

Effect of solid residence time on CO₂ selectivity in a semi-continuous chemical looping combustor

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Abstract—Chemical looping combustion (CLC) is a promising technology for fossil fuel combustion with inherent CO₂ capture and sequestration, which is able to mitigate greenhouse gases (GHGs) emission. In this study, to design a 0.5 MW_{th} pressurized chemical looping combustor for natural gas and syngas the effects of solid residence time on CO₂ selectivity were investigated in a novel semi-continuous CLC reactor using Ni-based oxygen carrier particle. The semi-continuous chemical looping combustor was designed to simulate the fuel reactor of the continuous chemical looping combustor. It consists of an upper hopper, a screw conveyor, a fluidized bed reactor, and a lower hopper. Solid circulation rate (G_s) was controlled by adjusting the rotational speed of the screw conveyor. The measured solid circulation rate increased linearly as the rotational speed of the screw increased and showed almost the same values regardless of temperature and fluidization velocity up to 800 °C and 4 U_{mf}, respectively. The solid circulation rate required to achieve 100% CH₄ conversion was varied to change G_s -fuel ratio (oxygen carrier feeding rate/fuel feeding rate, kg/Nm³). The measured CO₂ selectivity was greater than 98% when the G_s -fuel ratio was higher than 78 kg/Nm³.

Keywords: Chemical Looping, Oxygen Carrier, Fuel Conversion, CO₂ Selectivity, Solid Residence Time

INTRODUCTION

The need to develop greenhouse gas (GHGs) mitigation technologies is increasing in response to climate change. To ensure a sustainable supply of energy while minimizing GHGs emissions, the use of renewable energy and nuclear energy are considered as viable alternatives [1,2]. Despite the fact that alternative energy sources are considered as a clean form of energy without emission of pollutant, approximately 80% of world energy consumption through 2040 is projected to be related to fossil fuel, which is the dominant source of CO₂ emissions [3-6]. CO₂ capture and storage (CCS) technologies are divided into pre-combustion, post-combustion, and oxy-combustion. Among current technologies for CO₂ capture, chemical-looping combustion (CLC) is expected to be a promising oxy-combustion technology that is able to capture CO₂ with a low energy penalty resulting in the largest cost reduction benefit for CO₂ recovery in the power generation sector [3,7,8].

CLC is a combustion technology that indirectly supplies oxygen gas for combustion by separating the combustion reactor into the air reactor and the fuel reactor, and employing oxygen carrier which transfers oxygen from the air reactor to the fuel reactor, unlike conventional combustion processes. The oxygen carrier in the form of a metal oxide circulates through the two reactors and supplies pure oxygen to the fuel reactor [9-11]. The concept of CLC technology is shown in Fig. 1.

Since the reaction in the air reactor of CLC system is a gas-solid

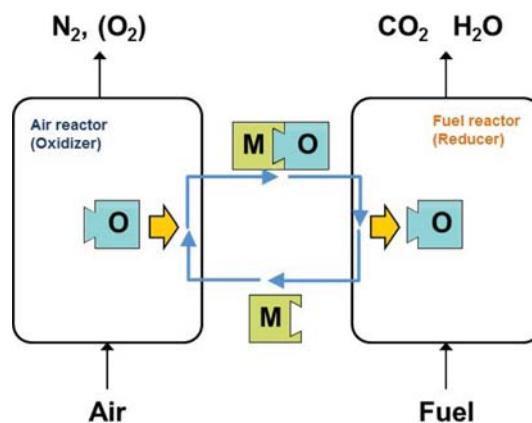


Fig. 1. The conceptual schematic of CLC process.

reaction occurring under the condition of no flame, the generation of thermal NO_x can be minimized and only oxygen is consumed in the air reactor. The use of an air separation unit (ASU) for the production of pure oxygen in existing oxy-fuel combustion technology reduces the CO₂ capture efficiency by 6.6%, while the chemical looping system supplies oxygen without the ASU [12]. In addition, since the flue gas from the fuel reactor contains mainly CO₂ and H₂O, a high concentration of CO₂ can be inherently separated by condensation of H₂O. Thus, additional CO₂ capture facility (CCS) is not required [13,14].

The most important factor determining the performance of CLC system is redox reaction characteristics of oxygen carrier circulating between two reactors. To increase the efficiency of CLC system, a large amount of oxygen needs to be transported from the

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air reactor to the fuel reactor by the oxygen carrier at a high rate, while maintaining physical properties such as strength and morphology of oxygen carrier particles [14-16]. The reduction reactivity of oxygen carriers is mainly compared to analyze the performance of oxygen carriers, since the reduction reaction rate is slower than the oxidation reaction rate [17-19].

Many studies have focused on system evaluation and oxygen carrier development [20-22]. However, limited research related to the pressurized CLC, which facilitates the industrial deployment of CLC process using gaseous fuel by achieving a high efficiency with gas turbine technology in a combined cycle, has been reported [23-25]. Lu et al. investigated the effects of the total pressure and partial pressure of CO on kinetics and oxygen-transport capacity in a pressurized thermogravimetric analyzer (PTGA). They reported that the reduction rate of oxygen carrier was faster with increasing the partial pressure of CO, while increasing the total pressure resulted in a slower reduction rate [26].

The Korea Institute of Energy Research (KIER) has carried out research on the CLC process, and collaborated with Korea Electric Power Research Institute (KEPCO RI) to develop an oxygen carrier since 2000 [18,27,28]. Long-term operation of a 50kW_{th} lab-scale chemical looping combustor with natural gas and syngas was performed in 2008 [29,30]. Two kinds of oxygen carriers, mix-

ture of NiO/bentonite and Co₃O₄/CoAl₂O₄, and spray-dried Ni-based oxygen carrier prepared by KEPCO RI, were used for the demonstration. As a next step, a 200 kW_{th} chemical looping combustor was designed and demonstrated to investigate operation stability of CLC process. Increasing the solid circulation rate led to increasing reactor power up to 263 kW_{th}. Consecutively, a 0.5 MW_{th} pressurized chemical looping combustor was considered to develop a pressurized CLC system up to 5 bar-abs using natural gas and syngas from coal gasification as fuels. The conceptual design of 0.5 MW_{th} chemical looping combustor was performed by means of mass and energy balance calculations [31]. Fig. 2 shows a schematic diagram of a 0.5 MW_{th} chemical looping combustor. The operation of a 0.5 MW_{th} pressurized CLC system is expected to be demonstrated in the near future, and further studies are needed on scale-up and application of the system to facilitate the industrial deployment of CLC process.

As mentioned, the pressurized CLC process has several benefits such as compact volume of the system, reduction of cost and energy consumption for CO₂ compression, and higher system efficiency. However, it requires high oxygen transfer capacity and high solid circulation rate of oxygen carrier to achieve the desired system capacity. As the system pressure increases, the mole flow rate of gaseous fuel increases at the same volume, when oxygen carrier circu-

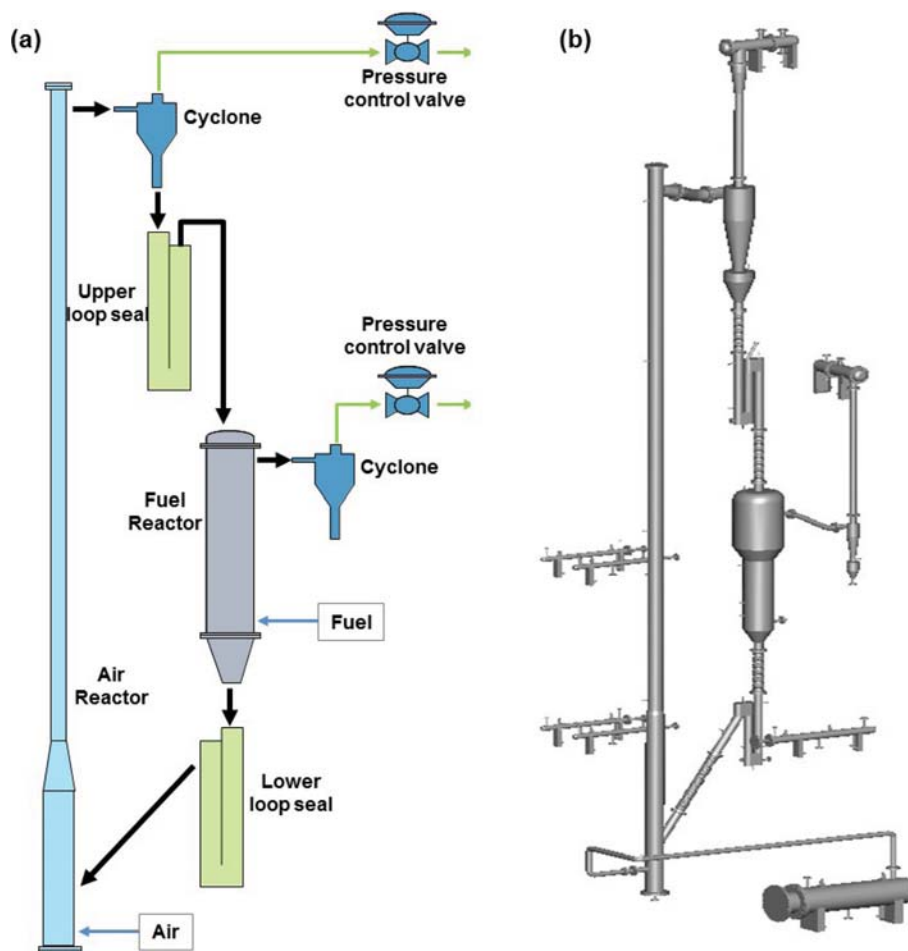


Fig. 2. A pressurized 0.5 MW_{th} chemical looping combustor, (a) schematic diagram, (b) 3D view.

lation rate is constant. This work investigates the effect of solid residence time on the reactivity of oxygen carrier in a novel semi-continuous CLC reactor to simulate the pressurized CLC process. The reactivity of Ni-based oxygen carrier particle was evaluated in terms of fuel conversion and CO₂ selectivity.

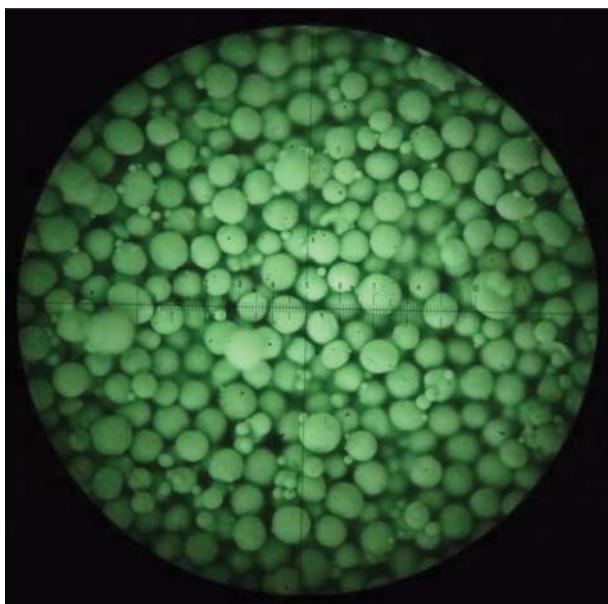


Fig. 3. Photograph of Ni-based oxygen carrier particle prepared by spray drying method.

EXPERIMENTAL

1. Oxygen Carrier

Ni-based oxygen carrier particle was prepared using spray drying method by KEPCO RI [32] in this study. Fig. 3 shows a photograph of the oxygen carrier. The particle contains about 70 wt% of NiO and measured bulk density is 2,285 kg/m³. The particles were sieved to a size range of 106–212 μm in diameter.

2. Bubbling Fluidized Bed Reactor

To examine the reduction reactivity of oxygen carriers with CH₄

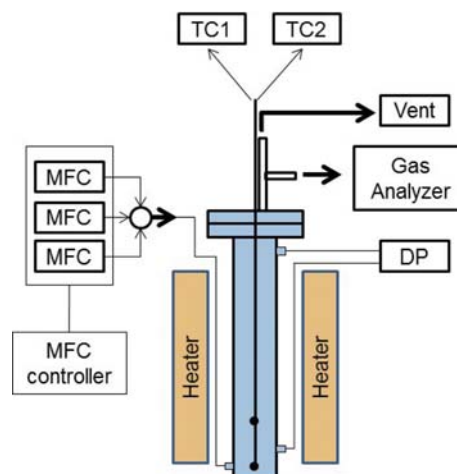


Fig. 4. Schematic diagram of bubbling fluidized bed reactor.

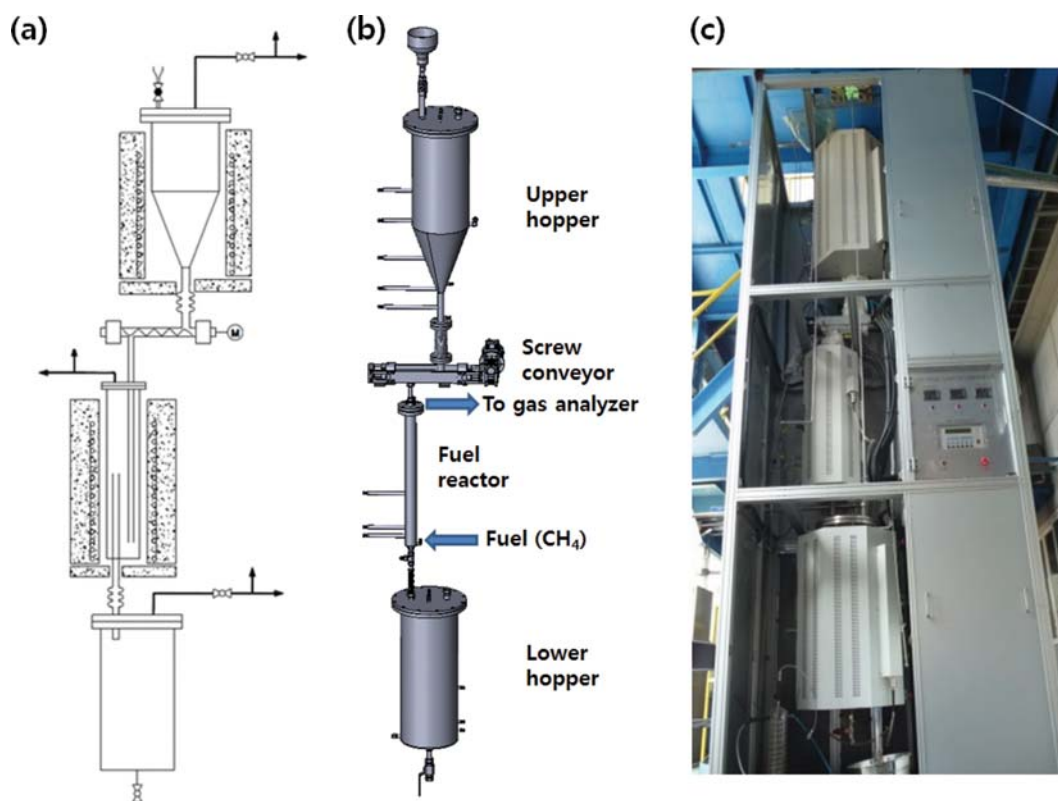


Fig. 5. Semi-continuous chemical looping combustor, (a) schematic diagram, (b) 3D view, (c) photograph.

concentration, a bubbling fluidized bed reactor was designed and used in this study. The reactor was made of SUS310S with an inner diameter of 0.05 m and a height of 0.8 m. Fig. 4 shows a schematic diagram of a bubbling fluidized bed reactor. The fluidizing gas was injected through a sparger located 0.005 m above the bottom of the reactor via a mass flow controller (MFC). The differential pressure data was obtained through the pressure transducers connected to the pressure taps located 0.05 m and 0.65 m from the bottom of the reactor. K-type thermocouples were inserted from the top of the reactor, and the inner temperature of the fluidized bed was measured at height of 0.1 and 5 m from the bottom of the reactor. The oxygen carrier was charged into the fluidized bed reactor corresponding to the height of 0.3 m and the temperature was increased to 900 °C while 0.072 m/s of air was introduced. After purging with N₂, CH₄ was introduced into the reactor to perform the reduction reaction of oxygen carrier for ten minutes. The concentration of CH₄, CO₂, CO, H₂ and O₂ was analyzed in real time with an online gas analyzer (Advance Optima, AO2020, ABB, Germany).

3. Semi-continuous Chemical Looping Combustor

A novel semi-continuous chemical looping combustor was developed to easily investigate the reactivity of oxygen carrier at different solid circulation rates. Fig. 5 shows a schematic diagram of the semi-continuous chemical-looping combustor. The general features of the system include an upper hopper, a screw conveyor, a bubbling fluidized bed reactor with an inner diameter of 0.054 m and a height of 0.85 m for simulating the fuel reactor of CLC, and a lower hopper. It has a sparger tube with ten holes of 1 mm in diameter, a solid intake tube, a solid output tube, and a gas exit tube connected with a gas analyzer. To maintain a solid height inside the fluidized bed reactor, the end of solid output tube was installed at 0.4 m from bottom of the reactor. Two thermocouples were installed at 0.1 and 0.3 m high from the bottom of the reactor. One differential pressure transducer was connected with two ports at 0.05 and 0.805 m from the bottom of the reactor to measure pressure drop inside the reactor. The on-line gas analysis system was used to measure concentration of O₂, CO₂, CO, CH₄, and H₂ continuously (Advance Optima, AO2020, ABB, Germany). Air and methane were introduced to the reactor for oxidation and reduction of oxygen carrier, respectively, and the solid circulation rate in the fuel reactor was controlled by adjusting the rotational speed of the screw conveyor.

RESULTS AND DISCUSSION

To analyze the reduction reactivity of oxygen carrier, fuel conversion and CO₂ selectivity was calculated as below (Eqs. (1)-(2)). Fuel conversion is defined as the molar ratio of the reacted fuel to the fuel feed, and the moles of reacted fuel are calculated by measured concentration of CO₂ and CO in the exhaust gas. CO₂ selectivity indicates the volumetric fraction of CO₂ per total carbon in gaseous products, and the higher the CO₂ selectivity, the easier it is to separate CO₂ from the flue gases.

Fuel conversion:

$$\frac{\text{Moles of reacted fuel}}{\text{Moles of input fuel}} \times 100 \quad (1)$$

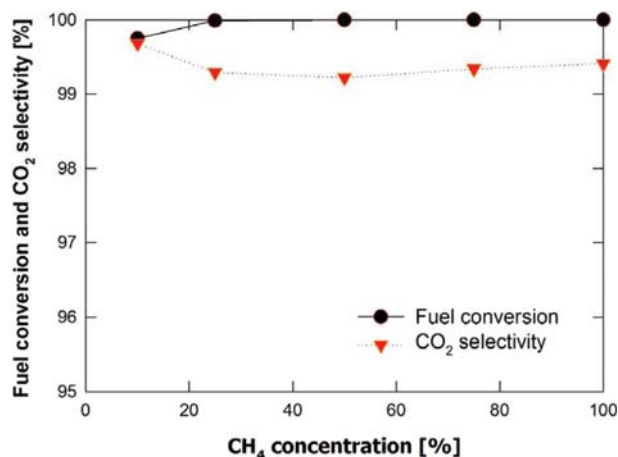


Fig. 6. Fuel conversion and CO₂ selectivity with CH₄ concentration.

CO₂ selectivity:

$$\frac{\text{CO}_2 \text{ in output gas}}{\text{Total carbon in output gas}} \times 100 \quad (2)$$

Fig. 6 shows the effect of the concentration of reducing agent (10, 25, 50, 75, 99.995% CH₄, N₂ balance) on fuel conversion and CO₂ selectivity of Ni-based oxygen carrier in a bubbling fluidized bed reactor at 900 °C. The fuel conversion was maintained at almost 100%, and the CO₂ selectivity was over 99% as the injected CH₄ concentration decreased from 99.995% to 25%. With decreasing the CH₄ concentration to 10%, the CO₂ selectivity was slightly increased, which means that it was possible to recover high concentrations of CO₂ at low CH₄ concentrations. Although it was confirmed that the fuel conversion and CO₂ selectivity were maintained high enough regardless of the CH₄ concentration, it was necessary to investigate the effect of the oxygen carrier residence time on the fuel conversion and CO₂ selectivity with oxygen carrier circulation. By using a novel semi-continuous CLC reactor to simulate the actual CLC process, the effect of solid (oxygen carrier) residence time on the reactivity of oxygen carrier was investigated.

Fig. 7 shows the solid circulation rate with the rotational speed of the screw conveyor at different gas velocity and bed temperature. To evaluate the effect of the rotational speed of the screw conveyor, gas velocity, and bed temperature on solid circulation rates in the semi-continuous chemical looping combustor, the lower hopper was disconnected and solid circulation rate was measured at different conditions by weighing discharged solid through solid output tube in the fluidized bed reactor. As shown in Fig. 7, the solid circulation rate increased as the rotational speed of the screw conveyor increased; however, the measured solid circulation rates showed almost the same values with increasing fluidization velocity and temperature from 0.032 to 0.063 m/s and from ambient to 800 °C, respectively. The controllable solid circulation rate range was from 6.1 to 60.0 kg/h in this system.

After these experiments, a series of reduction tests were carried out with different rotational speed of the screw conveyor, that is, at different solid circulation rates. High purity methane (CH₄, 99.995%) was used as fuel with a flow rate of 0.12 Nm³/h and bed temperature of 854-859 °C (U_o=0.63 m/s). During experiments, the rota-

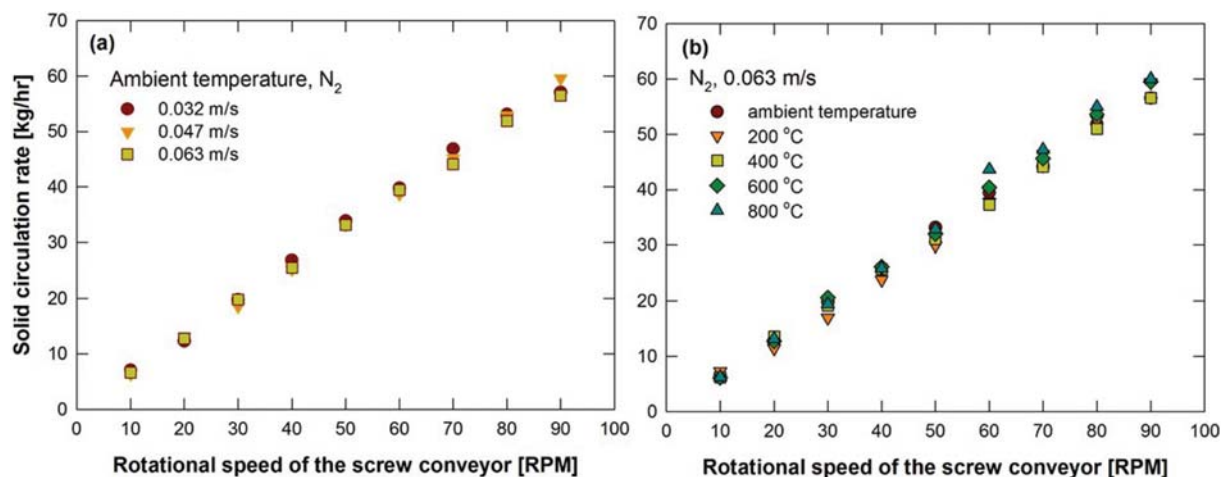


Fig. 7. Solid circulation rate with the rotational speed of the screw conveyor (a) at different gas velocity, (b) at different temperature.

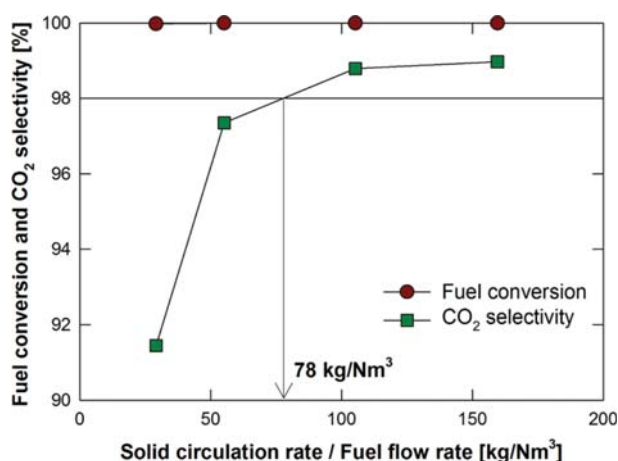


Fig. 8. Fuel conversion and CO₂ selectivity with ratio of solid circulation rate to fuel flow rate.

tional speed of the screw conveyor was varied from 5 to 30 RPM, and this variation corresponds to solid circulation rate of 3.5–19.1 kg/h. Consequently, the ratio of solid circulation rate to fuel flow rate was varied from 29.1 to 159.5 kg/Nm³. Fig. 8 shows the measured fuel conversion and CO₂ selectivity versus the ratio of solid circulation rate to fuel flow rate. The fuel conversion was maintained at almost 100% for all experimental conditions; however, the CO₂ selectivity increased as the ratio of solid circulation rate to fuel flow rate increased. This result indicates that more solid circulation rate, which means more oxygen feeding, is favorable for obtaining high purity CO₂ stream from flue gas. In principle, a harmonious solid circulation is vitally important in an interconnected fluidized bed system such as CLC [33]. Operating CLC unit with lower solid circulation rate would lead to a low temperature of the fuel reactor, causing a low fuel conversion and CO₂ capture efficiency. A high solid circulation rate could disturb the heat balance of the system due to undesired solid residence time, thus lowering CO₂ capture as well [34]. To achieve more than 98% of CO₂ selectivity, the ratio of solid circulation rate to fuel flow rate was confirmed to be greater than 78 kg/m³. Assuming that the fuel flow rate

is 50 Nm³/h in a 0.5 MW_{th} CLC system based on the heat of combustion of methane, the required solid circulation rate is obtained as 3,900 kg/h (22.7 kg/m²s, based on our conceptual design of air reactor) from the Fig. 8. This solid circulation rate is considered to be achievable and adjustable in the two-interconnected fluidized bed system based on previous works; consequently, high fuel conversion and CO₂ selectivity would be achieved with increasing solid circulation rate.

CONCLUSIONS

With the aim of developing a pressurized chemical looping combustion system with gaseous fuel, we investigated the effects of solid residence time on CO₂ selectivity in a novel semi-continuous CLC reactor using Ni-based oxygen carrier particles to design a 0.5 MW_{th} pressurized chemical looping combustor for natural gas and syngas. The semi-continuous chemical looping combustor was designed to simulate the fuel reactor of the continuous chemical looping combustor. The conceptual design of a 0.5 MW_{th} chemical looping combustor was by means of mass and energy balance calculations. Based on the conceptual design, the reactivity of oxygen carrier and solid circulation rate were selected as key parameters, and sensitivity analysis of those key parameters was conducted with the change of oxygen carrier utilization from 5 to 50%. Consequently adequate solid circulation rate to achieve 98% of CO₂ selectivity was confirmed.

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