VOLATILE MATTER CAPTURE BY CALCINED LIMESTONE UNDER CALCIUM-LOOPING PROCESS CONDITIONS

Tadaaki Shimizu*, Keisuke Koseki

Department of Chemistry and Chemical Engineering, Niigata University, 2-8050 Ikarashi, Niigata, Japan

*Email: tshimizu@eng.niigata-u.ac.jp

Abstract – Calcium-Looping (CaL) process that utilizes CaO as sorbent has been developed as a low energy-penalty CO_2 separation process. This process consists of two fluidized bed reactors, carbonator to capture CO_2 and regenerator to decompose $CaCO_3$, in the latter of which fuel (coal) is burned using pure oxygen. To avoid hot-spot formation in the regenerator, pure O_2 is diluted by recycled CO_2, but the dilution by CO_2 increases heat loss. Therefore, operation with higher O_2 concentration is favorable. This work presents an approach to avoid hot-spot formation in the regenerator under high-O_2 conditions. It is known that volatile matter from fuel can be captured by porous solids (such as porous alumina) and carbon deposit is formed within the pores. If the same phenomenon occurs in recirculating sorbent (porous $CaO/CaCO_3$ particles), rapid evolution of volatile matter in the regenerator can be suppressed and the heat of carbon deposit combustion can be directly transferred to the sorbent. Experimental work was carried out to assess the volatile matter capture by CaO particles in a fixed bed. Higher temperature was found to be favorable to capture volatile matter. Also combustion rate of carbon deposit was measured. The influences of temperature and oxygen concentration on deposit combustion rate were not remarkable. Several designs for fuel feed modification that enable volatile matter capture by recirculating sorbent are proposed.

INTRODUCTION

Carbon capture and storage (CCS) technologies have been investigated extensively to suppress CO_2 emissions to the atmosphere. Calcium-looping (CaL), a dry absorption-desorption process using a dual-fluidized bed solid circulation system, is a post-combustion CO_2 capture process. Carbon dioxide in flue gas from an air-blown combustor is captured by CaO to form $CaCO_3$ in a carbonator at about 600 – 650 ºC and decomposition of $CaCO_3$ to CaO and CO_2 is conducted in a regenerator at about 900 – 950 ºC, as portrayed in Fig. 1 (Shimizu et al., 1999). The heat necessary to decompose $CaCO_3$ in the regenerator is supplied by burning fuel such as coal using pure O_2 so that the flue gas consists ideally only of CO_2 and H_2O. The CaL process is regarded as an energy-efficient and low-cost post-combustion CO_2 capture process (Atsonios et al., 2016, Clarens et al., 2016, Cormos, 2015, Hanak, et al., 2015, Zhao et al., 2013). Therefore, this process has been extensively investigated using dual-fluidized bed systems. Numerous reports have described CO_2 capture by CaO-based sorbents (Abanades et al., 2009, Alonso et al., 2010, Arias et al., 2013, Charitos et al., 2010, 2011, Dieter et al., 2013, 2014, Fang et al., 2009, Kremer et al., 2013, Lu et al., 2008, Rodríguez et al., 2011, Sánchez-Biezma et al., 2013, Symonds et al., 2016).
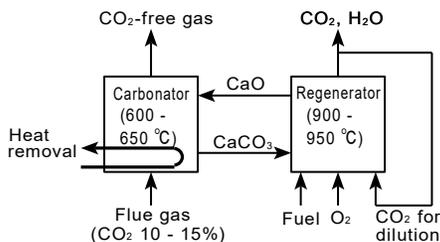

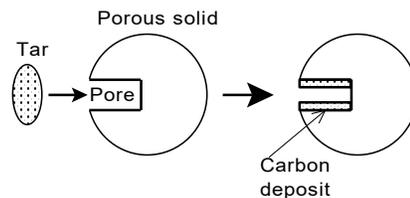Fig. 1. Concept of Calcium Looping (CaL) process.   Fig. 2. Capacitance effect of porous material.

In practice, pure O_2 fed to the regenerator must be diluted by recycled CO_2 to avoid hot-spot formation due to rapid combustion of fuel in high O_2 concentration atmosphere. Especially, care must be given when high-volatile fuels are burned because volatile matter is rapidly oxidized in gas phase and char from such fuels is reactive; both volatile matter combustion and rapid char combustion are anticipated to cause hot-spot

formation. However, dilution of O_2 by CO_2 increases the heat loss from the regenerator in the form of sensible heat of CO_2, thus it increases energy penalty (Shimizu, 2011).

To suppress the rapid combustion of volatile matter, the present authors propose the use of "capacitance effect" of porous solids, i.e., capture of gaseous hydrocarbons such as tar or volatile matter in the pores of porous solids followed by carbon deposition, as illustrated in Fig. 2 (Miyauchi et al., 1987, Franke et al., 1999, Shimizu et al., 2007). Capacitance effect of porous bed materials such as alumina has been proven to be effective to capture volatile matter, to suppress the rapid volatile matter combustion, and to enhance horizontal carbon dispersion under fluidized bed combustion conditions (Franke et al., 1999, Shimizu et al., 2007). However, previous works on capacitance effect were carried out by using mainly alumina and silica, both of which are solid acid. Teramae (2007) reported that tar capture of porous solids increased with increasing acid points on the surface. Thus it is not yet unclear whether porous CaO can capture volatile matter under conditions of CaL process.

The objective of this work is to assess the tar capture by CaO particles. Experiments of volatile matter feed to a fixed bed of CaO were carried out and the ratio of captured carbon in the volatile matter was determined. Also combustion rate of carbon deposit was measured. The effect of temperature on tar capture and combustion rate of carbon deposit was investigated. Based on the experimental results, designs of fuel feed system that enable volatile matter capture are proposed.

EXPERIMENTAL

Volatile matter capture by calcined limestone was evaluated by using a quartz fixed bed reactor schematically shown in Fig.3. The reactor system consisted of three parts, namely reactor A, B and C. They were made of quartz glass. They were all heated by an electric heater. Reactor B was the main body of the system and its size was 27 mm in inner diameter and 1 m in length. In the rector B, limestone of 28 cm^3 in bulk volume was packed on a quartz sintered plate. The reactor A, a quartz tube with a sintered plate at the bottom, was inserted in the reactor B. Fuel particles were fed into the reactor A onto the sintered plate and devolatilization occurred there. Only the evolved volatile matter passed through the sintered plate and fed into the reactor B. Part of the volatile matter was captured by the solid sample in the reactor B, whereas the rest of volatile matter reached reactor C. In reactor C, Pt/Al_2O_3 catalyst pellets were packed so that the unreacted part can be oxidized to form CO_2 and CO by feeding O_2 through valve V_1. The produced CO_2 and CO were measured by non-dispersive infrared absorption analyzers. After devolatilization, valve V_1 was closed and valve V_2 was opened to feed oxygen to reactor B. The carbon captured by the solid sample was burned to form CO_2 and CO. Finally, oxygen was fed to reactor A trough valve V_3 and the char was converted to CO_2 and CO.
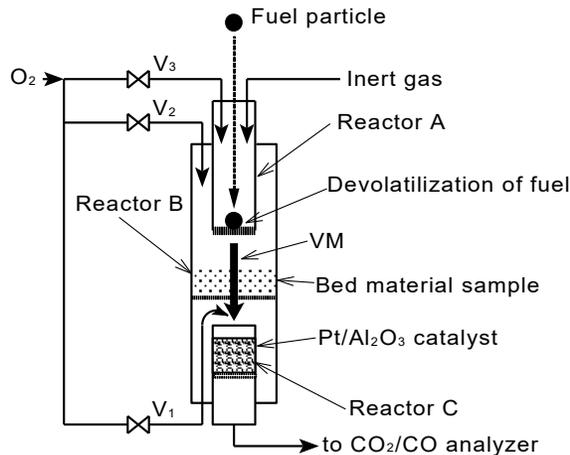

Fig. 3. Fixed bed system for tar capture and combustion of carbon deposit.

Chichibu limestone from Japan was employed as sample. The composition (wt-%) of raw limestone included $CaCO_3$ 96.9, $MgCO_3$ 1.4, SiO_2 0.6, Al_2O_3 0.8, and Fe_2O_3 0.3. The particle size was 0.35 – 0.42 mm. The limestone was calcined at 880 ºC in O_2-N_2 mixture, then the temperature was fixed at experimental temperature. Polyethylene pellets were employed as volatile matter source because it formed only negligible amount of char.

RESULTS AND DISCUSSION

A typical result of CO_2 formation after feeding PE pellets to the reactor system is shown in Fig.4. The first peak (0 – 120 s) corresponds to the combustion of volatile matter which was not captured by the calcined limestone bed. The second peak (120 – 240 s) corresponds to the combustion of carbon deposited on the calcined limestone bed. After 240 s oxygen was fed to the reactor A to burn residual char, but only slight formation of CO_2 was observed. The result shown in Fig.4 indicates that a considerable amount of volatile matter was captured by calcined limestone.

Fig.5 shows the effect of temperature on carbon retention. Carbon retention was calculated from the total formation of CO_2 and CO during deposit combustion. Carbon retention increased with increasing temperature, though scattering of the data was observed. These results imply that higher temperature is favorable for volatile matter capture. The amount of pellet had only little influence on the carbon retention.
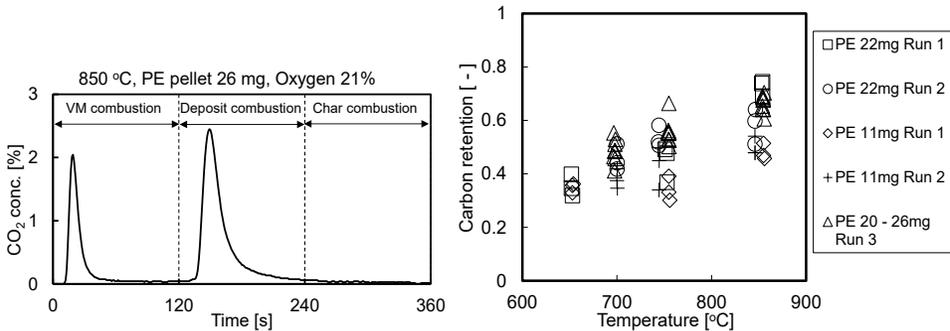

Fig. 4. Typical result of CO_2 formation after feeding a batch of plastic pellet to the fixed bed system.

Fig. 5. Effect of temperature on carbon retention over calcined limestone

Fig. 6 shows the impulse response of CO_2 analyzer (a) and estimation of true CO_2 formation profile from the CO_2 analyzer output signal (b). As shown in Fig. 6-(a), the half-height width of the impulse response of CO_2 analyzer was about 10 s. This value was not negligible for determine the combustion rate of carbon deposit. Thus the influence of analyzer's response on output signal was eliminated and true CO_2 formation profile was estimated. First, the impulse response was approximated by a three-stage complete mixing vessels. The input ($C_{IN,i}$) – output ($C_{OUT,i}$) relationship of i-th vessel is given by a differential equation as:

$$dC_{OUT,i}/dt = (C_{IN,i} - C_{OUT,i})/\tau_i \tag{1}$$

where τ_i refers to the residence time in i-th vessel. As shown in Fig. 6-(a), the impulse response of this CO_2 analyzer could be well described by a three-stage complete mixing vessels model. When an output of the i-th vessel is given by an experiment, the input of the i-th vessel (*i.e.* output of former vessel, $C_{OUT,i-1}$) can be estimated by transforming Eq.(1) as:

$$C_{IN,i} = C_{OUT,i-1} = C_{OUT,i} + \tau_i(dC_{OUT,i}/dt). \tag{2}$$

By turning back from the third vessel to the first vessel, the true inlet signal of the first vessel (true CO_2 formation profile) can be estimated from the output of the third vessel (CO_2 analyzer output). However, it should be noted that this estimation method amplifies high-frequency noise. A complete mixing vessel works as a low-pass filter that reduces the amplitude of high-frequency components of the signal, thus the present estimation method compensates the lost high-frequency components but it also amplifies unnecessary high-frequency noise. To suppress noise amplification, time-resolution of the signal was reduced. Fig. 6-(b) shows a result of the estimation of true CO_2 formation profile. The stepwise change in the estimated value corresponds to the reduction of time-resolution of the signal.
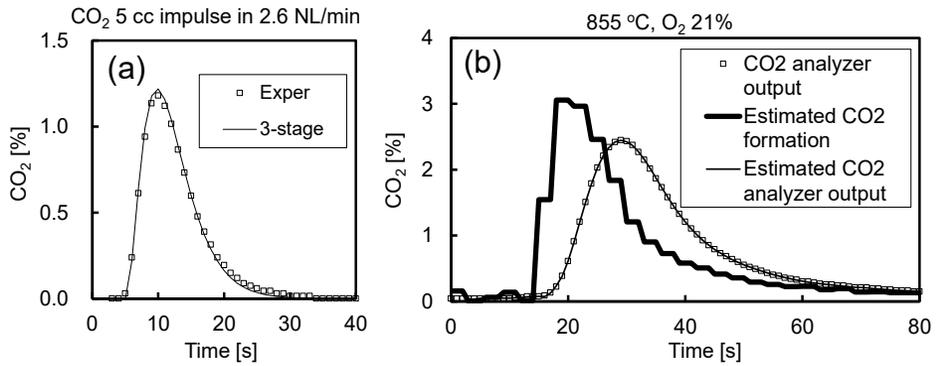
Fig. 6. Impulse response of CO_2 analyzer (a) and estimation of true CO_2 formation profile from the CO_2 analyzer output signal during carbon deposit combustion (b).

The estimated true CO_2 formation profile was integrated to calculate the conversion (X) of deposit carbon during combustion. Fig. 7 shows the change in unreacted fraction of carbon ($1 - X$) with time. The logarithm of unreacted fraction had a straight line relationship with time. Thus the change in carbon conversion with time was expressed as a first-order equation with respect to the unreacted fraction as:

$$dX/dt = k(1 - X) \tag{3}$$

where k is the apparent first-order rate constant.
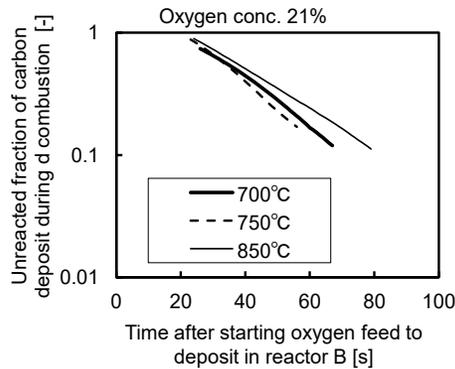

Fig. 7. Change in unreacted fraction of carbon deposit with time during carbon deposit combustion.
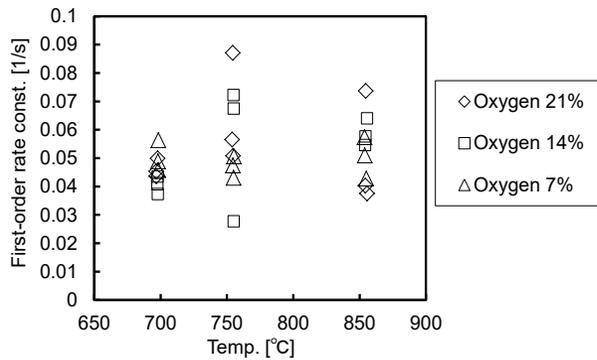

Fig. 8. Effect of temperature on apparent first-order rate constant of carbon deposit combustion

Fig. 8 shows the effect of temperature on apparent first-order rate constant of carbon deposit combustion. The temperature influenced the combustion rate constant only slightly. Fig. 9 shows the effect oxygen concentration on apparent first-order rate constant of carbon deposit combustion. The oxygen concentration affected the reaction rate only slightly, within the range of scattering of data. The above findings suggest that the carbon deposit combustion rate can be maintained low even in high O_2 concentration atmosphere under elevated temperature, i.e., capturing volatile matter to form carbon deposit on CaO surface is expected to suppress hot-spot formation within the regenerator by suppressing rapid combustion of volatile matter.
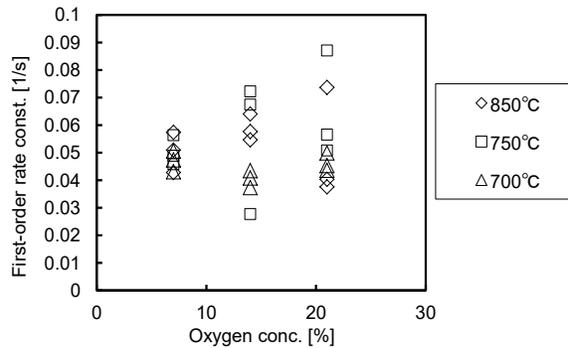

Fig. 9. Effect of oxygen concentration on apparent first-order rate constant of carbon deposit combustion

Fig. 10 illustrates proposed designs of fuel feed with volatile matter capture by porous recirculating bed material. Fig. 10-(a) shows the base case in which fuel is directly fed to the regenerator. One modification is to feed fuel to low-temperature recirculating solids from the carbonator as shown in Fig. 10-(b). The temperature of carbonator is maintained at 600 – 650 ºC, thus the temperature of the solids at the exit is within this temperature range. It is expected that carbon deposit is formed on $CaCO_3$-rich recirculating solids, thus the heat of carbon deposit combustion can be transferred to $CaCO_3$ effectively in the regenerator. One disadvantage is that such low temperature is not favorable for the volatile matter capture, as shown in Fig.5; only 30 – 40 % of volatile matter was captured at 650 ºC.

The second modification (Fig. 10-(c)) is to form O_2-lean zone at the bottom of the regenerator by feeding solely CO_2 to the bottom and by feeding fuel to the oxygen-lean zone. Because of the back-mixing of solids in the regenerator, the temperature in the O_2-lean zone can be maintained high; slightly lower temperature is expected than that of the regenerator because heat is consumed to heat up fed CO_2 and to evaporate water in the fuel. High temperature is favorable for volatile matter capture as shown in Fig.5. However, a part of volatile matter is captured by fully-calcined CaO particles which fall down from the top, thus heat of combustion from such particles should be transferred to $CaCO_3$ through solid-solid heat transfer via gas phase. Also the penetration of pure O_2 injected through the nozzles in the reactor above the O_2-lean zone may be insufficient when the size of the regenerator increases.

Modifications that enable the temperature control of volatile capture reactor are illustrated in Figs. 10-(d) and 10-(e). In Fig. 10-(d), a part of pure O_2 fed to the regenerator is fed to the volatile capture reactor to increase the temperature by burning a part of fuel/carbon deposit. The temperature in the reactor is measured and the O_2 feed rate is controlled so that a desired temperature can be maintained. In Fig. 10-(e), a part of the solids entrained from the regenerator to the carbonator is bypassed to the volatile capture reactor to increase the temperature. A solid-flow control valve (mechanical gate valve or pneumatic solid flow control device such as L-valve) is installed at the loopseal below the solid capture device (cyclone) to control the solid flow to the volatile capture reactor. The solid valve is operated so that a desired temperature can be attained in the volatile capture reactor. Comparing Fig. 10-(d) with Fig. 10-(e), controlling the O_2 flow to the volatile capture reactor is considered to be easier and more precise than controlling the solid flow, because solid flow is usually difficult and sometimes not so stable. Table 1 summarizes brief description, advantages, and disadvantages of proposed fuel feed modifications to enhance volatile matter capture by sorbent particles. Among them, O_2 feed to the volatile capture reactor (Fig. 10-(d)) is considered to be the most feasible and effective if O_2 feed rate to increase the temperature is within a feasible range.
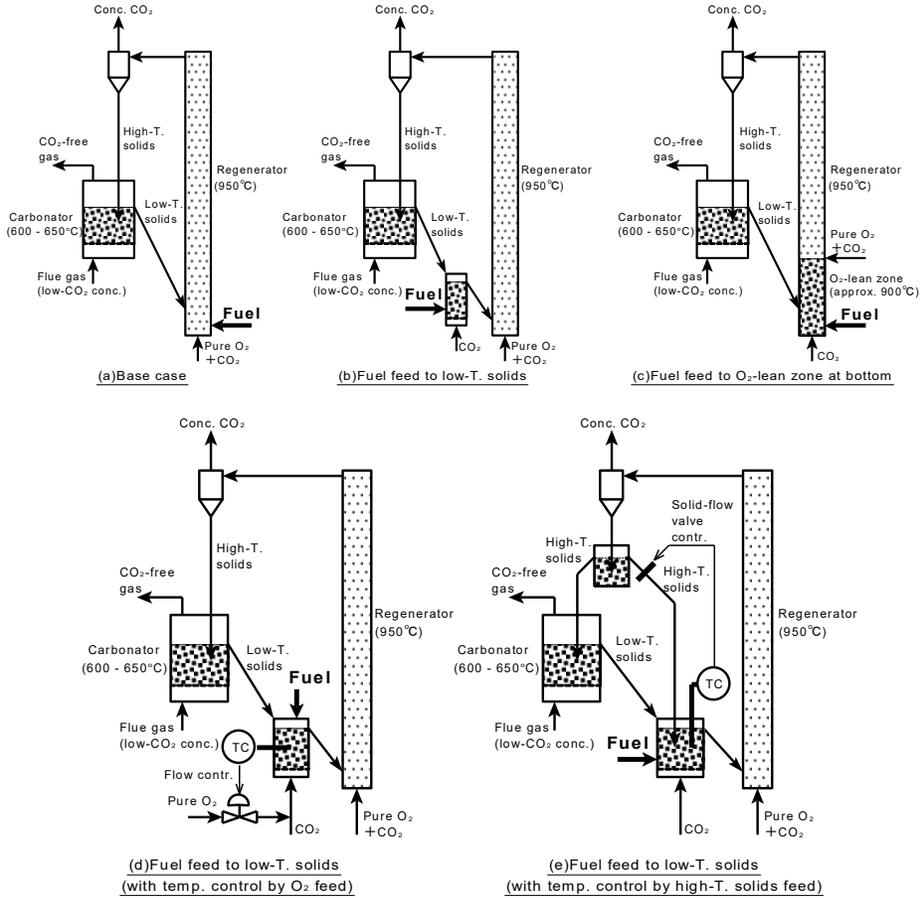
Fig.10. Proposed designs of fuel feed that enable volatile matter capture by porous recirculating bed material

Table 1 Description and advantage/disadvantage of proposed fuel feed modifications to enhance volatile matter capture by sorbent particles (Types b – e correspond to (b) –(e) in Fig. 10)

type	Description	Advantage	Disadvantage
b	Fuel feed to recirculating low temperature solids (600 – 650 ºC)	Volatile matter capture by solids rich in $CaCO_3$, thus efficient contact between heat source and heat sink	Low volatile matter capture efficiency at lower temperature
c	Fuel feed to O_2-lean zone in the bottom of regenerator (900 ºC)	High volatile matter capture efficiency at high temperature	Carbon capture by calcined solids, insufficient O_2 penetration into the regenerator
d	Fuel feed to recirculating low temperature solids with O_2 feed to achieve desired temperature	Temperature control to improve volatile matter capture, volatile matter capture by solids rich in $CaCO_3$, and reduced concentration of volatile matter diluted by CO_2	Somewhat complicated system
e	Fuel feed to recirculating low temperature solids with hot-solid feed from cyclone to achieve desired temperature	Temperature control to improve volatile matter capture and volatile matter capture by solids rich in $CaCO_3$	Complicated system, solid flow control not so easy

914

Required O_2 to increase the temperature of volatile matter capture reactor is calculated for the case of Fig. 10-(d). It is assumed that the inlet temperature of solids is 600 °C. The reactor is fluidized by pure CO_2 (recirculated gas from regenerator). Only CO_2 is formed when O_2 is fed. The heat of combustion is carried out of the reactor as sensible heat of solids and sensible heat of CO_2. $CaCO_3$ is stable in the reactor because temperature is lower than the decomposition temperature. Table 2 shows the design condition of the present calculation. The value employed in this calculation is the same as that employed for the process conceptual design by Shimizu (1999). The calculation result is shown in Fig. 11. To heat up the solids in the volatile capture reactor from 600 to 800 °C, about 30% of total O_2 should be fed into the volatile capture reactor. This value is considered to be feasible for the practical use.
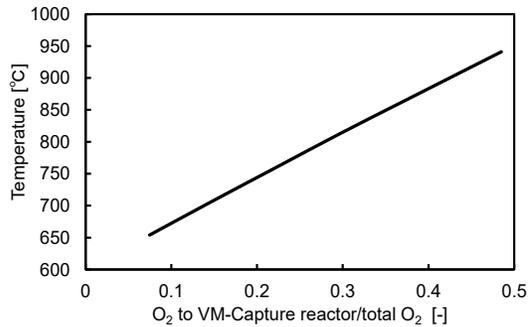

Fig.11. Estimated O_2 consumption to increase the temperature in volatile matter capture reactor for Fig.10-(d)

Table 2 Design condition of O_2 feed to volatile matter capture reactor for Fig.10-(d)

$CaCO_3$ flow	CaO flow	Fluidizing CO_2	Coal HHV	Coal feed	Total O_2 feed
kmol/s	kmol/s	kmol/s	MJ/kg-daf	kg-daf/s	kmol/s
2.41	21.71	0.086	33.2	32.0	2.66

The use of the volatile capture reactor with O_2 feed is considered to have an advantage of reduced volatile matter concentration in the gas mixture fed to the regenerator. Besides the volatile matter capture, the rest of volatile matter will be diluted by both fluidizing CO_2 and CO_2 formed by combustion. Thus higher temperature in the volatile capture reactor is considered to be favorable not only for volatile matter capture but also dilution of the rest of volatile matter because more CO_2 will be formed with increasing O_2 feed to increase temperature.

CONCLUSION

As an approach to prevent hot-spot formation in the regenerator of CaL process operated using high-O_2 concentration gas at high temperatures, use of capacitance effect (volatile matter capture and carbon deposit formation) of porous sorbent particles is proposed. A basic study was conducted to assess the volatile matter capture and deposit combustion rate. CaO particles were found to capture volatile matter in a temperature range of CaL process. Process modifications were proposed to enhance volatile matter capture by recirculating solids.

NOTATION

$C_{IN,i}$	Concentration at inlet of i-th stage %		t	time, s
$C_{OUT,i}$	Concentration at outlet of i-th stage %		X	solid carbon conversion, -
k	apparent reaction rate constant, 1/s		τ_i	residence time of i-th stage, s

REFERENCES

Abanades, J.C., Alonso, M., Rodríguez, N., González, B, Grasa ,G., Murillo, R. 2009. Capturing CO_2 from combustion flue gases with a carbonation calcination loop. Experimental results and process development. Energy Procedia 1, 1147–1154

Alonso, M., Rodríguez, N., González, B., Grasa, G., Murillo, R., Abanades, J. C. 2010. Carbon dioxide capture from combustion flue gases with a calcium oxide chemical loop. Experimental results and process development. Int. J. Greenhouse Gas Control 4, 167–173

Arias, B., Diego, M. E., Abanades, J. C., Lorenzo, M., Diaz, L., Martínez, D., Alvarez, J., Sánchez-Biezma, A. 2013. Demonstration of steady state CO_2 capture in a 1.7 MWth calcium looping pilot. Int. J. Greenhouse Gas Control, 18, 237–245

Atsonios, K., Panopoulos, K., Grammelis, P., Kakaras, E. 2016. Exergetic comparison of CO_2 capture techniques from solid fossil fuel power plants. Int. J. Greenhouse Gas Control 45, 106–117

Charitos, A., Hawthorne, C., Bidwe, A.R., Sivalingam, S., Schuster, A., Spliethoff, H., Scheffknecht, G. 2010. Parametric investigation of the calcium looping process for CO_2 capture in a 10 kWth dual fluidized bed. Int. J. Greenhouse Gas Control 4, 776–784

Charitos, A., Rodríguez, N., Hawthorne, C., Alonso, M., Zieba, M., Arias, B., Kopanakis, G., Scheffknecht, G., Abanades, J. C. 2011. Experimental validation of the calcium looping CO_2 capture process with two circulating fluidized bed carbonator reactors. Ind. Eng. Chem. Res. 50, 9685–9695

Clarens, F., Espí, J. J., Giraldi, M. R., Rovira, M. ,Vega, L. F. 2016. Life cycle assessment of CaO looping versus amine-based absorption for capturing CO_2 in a subcritical coal power plant. Int. J. Greenhouse Gas Control 46, 18–27

Cormos, C. C. 2015. Assessment of chemical absorption/adsorption for post-combustion CO_2 capture from Natural Gas Combined Cycle (NGCC) power plants. Appl. Therm. Eng. 82, 120-128

Dieter, H., Hawthorne, C., Zieba, M., Scheffknecht, G. 2013. Progress in calcium looping post combustion CO_2 capture: Successful pilot scale demonstration. Energy Procedia 37, 48-56

Dieter, H., Bidwe, A.R., Varela-Duelli, G., Charitos, A., Hawthorne, C., Scheffknecht, G. 2014. Development of the calcium looping CO_2 capture technology from lab to pilot scale at IFK, University of Stuttgart. Fuel 127, 23-37

Fang, F., Li, Z. S., Cai, N. S. 2009. Continuous CO_2 capture from flue gases using a dual fluidized bed reactor with calcium-based sorbent. Ind. Eng. Chem. Res. 48, 11140–11147

Franke, H.J., Shimizu, T., Nishio, A., Nishikawa, H., Inagaki, M., Ibashi, W. 1999. Improvement of carbon burn-up during fluidized bed incineration of plastic by using porous bed materials. Energy & Fuels 13, 773-777

Hanak, D. P., Biliyok, C., Anthony, E. J., Manovic, V. 2015. Modelling and comparison of calcium looping and chemical solvent scrubbing retrofits for CO_2 capture from coal-fired power plant. Int. J. Greenhouse Gas Control 42, 226–236

Kremer, J., Galloy. A., Ströhle, J., Epple, B. 2013. Continuous CO_2 capture in a 1-MWth carbonate looping pilot plant. Chem. Eng. Technol., 36, 1518–1524

Lu, D. Y., Hughes, R. W., Anthony, E. J., 2008. Ca-based sorbent looping combustion for CO_2 capture in pilot-scale dual fluidized beds. Fuel Process. Technol. 89, 1386–1395

Miyauchi, T., Tsutsui, T., Nozaki, Y. 1987. A new fluid thermal cracking process for upgrading residues. presented at the AIChE National Meeting (Houston, TX, USA)

Rodríguez, N., Alonso, M., Abanades, J. C., 2011. Experimental investigation of a circulating fluidized-bed reactor to capture CO_2 with CaO. AIChE J. 57, 1356–1366

Sánchez-Biezma, A., Paniagua, J., Diaz, L., Lorenzo, M., Alvarez, J., Martínez, D., Arias, B., Diego, M. E., Abanades, J.C. 2013. Testing postcombustion CO_2 capture with CaO in a 1.7MW$_t$ pilot facility. Energy Procedia 37, 1–8

Shimizu, T., Hirama, T., Hosoda, H., Kitano, K., Inagaki, M., Tejima, K. 1999. A twin fluid-bed reactor for removal of CO_2 from combustion processes. Chem. Eng. Res. Des. 77, 62-68

Shimizu, T., Franke, H.J., Hori, S., Asazuma, J., Iwamoto, M., Shimoda, T., Ueno, S. 2007. Capacitance effect of porous solids - an approach to improve fluidized bed conversion processes of high-volatile fuels. Chem. Eng. Sci. 62, 5549-5553

Shimizu, T., Takahashi, T., Narisawa, H., Murakami, Y., Li, L.-Y., Kim, H.-J. 2011. CaO looping cycle for CO_2 separation. Proc. 10th Int. Conf. on Circulating Fluidized Beds and Fluidization Technology - CFB-10, pp.329-336

Symonds, R. T., Champagne, S., Ridha, F. N., Lu, D.Y. 2016. CO_2 capture performance of CaO–based pellets in a 0.1 MW$_{th}$ pilot-scale calcium looping system. Powder Technol. 290, 124–131

Teramae, T. 2007. Effect of catalysis on tar elimination and gas production from fluidized bed gasification of biomass. Kagaku-Kogaku-Ronbunsyu 33, 246-256

Zhao, M., Minett, A. I., Harris, A. T. 2013. A review of techno-economic models for the retrofitting of conventional pulverised-coal power plants for post-combustion capture (PCC) of CO_2. Energy Environ. Sci. 6, 25–40