Carbon Recycling for Reduction of Carbon Dioxide Emission from Iron-making Process

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A new energy transformation concept based on carbon recycling, called the Active Carbon Recycling Energy System, ACRES, is discussed. In this system, hydrocarbons are regenerated from carbon dioxide by using a heat source that does not emit carbon dioxide, allowing the hydrocarbons to be re-used cyclically as energy carrier media. The thermodynamic feasibility of ACRES is compared with that of a hydrogen energy system. Carbon monoxide has a higher energy density than hydrogen and is highly compatible with conventional chemical, steel, and high-temperature manufacturing processes. Thus, it is a suitable carbon medium for ACRES. A high-temperature gas type nuclear reactor is a good power source for ACRES. The combination of the nuclear reactor and ACRES with carbon monoxide is expected to form the basis of a new iron-making process that has low carbon dioxide emissions.

KEY WORDS: energy; energy system; carbon recycling; carbon monoxide; hydrogen.

1. Introduction

Energy security is critical to the industrial and economic development of a society. Rapid changes and instability in the market prices of primary energy sources will lead to economic confusion in any age. This paper discusses the establishment of energy security from the standpoint of carbon recycling. Carbon is the most important energy medium for the manufacturing industry and in the daily life of a human being, making carbon security essential for a sustainable society. In Japan, the supply of fossil fuels depends almost entirely on imports. The enthalpy of imported fossil fuels is 82% (18.9×10^{18} J) of the total enthalpy of primary fuels used in Japan.¹⁾ Seventeen percent of fossil fuels are converted into plastics, while the rest is consumed solely for heat generation. Japan undertook the obligation of adhering to the Kyoto Protocol, which came into effect in 2005, and will therefore need to drastically reduce its carbon dioxide (CO₂) emissions. However, any limits imposed on CO₂ emissions will directly restrict the use of carbon resources, which will, in turn, severely affect the manufacturing and service industries. The simultaneous establishment of carbon security and lower CO₂ emissions is thus an important subject for the development of a modern society.

Here, a new energy system in which carbon is reused cyclically is discussed to reduce the emission of carbon dioxide into atmosphere from industrial processes. A carbon recycling system already exists in nature. In this paper, the concept of the Active Carbon Recycling Energy System, ACRES, is discussed. In ACRES, CO₂ is converted artificially into hydrocarbons by using a primary energy

source that has no CO₂ emissions, allowing the hydrocarbons to be re-used cyclically as energy carrying media. ACRES recycles carbon and transforms energy without CO₂ emission. Because ACRES is expected to solve the CO₂ emission problem, the feasibility of ACRES is discussed thermodynamically.

2. Proposal

2.1. Conventional Water Recycle Energy Systems and ACRES

ACRES is compared with conventional recycle energy systems in this section. Conventional recycling energy systems based on water are depicted in **Fig. 1**. Figure 1(a) shows a conventional steam engine in which the water/vapor phase change is used for energy conversion. Primary energy is used for the evaporation of water, and a phase change from steam to water provides the energy output. Figure 1(b) indicates a hydrogen system in which water is decomposed into hydrogen (H₂) and oxygen by an energy input, and the oxidation of H₂ provides the energy output.

Fig. 1. Conventional water recycling energy systems.

Fig. 2. Carbon recycling energy system.

The H₂ energy system is superior to the vapor system at long-term energy storage with a small loss and a high energy density. However, H₂ requires considerable work for compression up to 700 bars in storage, high-cost security for explosion prevention, and system complexity for energy conversion of the energy output as in fuel cells. These requirements are still a hindrance to the market development of a H₂ energy system.

The proposed concept of ACRES is shown in Fig. 2. Carbon dioxide (CO₂) with/without water is the ground state of carbon. CO₂ is converted into hydrocarbons or alcohols by an energy input using some catalytic technologies.²⁾ The produced hydrocarbons are useful for conventional manufacturing industry as thermal energy sources and raw materials. These hydrocarbons provide thermal and electrical energies during the oxidation into CO₂. The hydrocarbons can be used as raw materials for making industrial materials. These hydrocarbons are easy to be stored and can be transferred under a low compression pressure with a small explosion risk in comparison with H₂. The hydrocarbons have a considerable potential for use in common manufacturing industries. If the carbon recycling system can be established thermally and kinetically, it is expected that the system is diffused easily into conventional industries. A natural carbon recycle energy system already exists in the plant kingdom and is an ideal recycling system. However, the potential amount of bio-mass recycled by this system is not sufficient to meet the demands of a modern society. In particular, the domestic bio-mass potential in Japan is less than 10% of the total domestic energy demand.³⁾ The natural recycling system is not sufficient to meet the energy demands in Japan. Therefore, an artificial active recycling system for carbon, *viz.*, ACRES, is proposed in this study. The feasibility of ACRES is discussed from the viewpoint of enthalpy balances in this paper.

2.2. Structure of ACRES

The structure of ACRES shown in Fig. 3 consists of three elemental processes of hydrocarbon usage, CO₂ recovery and separation, and hydrocarbon regeneration. In the usage process, hydrocarbons can be used as both a heat source and a material. CO₂ generated from hydrocarbon consumption is recovered by physical and chemical sorptions. Recovered CO₂ in a sorption material is separated thermally from the material by a heat input. This process produces highly concentrated CO₂. Recovered CO₂ is regenerated into hydrocarbons in the regeneration process. The regeneration process is endothermic and requires an energy input. In ACRES, the total energy input at recovery and separation (E_S), and regeneration (E_R) should be larger than the energy output of the usage process (E_U).

Fig. 3. Principle of ACRES with three elemental processes.

$$E_S + E_R > E_U \dots\dots\dots(1)$$

ACRES is an energy consumption process; hence, a discussion of the energy balance of the system is required for the feasibility evaluation of the system.

3. Enthalpy Evaluation of ACRES

Practical hydrocarbons are examined those availability in ACRES by an enthalpy balance evaluation.

3.1. Availability of ACRES with Methane

Methane as a basic hydrocarbon is discussed first. In the usage process of methane, methane combustion (Eq. (2)) produces heat, methane steam reforming (Eq. (3)) produces hydrogen, and the polymerization of methane (Eq. (4)) produces polymeric materials.

CO₂ is recoverable by physical adsorptions of active carbons or zeolites, or a chemical sorption by the carbonation of calcium oxide (CaO) in the CO₂ recovery and separation process. CaO can chemically absorb CO₂ at temperatures of 500–800°C (Eq. (5)). CaO can remove CO₂ from a hydrocarbon reaction system at the reaction temperature for CO₂ production with a small sensible heat loss and enhance the reaction rate and yield of the CO₂ production reaction.⁴⁾

In the process of methane regeneration from CO₂, a two-step reaction of hydrogen production by water electrolysis and the methanation of CO₂ with hydrogen (Eqs. (6) and (7)) is available.

The enthalpy balance of ACRES for methane is shown in Fig. 4. Because Eq. (7) needs 4 mol of H₂, then fourfold large of ΔH of Eq. (6) is required for H₂ production in the figure. Required enthalpies per one molecule of methane for the processes of usage and regeneration are depicted by the lower-heating value (LHV). Thermodynamic property values of reactions in the following were calculated on the basis of LHV because these reactions generally proceed at a sufficiently high temperature of more than 100°C. The re-

Fig. 4. Enthalpy balance of ACRES based on methane.

covery and separation process requires a relatively smaller enthalpy than one of other processes; further, it can be driven by waste heat at a relatively low temperature (less than 100°C). Because the enthalpy evaluation for the recovery and separation process had uncertainties, the process was not taken into account in this system evaluation. The regeneration process assumed that hydrogen was used for hydrocarbon regeneration by the two-step reaction given in Eqs. (6) and (7). Production of H₂ (4 mol) needs an enthalpy of 967 kJ/mol-CH₄. The methanation of CO₂ with H₂ is an exothermic reaction of 165 kJ/mol-CH₄. Regenerated methane has a reaction enthalpy of 802 kJ/mol-CH₄. The circulation rate (η_c) which is the formation enthalpy ratio of the regenerated hydrocarbon to the required hydrogen is defined as follows:

$$\eta_c = \frac{\text{Formation enthalpy of regenerated hydrocarbon}}{\left(\frac{\text{Formation enthalpy of hydrogen of required amount for hydrocarbon regeneration}}{\dots\dots\dots} \right)} \quad \dots\dots\dots(8)$$

η_c of methane for ACRES was 83%. This means that an enthalpy loss is observed in the methanation process. However, when the same amount of enthalpy is stored in methane or H₂, the methane storage pressure is reduced to one-third of the H₂ storage pressure. Compression work can also be reduced to 1/3 for methane storage in comparison with H₂ storage. For comparison of energy efficiency between ACRES and the H₂ system, a discussion considering comprehensive energy consumption in each system is needed. η_c of some hydrocarbons were calculated in Fig. 5. A higher η_c implies that enthalpy loss for the regeneration of the hydrocarbon becomes smaller. Methanol and ethanol are generally in liquid phase, easy to transport and store, and applicable to vehicles. Carbon monoxide (CO) has the highest η_c in the hydrocarbons.

4. ACRES Based on CO

4.1. Enthalpy Analysis of ACRES Based on CO

η_c of CO is 117%. This shows that CO has a higher energy density than H₂. CO is a popular energy material in conventional chemical, steel, and other manufacturing industries. Therefore, ACRES for CO is evaluated second. In the usage process of CO, the oxidation of CO (Eq. (9)) for the heat output and the shift reaction of CO for H₂ production (Eq. (10)) is available. CO can be also converted into polymeric materials by polymerization (Eq. (11)).

Fig. 5. Recycle ratios of ACRES based on some hydrocarbons using water electrolysis.

Fig. 6. Enthalpy balance of ACRES based on carbon monoxide.

CO is regenerative from CO₂ by electrolysis (Eq. (12)).

A two-step reaction of hydrogen production by water electrolysis and reduction of CO₂ with the hydrogen (Eqs. (6) and (13)) is a practical process for CO regeneration.

The enthalpy balance of ACRES for CO is shown in Fig. 6. Required enthalpies per molecule of CO for the processes of usage and regeneration are shown in LHV. The regeneration process is assumed to use hydrogen for CO regeneration by the two-step reaction given in Eqs. (6) and (13).

Production of H₂ (1 mol) requires an enthalpy of 242 kJ/mol-CO. Reduction of CO₂ into CO with H₂ is an endothermic reaction and requires a heat input of 41 kJ/mol-CO. Because CO has a higher energy density than H₂, CO is one of the most popular media in chemical processes.

CO is a considerably acceptable medium for conventional chemical and manufacturing industries. Hence, it is expected that CO is the most appropriate candidate for a regenerative medium in ACRES.

4.2. Regeneration of CO

Efficient regeneration of CO is a key technology for ACRES based on CO. The feasibility of the regeneration

methods of CO is evaluated.

4.2.1. CO₂ Hydrogenation

The chemical reaction equilibrium for the H₂/CO₂/CO/H₂O system of Eqs. (6) and (13) is shown in Fig. 7. It was assumed in the evaluation that the reaction proceeded under an equivalent ratio and a total pressure of 100 kPa. CO₂/CO is reversible around 700°C. This implies that the CO regeneration by CO₂ hydrogenation in Fig. 6 requires a heat input of more than 700°C. Because η_c of ACRES based on CO is 117%, CO regeneration can recover all of the enthalpy of H₂. Waste heat at a high temperature of around 700°C generated from the high-temperature processes can be utilized in the reaction. Energy saving of the high-temperature processes is achievable by which the waste heat generated from the processes is utilized for the regeneration process in the ACRES.

4.2.2. CO₂ Electrolysis

CO₂ electrolysis is one method of CO regeneration. Solid-oxide electrolysis cell (SOEC) in which a reverse operation of a solid-oxide fuel cell (SOFC) proceeds has a possibility for the electrolysis.⁵⁾ SOEC has been discussed for the production of a syngas, which is a mixture of H₂ and CO generated from H₂O and CO₂. Temperature dependencies of enthalpy and Gibb's free energy changes, ΔH_i [kJ/mol] and ΔG_i [kJ/mol], of Eq. (12) for the electrolysis of CO₂ and Eq. (6) for H₂O were calculated by a reaction equations module of HSC Chemistry (Ver. 6.12), Outotec. Electromotive forces, V_i [V], for Eqs. (12) and (6) were derived from Eq. (14).

$$V_i = \frac{-\Delta G_i}{n_i F}, \quad F = 9.65 \times 10^4 \text{ C/mol} \quad \dots\dots\dots(14)$$

n_i is the mole number of migrated electrons in a reaction. ΔG_i corresponds to the electrical energy for electrolysis. Electricity consumption ratio for electrolysis, η_{el-i} , is defined as follows:

$$\eta_{el-i} = \Delta G_i / \Delta H_i \quad \dots\dots\dots(15)$$

Both V_i and η_{el-i} of Eqs. (12) and (6) are shown in Fig. 8. At higher temperatures, η_{el-CO} and η_{el-H_2} decreases. This implies that electrical energy consumption of CO₂ electrol-

Fig. 7. Chemical reaction equilibrium for H₂/CO₂/CO/H₂O reaction system under 100 kPa.

ysis becomes lower at a higher temperature like H₂O. V_{CO} becomes smaller than V_{H_2} at a temperature higher than 820°C. This implies that higher-temperature CO₂ electrolysis has a smaller demand for electrolysis than the H₂O electrolysis.

5. Application of ACRES

The value of ACRES is that the system uses carbon cyclically and does not emit CO₂ into atmosphere. The use of non-carbon primary energy sources is an essential requirement for a practical realization of ACRES. ACRES based on CO is the most effective recycling system in this evaluation. A high-temperature gas reactor type nuclear reactor (HTGR) is the most suitable energy source for ACRES because of the high-temperature output of up to 950°C with non-carbon emission and a sufficient amount of nuclear fuel to meet a country's demand.⁶⁾ High-temperature electrolysis of CO₂ using both heat and electricity outputs from HTGR is expected to have high efficiency than high-temperature electrolysis of water. The application of ACRES based on CO regenerated by high-temperature electrolysis driven by HTGR is proposed in Fig. 9. CO is used for the reduction of metal oxides or raw industrial materials (MO) into metals or reduced materials (M), and CO₂ is generated from the reduction process. The generated CO₂ is regenerated into CO during the high-temperature electrolysis using electricity and high-temperature (up to

Fig. 8. Temperature dependencies of electricity consumption ratio for electrolysis and electromotive force for electrolyses of CO₂ and H₂O (LHV base).

Fig. 9. ACRES with high-temperature CO₂ electrolysis driven by HTGR. (MO: metal oxides or raw industrial materials, M: metals or reduced materials).

950°C) heat. The electrolysis at 850°C has $\eta_{\text{el-CO}}$ of 65.5%. The ratio at 25°C under atmospheric pressure is 90.9%. Higher-temperature electrolysis can theoretically reduce 28% of the electricity consumption as compared to atmospheric electrolysis and has an advantage in terms of energy efficiency. The thermo-chemical reduction of CO_2 is an ideal process for a reduction method like water decomposition because it does not consume any electricity. ACRES introducing a thermo-chemical CO_2 decomposition process is shown in Fig. 10. High-temperature thermo-chemical CO_2 decomposition has the highest energy efficiency. Thermo-chemical water decomposition into H_2 requires multiple elemental reactions like the IS cycle.⁷⁾ A set of reactions for the thermo-chemical CO_2 reduction needs to be found in future.

Application of ACRES to an iron-making process is proposed in Fig. 11. The application is based on the process shown in Fig. 9. The system is driven by electricity and thermal energy generated from HTGR. Regenerated CO is used for the reduction of iron monoxide into pure iron. CO_2 generated from the reduction is regenerated into CO again by the CO_2 decomposition process. Oxygen as the by-products of CO can be a useful material for other oxidation processes.

An iron-making process using hydrogen is discussed in a previous work.⁸⁾ Iron(III) oxide (hematite), Fe_2O_3 , is employed as a raw material for the process in the following discussion. Fe_2O_3 reduction by hydrogen is an endothermic reaction and requires an external heat input.

In contrast, Fe_2O_3 reduction by CO is an exothermic reaction and proceeds spontaneously with self-heating.

CO reduction is advantageous for the iron-making process in comparison with hydrogen reduction. The reac-

tion is usual in conventional iron making. Direct reduction processes for Fe_2O_3 , in which CO and H_2 gasses are used directly for the reduction, have been discussed.⁹⁾ ACRES based on CO has a high affinity to such conventional processes. The iron-making process with ACRES is fundamentally a zero CO_2 emission process. This process could be a possible way to reduce CO_2 emission.

ACRES is an energy transformation system with energy consumption. The direct supply of a primary energy in an energy-demanding process without ACRES has the highest efficiency with the smallest energy loss. When a hydrocarbon recycled in ACRES is useful for energy demanding process compared with primary energies of heat or electricity, the ACRES is expected to have a practical value. In conventional chemical, steel, and other high-temperature manufacturing industries, CO has a higher affinity to processes than electricity and heat of primary energies. ACRES has the potential applicability in these industries as shown in Fig. 9. ACRES still requires efficient technologies for CO_2 recovery and hydrocarbon regeneration. The development of a practical process using ACRES and the optimization of the process will be the focus of the next study.

6. Conclusions

For an establishment of a practical ACRES, appropriate selections of a recycling hydrocarbon medium and a primary energy source for the system drive were important. CO was the most suitable as the recycle medium in ACRES because CO had a higher energy density and affinity than H_2 to chemical processes in conventional manufacturing industries. HTGR was a candidate of a primary energy source of ACRES. CO_2 electrolysis at a high temperature had a higher efficiency than low temperature electrolysis. ACRES with CO driven by the heat output from HTGR was the most applicable combination. Application of ACRES to an iron-making process had the possibility to realize a zero CO_2 emission process. ACRES was expected to be a candidate of energy systems for the establishment of carbon supply security in a modern society.

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Fig. 10. ACRES with thermo-chemical CO_2 decomposition driven by HTGR.

Fig. 11. ACRES for an iron-making process.