5A1. Hydrogen Production by Reaction Integrated Novel Gasification Process (HyPr-RING)

Research and development: Japan Coal Energy Center; National Institute of Advanced Industrial Science and Technology; Ishikawajima-Harima Heavy Industries Co., Ltd.; Babcock Hitachi K.K.; Mitsubishi Materials Corporation; JGC Corporation

Project type: Subsidized by the Ministry of Economy, Trade and Industry

Period: 2000-2008 (9 years-planned)

Technology overview

1. Background

In addition to its position as the world's most abundant energy reserve, coal is used as an important primary energy source due to its economic advantages as well. Future consumption is expected to increase with economic growth as well as an increasing population.

Meanwhile, in response to global warming caused by CO_2, there is an earnest need to develop technology to use coal cleanly and more efficiently. In response, a process called HyPr-RING that enables the hydrogen necessary for future hydrogen-energy communities to be produced from coal is now under development for commercialization.

2. Theory of HyPr-RING process

HyPr-RING is a process in which a CO_2-sorbent, CaO, is directly added into a coal gasifier and the CO_2 generated by coal gasification is fixed as $CaCO_3$, together with the produced hydrogen. The reaction between CaO and H_2O produces the heat necessary for subsequent coal gasification in the gasifier. Within the gasifier, a series of reactions from equation (1) to equation (4) and the overall reaction of equation (5) take place.

$$CaO + H_2O \rightarrow Ca(OH)_2 ; \quad \Delta H^{o}_{298} = -109 kJ/mol \quad (1)$$

$$C + H_2O \rightarrow CO + H_2 ; \quad \Delta H^{o}_{298} = 132 kJ/mol \quad (2)$$

$$CO + H_2O \rightarrow CO_2 + H_2 ; \quad \Delta H^{o}_{298} = -41.5 kJ/mol \quad (3)$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O ; \quad \Delta H^{o}_{298} = -69 kJ/mol \quad (4)$$

$$C + 2H_2O + CaO \rightarrow CaCO_3 + 2H_2 ; \quad \Delta H^{o}_{298} = -88 kJ/mol \quad (5)$$

This overall reaction is an exothermic reaction with C, H_2O, and CaO as initial reactants. This means that, in theory, there is no need for external heat. It was also discovered that CO_2 fixation enhances reactions (2) and (3) for H_2 generation. Figure 1 shows the process concept of HyPr-RING. $CaCO_3$ is regenerated by calcination into CaO for its recycle as a sorbent. Most of the heat energy required for calcination is carried as the chemical energy of CaO and made available for coal gasification to produce H_2 in the gasifier.

How is this different from conventional gasification?

Conventional gasification secures the heat necessary for gasification through a partial combustion of coal, with a reaction taking place in the gasifier expressed by the following equation:

$$C + 0.5O_2 + 0.5H_2O \rightarrow 0.5CO_2 + 0.5CO + 0.5H_2 \quad (6)$$

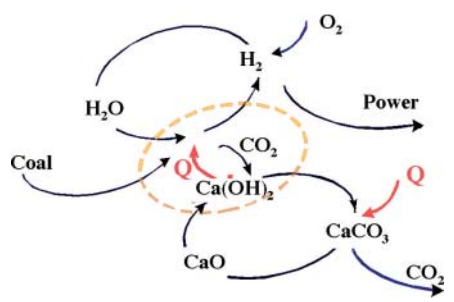


Fig. 1 Concept of HyPr-RING process

Gasification gas must be sent through a low-temperature shifter and then exposed to a low-temperature absorbent such as amine for CO_2 separation. At that time, the amount of CO_2 gas separated is one mole per mole of hydrogen.

On the other hand, the HyPr-RING process uses dry CaO to absorb CO_2 in the furnace (650°C, 30 atm). In this case, heat is released during CO_2 absorption to maintain a high temperature in the gasifier.

Here, post-CO_2 absorption $CaCO_3$ is returned to CaO by calcination (reproduction) and, at that time, 50-80% of the thermal energy required is converted into CaO for reuse in the gasifier (Fig. 2).

As seen from equation (5), 2-mole hydrogen production from one mole of carbon is another important feature.

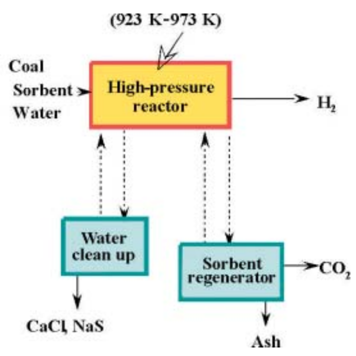


Fig. 2 Hydrogen production using HyPr-RING process

Table 1 CO_2 separation energy and temperature level

	HyPr-RING (CaO absorption process)	Partial combustion (Monoethanolamine absorption process)
Heating value of carbon ($C \rightarrow CO_2$)	393 kJ/mol	393 kJ/mol
CO_2 absorption energy	178 kJ/mol	84.5 kJ/mol
CO_2/H_2 generation ratio	0.5 mol/mol	1 mol/mol
CO_2 separation energy per mole of H_2 generated	89 kJ/mol	84.5 kJ/mol
Temperature level	973-1073 K	about 323 K

3. Characteristics of HyPr-RING process

Cold gas efficiency

The HyPr-RING process gasifies the easy-to-gasify portion of coal under low-temperature (600-700°C) conditions into hydrogen and uses the remaining difficult-to-react char as fuel for $CaCO_3$ calcination.

Figure 3 shows an example of a HyPr-RING process configuration with a fluidized-bed gasifier and an internal combustion-type calcining furnace. For product gas composition of 95% H_2 and 5% CH_4, the cold gas efficiency proved to be about 0.76.

CaO absorbent

At the gasifier inlet, where the temperature is low, CaO first reacts with H_2O to produce $Ca(OH)_2$, providing heat-to-coal pyrolysis. Then, at a high-CO_2 partial pressure region, $Ca(OH)_2$ absorbs CO_2 to produce $CaCO_3$, and releases heat. This heat is used for the gasification of char. To prevent CaO from becoming less active due to high-temperature sintering, a method of absorbing CO_2 in the furnace, by way of $Ca(OH)_2$, is employed. Gasification at a temperature as low as possible is also employed to prevent the eutectic melting of calcium minerals. In such cases, unreacted product carbon can be used as a heat source for CaO reproduction.

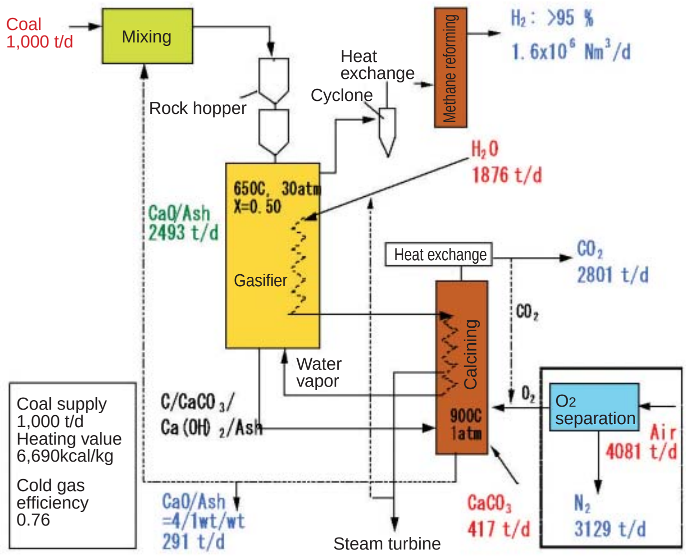


Fig. 3 Analysis of HyPr-RING process

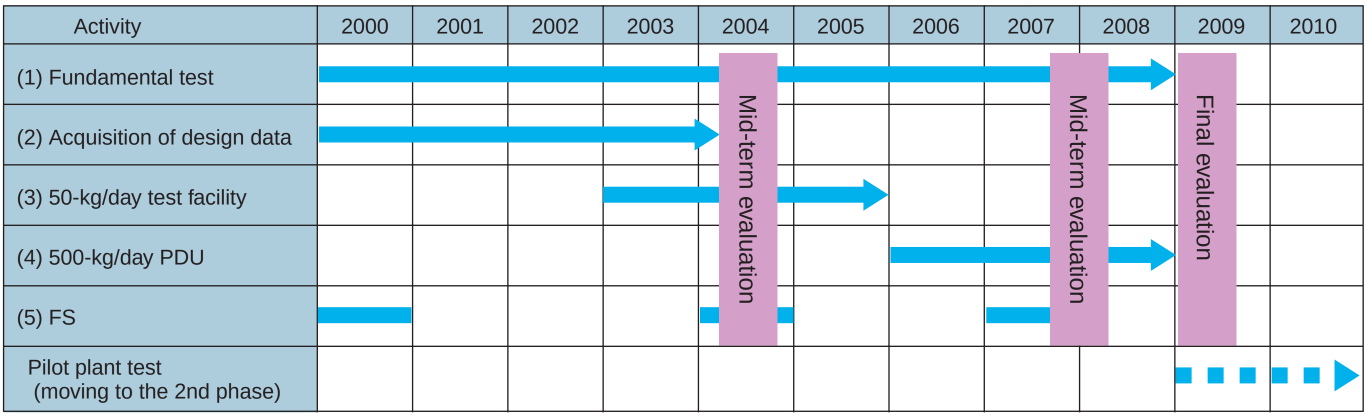
4. Project overview

Under this project, which commenced in 2000, process configuration identification and FS through testing with batch/semi-continuous equipment were paralleled with a variety of factor tests required. In and after FY2003, it is expected that 50-kg/day (coal base) continuous test equipment will be fabricated for continuous testing and then, based on the results, running tests and a FS of a 5 ton/day-scale pilot plant are to be carried out in and after 2006 to establish a commercialization process. Table 2 shows development targets of the project and Table 3 shows, the project timetable.

Table 2 Targets

Item	Target
1. Gasification efficiency 2. Product gas purity 3. CO_2 recovery	1. Cold gas efficiency: 75% or greater 2. Sulfur content of product gas: 1ppm or less 3. High-purity CO_2 recovery rate: 40% or greater of inputed coal carbon to be recovered (per-unit of energy CO_2 exhaust to be less than that from natural gas)

Table 3 Development timetable



References

1) Shiying Lin, Yoshizo Suzuki & Hiroyuki Hatano, Patent No. 29791-49, 1999.

2) Energy Technology and the Environment, Editors: A. Bisio and S. Boots, John Wiley & Sons, New York, 1995.