The high efficiency CO_2 separation by the innovative combustion concept "Chemical Looping Combustion"

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Abstract

Chemical Looping Combustion is a novel concept to capture CO_2 simultaneously with generating the heat. An originality of this technology is the utilization of metric particles which transport oxygen from the combustion air to the fuel. These metric particles are called oxygen carrier.

Experimental studies are conducted using a cyclic system of reactor where oxidation and reduction are exchanged in a several residence time. Solid particles of Fe_2O_3 are poured into reactor. It can be observed that reaction rate depends greatly on residence time. Reduction takes longer than oxidation, so it has an influence on a reactor size.

Moreover, to evaluate the durability of the oxygen carrier, over 60 times continuous redox was tested. It can be confirmed that the peak of the CO_2 concentration remains unchanged, so activity of the oxygen carrier was kept in this term.

Background

Recently, the influence of global warming appears obvious causing many natural disasters such as great typhoons, floods, tornados and long term droughts.

After the Great East Japan Earthquake on March 11, 2011, the direction of national energy policy is discussed all over the world, concerning the introduction and operation of nuclear power plants. In Germany, it is decided to stop all of 17 nuclear power plants until 2022. In Italy, the referendum results that 94% of voters reject to continue the operation of nuclear plant. At the Fukushima in Japan, an effort is made to shut down nuclear plant safely obtaining much of support from the international society. We make a grateful acknowledgement for that.

However, reduction of CO_2 emissions is one of the most important issues which the international society should make effort cooperatively.

There are three effective measures to reduce CO_2 emissions.

(1) Energy sources without CO_2 emissions
ex) nuclear power, natural energy, hydrogen etc.

(2) Energy systems with lower CO_2 emissions
ex) shift from oil to natural gas, high efficiency, smart energy network etc.

(3) CO_2 capture and storage

Tokyo Gas Co., Ltd., is a first city gas supplier to introduced LNG in 1969 and has been trying to reduce CO_2 emissions for more than 40 years. Particularly in an industrial field, where a large volume of energy is consumed, we developed a novel combustion technologies such as FDI regenerative burner [1] [2], radiant tube burner and oxy-fuel combustion [3] [4]. Those technologies enhance the high efficiency of energy and reduce CO_2 emissions.

Considering about ages after 2020, and taking advantage of combustion technologies, we have contended with separating and capturing CO_2 generated from natural gas in an industrial field. Chemical absorption technologies were developed several years ago to capture CO_2 from the flue gas at the power plant. Some of the power plants have already operated with capturing CO_2.

For the high temperature industrial furnaces, we try to apply the oxy-fuel combustion to save energy consumption and storage CO_2 [5]. However, it is difficult to introduce this technology to the low temperature range. Therefore, new technology is required to separate and capture CO_2 from applications, such as boiler, with high efficiency.

Purpose of this study

We focused on the technology,"Chemical Looping Combustion (CLC)" that captures CO_2 simultaneously with generating the heat. This new concept combustion overturns the idea of conventional one that mixes fuel and air. It is characterized by using metal particles as oxygen carrier. Thermal NOx hardly occurs because combustion flame does not exist.

Moreover, fuel reacts with O_2 from metal particles, so only CO_2 and H_2O occur. For this reason, it is easily to separate CO_2 in high concentration. This technology is the next generation combustion system with the potentiality of zero emission.

We promote technological developments to apply CLC system to boiler and so on. CO_2 can be captured at high efficiency onsite.

Principle of Chemical Looping Combustion

The Chemical Looping Combustion consists of two reactions, "oxidation of metallic particles" and "reduction of oxidized metallic particles". In the system, combustion concludes by physically cycling the particles between the two reactors.

In the oxidation reactor, the exothermic reaction occurs from the metal oxidation.

$2M + O_2 \rightarrow 2MO$

In the reduction reactor, the endothermic reaction occurs from reduction of the oxidized metal.

$4MO + CH_4 \rightarrow 4M + CO_2 + 2H_2O$

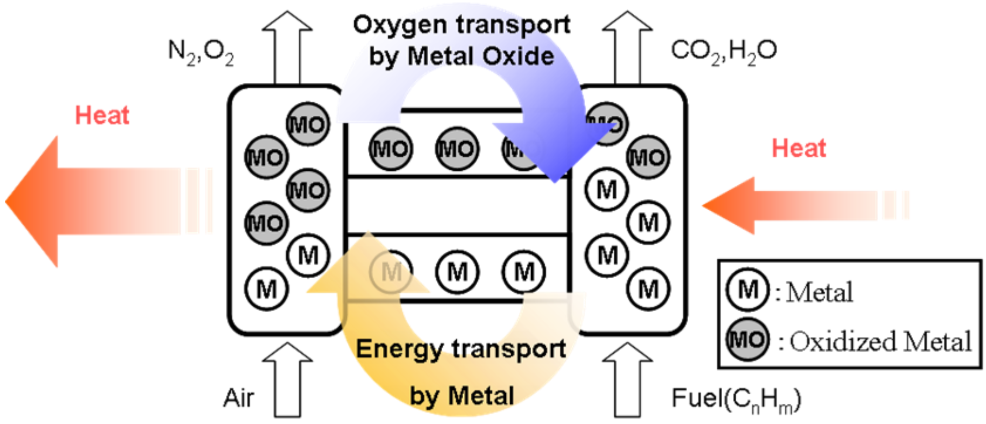

Fig. 1 Conceptual diagram of Chemical Looping Combustion

The Chemical Looping Combustion has several unique features as below.

(1) Hydrocarbon such as Methane work as reductant on oxidized metals, and this metal principle generates heat from oxidation

(2)In part of oxidation, only air and metal particles supply the reactor. It is relatively low of combustion temperature, so CLC system emits hardly thermal NOx

(3)In the reduction reactor, there are only two components, Hydrocarbon and O_2 from the oxidized metal. So flue gas from the redactor is CO_2 and H_2O. For removing H_2O by cooling flue gas, more than 90% concentration of CO_2 can be separated in the reduction reactor. The candidates of oxygen carrier are metals as Ni, Cu, Fe, Co, and Mn, and those are supported by Al_2O_3, SiO_2, ZrO_2, and TiO_2 and so on.

A Pioneer of this technology is Professor Ishida of Tokyo Institute of Technology in Japan [6]. He succeeded in the reaction experiment at 1200℃ using Fe_2O_3 supported alumina that the diameter about 100 μm in 1980's. Now, this technology is studied actively in Europe. GDF SUEZ reported about CO_2 capturing for using CLC in power plant [7].

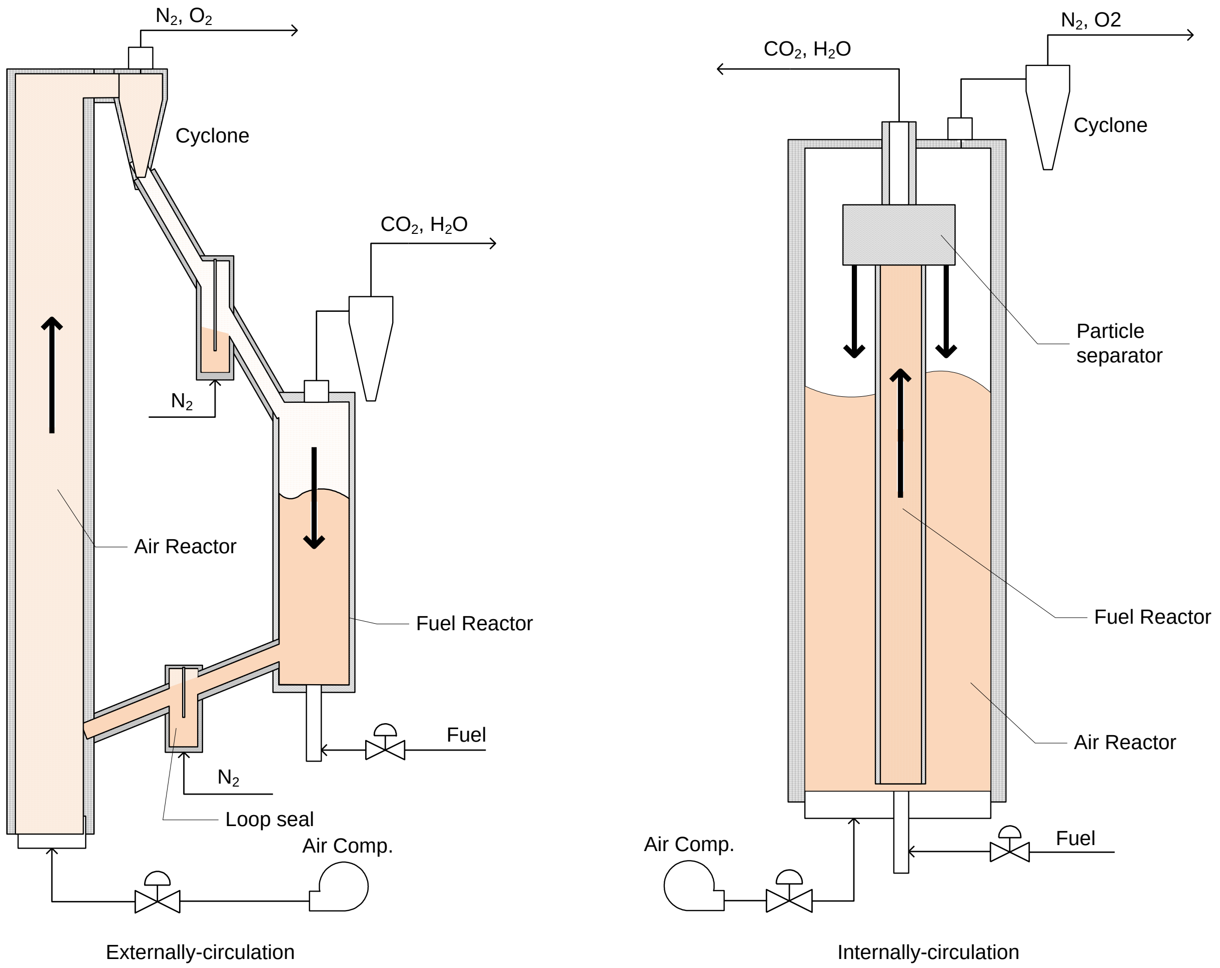

Fig. 2　Comparison of cycle system

The metal particles circulate between the two reactors, oxidation and reduction. The size of metal particles is about 50～200 μm. There are two types of circulation, internally-circulating fluidized bed and externally one. Almost all researchers study the later. We study both types to use onsite.

Experimental results

To clarify a reaction characteristic in a reactor for design of the pilot scale reactor, a redox reaction was carried out with switch type test equipment. Schematic diagram of the experimental equipment is shown in Fig. 3. Moreover, Fe_2O_3 supported Alumina (Al_2O_3) was used as the oxygen carrier that the diameter about 100μm as shown in Fig. 4. These particles were developed by Ohba laboratory of Kanagawa Institute of Technology.

In the test, N_2 gas was used as purge gas, and natural gas（16.6%/ N_2 balance） and air were used as reduction gas and oxidation gas respectively.

The test condition is shown in Table 1. Six case tests were carried out, these tests were changed the gas volume flow and amount of reduction gas. The results are shown in Table 2. It is understood that reaction rate depends on the residence time. In the same residence time, as the amount of the reduction gas increases, a reaction rate comes down therefore the oxidation metal proportion decreases in the reactor.

The gas analysis result of the continuous reduction test (in case 1-2; 6 times) is shown in Fig. 5. It can be confirmed that CO_2 concentration in flue gas decreases and the concentration of CH_4 and CO increases because the proportion of the oxidation metal decreases while reduction repeating. Moreover, CO_2 concentration increase immediately after air was injected because of carbon deposition on the carrier. O_2 concentration is almost 0% for a while after air is injected. Oxidation and reduction gas volume flow are equal, so oxidation is remarkably earlier than reduction.

As shown in Table 2, in case residence time was about 12 seconds (case3-1), reaction rate was more over 97%. The results of gas analysis were shown in Fig. 6. Un-reacted CH_4 and CO were hardly found.

Fig. 7 shows the gas analysis results of continuous redox test (63 times) on the condition of case 3-1 to evaluate the durability of the oxygen carrier. It can be confirmed that the peak of the CO_2 concentration remains unchanged, so activity of the oxygen carrier was kept in this term.

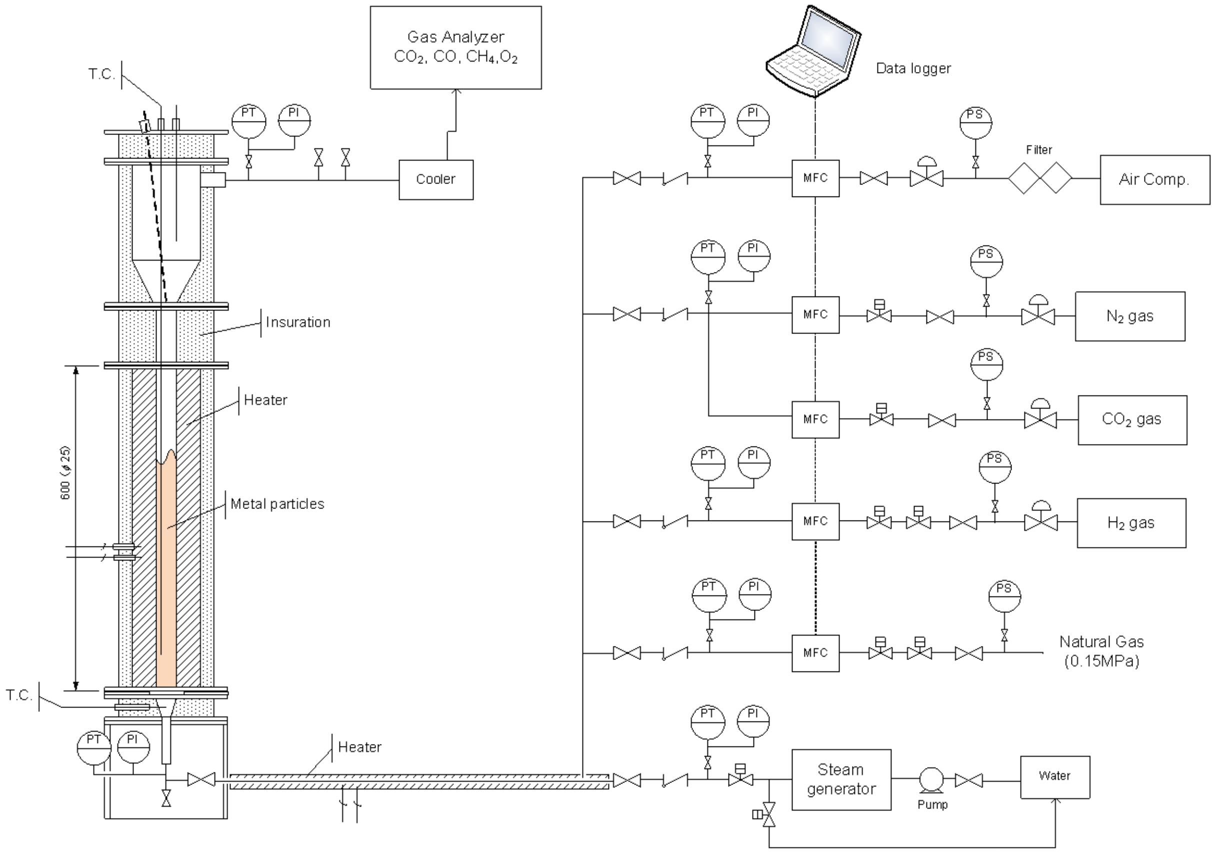

Fig. 3　Schematic diagram of CLC test system

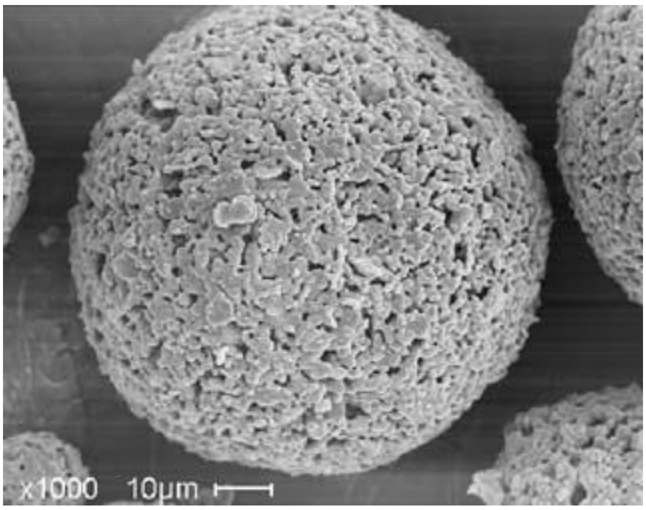

Fig. 4　Metal particles (oxygen carrier)

Table 1 Test condition

Parameters	Operating Condition
Reactor	ϕ25.4mm × 600mm
Particles	Fe_2O_3 / Alumina（25:75）
Fill amount and height	250g（300mm）
Temperature	900℃(1173K)
Oxidation gas	Air
Reduction gas	*Natural gas / N_2 Balance (Natural gas 16.6%)
Purge Gas	N_2

*CH_4 89.6% C_2H_6 5.62% C_3H_8 3.43% C_4H_{10} 1.35%

Table 2 Reaction rate in Six case test

		case 1-1	case 1-2	case 2-1	case 2-2	case 3-1	case 3-2
volume flow	liter/min	1.2		0.48		0.24	
reduction time	s	30	180	75	450	150	900
amount of reduction gas	liter	0.1	0.6	0.1	0.6	0.1	0.6
velocity	cm/s	12.3	12.3	4.9	4.9	2.5	2.5
residence time	s	2.44	2.44	6.09	6.09	12.18	12.18
reaction rate	-	63.0%	45.7%	85.7%	54.0%	97.6%	77.2%

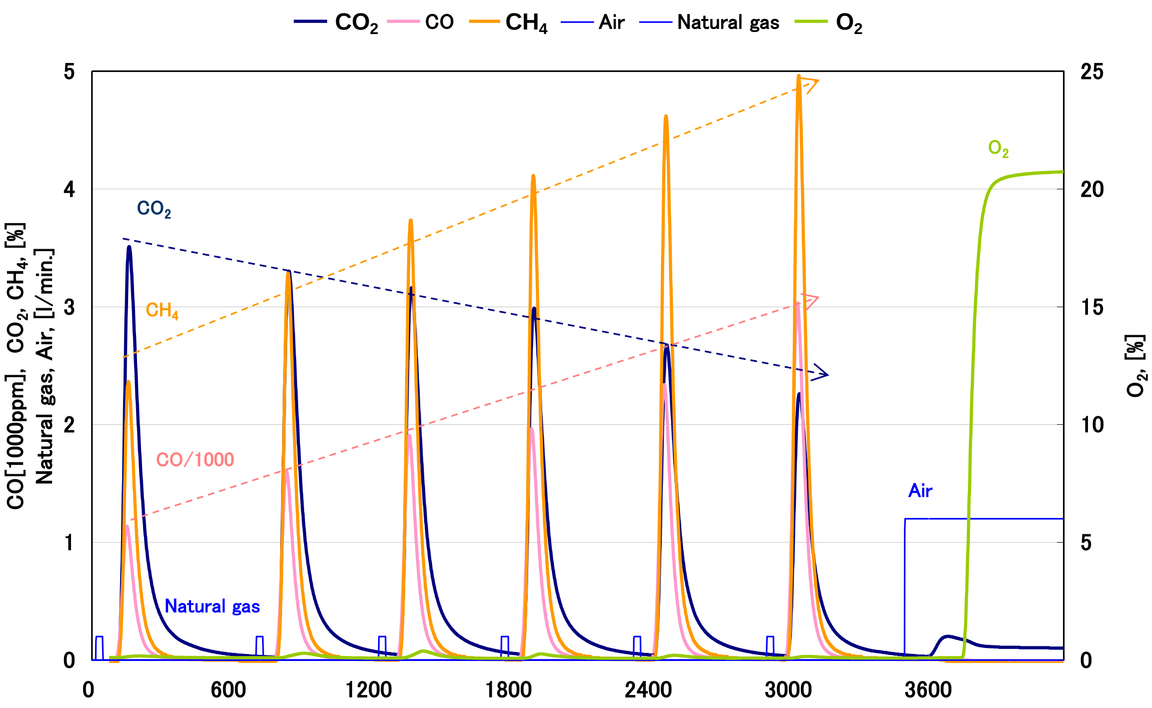

Fig. 5 Gas analysis of continuous reduction test (case1-2)

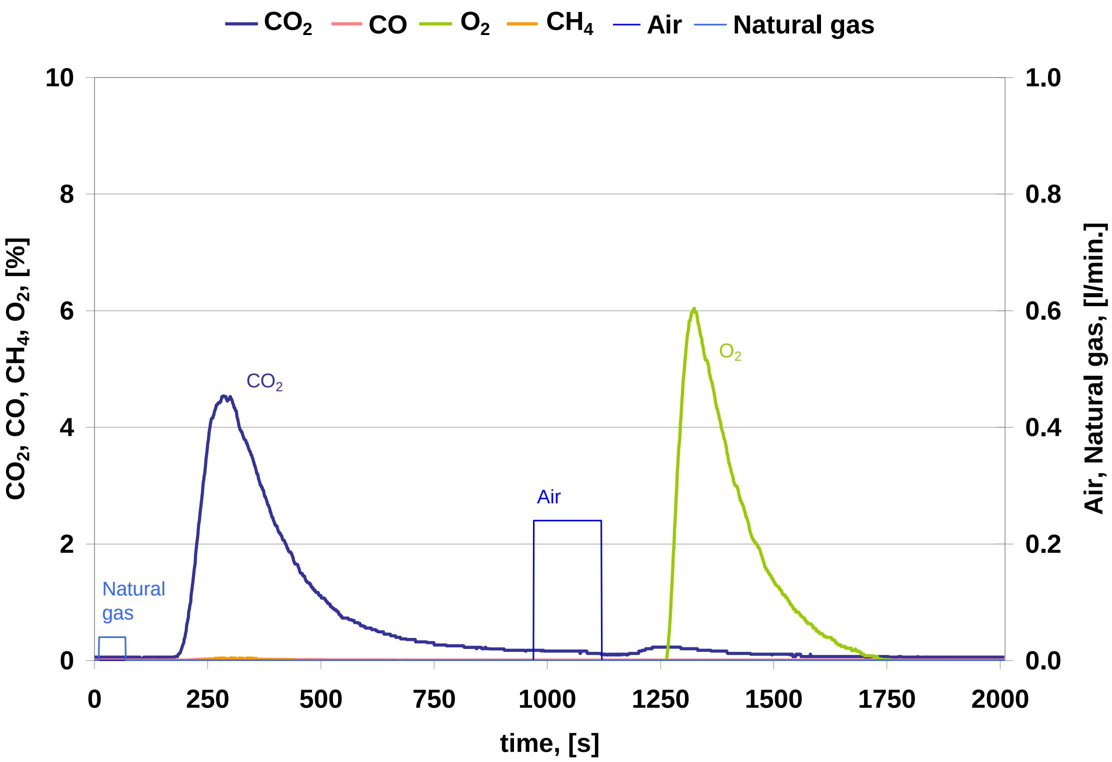

Fig. 6 Gas analysis of redox test (case3-1)

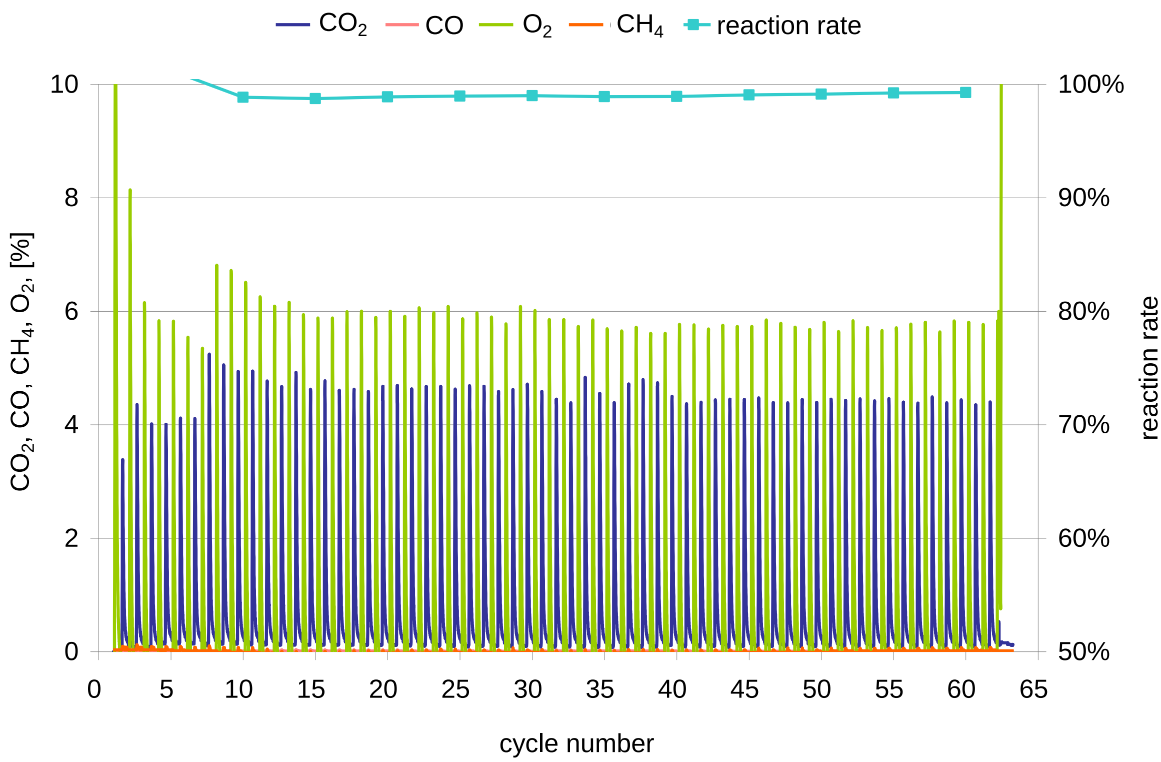

Fig. 7　Gas analysis of continuous redox test (case3-1)

Future Plan

- Investigation of reaction speed and oxygen transportation capacity of oxygen carrier by TG-DTA
- Investigation of fluidized state and circulation state in the reactor with cold flow equipment
- Durability evaluation of oxygen carrier by additional continuous test for a long period of time

Moreover, to evaluate other oxygen carriers except iron is planned. And Feasibility Study of the CLC boiler system is also scheduled.

Fig. 8 shows the schematic of CLC boiler system that generates steam, the hot air and CO_2 onsite. We think that target of this system is steel, chemistry, or food industry fields, and the capacity of CLC system is assumed as 1MW - 50MW.

We will develop this CLC system to introduce in a market after 2020.

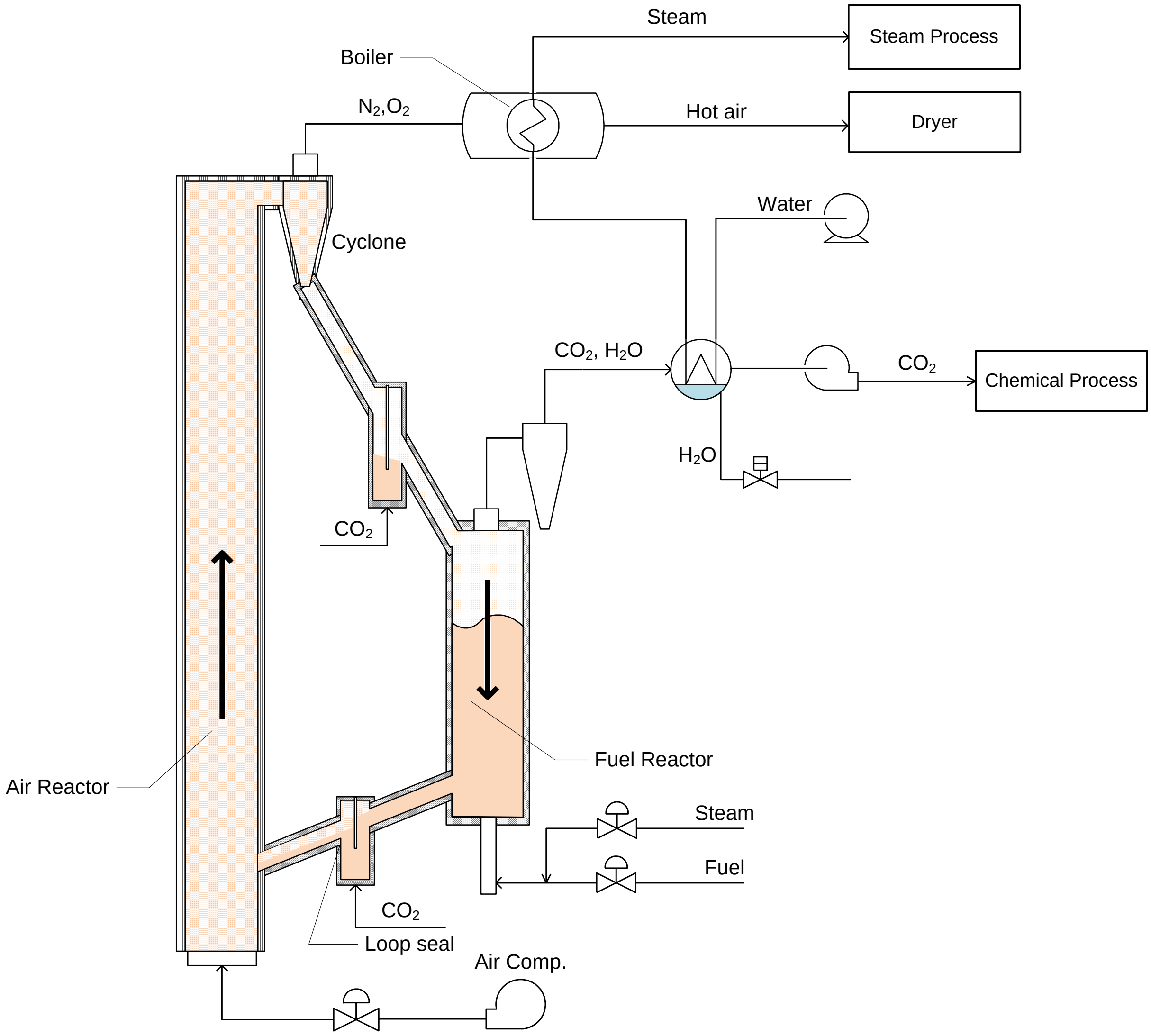

Fig. 8 CLC boiler system

Acknowledgment

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