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매체 순환식 연소 공정용 산소 공여체 입자의 경제성 분석

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Economic analysis of oxygen carrier particles for chemical-looping combustion process

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1. Introduction

It has been known that carbon dioxide (CO_2) is a greenhouse gas that is mainly releasing from fossil fuel combustion [1]. In the developing countries, the economic growth results in a rapid increase in demand for energy supply of fossil fuels, while the developed countries have not yet found the means for substantially decreasing the use of these fuels. In the near future, it is not unlikely that radical measures to decrease CO_2 emissions should be implemented [2].

From these demands, a reversible combustion was proposed to utilize oxidation and reductions of the metals [3] as a novel concept of the chemical-looping combustion (CLC) [4]. It is composed of two reactors, an air and a fuel reactor, as shown in Fig. 1. The CLC has the advantage of no energy lost for separation of CO_2 and no NO_x formation. This system consists of oxidation and reduction reactors where metal oxides particles are circulating through these two reactors. The metal particles are oxidized with air in air reactor and the oxidized metal particles are reduced by fuel in a fuel reactor.

The reactivity of various oxygen carrier particles has been studied to find higher conversion of metal oxides. However, the effective carrier particles are rather expensive chemical agents so that cheaper oxygen carrier materials are needed for large-scale power plants. We has been studied reactivity and physical properties of NiO and Fe_2O_3 as the oxygen carrier particles on the cheap supports [5, 6, 7]. In the present study, the best oxygen carrier candidate is selected from nine different kinds of NiO and Fe_2O_3 particles based on the experimental data of conversion in the CLC reactor [2,8], properties and price of the raw materials. Especially, the attrition characteristics of the carrier particles are mainly considered because this property is the most important factor in the real CLC operation [9].

2. Theory

As shown in Fig. 1, fuel is introduced into the fuel reactor in a gaseous form where it reacts with the oxygen carrier particles as

$$(2n + m)\,MO + C_nH_{2m} \rightarrow (2n + m)\,M + m\,H_2O + n\,CO_2 \qquad (1)$$

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 with H_2O condensation. The reduced metal oxide is then circulated to the air reactor where it is oxidized according to

$$M + 1/2\,O_2 \rightarrow MO \qquad (2)$$

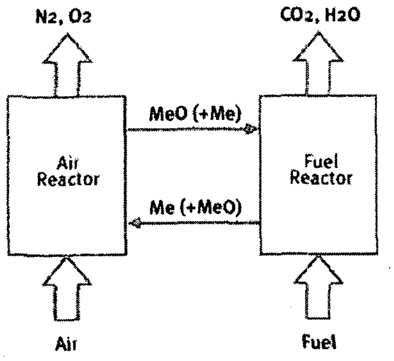

Figure 1. Schematic diagram of chemical-looping combustion by Lyngfelt et al. [2]

The flue gas from the air reactor will contain N_2 and unreacted O_2. The extent of the reactions may vary depending on the metal oxides and the reaction conditions. The total amount of heat evolved from the reactions (1) and (2) would be the same as the normal combustion where the oxygen is in direct contact with the fuel. However, the advantage of this system compared to the normal one is that CO_2 and H_2O are inherently separated from the rest of the flue gases, and no energy is expended for this separation [10].

For designing of a CLC reactor, required parameter values are determined as follows: Assuming that the fuel is completely burnt, the amounts of fuel and oxygen can be decided by stoichiometric calculation. It also gives the air mass by mass fraction of oxygen in air. The cross-sectional areas of oxidizer and reducer can be determined by the each fluidizing gas velocity, the specific volume of gases, the ambient temperature, the reaction temperature, and the calculated gas amount. From these calculated values with the known values of bed height, density of bed material, and the bed voidage, the amount of bed material can be determined.

The degree of oxygen conversion, henceforth called conversion, is the actual mass of oxygen divided by the mass of oxygen then fully oxidized. The capacity of the carrier particles defined as the ratio of a fractional mass increase to an increase in conversion, is a measure of how much oxygen is able to transfer for a given charge of carrier in conversion. The mass flow of entrained solids from the oxidizer to the reducer is related to the difference in conversion, and the mass flow of solids returned from the reducer to oxidizer is somewhat smaller, because of the oxygen used in the reducer [2, 8].

3. Analysis of Data

Design criteria are chosen for the layout of an atmospheric boiler that is suitable for semi-commercial scale. The design resembles that of a circulating fluidized bed (CFB) boiler for combustion of solid fuels, thus using the elements of proven technology. However, a full optimization is premature at this state of knowledge. Instead, the design data are chosen according to the following considerations, which to some extent rely on the experience from CFB boilers [2]:

- The fuel is methane.
- The air ratio aims at keeping down the gas flow in the reactor, and yet have a sufficient oxygen concentration for high conversion rate of the solids.
- The temperatures reflects the level where most of the experimental data are available at present.
- The recirculation ratio is low to minimize the power needed for compression of CO_2.
- The pressure drop and the cross-section area are similar to that of CFB combustors.
- The conversion difference is small, which will give a large recirculation rate of solids.
- The oxygen carriers are NiO/TiO_2, Fe_2O_3/TiO_2, NiO/Al_2O_3, Fe_2O_3/Al_2O_3, NiO/bentonite, Fe_2O_3/benonite, and three kinds of NiO-Fe_2O_3/bentonite.

The design values and the constants are used those in a previous study [8] with nine kinds of metal oxides (Table 1). Molecular weight of iron oxide is based on the oxygen carrying capacity of one atom of iron, so the values in Table 1 are half of the real molecular weight of Fe_2O_3. The economic analysis of the oxygen carrier particles is based on the quantity of power generation and operation time.

The reactivity data of the oxygen carrier particles are adopted in a previous study [5]. The design values provide the mass of carrier material and the fractional conversion rate in the oxidizer and reducer with the reactivity data.

The carbon deposition on metal particles occurs due to incomplete combustion. The factor related on carbon deposition is a function of residence time in the bed, so it is considered only when the residence time is longer than the time that carbon deposition can occur [6]. But, this is not a quantitative factor, so not considered on calculating.

Attrition of oxygen carrier particles is the most important factor to operate the CLC system [9] and the attrition data of the present carrier particles have been determined [7].

The cost of looping materials are decided from the calculated mass of the carrier particles. Prices of the raw materials are quoted from the fine chemicals of the Sigma-Aldrich Korea 2003-2004 for economic analysis of the oxygen carrier particles.

4. Result and Discussion

For the all carrier particles, the calculated values of fuel flow, air mass flow, bed mass and the required conversion rate in the oxidizer and reducer, residence time in the reducer, and the bed mass loss by attrition are determined. Table 2 shows an example of NiO-Fe_2O_3(2:2)/bentonite particle. The properties are calculated, based on the power range from 50 kWth to 1,000 MWth. The attrition index is not exact value for calculating the factor of attrition, but the effect of attrition can be determined by direct substitution of the corrected attrition index as that is enough.

The mass of oxygen carrier particles were determined by the sum of the particle mass in the oxidizer and the reducer with the knowledge of the attrition and reactivity of the carrier particles. The conversion of all oxygen carriers are sufficient for the pilot plants having power greater than 10 MWth. Although those pilot plants having power output below 1 MWth are satisfied, we can assumed that two times of the required conversion is sufficient for the excess oxygen for complete methane combustion. Thus, the mass

Item	Symbol	Value				Unit
		NiO/TiO_2	Fe_2O_3/TiO_2	NiO/Al_2O_3	Fe_2O_3/Al_2O_3	
Molecular weight of metal oxide	$M_{r,ox}$	74.69	79.85^{*}	74.69	79.85^{*}	g/gmol
Molecular weight of metal	$M_{r,red}$	58.69	55.85	58.69	55.85	g/gmol
Oxygen ratio	R_O	0.1285	0.1803	0.1285	0.1803	-
Particle density	ρ_p	4558	4062	4431	3934	kg/m^3

Item	Symbol	Value of NiO-Fe_2O_3/bentonite (ratio of NiO:Fe_2O_3)					Unit
		4:0	3:1	2:2	1:3	0:4	
Molecular weight of metal oxide	$M_{r,ox}$	74.69	75.98^{*}	77.27^{*}	78.56^{*}	79.85^{*}	g/gmol
Molecular weight of metal	$M_{r,red}$	58.69	57.98	57.27	56.56	55.85	g/gmol
Oxygen ratio	R_O	0.1285	0.1421	0.1553	0.1680	0.1803	-
Particle density	ρ_p	3450	3359	3290	3249	3155	kg/m^3

Table 1. Solid properties of oxygen carrier particles (*Molecular weight of iron oxide is based on oxygen carrying capacity of one atom of iron.)

Item	Symbol	Power					Unit
		50 kWth	1 MWth	10 MWth	100 MWth	1,000 MWth	
Fuel flow	m_{fuel}	0.0010	0.0200	0.2000	2.0000	20.0000	kg/s
Air mass flow	m_{air}	0.0204	0.4072	4.0717	40.7170	407.1699	kg/s
Bed mass in the oxidizer	$m_{bed,ox}$	10.61	948.7	30000	948670	30000000	kg
Bed mass in the reducer	$m_{bed,red}$	47.06	4209.6	133120	4209600	133120000	kg
Required conversion rate in the oxidizer	r_{ox}	14.53	3.248	1.027	0.3248	0.1027	%/min
Required conversion rate in the oxidizer	r_{red}	3.27	0.731	0.231	0.0731	0.0231	%/min
Residence time in the reducer	t_{red}	186.2	832.7	2633.2	8327.0	26332	sec
Bed mass loss by attrition	m_{loss}	0.00712	0.6366	20.13	636.6	20130	kg/s

Table 2. Effect of power and particles on the design values for the example of NiO-Fe_2O_3(2:2)/bentonite

of oxygen carriers are multiplied by the factor of their conversion rate in the plants having power capacity of 50 kWth and 1 MWth.

The required mass of looping materials and prices increase linearly with the power on log scale as shown Figures 2-5. Figures 2 and 3 show the needed mass of the carrier particles as a function of power output for one year operation. As can be seen, there are two groups of three different particles. Although small changes are seen between the required bed mass and price, they lie within each group. It can be attributed to its attrition characteristics that is known as the most important factor in the CLC operation. In the present study, Fe_2O_3/Al_2O_3 is the most economical material since it has low attrition rate and it is a rather cheap raw material. Also, bentonite support is also cheap material, but it has relatively high attrition rate so that it may cause additional cost to preparing the oxygen carriers. The effect of NiO-Fe_2O_3 loading on the required mass and prices for one year operation are shown in Figures 4 and 5. The required mass of carriers increases with increasing Fe_2O_3 content, but the high content of Fe_2O_3 is profitable since Fe_2O_3 is much cheaper than NiO.

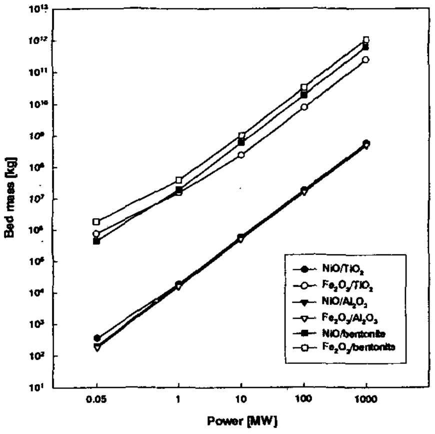

Figure 2. Required mass of looping materials by change of materials in one year operation.

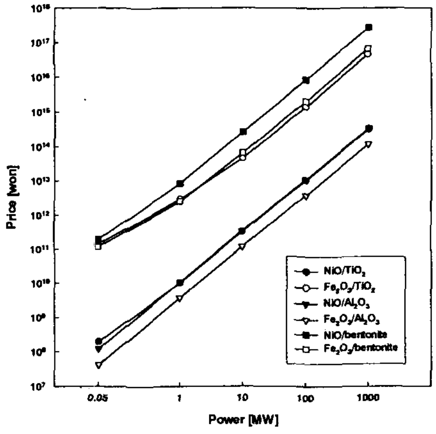

Figure 3. Prices of looping materials by change of materials in one year operation.

Figures 6 and 7 show the prices as a function of operation time in a 100 MWth pilot paint. As can be seen, the price increases with the operation time as incase of power (Figs. 4 and 5). Also, they lie in two groups that is also caused by particle attrition. Especially, the materials having low attrition rates would be profitable for long-time operation. Consequently, Fe_2O_3/Al_2O_3 is the most economical material in this respect.

Although NiO/TiO_2, NiO/Al_2O_3, and Fe_2O_3/Al_2O_3 are shown good candidates for the CLC operation based on the economic analysis, they have a fatal problem of carbon deposition. Carbon deposition occurs for the time period of 7,000 - 38,000 seconds in the pilot plants having power output of 100 - 1,000 MWth with enough residence time in the reducer. But the previous three materials, NiO/TiO_2, NiO/Al_2O_3,

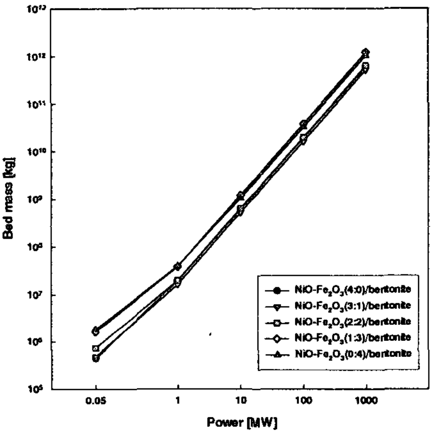

Figure 4. Required mass of $NiO-Fe_2O_3$/bentonite for one year operation.

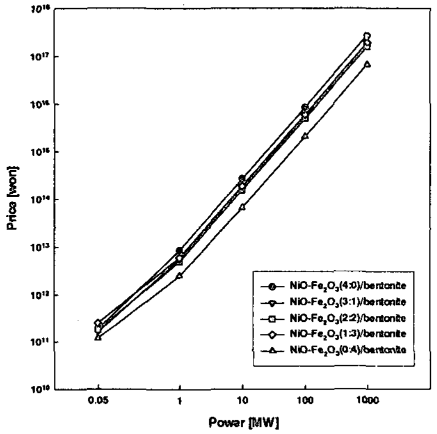

Figure 5. Prices of $NiO-Fe_2O_3$/bentonite as a function of power for one year operation.

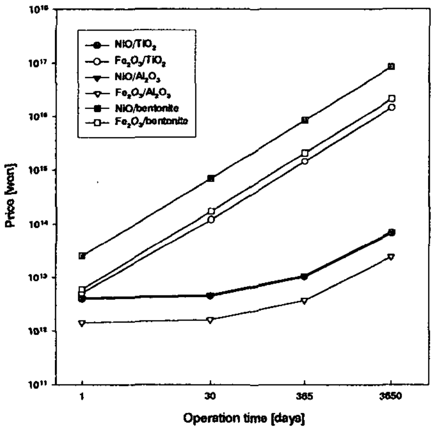

Figure 6. Prices of different looping materials as a function of operation time for a 100 MWth pilot plant.

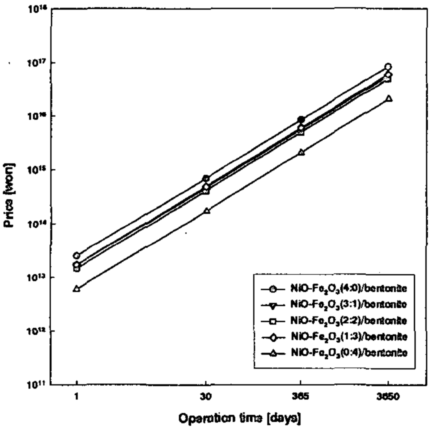

Figure 7. Prices of $NiO-Fe_2O_3$/bentonite as a function of operation time for a 100 MWth pilot plant.

and Fe_2O_3/Al_2O_3, carbon is deposited on the particles before 1,000 seconds in the reduction reaction. Although numerical interpretation cannot be performed for carbon deposition, large emission of CO_2 from the oxidizer by combustion of the deposited carbon is a fatal problem that may hurt the originality of the CLC process. Therefore, we must be careful to select an oxygen carrier.

5. Conclusion

Economic analysis of the oxygen carrier particles were performed for the CLC operation. The ranking of the tested oxygen carrier particles for the economic analysis is based on the reactivity, attrition rate and price of each carrier particles. The required mass of the carrier materials and prices increase linearly with both the power and operation time of a power plant. The tested particles are divided into two groups according to their attrition characteristics. The attrition rate affects strongly both the required mass and prices of the carrier particles. From the economic analysis, the most economic oxygen carrier particle is found to be Fe_2O_3/Al_2O_3 because it has low attrition rate and material cost. The bentonite support was considered a cheap material, but it has relatively high attrition rate that may cost more for making the oxygen carriers. Also, other good carrier materials having good economic analysis exhibit carbon deposition problem that may cause environmental and technical problem with CO_2 emission.

6. References

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