon consumption in the conventional blast furnace and the carbon recycling blast furnace. In the conventional blast furnace, carbon is mainly consumed in the reaction with oxygen in front of the tuyeres, in the direct reduction reaction and the hot metal carburization reaction.

Fig. 8 Rist diagrams of conventional blast furnace and carbon recycling blast furnace
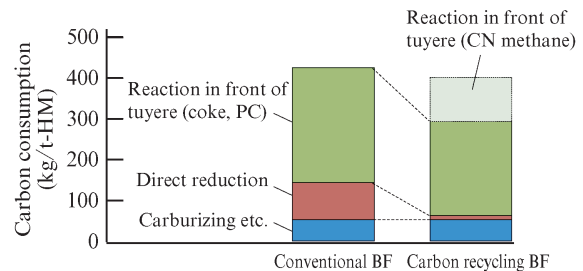

Fig. 10 Breakdown of carbon consumption of conventional blast furnace and carbon recycling blast furnace
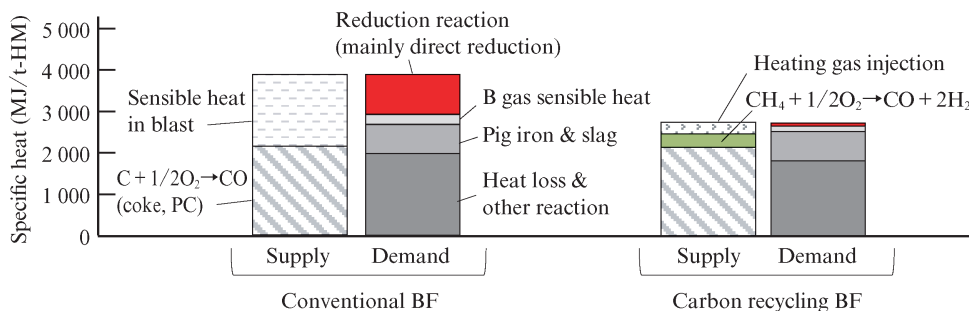

Fig. 9 Heat balance of conventional blast furnace and carbon recycling blast furnace

Among these reactions, in the carbon recycling blast furnace, carbon consumption by direct reduction decreases greatly. Carbon consumption by combustion in front of the tuyeres to compensate for the decrease in the sensible heat of the blast is larger in the carbon recycling blast furnace than in the conventional blast furnace, but because part of this carbon consumption is carbon in the CN methane, the amount of coke consumed in front of the tuyeres is approximately the same as that in the conventional blast furnace.

4.4 Technologies to be Developed and Issues for Realization

When examining the operating parameters by the Rist diagram in this study, several calculation assumptions were made based on past knowledge, for example, the transition of the thermal reserve zone temperature in response to the O_2 concentration in the blast, shaft efficiency, and so on. Although it is thought that these conditions can be controlled by the volume and temperature of preheating gas injection, evaluation by a numerical simulation model which considers kinetics will be essential for verifying this point. Moreover, because the volume and composition of the gas in the carbon recycling blast furnace differ greatly from those in the conventional blast furnace process, it is considered necessary to improve simulation accuracy through verification by laboratory tests and demonstration with a small-scale blast furnace.

In the establishment of this technology, in addition to the above-mentioned improvement of operation prediction techniques, it will also be necessary to develop equipment technologies, namely, optimization of the tuyere structure and the furnace body profile to enable massive injection of hydrogen and methane, and a carbon recycling technology for synthesizing CN methane from blast furnace gas, which contains impurities. While steady progress is being made in these technologies by development which includes demonstration tests, obtaining green hydrogen, which is necessary in order to produce CN methane, is still a challenge. Thus, early practical application of a green hydrogen production technology is also desired for realization of this technology.

5. Conclusion

Reduction of CO_2 emissions by the carbon recycling blast furnace was studied using the Rist diagram approach, and the following knowledge was obtained.

(1) Use of carbon neutral (CN) methane reduces the CO_2 emission of the blast furnace by the following two effects.
  i) CN methane decreases the amount of direct reduction, which is a large endothermic reaction, by increasing the amount of reducing gas.
  ii) CN methane supplies heat by reaction with oxygen in front of the tuyeres.
(2) It is possible to reduce CO_2 emissions more than 30 % at a maximum by using CN methane in the blast furnace.
(3) In maximizing CN methane injection, oxygen blowing and preheating gas injection from the upper shaft level are effective.

References

1) For example, United Nations: The Paris Agreement, https://www.un.org/en/climatechange/paris-agreement, (accessed 2021-9-13).
2) National Institute for Environmental Studies, Japan. National Greenhouse GasInventory Report of JAPAN 2021, https://www.nies.go.jp/gio/aboutghg/, (accessed 2021-9-13).
3) Ariyama, T. Perspective toward Long-term Global Goal for Carbon Dioxide Mitigation in Steel Industry. *Tetsu-to-Hagané*. 2019, vol. 105, no. 6, p. 567–586.
4) Watakabe, S.; Takeda, K.; Nishimura, H.; Goto, S.; Nishimura, N.; Uchida, T.; Kiguchi, M. Development of High Ratio Coke Mixed Charging Technique to the Blast Furnace. ISIJ Int. 2006, vol. 46, p. 513–522.
5) ThyssenKrupp: Press release, https://www.thyssenkrupp-steel.com/en/ newsroom/press-releases/thyssenkrupp-steel-concludes-first-test-phase-successfully.html, (accessed 2021-9-13).
6) Naito, M.; Takeda, K.; Matsui, Y. Ironmaking Technology for the Last 100 Years: From adopted Technologies to a Position of Leadership in Advanced and Next-Generation Technology. *Tetsu-to-Hagané*. 2014, vol. 100, no. 1, p. 2–30.
7) Ministry of Finance Japan. Trade Statistics of Japan. https://www.customs.go.jp/toukei/info/, (accessed 2021-9-13).
8) Senderens, J.-B.; Sabatier, P. Nouvelles synthèses du méthane. Comptes Rendus Acad. Sci. 1902, vol. 82, p. 514–516.
9) EtoGas Power-to-Gas, https://www.hz-inova.com/renewable-gas/etogas/, (accessed 2021-9-13).
10) Rist, A.; Meysson, N. Recherche graphique de la mise au mille minimale du haut fourneau a faible temperature de vent. Rev. Mét. 1964, vol. 61, no. 2, p. 121–146.
11) Rist, A.; Meysson, N. Étude graphique de la marche du haut fourneau avec vent humide et injections aux tuyères. Rev. Mét. 1965, vol. 62, no. 11, p. 995–1040.
12) Kato, K.; Hashimoto, S.; Mori, K.; Murai, Y. On the Influences of the Theoretical Combustion Temperature upon Operating Conditions. *Tetsu-to-Hagané*. 1961, vol. 47, no. 3, p. 229–232.
13) Ramm, A. N. Contemporary problems of metallurgy, ed. By Samarin (Translated from Russian), Consultants bureau, 1960.
14) Ohno, Y.; Hotta, H.; Matsuura, M.; Mitsufuji, H.; Saito, H. Development of Oxygen Blast Furnace Process with Preheating Gas Injection into Upper Shaft. *Tetsu-to-Hagané*. 1989, vol. 75, no. 8, p. 1278–1285.
15) Miyashita, T.; Ohtsuki, M. Phenomena of Oxygen Enrichment in a Blast Furnace Process and its Limit. *Tetsu-to-Hagané*. 1971, vol. 57, no. 14, p. 2184–2196.