Hydrogen Utilization for Carbon Recycling Iron Making System

Yukitaka KATO*

Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, 2-12-1-N1-22, Ookayama, Meguro-ku, Tokyo, 152-8550 Japan.

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A new energy transformation concept based on carbon recycling, called the Active Carbon Recycling Energy System, ACRES, had been proposed for a zero carbon dioxide emission process. A smart ironmaking system based on ACRES (iACRES) was discussed thermodynamically. Efficient regeneration of carbon material from carbon dioxide (CO2) emitted from ironmaking system was a key technology for establishment of iACRES. Carbon monoxide (CO) was the appropriate carbon material in recycling system of iACRES because CO had high enthalpy for reduction of iron oxide. CO regeneration by CO2 hydrogenation was employed for carbon recycling because the regeneration was the most practical technology in regeneration ways. Equilibrium analysis for CO recycling in iACRES was discussed. Effluent gas of an ironmaking process is generally mixture of CO2 and CO. Effect of concentration of CO2 in gas for reduction on CO regeneration was discussed. CO2 had small negative effect on CO reduction. Then, CO and CO2 separation process for effluent gas from ironmaking process was capable to be omitted in iACRES. The omission of the process would realize simplification and cost-reduction of processes in iACRES. A structure of iACRES using external H2 and high-temperature heat was proposed. It was shown that hydrogen was useful material as reductant for CO2 reduction in iACRES.

KEY WORDS: carbon recycling; hydrogen; carbon dioxide hydrogen reduction; carbon dioxide; carbon monoxide.

1. Introduction

Energy supply security is important matter for industrial and economical developments of a society. Steep change and instability of the market prices of primary energy sources is causing economic confusion in any ages. Carbon is the most important energy media for manufacturing industry and social life of human being. Carbon supply security is an essential condition for a sustainable society. In Japan, the supply of fossil fuels of primary energy almost depends on import. Enthalpy of import fuel is 82% (18.9×1018 J) of all of using primary energy in Japan.1) 7% of fossil fuel is consumed for ironmaking process. The Kyoto protocol came into effect in 2005. Japan has undertaken obligation to follow the protocol, and is required drastic reduction of carbon dioxide (CO2) emission. However, CO2 reduction connects with restriction of usage of carbon resources and causes depression of activity of manufacturing and service industries. Co-establishment of carbon supply security and reduction of CO2 emission is an important subject for a development of a modern society.

A new energy system in which carbon is reused cyclically was discussed. A carbon recycle system has already existed in nature as a natural carbon neutral system. A concept of an Active Carbon Recycling Energy System, ACRES, had been proposed against natural carbon recycling energy system.2) CO2 is regenerated artificially in hydrocarbons consuming a primary energy source with no-CO2 emission, and re-used cyclically in ACRES. ACRES recycles carbon, and transforms energy without CO2 emission. ACRES can be applicable for ironmaking process. An ironmaking system based on ACRES was proposed and discussed thermodynamically its energy feasibility in this paper. Then, contribution of hydrogen as a reductant of CO2 reduction in the system was evaluated.

2. Smart Ironmaking System Based on ACRES

A smart ironmaking system based on ACRES2) named as iACRES is proposed in Fig. 1. The system is assumed to use CO as recycling carbon material for reduction of iron(III) oxide (hematite, Fe2O3) which is employed as representative raw material in ironmaking process in this study. The total

* Corresponding author: E-mail: yukitaka@nr.titech.ac.jp
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Fig. 1. Basic structure of smart ironmaking system based on ACRES, iACRES.
reaction for ironmaking in iACRES will be as following.

\[
\text{Fe}_2\text{O}_3(s) + (3 + n) \text{CO(g)} = 2\text{Fe(s)} + 3\text{CO}_2(g) + n\text{CO(g)} \quad (1)
\]

Reaction enthalpy values in this paper were calculated from a reference data. \(^3\) The ironmaking process emits mixture of CO\(_2\) and CO by reduction of Fe\(_2\)O\(_3\) into pure iron (Fe) by CO. The mixture is separated into CO\(_2\) and CO by a CO\(_2\) separator. It is assumed that the primary energy for CO\(_2\) regeneration from CO\(_2\) in CO\(_2\) reduction process is supplied from energy sources as electricity, heat and hydrogen. Regenerated CO is mixed with separated CO and the mixture is used again for the reduction of Fe\(_2\)O\(_3\). Oxygen as the by-products of CO in CO\(_2\) reduction process can be a useful material for other oxidation processes.

Renewable energies, industrial waste heats and nuclear heat would be candidates of the primary energy sources. Renewable energy is one of ideal energy sources because it is environmental friendly. However, instability of renewable energies, especially, from sun and wind cause reduction of electricity quality in frequency and voltage in an electricity supply grid. iACRES can be acceptable the instable energies. Industrial high-temperature waste heat is also able to be energy source for heat supply into endothermic reaction of CO\(_2\) reduction. High temperature gas cooled type nuclear reactor (HTGR) which has demonstrated heat output at 950°C \(^4\) is a candidate of the primary energy source. Because iACRES is able to accept various non-carbon energy resources as electricity, heat and hydrogen for ironmaking system and have robustness to carbon supply security, then, it would be categorized in smart ironmaking system.

3. Utilization of Hydrogen in iACRES

Enthalpy balances for carbon recycling and iron oxides reduction is shown in Fig. 2. Required enthalpies per one molecule of CO for the processes of usage and regeneration are depicted in low heating value (LHV). CO has higher energy density than H\(_2\). Fe\(_2\)O\(_3\) is employed as a raw material for the process in the following discussion. An ironmaking process using hydrogen has been discussed in previous works. \(^5\) Fe\(_2\)O\(_3\) reduction by hydrogen is an endothermic reaction and requires an external heat input.

\[
\text{Fe}_2\text{O}_3(s) + 3\text{H}_2(g) \rightarrow 2\text{Fe(s)} + 3\text{H}_2\text{O(g)}, \quad \Delta H = +104.9 \text{ kJ mol}^{-1} \quad (2)
\]

In contrast, Fe\(_2\)O\(_3\) reduction by CO is an exothermic reaction and proceeds with self-heating.

\[
\text{Fe}_2\text{O}_3(s) + 3\text{CO(g)} \rightarrow 2\text{Fe(s)} + 3\text{CO}_2(g), \quad \Delta H = -18.4 \text{ kJ mol}^{-1} \quad (3)
\]

CO reduction is advantageous for the ironmaking process in comparison with hydrogen reduction, then, the reaction is usual in conventional iron making.

Development of efficient CO regeneration process is the most important for the establishment of iACRES. CO is regenerative from CO\(_2\) by electrolysis (Eq. (4)) using a solid oxide fuel cell [\(^4\)].

\[
\text{CO}_2(g) \rightarrow \text{CO(g)} + 1/2\text{O}_2(g), \quad \Delta H = +283.0 \text{ kJ mol}^{-1} \quad (4)
\]

A two-step reaction of hydrogen production by water electrolysis (Eq. (5)) and hydrogen reduction of CO\(_2\) with the hydrogen, that is, reverse water-gas shift reaction (Eq. (6)), is more practical process for CO regeneration, because hydrogen production and CO\(_2\) hydrogen reduction processes are well studied in comparison with CO\(_2\) electrolysis.

\[
\text{H}_2\text{O(g)} \rightarrow \text{H}_2(g) + 1/2\text{O}_2(g), \quad \Delta H = +241.8 \text{ kJ mol}^{-1} \quad (5)
\]

\[
\text{CO}_2(g) + \text{H}_2(g) \rightarrow \text{CO(g)} + \text{H}_2\text{O(g)}, \quad \Delta H = +41.2 \text{ kJ mol}^{-1} \quad (6)
\]

Introduction of H\(_2\) from other H\(_2\) production processes and H\(_2\) as by-product from other processes is also practical choice. Production of H\(_2\) of 1 mol needs an enthalpy of 242 kJ (mol-CO)\(^{-1}\). Reduction of CO\(_2\) into CO with H\(_2\) is endothermic reaction required heat input of 41 kJ (mol-CO)\(^{-1}\). The reduction heat is possible to be supplied from industrial high-temperature waste heat and HTGR. H\(_2\) usage in CO\(_2\) reduction is the most conventional way for iACRES. Reduction processes for Fe\(_2\)O\(_3\), in which CO and H\(_2\) mixed gas is used for the reduction, have been discussed. \(^6\) The unique point of iACRES is to use positively H\(_2\) for regeneration of CO from CO\(_2\) and cyclically regenerated CO in the ironmaking process.

4. Chemical Equilibrium Analysis for H\(_2\) Reduction of CO\(_2\)

4.1. Recycle of CO in iACRES

Feasibility of iACRES based of CO\(_2\) hydrogen reduction was discussed thermodynamically. Material flows in CO\(_2\) hydrogen reduction process and ironmaking process in iACRES depicted in Fig. 1 is shown in Fig. 3 in which a

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Fig. 2. Enthalpy balances for carbon recycling and iron oxides reduction.

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Fig. 3. Material flows in CO\(_2\) hydrogen reduction process and ironmaking process in iACRES.
CO₂ separation process is not considered, however, the separation process is acceptable occasionally in the system. Abscissas and ordinates in Fig. 3 show reactor length and material amount, respectively, for both processes. At the ironmaking process, CO gas flows counter to the supply direction of Fe₂O₃. Fe₂O₃ is reduced by CO and Fe is produced. CO and CO₂ mixture which reaches equilibrium is emitted from opposite side of ironmaking process. CO₂ and CO mixture is recycled again CO₂ hydrogen reduction process, and CO₂ is reduced by using external H₂ which is produced from H₂O electrolysis processes using electric power from renewable energies of sun and wind, and HTGR, and by-product of another carbon processes. Heat for the reduction is supplied from industrial high-temperature processes and HTGR. CO is regenerated in the process, and supplied cyclically to iron making process.

4.2. Equilibrium Analysis of CO₂ Reduction

4.2.1. Effect of Temperature on CO Regeneration

Chemical reaction equilibrium for H₂ reduction of CO₂ in Eq. (6) was calculated by a chemical equilibrium calculator of HSC Chemistry ver. 7.0 (Outotech). It was assumed in the evaluation that the reaction proceeded in an ideal equilibrium reactor under a total pressure of 1.00 bar, initial mixture consists of CO₂, CO and H₂, and product of the reaction consisting of CO₂, CO, H₂O, O₂, carbon (C) and methane (CH₄). Equilibrium composition was calculated by a Gibbs energy minimization method. Figure 4 shows relationship between reaction temperature and equilibrium mole amount of products under initial state consisting of CO₂ of 1 mol, CO of 1 mole and H₂ of 0.5, 1.0 and 2.0 mol. Higher H₂ amount induces higher yield of CO. On the other hand residue of H₂ increased with increase of initial H₂ amount. Remained H₂ would be consumed in the next iron oxide reduction process in the ironmaking process in Fig. 3. It is preferable to enhance H₂ consumption for CO regeneration because of thermodynamic advantage of CO in iron oxide reduction.

Figure 5 shows effect of initial charged H₂ amount on reaction enthalpy change in CO₂ hydrogen reduction for conditions in Fig. 4. From Fig. 5, at up to 660°C, reaction enthalpy change is negative which means exothermic, and CO₂ and CO hydrogenation into C proceeds mainly. At over 660°C, reaction enthalpy change becomes positive which means endothermic, and CO₂ hydrogen reduction into CO proceeds. Over 800°C, enthalpy change varies monotonously with temperature increase, CO production from CO₂.

Fig. 4. Chemical reaction equilibrium for H₂ reduction of CO₂ under initial state consisting of CO₂ and CO of 1 mole each and H₂ of (a) 0.5 mol, (b) 1.0 mol and (c) 2.0 mol.

Fig. 5. Effect of initial charged H₂ amount on reaction enthalpy change in CO₂ hydrogen reduction under initial state consisting of CO₂ and CO of 1 mol each.
hydrogen reduction proceeds mainly. Then, CO was dominant products at over 800°C. It means that CO regeneration needs heat input over 800°C. Surplus heats at high-temperatures around 800°C generated from high-temperature processes can be utilized in the reaction. Energy recovery from waste heats of the high-temperature processes is achievable by endothermic CO regeneration in iACRES. Because formation enthalpy of CO is higher than one of H₂ as shown in Eqs. (4) and (5), the ACRES for CO can recover all of enthalpy of H₂. Then, it was expected that CO is one of appropriate candidates for a regenerative media in iACRES.

4.2.2. Effect of CO Existence in Initial State

As shown in Fig. 1, CO₂ removal from CO₂ and CO mixture effluent from iron making process is expected to enhance CO₂ reduction. For evaluation of effect of CO₂ separation from mixture of CO₂ and CO on CO₂ reduction, equilibrium composition of CO₂ hydrogen reduction under a condition without initial CO was evaluated. Calculation result at initial H₂ amount of 0.5, 1.0 and 2.0 are shown in Fig. 6. Higher temperature over 800°C and larger amount of initial H₂, CO production was enhanced well. However, remained H₂ became larger also. The CO production has similar trend with the results for accounting initial CO existence as shown in Fig. 4. Then, CO existence in initial state had small effect on CO₂ reduction and CO regeneration.

Figure 7 shows H₂ concentration effect on CO₂ reduction under initial amount of CO₂ and CO of 1 mole each at 900°C. CO₂ equilibrium amount increases gradually with increase of initial H₂ amount. However, H₂ equilibrium amount increases to increase of H₂ initial amount is more steeply than one of CO. CO regeneration amount is not proportional to H₂ initial amount. Equilibrium molar ratios between CO and H₂, \( R_{CO/H2} \), and CO and CO₂, \( R_{CO/CO2} \), are defined as following, respectively.

\[
R_{CO/H2} = \frac{\text{CO equilibrium amount [mol-eq.]} }{\text{H₂ equilibrium amount [mol-eq.]} } ............... (7)
\]

\[
R_{CO/CO2} = \frac{\text{CO equilibrium amount [mol-eq.]} }{\text{CO₂ equilibrium amount [mol-eq.]} } .............. (8)
\]

H₂ concentration effect on \( R_{CO/H2} \) and \( R_{CO/CO2} \) at 900°C is shown in Fig. 8. Cases under initial CO amount of 1 mole and null are compared in the figure. \( R_{CO/H2} \) increased at low-
er H₂ initial amount, then, lower H₂ initial amount was benefi-
cial to reduction of H₂ equilibrium amount. R_{CO:CO₂} increased at higher H₂ initial amount, then, higher H₂ initial
amount was better for CO₂ reduction into CO. Optimization
of H₂ initial amount will be required for design of the iron-
making process.

Figure 8 shows also effect of CO initial existence on CO₂
hydrogen reduction. CO existence in initial state did not pro-
hibit CO production. Both R_{CO:H₂} and R_{CO:CO₂} of a state with
initial CO existence was higher than one of no initial CO.
From Fig. 8, it was concluded that separation process of CO
from off-gas of iron making process was able to be elimi-
nated. The elimination induces reduction of separation en-
ergy, separation facility cost and complexity of process op-
eration. Then, CO₂ hydrogen reduction from mixture of CO₂
and CO without separation process was effective and prac-
tical process for iACRES. H₂ had important contribution on
iACRES.

5. Scale Evaluation of iACRES

External H₂ utilization with heat supply from high tem-
perature heat sources was one of candidates for CO regen-
eration in iACRES as shown in Fig. 9. Scale of iACRES
having the structure of Fig. 9 with assumption of application
on a conventional blast furnace was evaluated. Evaluation
result is shown in Table 1. HTGR combined with a helium
gas-turbine power generator which had capacity of thermal
output of 600 MW-thermal was employed for supply of pri-
mary energy sources for process. It was assumed that exter-
nal H₂ was used for CO₂ hydrogen reduction and the
HTGR supplies heat for the CO₂ reduction as shown in Eq.
(6). A case of CO₂ electrolysis reduction into CO based on
Eq. (4) was also evaluated. It was assumed that both reac-
tion energies were supplied by electricity generated from the
gas-turbine generator of HTGR. From a previous research
for conventional blast furnace in Japan, it was assumed
that carbon amount emitted as off gas from a blast furnace
is around 400 kg-C·(ton-pig iron)⁻¹ and mole ratio between
CO and CO₂ in the off gas is around 1:1. CO₂ of 16.7
kmol·(ton-pig iron)⁻¹ is emitted from a blast furnace. It was
concluded that 0.25 unit of HTGR was capable to regenerate
CO by CO₂ hydrogen reduction and 1.72 unit of HTGR was
required for CO₂ electrolysis reduction into CO. When hydrogen for CO₂ hydrogen reduction was produced by
water electrolysis in Eq. (5) in iACRES system, total energy
requirement of CO₂ hydrogen reduction will be equal to one
of CO₂ electrolysis. When low-cost external H₂ was able to
be utilized in iACRES, CO₂ hydrogen reduction had advan-
tage to CO₂ electrolysis for iACRES. Then, CO₂ hydrogen
reduction using external H₂ was one of candidates for CO
regeneration in iACRES.

6. Conclusions

For an establishment of iACRES, CO was suitable for a
recycle medium in iACRES, because CO had higher energy
density and affinity to conventional iron making process in
comparison with H₂. Instability of renewable energies from
sun and wind was acceptable into the system. HTGR was
also a candidate of primary energy source of iACRES.
Hydrogen reduction of CO₂ was practical way for CO
regeneration. Mixture of CO₂ and CO which was emitted as
off-gas from blast furnace was capable to be used directly for the CO₂ reduction. The reduction could eliminate CO₂ separation process from the mixture, and was expected to have higher economic efficiency than other CO regeneration process. Usage of low-cost external H₂ for CO₂ hydrogen reduction with heat supply from high temperature heat sources such as industrial waste high temperature process and HTGR was the one of appropriate set for CO regeneration in iACRES.

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