# Continuous and Semi-Continuous Operations of Chemical-Looping Combustion in an Annular Fluidized Bed Reactor with Solids Circulation

Sung Real Son[*]        Sang Done Kim[†]

Jea-Keun Lee[‡]

[*]Korea Advanced Institute of Science and Technology, rreal@kaist.ac.kr

[†]Korea Advanced Institute of Science and Technology, kimsd@kaist.ac.kr

[‡]Pukyong National University, leejk@pknu.ac.kr

# CONTINUOUS AND SEMI-CONTINUOUS OPERATIONS OF CHEMICAL-LOOPING COMBUSTION IN AN ANNULAR FLUIDIZED BED REACTOR WITH SOLID CIRCULATION

Sung Real Son[1,*], Sang Done Kim[1,*] and Jea-Keun Lee[2]
[1]Department of Chemical & Biomolecular Engineering and
Energy & Environment Research Center,
Korea Advanced Institute of Science and Technology,
373-1 Guseong-dong, Yuseong-gu, Daejeon, 305-701, Korea
[2]Department of Environmental Engineering, Pukyong National University,
599-1 Daeyeon-dong, Nam-gu, Busan, 608-737, Korea
[*]Tel: +82-42-869-3913, Fax: +82-42-869-3910. E-mail: kimsd@kaist.ac.kr

## ABSTRACT

Chemical-looping combustion (CLC) of methane was carried out in an annular shape fluidized bed reactor with double circulations. Combustion efficiency of the continuous and semi-continuous operations with $NiO$ and $Fe_2O_3$ supported on bentonite were determined. Combustion efficiencies of the semi-continuous operations with $NiO$/bentonite and $Fe_2O_3$/bentonite are over 99 % in both cases, and those of the continuous operations are around 97% and 72%, respectively. The chemical reactivity of $NiO$ is higher than $Fe_2O_3$ in the CLC process. The concentration of CO in flue gas was below 1% and no $H_2$ emission was detected.

## INTRODUCTION

It has been known that carbon dioxide ($CO_2$) is one of greenhouse gases that is mainly releasing from fossil fuel combustion. In the near future, it is not unlikely that radical measures to decrease $CO_2$ emissions should be implemented. (Lyngfelt et al. ([1])) Richter and Knoche ([2]) proposed a reversible combustion to utilize oxidation and reduction of the metals, and Ishida et al. ([3]) proposed a novel concept of the chemical-looping combustion (CLC). This system consists of oxidation and reduction reactors where metal oxide particles are circulating through these two reactors. The metal or partially oxidized metal oxide particles are oxidized with air in an air reactor (oxidation reactor) and the oxidized metal oxide particles are reduced by fuel in a fuel reactor (reduction reactor) as shown in Fig. 1. Separation of two reaction zones makes it possible to concentrate $CO_2$ from flue gas and indirect combustion at lower temperatures does not produce thermal $NO_x$. At complete conversion of the fuel gas, the exit gas stream from the fuel reactor contains only $CO_2$ and $H_2O$, thereby, pure $CO_2$ can be obtained by $H_2O$ condensation. The flue gas from the air reactor will contain only $N_2$ and unreacted $O_2$. The extent of the reactions may vary depending on the metal oxides and the reaction conditions.

The CLC reactors could be designed by two interconnecting fluidized beds that have
an advantage over the other alternative designs since the process requires a good
contact between gas and solid phases and continuous smooth flow of solid particles
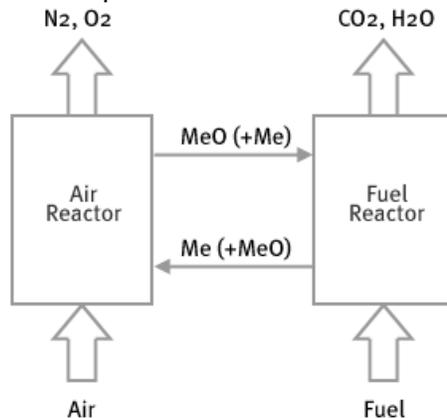


Figure 1. Schematic diagram of chemical-looping combustion (Lyngfelt et al, (1))

between the two reactors. (Ishida et al. (3)) Circulating fluidized bed (CFB)
combustors could be considered for CLC since they have excellent gas-solid mixing
characteristics. The reactivity of various oxygen carrier particles has been studied to
find suitable metal oxides for higher conversion. However, the effective carrier
particles are rather expensive chemical agents so that cheaper oxygen carrier
materials are needed for large-scale power plants. In the present study, the chosen
metal oxides are $NiO$ and $Fe_2O_3$ those are supported on bentonite. The CLC
experiment was carried out in an annular shape fluidized bed reactor to optimize
heat transfer from the oxidation (exothermic) to the reduction reactors (endothermic)
(Son and Kim (4)). In the present study, continuous and semi-continuous operations
were performed in a fluidized bed reactor. Continuous operation may provide easy
control as needed only first start-up, while it needs lots of inert gas to transport solid
particles. Semi-continuous operation is composed of the cycles of batch operation,
and may spend less transporting gas. The performance of CLC in the fluidized bed
reactor was characterized by analyzing the flue gas of $CO_2$, $CO$, $CH_4$, and $H_2$.

## EXPERIMENT

### Preparation of Oxygen Carrier Particles
Nickel oxide ($NiO$, Nihon Kagaku Sangyo Ltd., Japan) and iron oxide ($Fe_2O_3$, Bayer
AG, Germany) particles were used as the oxygen carriers, and bentonite (Donghae
Chemical, Korea) as a support material. Those particles were prepared by the direct
mixing of fine metal oxides whose size is less than 10 μm. The ratio of the
carrier/support was 3/2, and distilled water was added into the well mixed metal
oxides particles to form paste. The paste was dried at 383 K for 24 h, and calcined at
1273 K for 6 h. Then it was crushed, and sieved for preparing particle size range of
90-212 μm. Properties of the prepared oxygen carrier particles are listed in Table 1.

### Experimental Conditions in a Fluidized Bed Reactor with Solid Circulation

Previous CLC reactor systems in the literature are mostly composed of one bubbling
fluidized bed with switching the reduction and oxidation reactions (Cho et al. (5));

Mattisson et al. (6); Adánez et al. (7)), or a CFB with a riser and a bubbling fluidized bed (Lyngfelt et al. (1); Ryu and Jin (8)). The oxygen carrier particles are circulating between the two fluidized beds. In the air reactor, or the riser, oxygen is transferred from the combustion air to the oxygen carrier. In the low velocity fluidized bed, or the fuel reactor, oxygen is transferred from the oxygen carrier to the fuel. The gas velocity in the riser provides driving force for circulation of particles between the two beds. Thus, the particles carried upward from the riser are collected by a cyclone and flow into the fuel reactor.

Table 1. Properties of the prepared oxygen carrier particles

| Specimen | NiO/bentonite | $Fe_2O_3$/bentonite |
|---|---|---|
| Main crystalline phase | NiO | $Fe_2O_3$ |
| Particle density [kg/m$^3$] | 3450 | 3160 |
| Surface area [m$^2$/g] | 2.11 | 1.39 |
| Pore volume [cc/g X 10$^{-3}$] | 8.07 | 3.12 |
| Metal oxide loading [%] | 54.5 | 65.0 |
| Characteristic size [μm] | $\cong$150 | $\cong$150 |
| Shape | amorphous | amorphous |
| Geldart group | D | D |

In the present study, however, the air reactor was also designed as a bubbling fluidized bed, since the oxidation reaction is not sufficiently fast to complete the oxidation reaction in the fast fluidized bed riser (Son and Kim (4)). The present annular shape reactor is shown in Figure 2. To transport oxygen carrier particles between two bubbling fluidized beds, two risers are needed to transport the particles from the oxidation to the reduction zone and the other riser provides the particle transport from the reduction to the oxidation reactors. The design values and constants are adopted from the theoretical equations of Lyngfelt et al. (1) and Ryu and Jin (8). Loop-seal is one kind of non-mechanical solid feeding control valve with variation of aeration velocity. The seal-pot type loop-seal was selected for the present reactors. Dimensions of the two loop-seals are the same based on the study of Basu and Fraser (10).

The oxygen carrier particles in the annular section were reduced by $CH_4$, and then flowing down to the loop-seal. The loop-seal controls solid circulation by aeration to the riser where the particles were transported by air to the oxidation reactor. The particles are oxidized by air and then flowing down to another loop-seal where the particles were aerated by $CO_2$ and the particles were transported via another riser to the reduction reactor. In this way, the oxygen carrier particles go through one cycle of the CLC reaction. In the continuous CLC operation, all the gases are supplied simultaneously so that the particles are passed smoothly through the circulation loop. Whereas, in the semi-continuous mode, the reaction gases, $CH_4$ and air, were introduced into the annular and core section, respectively, and the oxygen carrier particles were reacted with the reacting gases in the bubbling fluidized bed state. After completing the reactions, the particles were transported via each riser to the other reactor zone. The metal oxides were loaded in both reactors, 0.6 kg in the reduction reactor and 0.2 kg in the oxidation reactor for each operation. After feeding the bed materials in each section, the reactor was heated to a desired temperature and then reactant gases, air and $CH_4$, were introduced into the core and annular regions, respectively. $CO_2$ and air were used to aerate particles for smooth solid

circulation in the loop-seals, and the same gases at the velocity of around 1.5 m/s
were supplied into the risers for solid transportation. The solid circulation rate,
around 13 kg/m$^2$s, was controlled by aeration in the loop-seals.
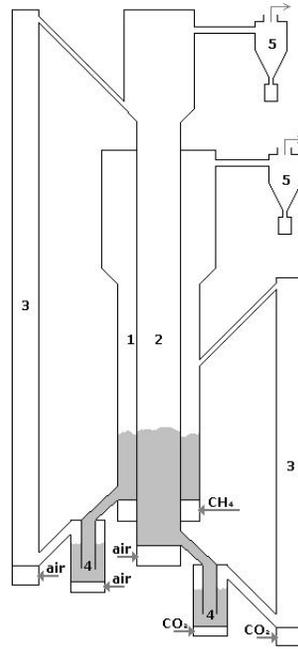


Figure 2. Schematic diagram of annular fluidized bed reactor for CLC. (1) Reduction
zone, annular column, 55 mm i.d., 0.9 m height; (2) oxidation zone, inner column,
23 mm i.d., 1.5 m height; (3) riser, 17 mm i.d., 2.1 m height for oxidizer, 1.15m
height for reducer; (4) loop-seal, 23 mm i.d., seal-pot type; and (5) cyclone.

The bed weights and solid circulation rate could be estimated by residence time for
the complete reaction by using the estimation standard of Lyngfelt et al. (1) and Ryu
and Jin (5) based on the 1 kW combustor. The present continuous and semi-
continuous chemical-looping combustion with NiO and $Fe_2O_3$ supported on bentonite
was carried out at 1123 K. The fuel gas, $CH_4$, was introduced into the reduction
reactor at 75 mm/s ($\cong$ 3 $u_{mf}$, 0.14 L/s) and air was injected into the oxidation reactor
at 200 mm/s (0.08 L/s). The stoichiometric ratio of oxygen is 2 based on the study of
Lyngfelt et al. (1). The composition of flue gas from the reduction reactor was
analyzed by infrared gas analyzer (Fuji Electric System, ZRJ-5 type) for $CO_2$, CO,
and $CH_4$ gases and thermal conductivity gas analyzer (Fuji Electric System, ZAF
type) was used to determine $H_2$ gas concentration.

**RESULTS AND DISCUSSION**

The performance of CLC in the fluidized bed reactor could be characterized by
analyzing the composition of flue gas. If the desired reaction occurs, only $CO_2$ and
$H_2O$ should be detected in flue gas from the reduction reactor. However, CO and $H_2$
may be formed by the side reactions and $CH_4$ could be emitted due to the
incomplete reduction reaction and $NO_x$ from the oxidation reactor. With ND-IR type
$NO$ analyzer, $NO_x$ from the oxidation reactor was detected only within the error

bound in a previous study (4). It may imply that the thermal NO$_x$ emission is negligibly small. The reaction efficiency can be determined by the analysis of flue gas from the reduction reactor. The possible composition of the flue gas is mixtures of CO$_2$, CO, H$_2$, and CH$_4$. Based on the flue gas analysis, most of CH$_4$ was converted to CO$_2$, and very low concentration of CO was detected from the side reaction. H$_2$ was detected within the error bound.

In the semi-continuous operation, one cycle of reaction time was assigned about 4 min for each cycle. From the full reduction time test, the breakthrough times are found to be around 15 min and 12 min for the oxygen carrier particles of NiO/bentonite and Fe$_2$O$_3$/bentonite, respectively. The breakthrough time is the starting time when unwanted gases such as CO and/or CH$_4$ were detected after complete combustion of the fuel (Corbella et al. (11)). Since the amount of particle circulation in one cycle is one third of the bed mass in the reduction reactor, one cycle of the reaction time was assigned about 4 min.

In the semi-continuous operation, concentrations of CO$_2$, CO, and CH$_4$ in flue gas from the reduction reactor in the number of reduction and oxidation reactions cycles with NiO/bentonite and Fe$_2$O$_3$/bentonite particles are shown respectively in Figs. 3 (a) and (b). In case of NiO/bentonite, methane was combusted almost completely with the oxygen carrier particles up to 13th cycle. As can be seen in the figure, the reactivity of the oxygen carriers at the initial and after reaction are high and not affected by number of cycles within 13 cycles. In case of Fe$_2$O$_3$/bentonite, CH$_4$ is combusted to CO$_2$ almost completely to the 8th cycle. It is also found that the reactivities of the oxygen carriers at the initial and after reactions are high and not affected by number of cycles within 8 cycles. In all the cases, concentration of CO was below 1%, and CH$_4$ and H$_2$ were not detected in this reaction process.

Combustion efficiencies of the semi-continuous in the present study and the continuous CLC operation of our previous study (Son and Kim (4)) is shown in Fig. 4 where combustion efficiency, γ, is defined as

$$\gamma = \frac{P_{CO_2}}{P_{CH_4} + P_{CO_2} + P_{CO}} \tag{1}$$

where $P_a$ is the partial pressure of gas component "a" (Lyngfelt et al. (1)). In other words, combustion efficiency indicates the quantity of completely combusted gas, CO$_2$, in flue gas to that of the fuel injected. In general, the combustion efficiency of the semi-continuous operation is a little higher than that of the continuous operation with NiO/bentonite and much higher than that with Fe$_2$O$_3$/bentonite particles. Combustion efficiencies of the semi-continuous operations with NiO/bentonite and Fe$_2$O$_3$/bentonite are over 99 % in both cases, and those of the continuous operations are around 97 % and 72 %, respectively. It is found that incomplete combustion gases, CO was detected in the range of 1% in the semi-continuous operation since the excess oxidized metal oxide particles may react completely with the supplied CH$_4$ gas, though CO and CH$_4$ were detected a little more in the continuous reactor mode. That indicates the semi-continuous operation is more effective in the CLC process in this study. In addition, transporting gases, CO$_2$ and N$_2$ are needed enormously in the risers in the continuous operation.

(a)
(b)
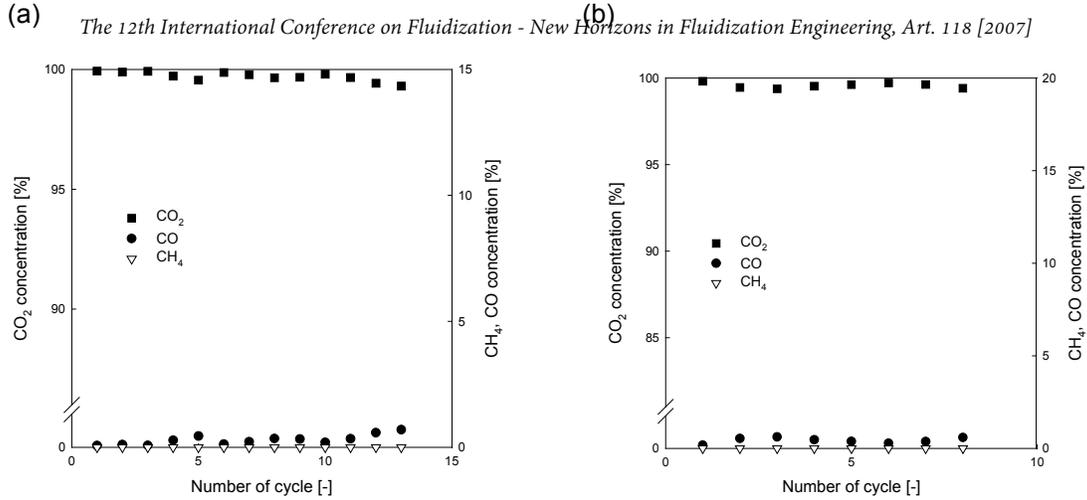


Figure 3. Effect of reaction cycles on the product gas composition in semi-continuous CLC operation with (a) NiO/bentonite; and (b) $Fe_2O_3$/benonite particles.
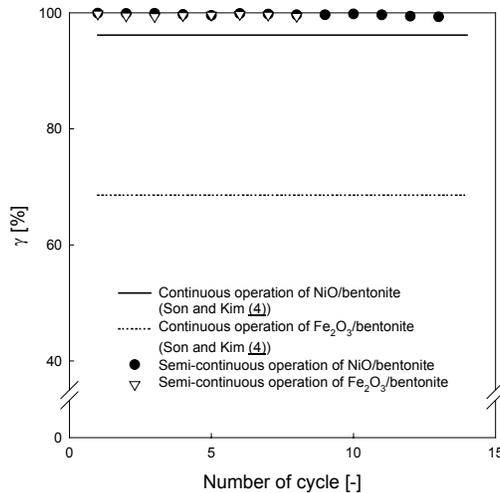


Figure 4. Combustion efficiency on cycle of semi-continuous operation and continuous operation with NiO/bentonite and $Fe_2O_3$/benonite particles.

## CONCLUSIONS

The chemical-looping combustion (CLC) was carried out in an annular shape fluidized bed reactor to provide enough reaction time for each reaction and optimize the heat transfer from the oxidation (exothermic) to the reduction reactors (endothermic). The reduction and oxidation reactions of NiO and $Fe_2O_3$ supported on bentonite as oxygen carriers were carried out in the continuous and semi-continuous mode operations. In the semi-continuous operation, stable reactivity can be attained through more than 10 cycles of batch mode fluidized bed operations. The reactivities of the oxygen carriers at the initial and after complete reaction are high and not affected by number of cycles within the 13th cycles with NiO/bentonite and 8th cycles with $Fe_2O_3$/bentonite. The combustion efficiencies of semi-continuous

operations with NiO/bentonite and Fe$_2$O$_3$/bentonite are over 99%, and those of continuous operations are around 97% and 72%, respectively. It is found that the efficiency of CLC in the semi-continuous operation is somewhat higher than that in the continuous operation with NiO/bentonite and much higher than that of Fe$_2$O$_3$/bentonite particles.

## ACKNOWLEDGEMENT

## NOTATION

$P_a$      partial pressure of gas component "*a*"
$u_{mf}$      minimum fluidizing velocity (mm/s)
$\gamma$      combustion efficiency (eq. 3) (%)

## REFERENCES

1. Lyngfelt, A., Leckner, B., and Mattisson, T. (2001). "A fluidized-bed combustion process with inherent CO$_2$ separation; application of chemical-looping combustion." *Chem. Eng. Sci.*, 56, 3101-3113.
2. Richter, H. J., and Knoche, K. F. (1983). "Reversibility of combustion process." *ACS Symp. Ser.*, American Chemical Society, Washington DC, 71-85.
3. Ishida, M., Zheng, D., and Akehata, T. (1987). "Evaluation of a chemical-looping combustion power-generation system by graphic exergy analysis." *Energy*, 12, 147-154.
4. Son, S. R., and Kim, S. D. (2006). "Chemical-looping combustion with NiO and Fe$_2$O$_3$ in a thermobalance and circulating fluidized bed reactor with double loops." *Ind. Eng. Chem. Res.*, 45, 2689-2696.
5. Cho, P., Mattisson, T., and Lyngfelt, A. (2004). "Comparison of iron-, nickel-, copper- and manganese-based oxygen carriers for chemical-looping combustion." *Fuel*, 83, 1215-1225.
6. Mattisson, T., Johansson, M., and Lyngfelt, A. (2006). "The use of NiO as an oxygen carrier in chemical-looping combustion." *Fuel*, 85, 736-747.
7. Adánez, J., García-Labiano, F., de Diego, L. F., Gayán, P., Celaya, J., and Abad, A. (2006). "Nickel-copper oxygen carriers to reach zero CO and H$_2$ emissions in chemical-looping combustion." *Ind. Eng. Chem. Res.*, 45, 2617-2625.
8. Ryu, H. J., and Jin, G. T. (2003). "Conceptual design of 50 kW thermal chemical-looping combustor and analysis of variables." *Energy Eng. J.*, 12, 289-301.
9. Mattisson, T., Järdnäs, A., and Lyngfelt, A. (2003). "Reactivity of some metal oxides supported on alumina with alternating methane and oxygen – application for chemical-looping combustion." *Energy Fuels*, 17, 643-651.
10. Basu, P., and Fraser, S. A. (1991). *Circulating Fluidized Bed Boilers: Design and Operations*, Butterworth-Heinemann, Boston.
11. Corbella, B. M., de Diego, L. F., García-Labiano, F., Adánez, J., and Palacios, J. M. (2005). "The Performance in a fixed bed reactor of copper-based oxides on titania as oxygen carriers for chemical looping combustion of methane." *Energy Fuels*, 19, 433-441.