



Innovative hydrogen production by reaction integrated novel gasification process (HyPr-RING)

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Synopsis

A new hydrogen production process, named the HyPr-RING, has been proposed. Fundamental concept of the HyPr-RING is integration of water carbon reaction, water-gas shift reaction and CO₂ absorbing reaction in a single reactor. Firstly, thermodynamic analysis was done to judge the possibility to realize the process. It was found that high pressure and temperature condition, such as 20 MPa and 1000 K, is required to promote this integrated reaction.

Next, experimental verification of the new process was done under the high pressure and temperature reaction conditions. As the results, integration of above three reactions in a single reactor can be done successfully and produced a large amount of hydrogen as estimated by thermodynamic analysis. Experiments showed that organic materials including coal, heavy oil, biomass, plastics can be used in this process. In the gaseous phase, no pollutants such as H₂S, SO₂, COS are detected so that gas cleanup system is not required for power generation when this process is used.

Finally, a process design was made to estimate process efficiency. Theoretically, 1 mole of carbon can generate 2 moles of hydrogen and cold gas efficiency of this process estimated as more than 80 per cent. The process potentially reduces hydrogen production cost compared with the conventional hydrogen production methods.

Keywords: Hydrogen, Fossil fuel, Energy, Process, Supercritical water

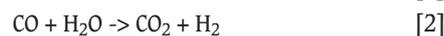
Introduction

Hydrogen will become important energy in the 21st century because it generates no pollutant and supplies sufficient energy for power generation, transportation and other applications. However, producing hydrogen consumes a lot of energy under the current technology which requires near twice as much as the energy produced from other energy sources: coal, oil, gas or electricity¹. To develop more appropriate methods based on sustainable energy sources will be very important. One of the effective methods for coal and organic waste recycle is to convert them to hydrogen, which is the most clean and useful energy source. We have developed a new hydrogen production process from coal and other organic materials. The principle, thermodynamic analysis, experimental verifi-

cation, process design and its performance analysis will be described in this paper.

Principle of a new hydrogen production process

It is well known that carbon-water reaction (Equation [1]) and water-gas shift reaction (Equation [2]) can be used to produce hydrogen from organic materials².



The reaction [1] converts C in coal or organic waste to CO, and the reaction [2] converts CO, produced by the reaction [1], to H₂ successively. A diagram of a typical conventional hydrogen production process based on coal is shown in Figure 1. In conventional processes, the reaction [1] takes place in the primary reactor with operating temperature above 1273 K, and the produced gases are then introduced into the secondary reactor, which is usually operated below 673 K, to promote the reaction [2]. The conventional processes requires two reactors to produce H₂ because reaction [1] and [2] proceed at different range of temperature. A gas cleanup system is usually required after the primary reactor to remove H₂S or COS which poison the catalyst in the second reactor. A CO₂ separator is also required to improve the purity of H₂ in the product gas.

From a viewpoint of heat balance, we must find a heat source since reaction [1] is a strong endothermic reaction. This is a reason why conventional gasification process is operated at high temperature. If the reaction [1] and [2]

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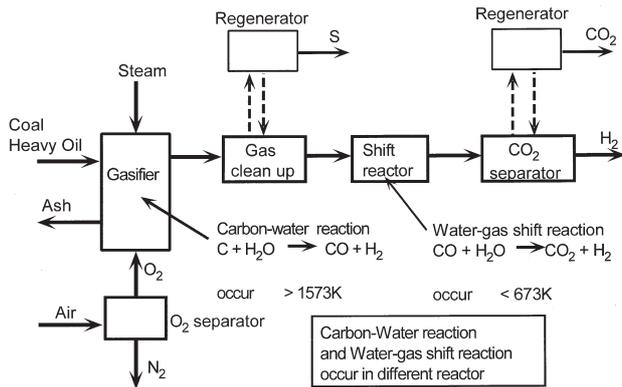
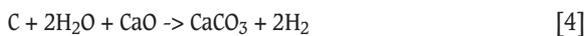


Figure 1—Typical flow sheet of present hydrogen production process based on coal

can be integrated within a single reactor by some means, hydrogen production process should be simplified. In order to integrate the two reactions in a single reactor, we propose the addition of CO₂ absorption reaction such as



By co-existence of reaction [3], chemical equilibrium of reaction [2] should be shifted to product side, and H₂ yield should be increased. By combining the reaction [1], [2] and [3], a general expression for this new reaction system is given as



Heat of above reactions is listed in Table I. It is shown that the heat generated in the reaction [3] is just the same magnitude of the heat required in the reaction [1]. The heat generated by reaction [3] can be directly supplied to gasification reaction [1] within the same reactor.

In order to know whether the integrated reaction [4] proceeds or not, a thermodynamic analysis was made. Figure 2 shows the thermodynamic equilibrium diagram of the equations [1], [2] and [3]. Calculations were made at the condition that CO and CO₂ concentration in gas phase was below 1000 ppm by dry base. It was found that high pressure and temperature condition, such as 20 MPa and 1000 K, is required to proceed the integrated reaction [4].

By coexistence of reaction [3], it is possible that reaction [1] proceeds at lower temperature and reaction [2] proceeds at higher temperature than each reaction equilibrium, even though higher operating pressure is required. Figure 2 shows the reaction equilibrium constants calculated, based on the thermodynamic data³. As shown in Figure 2 and Table I, the role of CO₂ absorber is as follows; (1) to improve hydrogen production, shifting the chemical equilibrium of reaction [2] by absorbing CO₂, (2) to supply heat required in gasification reaction [1].

Advantages of this new process are; (1) H₂ is the only product in gas phase, (2) exothermic and catalytic reaction may occur below 1173 K, (3) high H₂O partial pressure may enhance carbon conversion, and (4) CO₂ can be fixed simultaneously. This new hydrogen production process was named as the HyPr-RING (Hydrogen Production by Reaction Integrated Novel Gasification)⁴⁻⁸.

Reaction condition required by the HyPr-RING process is very severe for chemical process on the viewpoint of

materials for the reactor, control technology, handling of raw materials. However, development of a chemical process with this reaction conditions is realistic because some supercritical water processes have been already developed^{9,10}.

Supercritical water process such as supercritical oxidation of organic wastes, has very environmental friendly manner. Hetero atoms such as S, Cl, and F are fixed as a salt and no pollutant in the product gas is found, so that the HyPr-RING process is a quite clean hydrogen production process which requires no gas cleanup system.

Experimental

Since the HyPr-RING process is estimated as realistic by thermodynamic consideration, some experiments were carried out to verify with temperature and pressure range of 873-973 K and 10-100 MPa, respectively.

Experiments with micro autoclaves

Experimental procedure

Figure 3 shows a micro autoclave which is made of Inconel with 20 cm³ in volume. Coals and organic materials were crushed into 0.1 mm diameter. And then, 0.1 g of coal or organic materials, 0.6 g of CO₂ sorbent, 0.05 g of catalyst and some milliliters of water were mixed and put into the micro autoclave. Ca(OH)₂ powder was used as CO₂ sorbent and NaOH was used as catalyst. Organic materials used were coal, sewage sludge, wood chip, cellulose, glucose, plastics,

Table I

Heat of elementary reactions

1	$\text{C} + \text{H}_2\text{O} = \text{CO} + \text{H}_2$	H	$_{298} = 131.6\text{KJ}$
2	$\text{H}_2\text{O} + \text{CO} = \text{CO}_2 + \text{H}_2$	H	$_{298} = -41.5\text{KJ}$
3	$\text{CaO} + \text{CO}_2 = \text{CaCO}_3$	H	$_{298} = -178.1\text{KJ}$
Overall reaction:			
4	$\text{C} + 2\text{H}_2\text{O} + \text{CaO} = \text{CaCO}_3 + 2\text{H}_2$	H	$_{298} = -88.0\text{KJ}$

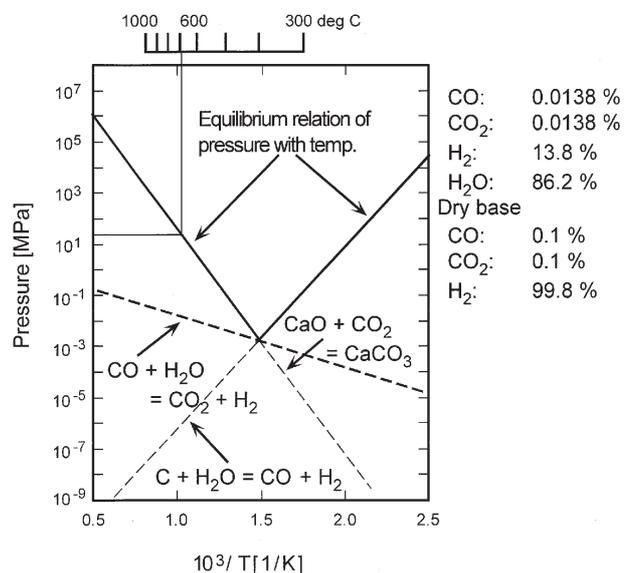


Figure 2—Chemical equilibrium of relating reactions

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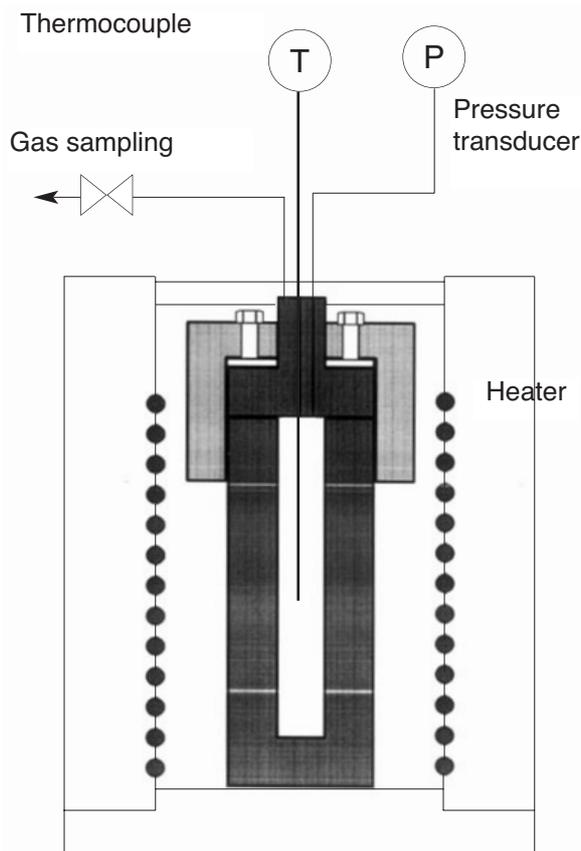


Figure 3—Schematic diagram of micro autoclave

benzene and graphite. Reaction pressure was controlled by changing the initial volume of water.

The autoclave was heated by an electric heater from the room temperature to the reaction temperature within 10 minutes and kept for 20 minutes at the temperature. And then, the autoclave was pulled up from the heater and cooled quickly down by air with a fan to quench the reaction. The volume of product gas was measured and its composition was analysed by a gas chromatograph. Also, liquid and solid residues remaining in the autoclave were weighed and carbon and CaCO_3 content of solid residue was analysed to know carbon balance.

Experimental results

Figure 4 shows the verification of principle of the HyPr-RING process when Taiheiyo coal was used at 923 K and 60 MPa. It can be seen that when the coal and water were put into the autoclave without both CO_2 sorbent and catalyst, gas was produced about 0.8 l/g-coal, measured at 298 K and 101 KPa. The gas contained about 55 per cent of H_2 , 13 per cent of CH_4 , 31 per cent of CO_2 and 1 per cent of C_2H_6 . About 0.2 per cent of CO was also found in the gas. With CO_2 sorbent ($\text{Ca}(\text{OH})_2$), a produced gas increased up to 1.3 l/g-coal. The composition of the gas was about 76 per cent of H_2 , 24 per cent of CH_4 and less than 1 per cent of C_2H_6 . CO_2 was 0.1 per cent and only trace CO was found in the product gas as estimated in thermodynamic consideration. With both CO_2 sorbent and the catalyst (NaOH), the product gas was increased more to 1.70 l/g-coal, including 85 per cent of H_2 ,

15 per cent of CH_4 and less than 0.1 per cent of CO_2 . In this case, carbon conversion exceeds more than 80 per cent and sulphur compounds such as SO_2 , H_2S , COS were not detected. Hydrogen should be only produced according to the overall reaction [4]. Methane, however, was produced in the experiments, which may be produced by the reaction between hydrogen and carbon.

Measurement of the reaction rate has not been completed. It is well known that steam gasification reaction rate is low in conventional reaction systems. However, higher reaction rates can be expected in the HyPr-RING process because more than 90 per cent of carbon conversion was achieved within 30 min. of reaction time.

Figure 5 shows the results when various organic materials including biomass, organic wastes, plastics were used as a raw material. It can be seen that these organic materials can produce hydrogen efficiently. In HyPr-RING process, major source of hydrogen produced is hydrogen atoms in water, and hydrogen gas is produced by the reaction between carbon atoms in the organic materials and

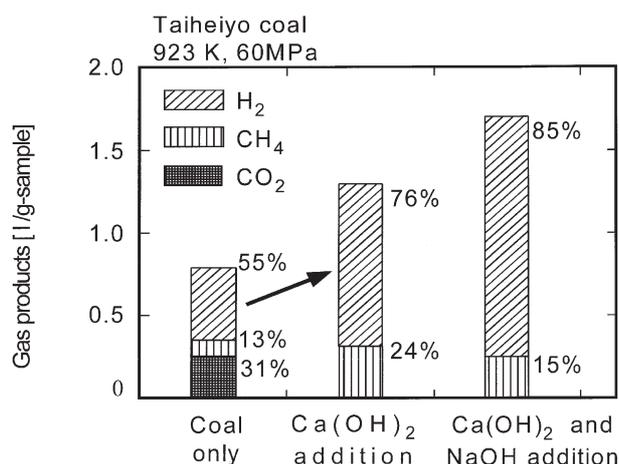


Figure 4—Effect of CO_2 sorbent and NaOH on the reaction between coal and steam

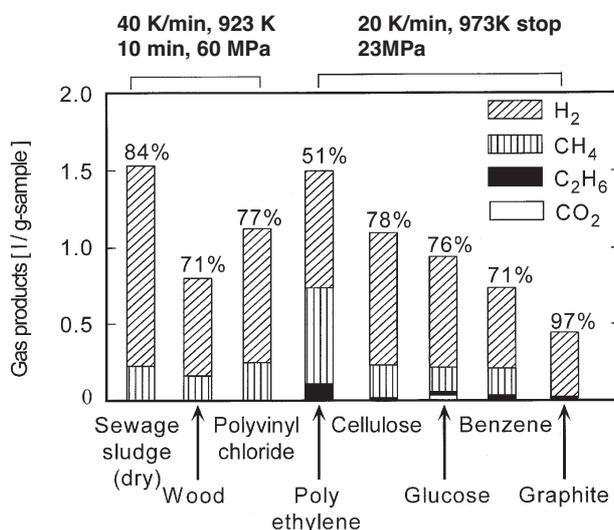


Figure 5—Gas production among various organic materials

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water. When graphite was used, both total gas volume and hydrogen volume was decreased. It is considered that hydrogen productivity depends not only on carbon content in raw material but also on the reactivity between the raw material and water. When polyvinyl chloride and sewage sludge which contain much chlorine or sulphur were used as a raw material, no chlorine or sulphur compounds were found in the product gas. S and Cl atoms should be fixed by $\text{Ca}(\text{OH})_2$ or NaOH and formed soluble salts.

Figure 6 shows the effect of pressure on the gas production. In theoretical consideration, the pressure higher than 20 MPa is required to produce hydrogen. A large amount of hydrogen was actually produced in lower pressure less than 20 MPa. And, Figure 7 shows the effect of temperature on the gas production, added both $\text{Ca}(\text{OH})_2$ and NaOH . About 0.70 l/g-coal gas was produced at 873 K, including 39 per cent of H_2 and 61 per cent of CH_4 . CO and CO_2 were not found in the gas. The carbon conversion rate was 63.2 per cent. At the temperature of 923 K, 1.70 l/g-coal gas was produced, including 77 per cent of hydrogen. The carbon conversion reached to 90 per cent. At the temperature of 973 K, product gas was increased more to 2.1 l/g-coal, including 89 per cent of hydrogen. Carbon in the coal was perfectly converted in this case. From the results of above experiments, it was shown that the effect of the reaction temperature was dominant in the HyPr-RING process. Gas compositions measured in the autoclave experiment were comparatively closed in equilibrium.

Experiment with flow reactor

Experimental procedure

Figure 8 shows the continuous flow reactor system. The system consists of a high pressure reactor, a high pressure steam generator, a condenser, gas/liquid and gas/solid separators. The high pressure reactor is made of iniconel, and inside surface of it was coated by Al_2O_3 to prevent the erosion caused by a high pressure and temperature environment. A sintered metal plate was attached to the centre of the reactor to support a fixed bed of a mixture of coal and CaO powder.

Mixture of 0.5 g of Taiheiyo coal and 3 g of CaO powder was charged on the plate. And, the system was pressurized by nitrogen gas to a desired pressure and the reactor was heated up to 923K by electric heaters. Coal was devolatilized during the heating period. Next, steam generated by the fluidized bed steam generator was introduced to the reactor. The temperature of steam was the same as that of the reactor. Generating gas volume and its composition were monitored in short intervals. The gas volume was measured by a mass flow meter and the composition was analysed by a gas chromatograph.

Experimental results

Figure 9 shows the change of temperature in the reactor and the volumes of hydrogen and methane at 9 MPa. Hydrogen is mainly produced with a trace of methane. Carbon conversion, calculated by the amount of hydrogen and methane, was reached to 63 per cent in 18 minutes after steam injection. When the steam was injected into the reactor, the temperature of the fixed bed was jumped about 100 degree C

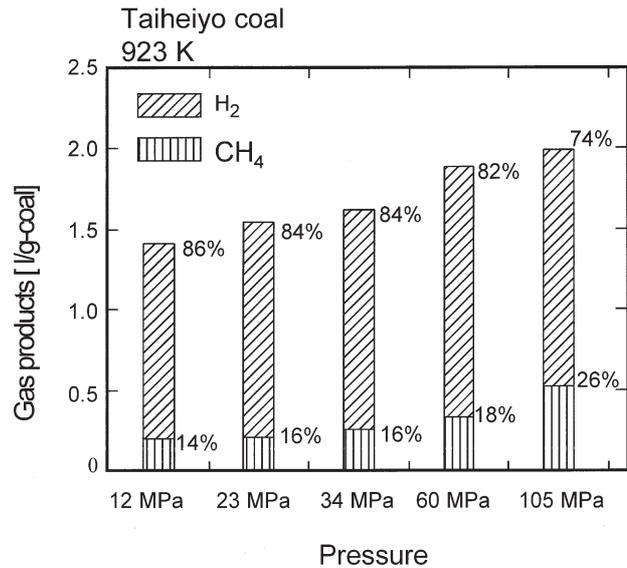


Figure 6—Effect of pressure on gas production

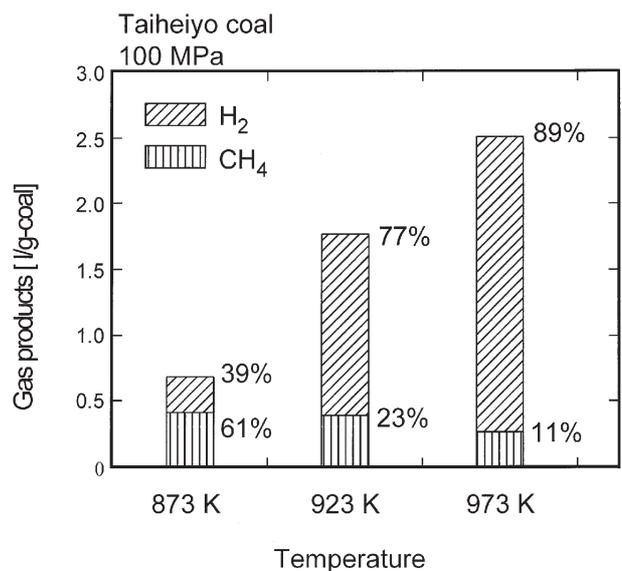


Figure 7—Effect of temperature on gas production

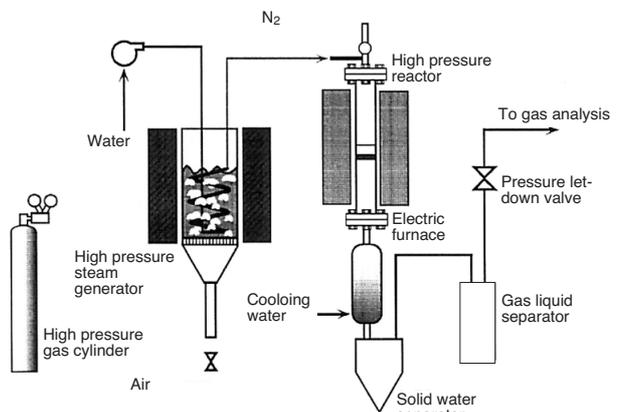


Figure 8—Schematic diagram of flow reactor system

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due to the reaction of calcium oxide with water. Methane can be produced during pyrolysis of coal and by the reaction of hydrogen with carbon. Methane was increased to about 2 per cent after steam injection as shown in Figure 9. It is considered that methane may be produced by the reaction between hydrogen and carbon as mentioned before.

Figure 10 shows hydrogen produced from coal with or without CaO in several experimental conditions. It can be seen that hydrogen produced with CaO is twice as much as that without CaO. And, the effect of particle size was smaller than the effect of temperature on the production of hydrogen.

In HyPr-RING process, calcination of CaCO₃ is very important to cycle CaO. It is well known that reactivity of CaO with CO₂ is decreased with regeneration times due to plugging of micro pore of CaO particle during each cycle¹¹. Reactivity change of CaO was tested by using a thermogravimetric analysis at atmospheric pressure in two different cases shown in Figure 11. In upper case, CaO reacts with steam and forms Ca(OH)₂, and reacts with CO₂. On the contrary, in lower case, CaO reacts directly with CO₂ and forms CaCO₃. The reactivity change of CaO is completely different for the two cases as shown in Figure 11. When CaCO₃ was formed via Ca(OH)₂, reactivity of regenerated CaO particle is kept high enough in more than 10 regeneration cycles. The reason to keep high reactivity may be explained by crystal structure of Ca(OH)₂. On the contrary, reactivity of CaO regenerated from CaCO₃, which is directly formed from the reaction between CaO and CO₂, is rapidly decreased with regeneration cycles. In this test, reactivity of regenerated CaO can be kept high with many regeneration cycles when Ca(OH)₂ forms in the cycle. According to thermodynamic analyses, formation of Ca(OH)₂ by the reaction between CaO and steam is dominant at 973 K and 7 MPa in the presence of CO₂. Thus, reactivity of regenerated CaO should be kept high under the condition.

Applications of the HyPr-RING process

The HyPr-RING process for power generation

Based on the theoretical and experimental verification, a new hydrogen production process, the HyPr-RING, was proposed. Figure 12 shows the simplified material and energy flow in the power generation system by the HyPr-RING process. Reactions between C and H₂O, CaO and CO₂ can be promoted in a single reactor. Two chemical loops are included in this process. The first chemical loop is the water cycle. Water reacts with organic materials and produces H₂ and CO₂. Hydrogen produced reacts with O₂ in air and forms water (H₂O-H₂-H₂O) and power. The second is calcium cycle. CaO absorbs CO₂ in the same reactor where water and carbon reacts, and releases heat (Q) during the formation of CaCO₃. This heat was consumed by water-carbon reaction, and CaCO₃ formed is transported to calcinator and regenerated to CaO again by calcination and releases CO₂. As calcination reaction is endothermic reaction, heat (Q) is absorbed during regeneration of CaCO₃ to CaO and released into the reactor which carbon reacts with water. This means the HyPr-RING process has a function converting heat energy to chemical energy. For the HyPr-RING process including power generation, raw materials supplied are the hydrocarbon,

water and oxygen and major products are hydrogen, power and pure CO₂. This seems very excellent power system.

A flow diagram of the HyPr-RING process is shown in Figure 13. Comparing with the conventional hydrogen production process shown in Figure 1, the HyPr-RING process is quite simple and has following advantages, (1) reaction takes place in single reactor, (2) low temperature gasification occurs, (3) no gas cleanup system is required, (4) CO₂ can be withdrawn by calcination which is very simple unit operation.

One of the most important issues in utilization of carbon rich fossil fuels may be how to reduce CO₂ emission. Thermal efficiency can be improved when hydrogen produced by the HyPr-RING process is used with the excellent power system such as fuel cell. Therefore, CO₂ emission per unit power can be reduced. An example of the combination of the HyPr-RING

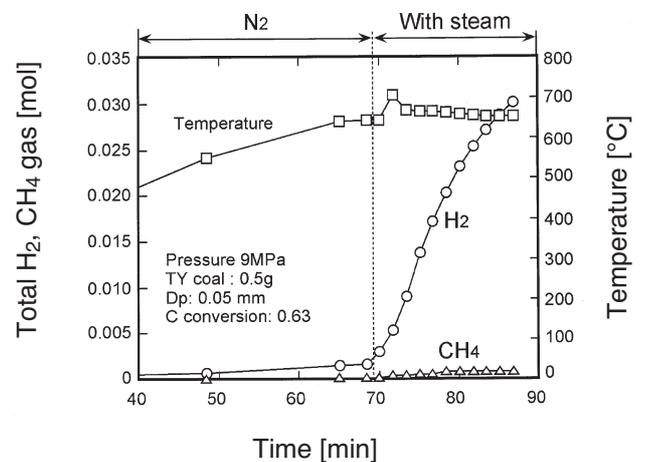


Figure 9—Gas production with steam injection

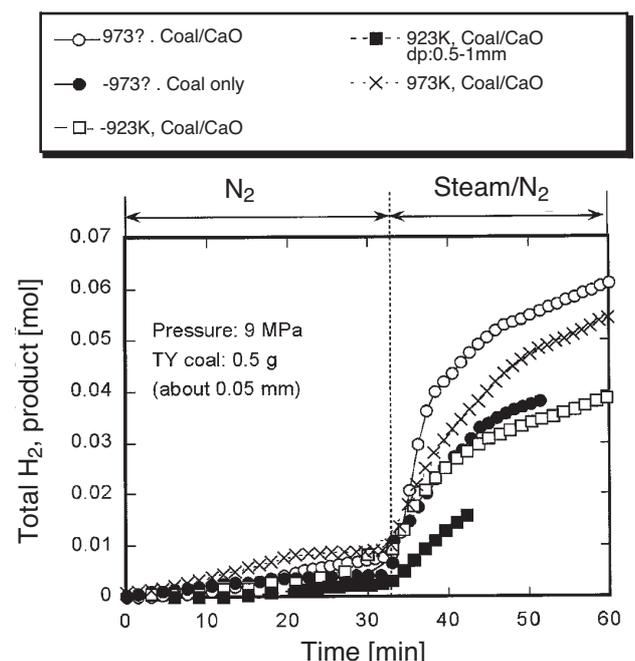


Figure 10—Effect of CaO addition and temperature on H₂ production with continuous flow reactor

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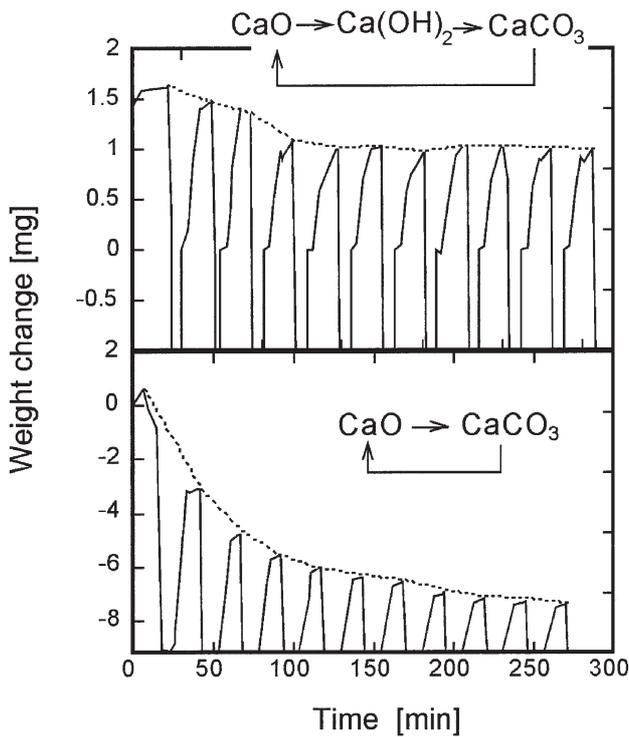


Figure 11—The change of reactivity in regeneration of CaCO₃

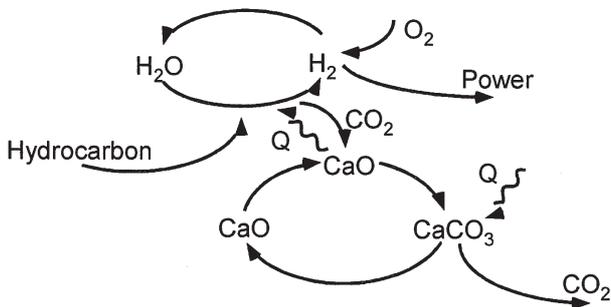


Figure 12—Mass and heat flow in the HyPr-RING process

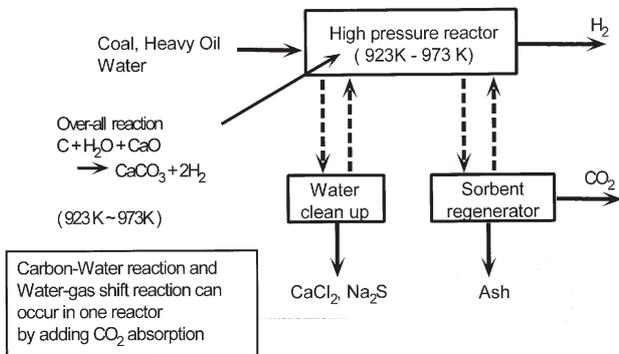


Figure 13— Flow sheet of the HyPr-RING process

process and the hydrogen gas turbine power generation system is illustrated in Figure 14. In usual hydrogen gas turbine power generation system, waste heat containing in

the outlet of gas turbine is recovered by a steam generator and power is also generated by a steam turbine. On the contrary, in the HyPr-RING process, the waste heat from gas turbine is used as a heat source of the regenerator as shown in Figure 14. Thermal efficiency can be improved comparing with the conventional hydrogen gas turbine power generation system because heat is regenerated to chemical energy. A system of combined HyPr-RING process and high temperature fuel cell can be also made as same as the system shown in Figure 14.

Mass and energy balances in the HyPr-RING process

Mass and energy flow were calculated to evaluate the process performance of the HyPr-RING process which coal is used. Figure 15 shows a calculation result of the mass and energy flow for a plant using 1 t/hr of coal. Japanese domestic coal (Taiheiyo coal) having the heating value of 25.8 MJ/kg is used in the calculation. In this case, reaction pressure is set as 10 MPa and a dry feeding system for coal and regenerated CaO is employed. By using the dry feeding system, total volume of water is reduced and thermal efficiency is improved. Carbon conversion at main reactor is set as 53 per cent and remaining unreacted carbon is burnt-up at the regenerator by air or oxygen and CaCO₃ is regenerated to CaO. Calculation shows that cold gas efficiency is about 82 per cent, which is higher than those of the conventional hydrogen production processes. The main reason is that the heat absorbed by CaO in the regenerator is released during absorbing CO₂ by CaO in the reactor and used directly in the

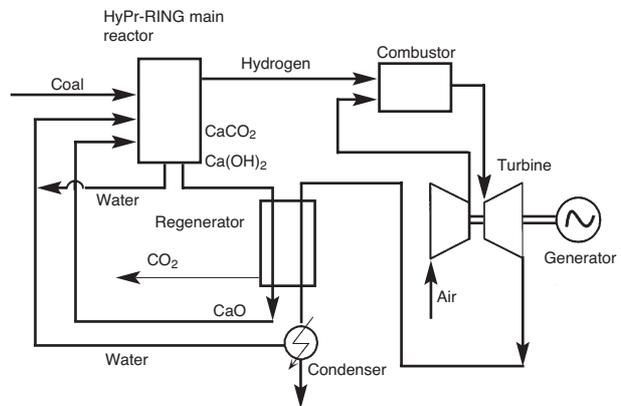


Figure 14— Power generation system by a combination of the HyPr-RING process and hydrogen gas turbine

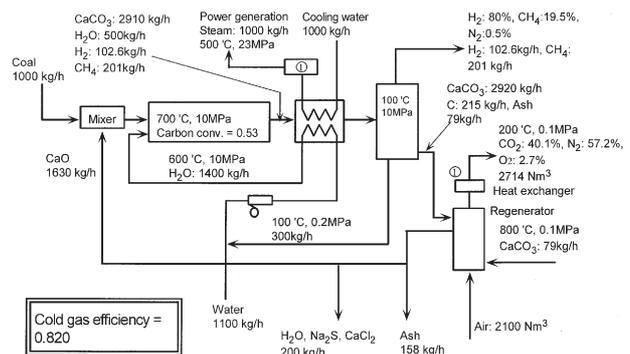


Figure 15— Material flow of a typical HyPr-RING process

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gasification reaction in the same reactor. The possibility to get higher thermal efficiency in the hydrogen production process based on the coal seems to be very attractive.

Conclusions

A new hydrogen production process, named the HyPr-RING, has been proposed. Fundamental concept of the process is integration of water carbon reaction, water-gas shift reaction and CO₂ absorbing reaction in a single reactor. By the theoretical and experimental verifications, and process performance analysis, the propriety of the concept of the HyPr-RING process was confirmed. Advantages of the HyPr-RING process are as follows.

- ▶ Coal and other organic materials can be converted to gas containing 80 per cent of hydrogen and 20 per cent of methane efficiently in a single stage reactor.
- ▶ Product gas is sulphur free and no gas cleanup systems are required. Hydrogen produced can be directly used with a hydrogen gas turbine and a fuel cell.
- ▶ Cold gas efficiency exceeds 80 per cent. This is higher than those of conventional processes.
- ▶ The HyPr-RING process can accept high water content materials such as brown coal, sub-bituminous coal, and also any other organic materials.
- ▶ CO₂, which is the by-product, can be withdrawn by very simple operation.

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