

## Design of acryogenic CO<sub>2</sub> capture system based on Stirling coolers

著者別名	宋 春風, 北村 豊
journal or publication title	International journal of greenhouse gas control
volume	7
page range	107-114
year	2012-03
権利	(C) 2012 Elsevier Ltd. NOTICE: this is the author's version of a work that was accepted for publication in International journal of greenhouse gas control. Changes resulting from the publishing process, such as peer review, editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version was subsequently published in International journal of greenhouse gas control, Vol.7, Pages:107-114. doi: 10.1016/j.ijggc.2012.01.004.
URL	<a href="http://hdl.handle.net/2241/117618">http://hdl.handle.net/2241/117618</a>

doi: 10.1016/j.ijggc.2012.01.004

# **Design of a cryogenic CO<sub>2</sub> capture system based on Stirling coolers**

Chun-Feng Song, Yutaka Kitamura\*, Shu-Hong Li, Kenji Ogasawara

*Graduate School of Life and Environmental Sciences, University of Tsukuba, 1-1-1,*

*Tennodai, Tsukuba, Ibaraki 305-8572, Japan*

\* Corresponding author. Tel.: +81 0298-53-4655; Fax: +81 0298-53-4655.

E-mail address: [kitamura.yutaka.fm@u.tsukuba.ac.jp](mailto:kitamura.yutaka.fm@u.tsukuba.ac.jp)

## **Abstract**

In this research, a novel cryogenic CO<sub>2</sub> capture system based on Stirling coolers has been developed. By the capture system designed, an effective separation can be achieved according to differences in condensation and desublimation. From the capture process, H<sub>2</sub>O and CO<sub>2</sub> can condense and desublimates at different parts of the capture system, while residual gas flows out without properties change. It is noteworthy that in the process, CO<sub>2</sub> can be captured in a solid form, thus avoiding the use of the solvents and consideration of pressure in other methods. Furthermore, two significant parameters (the temperature of Stirling coolers and the flow rate of the gas stream) were investigated in detail. The results showed that under the optimal temperature and flow rate, CO<sub>2</sub> recovery of the cryogenic process can reach 96%, which demonstrated that the system can capture CO<sub>2</sub> gas effectively.

*Keywords:* CO<sub>2</sub> capture, Stirling cooler, cryogenic, desublimation

## Nomenclature

$P_{sat,g}$	Saturated vapor pressure of CO <sub>2</sub> gas, Pa
$P_{sat,s}$	Saturated vapor pressure of CO <sub>2</sub> frost, Pa
$T_g$	Temperature of gas, K
$T_f$	Temperature of frost, K
$U$	Voltage, V
$I$	Current flow, A
$Q$	Total heat flux to the frost layer, W/m <sup>2</sup>
$Q_c$	Heat flux of convection, W/m <sup>2</sup>
$Q_p$	Heat flux of phase change, W/m <sup>2</sup>
$M_s$	Frost mass upon per unit surface area, kg/m <sup>2</sup>
$R_{CO_2}$	Gas constant, 8.314 J/(K·mol)
$Nu$	Nusselt number

$Pr$	Prandtl number
$Ra$	Rayleigh number
$Re$	Reynolds number
$m_t$	Mass flux of desublimated CO <sub>2</sub> , kg/(m <sup>2</sup> ·s)
$h_{m,CO_2}$	Mass transfer coefficient of solid CO <sub>2</sub> , m/s
$h_c$	Coefficient of convective heat transfer process, W/(m <sup>2</sup> ·K)
$h_{nc}$	Coefficient of natural convection, W/(m <sup>2</sup> ·K)
$h_{fc}$	Coefficient of forced convection, W/(m <sup>2</sup> ·K)
$t$	Time, s
$k_f$	Effective thermal conductivity of frost layer, W/(m·K)
$q$	Latent heat of sublimation, J/kg
<i>Greek letters</i>	
$v_{in}$	Flow rate of feed gas, L/min
$v_{out}$	Flow rate of vent gas, L/min
$\eta$	CO <sub>2</sub> recovery efficiency, %
$\rho_{CO_2,g}$	Density of CO <sub>2</sub> gas, kg/m <sup>3</sup>
$\rho_{CO_2,s}$	Density of CO <sub>2</sub> solid, kg/m <sup>3</sup>
$\omega_{CO_2,in}$	Percentage of CO <sub>2</sub> in feed gas, vol. %
$\omega_{CO_2,out}$	Percentage of CO <sub>2</sub> in vent gas, vol. %

$\delta_f$	Frost layer thickness, m
------------	--------------------------

*Abbreviations*

<i>CCS</i>	CO <sub>2</sub> capture and storage
------------	-------------------------------------

<i>SC</i>	Stirling cooler
-----------	-----------------

<i>EC</i>	Energy consumption
-----------	--------------------

## **1. Introduction**

Climate change caused by greenhouse gas has become a critical issue of worldwide

concern. Among greenhouse gas, CO<sub>2</sub> makes up a high proportion of the amount in the atmosphere and is responsible for 70% of global warming effect (U.S. Department of Energy, 2007). Although new renewable resources of energy production have been exploited (such as wind, solar, and biomass energy), the world will remain largely dependent on fossil fuels for the next decades. Thus, the capture and separation of CO<sub>2</sub> are significant for greenhouse effect control, and it is a serious global priority. In this case, CO<sub>2</sub> capture and storage (CCS) has been proposed as a sustainable technology to mitigate greenhouse gas by the Intergovernmental Panel on Climate Change (IPCC) (Metz et al., 2005).

In recent years, the focus of the researchers fastens on the fossil fueled power plants, which are the main emissions of CO<sub>2</sub>. There are three ways to capture CO<sub>2</sub> from coal-fired plants: post-combustion, pre-combustion and oxy-fuel combustion (Irons et al., 2007). Although capture of CO<sub>2</sub> contributes 75% to the overall CCS costs, the separation of CO<sub>2</sub> is also a crucial part of CCS. Nowadays, the technologies of CO<sub>2</sub> separation mainly contain absorption, adsorption, cryogenics and membranes (Jeremy, 2000; Audus, 2000). Among these technologies, chemical solvents absorption processes are considered to be the most feasible method and already at an advanced stage of development, but they still have several areas that need to be improved, such as energy penalty caused by solvents regeneration. In order to achieve

the aim of reducing energy consumption, the improvement of existing technologies and exploitation of novel capture processes have been paid an increasing attention.

As an available approach for CO<sub>2</sub> capture, the cryogenic separation technology has been researched for several decades. However, for the past years, this technology was not extensively studied due to the high expected cooling cost. In fact, by the application of cryogenic separation, no absorbents are required and CO<sub>2</sub> can be captured at atmospheric pressure. With these advantages, the research of cryogenic CO<sub>2</sub> capture technologies has made significant progress. In 2002, Clodic and Younes developed a cryogenic CO<sub>2</sub> capture process, in their process CO<sub>2</sub> could be desublimated as a solid onto the surfaces of heat exchangers, which were cooled by evaporating a refrigerants blend. The energy requirement of the whole process was in the range of 541 to 1119 kJ/kg CO<sub>2</sub> (Clodic et al., 2004a). In 2010, Tuinier et al. exploited a novel cryogenic CO<sub>2</sub> capture process using dynamically operated packed beds. By the developed process above 99% CO<sub>2</sub> could be recovered from a flue gas containing 10 vol. % CO<sub>2</sub> and 1 vol. % H<sub>2</sub>O with 1.8 MJ/kg CO<sub>2</sub> energy consumption.

In addition, as the most important part of the cryogenic system, Stirling cooler (SC) gets interest of researchers because of its significant advantages, such as high efficiency, high reliability and small size (Hu et al., 2010). The operation of SC contains four processes: expansion under an isothermal condition, refrigeration under

a constant volume condition, compression under an isothermal condition, and heating under a constant volume condition (Sun et al., 2008). As a typical mechanical cooler, Stirling cycle coolers have been widely applied to the area of infrared detectors, superconductor filters, space exploration and cryopumps (Park et al., 2002; Chen et al., 2009). Nevertheless, the application of Stirling cooler on greenhouse gas control is novel. Compared to current technologies, its advantage is low energy consumption. Furthermore, this method is mainly based on a thermal process for CO<sub>2</sub> capture and separation, thereby avoiding the use of any chemical solvents that can lead to increasing operating costs and environmental impact (Metz et al., 2005).

Based on the above discussion, it is significant to develop an efficient and convenient method of CO<sub>2</sub> capture. In this study, a completely different system of cryogenic CO<sub>2</sub> capture is developed according to the invention patent of Kitamura in 2006. The effect of temperature and flow rate on CO<sub>2</sub> recovery and process performance is researched, and the result of experiments showed that the SC-based CO<sub>2</sub> capture system can capture CO<sub>2</sub> gas effectively.

## **2. Process principle**

CO<sub>2</sub>, in its pure form, has a freezing point of -78.5°C (at atmospheric pressure CO<sub>2</sub> does not exist as a liquid) (Hart and Gnanendran, 2009). With the distinctive physical

characteristics, separation of CO<sub>2</sub> from other components of the emission sources can be realized.

Considering the post-combustion flue stream is typically composed by 13.9% CO<sub>2</sub>, 75.5% N<sub>2</sub> (which has a frost point approximately -209.86°C), 5.1% O<sub>2</sub> (which has a frost point approximately -218°C) and 5.5% H<sub>2</sub>O (Clodic and Younes, 2002), it is convenient to carry out this separation using cryogenic processes, and under the low temperature condition, most of the CO<sub>2</sub> can desublimates and be separated from the gaseous phase.

The schematic of the cryogenic process based on SCs is described in Fig. 1. In the process, the feed gas is separated into three flows: condensate water, dry ice and residual gas. At the first step, the water in flue gas condenses in the pre-cool process by SC-1 and then moves through the condensing pipe to the outlet to avoid plugging the vessel, which is the key issue of cryogenic separation technologies. Meanwhile, the other gas flows into the main freezing tower, at atmospheric pressure and the cryogenic temperature, CO<sub>2</sub> gas desublimates into solid form. At last, the solid CO<sub>2</sub> frosts onto the heat exchanger of SC-2, and by spinning the scraping rod on the heat exchanger of SC-2, it falls down to the storage column, where SC-3 provides a cryogenic condition for storage. On the other hand, residual gas exhausts from the gas outlet.

### 3. Numerical study

In order to enhance understanding of the frost process for improving efficiency of CO<sub>2</sub> capture, heat and mass transfer processes were investigated in this section. The process was described by a numerical model. Besides, due to the varying thermo physical properties during frost formation, some assumptions were employed to simplify the complex process: 1) Frost layer distribution is homogeneous over the cooling fin of the heat exchanger of SC-2; 2) The frosting process takes place at a quasi-steady state; 3) Frost thermal conductivity of the frost layer varies only with frost density; 4) Radiation heat transfer between the flue gas and frost layer is negligible. It is noted that owing to the desublimation process occurred on the heat exchanger of SC-2, the structure of its cooling fin and the direction of airflow is described in Fig. 2(1), and the temperature distribution in the main freezing tower is simulated in Fig. 2(2).

#### 3.1 Mass transfer

From the mass balance, the frost mass accumulated upon per unit surface area ( $M_s$ ) of the cooling fin of SC-2's heat exchanger is defined as:

$$\frac{dM_s}{dt} = m_t$$

where  $m_t$  is the mass flux of desublimated CO<sub>2</sub> from flue gas to the surface of

cooling fin, and it can be obtained in terms of:

$$m_t = h_{m,CO_2} (\rho_{CO_2,g} - \rho_{CO_2,s})$$

where  $h_{m,CO_2}$  is the mass transfer coefficient of solid CO<sub>2</sub>;  $\rho_{CO_2,g}$  and  $\rho_{CO_2,s}$  are the densities of CO<sub>2</sub> in flue gas and frost surface, respectively. Since the CO<sub>2</sub> gas is assumed to be an ideal gas,  $\rho_{CO_2,g}$  and  $\rho_{CO_2,s}$  can be calculated from the following ideal gas equations of state.

$$\rho_{CO_2,g} = \frac{\omega_{CO_2,in} P_{sat,g}}{R_{CO_2} T_g}$$

$$\rho_{CO_2,s} = \frac{P_{sat,s}}{R_{CO_2} T_f}$$

where  $\omega_{CO_2, in}$  is the percentage composition of CO<sub>2</sub> in flue gas,  $T_g$  and  $T_f$  are the temperature of flue gas and frost surface, respectively.  $P_{sat,g}$  and  $P_{sat,s}$  denote the saturation pressure of CO<sub>2</sub> at  $T_g$  and  $T_f$ , respectively, and  $R_{CO_2}$  is the gas constant of CO<sub>2</sub>. In addition, the frost layer thickness ( $\delta_f$ ) on cooling fin surface of SC-2's heat exchanger is calculated as:

$$\delta_f = \frac{M_s}{\rho_{CO_2,s}}$$

where  $\rho_{CO_2,s}$  is the density of frost layer.

### 3.2 Heat transfer

In order to describe the effect of heat transfer, the effective thermal conductivity of

frost layer ( $k_f$ ) is introduced, and the heat balance at cooling fin surface of SC-2 heat exchanger is determined from:

$$k_f \frac{T_f - T_g}{\delta_f} = Q$$

where  $Q$  is the total heat flux to the frost layer and is equal to the sum of heat fluxes by convection ( $Q_c$ ) and phase change ( $Q_p$ ) as following:

$$Q = Q_c + Q_p$$

The convective heat transfer can be calculated by the equations described by Y.A.

Cengel in 2003:

$$Q_c = h_c (T_g - T_f)$$

$$h_c = |h_{nc}^3 + h_{fc}^3|^{1/3}$$

$$Nu_{nc} = \left\{ 0.825 + \frac{0.387 Ra^{1/6}}{\left[ 1 + (0.492 / Pr)^{9/16} \right]^{8/27}} \right\}^2$$

$$Nu_{fc} = 0.3 + \frac{0.62 Re^{2/3} Pr^{1/3}}{\left[ 1 + (0.4 / Pr)^{2/3} \right]^{1/4}} \left[ 1 + \left( \frac{Re}{282.000} \right)^{5/8} \right]^{4/5}$$

where  $h_c$ ,  $h_{nc}$  and  $h_{fc}$  denote the heat transfer coefficients of the whole convective heat transfer process, natural and forced convection, respectively.  $Nu$  is Nusselt number,  $Ra$  is Rayleigh number,  $Pr$  is Prandtl number and  $Re$  is Reynolds number.

The phase change heat transfer is equal to:

$$Q_p = m_t q$$

where  $q$  is the latent heat of sublimation, which has been estimated by M. Fossa and G. Tanda in 2002:

$$q = 2.88 \times 10^6 - 195T_f$$

#### **4. Cryogenic capture system**

The experiments are implemented based on the setup shown in Fig. 3. The main parts of the system contain SC, vacuum pump, freezing tower, camera, control panel and computer. There are three SCs in the system. Firstly, SC-1 is used for precooling the feed gas stream and condensing the moisture in the gas mixture. Secondly, SC-2 maintains a cryogenic condition in the main freezing tower, and in that condition, CO<sub>2</sub> can desublimates into a solid form. At last, SC-3 is used for solid CO<sub>2</sub> storage.

In addition, the materials of the structure should be selected considering their influence on cryogenic performance. First of all, the materials used as the structure of experimental setup are stainless steel. Then as the key part, copper is used as the cold head of heat exchangers, since it has a well coefficient of heat transfer. The junctions between the cold head of the SCs and freezing tower are wrapped up by thermal insulating materials to reduce the heat loss. For some synthetic materials may become ineffective at low temperature (approximately -120°C), specific sealing materials and gaskets are typically required for the pipe fittings to avoid air leakage of the system.

The flow rate and pressure of the gas stream at the inlet and outlet are controlled by a flow controller (Bronkhorst El-flow) and analogue pressure controller. The temperature of the main parts of the cryogenic system is measured with thermocouples (Thermo-Electric K-type) every 0.1 seconds. The heat transfer parts are maintained under a vacuum condition and recorded by vacuum pump (Nakamura Seisakusho Co., Ltd.) and indicator (NVC-1100, Tokyo Rikakikai Co., Ltd.), respectively. The process of desublimation is monitored by a camera in the main freezing tower.

## **5. Results**

Through the tests, we found there were various parameters that influence the performance of the cryogenic system. To explore an efficient capture process, several key parameters were investigated. In this study, the effect of flow rate and temperature on the CO<sub>2</sub> recovery and capture performance was tested. The composition and condition of feed gas is listed in Table 1.

### *5.1. Effect of the flow rate of the gas stream on CO<sub>2</sub> recovery*

As a key parameter representing the efficiency of CO<sub>2</sub> capture process, CO<sub>2</sub> capture recovery is defined as:

$$\eta = 1 - \frac{v_{out} \omega_{CO_2,out}}{v_{in} \omega_{CO_2,in}} \quad (1)$$

here  $\eta$  is CO<sub>2</sub> recovery;  $v$  is the flow rate of gas mixture and  $\omega$  is the percentage of CO<sub>2</sub> in gas mixture. In addition, the subscripts *in* and *out* represent the state of inlet and outlet.

Owing to the limitation of the contact area of heat exchanger, the recovery of CO<sub>2</sub> gas depends on the flow rate of the gas stream. The condition of flow rate test is shown in Table 2, with the temperature of SCs kept constant, three different flow rates were tested.

Result in Fig. 4(1) shows that with the flow rate increasing, the recovery of CO<sub>2</sub> presents a declining curve. This can be explained by the fact that CO<sub>2</sub> gas desublimated onto heat exchanger of SC-2 decreased the cooling capacity of SC-2. That is due to frost layer insulated the cooling fin and hindered the contact of subsequent gas stream and heat exchanger. The temperature of frost surface increased rapidly and heat transfer consequently decreased. Hence, the temperature around the gas stream can not attain the condition of CO<sub>2</sub> desublimation. It suggested that the continuous scraping mechanism for the heat exchanger or freezing portion should be incorporated into the system. On the other hand, result in Fig. 4(2) shows that among three different flow rates, 1.5 L/min is the best with the lowest energy consumption per kg of CO<sub>2</sub>. When SCs in the system operated at full capacity and the flow rate was

set as 1.5 L/min, the system could capture 96% CO<sub>2</sub> from flue gas with 1.5 MJ/kg CO<sub>2</sub> energy consumption. That is because when the flow rate is set as 1L/min, a majority of flue gas flows through the cold head from the sides; while the flow rate is increased unto 1.5L/min, most of the gas can pass the gap of the cold head and only a small fraction slop over; when the flow rate is too fast as 2 L/min, although the flue gas can flow via the cooling fin, there is no time for most of it to undergo the frosting process.

## *5.2. Effect of temperature on capture performance*

Considering that the temperature of SC was also a critical factor for the system performance, the experiment of temperature was carried out to obtain the optimal capture efficiency. In this experiment,  $v$  was set to 1.5 L/min, which has been testified in the above section. Then, the effect of temperature of SC-1 on capture performance was investigated. The condition of the experiment is shown in Table 3.

The details in Fig. 5 show that when the temperature threshold of SC-1 changed from -60°C to -30°C before gas mixture flowed into the system, the temperature of SC-1 heat exchanger, pre-cooling tube and water condensate tube increased obviously; the temperatures of SC-2 heat exchanger and dry ice storage tank were consistent. Nevertheless, when the temperature threshold of SC-1 exceeded -30°C, the system

was not able to maintain a cryogenic condition. Although the temperature of SC-2 heat exchanger could also reach  $-90^{\circ}\text{C}$ , the gas stream could not be precooled adequately, and the temperature in the  $\text{CO}_2$  storage tank was far above the condition of cryopreservation. This led to a decline of capture efficiency.

It was obvious that in order to maintain high purity of frosted  $\text{CO}_2$ , the water in the gas stream should be separated as much as possible. According to the tests, an effective separation between  $\text{CO}_2$  and  $\text{H}_2\text{O}$  was obtained and the problem of plugging was intrinsically avoided by keeping the temperature threshold of SC-1 under  $-30^{\circ}\text{C}$ . With the range of  $-60^{\circ}\text{C}$  to  $-30^{\circ}\text{C}$ , the lower the temperature threshold of SC-1 was, the better efficiency of the capture system performed. However, when the temperature threshold of SC-1 was above  $-30^{\circ}\text{C}$  (e.g.,  $-20^{\circ}\text{C}$  in Fig. 5), the system could not separate  $\text{H}_2\text{O}$  from the gas stream effectively. Consequently, the upper limit of the temperature of SC-1 should be controlled below  $-30^{\circ}\text{C}$ .

The purpose of the experiment was also focused on the validation of the effect of temperature on cryogenic  $\text{CO}_2$  capture performance. Figure 6 presents the trend of temperature variation of SC-2 heat exchanger when flue gas flowed into the system, and indicates that when the temperature limit of SC-1 was lower than  $-30^{\circ}\text{C}$ , the trend of temperature variation of SC-2 heat exchanger was coincident; when the experiment was repeated with the temperature limit of SC-1 set to  $-20^{\circ}\text{C}$ , the variation presented a

different tendency. This alteration of temperature threshold of SC-1 led to the temperature change in the system. These results showed a close resemblance to the point of Fig. 5, when the temperature threshold of SC-1 exceeded  $-30^{\circ}\text{C}$ , the moisture in the gas stream could not be separated effectively, and the cryogenic performance dropped off substantially.

## **6. Discussion**

The novel cryogenic  $\text{CO}_2$  capture process has been tested under various conditions (including gas flow rate and cooling temperature) to achieve a full description of the performance of the system. Simultaneously, two important parameters were used for assessing the cryogenic separation system, *i.e.* cryogenic performance and capture efficiency.

### *6.1. Cryogenic performance*

In the cryogenic process, there was some ice crystal generated on the joints between the heat exchangers and freezing towers. This phenomenon indicated that the effect of heat insulation jacket was not optimal. In addition, the frost layer of  $\text{CO}_2$  onto the cooling fin of the heat exchanger of SC-2 is shown in Fig. 7(1); the deposition of captured  $\text{CO}_2$  in the storage column is shown in Fig. 7(2). It is observed

that the increasing layer of solid CO<sub>2</sub> onto the heat exchanger surfaces during the capture cycle would adversely affect the heat transfer and reduce the process efficiency. Figure 8 shows the temperature of the main parts of the cryogenic system during capture process.

In comparison, the novel cryogenic system based on SCs has several significant advantages. One of the most important advantages is that H<sub>2</sub>O and CO<sub>2</sub> can be separated simultaneously while condensing and desublimating at the different places in the system. In previous studies, the bottleneck of cryogenic CO<sub>2</sub> capture technology is plugging. Thus extra cost needs to be invested on dehydration. However, in the proposed process, there was no plugging occurred. In addition, the size of the CO<sub>2</sub> capture system was small, which could be used on the sources of small emissions and economize capture cost as much as possible.

## 6.2. CO<sub>2</sub> capture efficiency

The energy consumption (EC) of the cryogenic system for per unit mass CO<sub>2</sub> captured is defined as following:

$$EC = \frac{UI}{(v_{in} - v_{out}) \rho_{CO_2}} \quad (2)$$

where  $U$  and  $I$  are voltage and current in the system, respectively.  $v_{in}$  and  $v_{out}$  are the

volume flow rate of gas mixture at the inlet and outlet.  $t$  is the run time of the cryogenic system, and  $\rho_{CO_2}$  is the density of  $CO_2$  gas.

In addition, the effect of flow rate and temperature on  $CO_2$  capture efficiency has been investigated. Through the results, with decreasing temperature, the recovery of  $CO_2$  did not improve accordingly. Under the condition of flow rate of feed gas was 1.5 L/min and the temperature threshold of SC-1 was  $-30^\circ C$ , the  $CO_2$  capture efficiency could reach 96%. It indicated that although the minimum temperature threshold of SC-1 was  $-120^\circ C$ , after the optimal value ( $-30^\circ C$ ), the continuous decrease of temperature would lead to an extra energy penalty. Meanwhile, due to the restriction of contact area between gas stream and heat exchanger, when the flow rate of the gas stream was excessively fast, it presented a reduced recovery. Besides, it was found that as time passed,  $CO_2$  recovery presented decreasing tendency. That was due to the dry ice formed on the surface of heat exchanger adversely affected heat transfer.

At present, the main  $CO_2$  capture technologies are chemical absorption and membrane separation. For the two technologies, solvent regeneration and pressure difference as driving force lead to capital penalties, respectively. With respect to the capture efficiency, the comparison of these major technologies cannot be neglected. In previous studies, some researchers have attempted to make a quantitative comparison between each two methods, e.g. MEA and membranes by Favre in 2011, MEA and

cryogenic by Clodic et al. in 2005. In our work, a brief comparison among the three processes has been made. Ahead of comparison, it should be pointed out that for different technologies the types of requirement energy are also different. 1) For the MEA methods, there are two parts of the energy that should be considered. One is the thermal energy used for regenerating the solvent and extracting steam from the steam turbine, which dominates the energy consumption of the whole capture process. The other small part is electrical energy for the operation of the machines. 2) For the membrane methods, all the energy required is electrical energy to generate the partial pressure difference. 3) For the cryogenic separation process in this research, the cryogenic condition and operation of the system are both based on the electrical energy consumption. In addition, for these technologies, the compression energy of CO<sub>2</sub> to transport and storage pressure should also be considered as an important part. It is therefore not correct to make a direct comparison of the energy consumption between these methods without any calculation exchange. In order to obtain meaningful results, the condition of each technology should be stated accompanying with the comparison. The comparison results are presented in Table 4. The results indicate that the energy consumption for membrane process is substantially higher than that for MEA and cryogenic processes, which is due to its capital requirement for permeation under the flue gas condition.

In addition, the common characteristic of the present work and the other cryogenic processes described in section 1 (*i.e.* the outcomes of Clodic and Tuinier) are that no chemical absorbent is required, and the capture of CO<sub>2</sub> can be realized at atmospheric pressure. Meanwhile, each of these methods has their own features, and a comparison is shown in Table 5. From the comparison, it is observed that further investigation on this process is significant and promising.

## **7. Conclusion**

In this study, a novel cryogenic CO<sub>2</sub> capture system based on the commercial SC has been designed. The principle of operation and advantages of the system were demonstrated and verified in detail. According to the experimental results, an effective separation on the basis of differences in frost points can be achieved without increasing pressure drops and plugging problems. From the performance of system, it demonstrated that the system can separate CO<sub>2</sub> efficiently. Furthermore, the influence of flow rate of gas stream and temperature of SC-1 on the performance of system was investigated. Based on the designed cryogenic system, the recovery of CO<sub>2</sub> can achieve 96% with 1.5 MJ/kg CO<sub>2</sub> energy consumption, which demonstrated that the research of the CO<sub>2</sub> capture process based on Stirling coolers is promising. Meanwhile, further testing has been planned to determine the range and overall

performance of the system and solve the problem of heat loss. Besides, the test of CO<sub>2</sub> capture from flue gas and biogas will be carried out.

### **Acknowledgement**

This research is supported by Adaptable and Seamless Technology transfer Program through the target driven R&D (AS2115051D) of Japan Science and Technology Agency (JST). We thank Mr. Yamano and Mr. Yamasaki of Tanabe Engineering Corporation for their technological assistance.

### **References**

- Audus, H., 2000. Leading options for the capture of CO<sub>2</sub> at power stations. Presented at the 5th international conference on greenhouse gas control technologies, Cairns, Australia. 13-16 August.
- Cengel, Y.A., 2003. Heat Transfer: A Practical Approach, second ed., McGraw-Hill.
- Chen, X., Wu, Y.N., Zhang, H., Chen, N., 2009. Study on the phase shift characteristic of the pneumatic Stirling cryocooler. Cryogenics 49, 120–132.
- Clodic, D., Hitti, E.R., Younes, M., Bill, A., 2005. CO<sub>2</sub> capture by anti-sublimation thermo-economic process evaluation. 4th Annual Conference on Carbon Capture & Sequestration, May 2-5, Alexandria (VA), USA.

- Clodic, D., Younes, M., 2002. A new method for CO<sub>2</sub> capture: frosting CO<sub>2</sub> at atmospheric pressure. Sixth International Conference on Greenhouse Gas Control Technologies, GHGT6, Kyoto, Japan, 1-4 October, pp.155–160, [CD ROM].
- Clodic, D., Younes, M., Bill, A., 2004a. Test result of CO<sub>2</sub> capture by anti-sublimation capture efficiency and energy consumption for boiler plants. Seventh International Conference on Greenhouse Gas Control Technologies, GHGT7, Vancouver, Canada, 6-9 September.
- Clodic, D., Younes, M., EL Hitti, R., Boulawz Ksayer, E., Casier, F., Bill, A. 2004b. Feasibility study of CO<sub>2</sub> and water capture by anti-sublimation for power station units. Report for the French Agency for Environment and Energy Management (ADEME), confidential.
- Favre, E., 2011. Membrane processes and postcombustion carbon dioxide capture: challenges and prospects. *Chemical Engineering Journal* 171, 782 - 793.
- Fossa, M., Tanda, G., 2002. Study of free convection frost formation on a vertical plate, *Exp. Therm. Fluid Sci.* 26, 661–668.
- Hart, A., Gnanendran, N., 2009. Cryogenic CO<sub>2</sub> Capture in Natural Gas. *Energy Procedia*. 1, 697–706.
- Ho, M.T., Allinson, G.W., Wiley, D.E., 2011. Comparison of MEA capture cost for low CO<sub>2</sub> emissions sources in Australia. *International Journal of Greenhouse Gas*

Control 5, 49 - 60.

Hussain, A., Hägg, M.B., 2010. A feasibility study of CO<sub>2</sub> capture from flue gas by a facilitated transport. *Journal of Membrane Science* 359, 140 - 148.

Hu, J.Y., Dai, W., Luo, E.C., Wang, X.T., Huang, Y., 2010. Development of high efficiency Stirling-type pulse tube cryocoolers. *Cryogenics*. 50, 603-607.

Irons, R., Sekkapan, G., Panesar, R., Gibbins, J., Lucquiaud M., 2007. CO<sub>2</sub> capture ready plants. IEA Greenhouse Gas R & D Programme, [www.ieagreen.org.uk](http://www.ieagreen.org.uk).

Jeremy, D., 2000. Economic evaluation of leading technology options for sequestration of carbon dioxide. M.S thesis, MIT, Cambridge, MA.

Kitamura, Y., 2006. How to stabilize the concentration of methane in the biogas system and stabilize the concentration of methane in biogas, Patent Publication No. 2007-237112.

Metz, B., Davidson, O., Coninck, H., Loos, M., Meyer, L, 2005. IPCC Special Report on Carbon Dioxide Capture and Storage. Prepared by Working Group III of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, UK, New York, NY.

Park, S.J., Hong, Y.J., Kim, H.B., Koh, D.Y., Kim, J.H., Yu, B.K., Lee, K.B., 2002. The effect of operating parameters in the Stirling cryocooler. *Cryogenics* 42, 419 - 425.

- Sun, J.F., Kitamura, Y., Satake, T., 2008. Application of Stirling cooler to food processing: Feasibility study on butter churning. *Journal of Food Engineering*. 84, 21–27.
- Tuinier, M.J., van Sint Annaland, M., Kramer, G.J., Kuipers, J.A.M., 2010. Cryogenic CO<sub>2</sub> capture using dynamically operated packed beds. *Chemical Engineering Science*. 65, 114-119.
- Tuinier, M.J., van Sint Annaland, M., Kuipers, J.A.M., 2011. A novel process for cryogenic CO<sub>2</sub> capture using dynamically operated packed beds—An experimental and numerical study. *International Journal of Greenhouse Gas Control*, doi:10.1016/j.ijggc.2010.11.011.
- U.S. Department of Energy., 2007. Energy Information Administration (EIA). International energy outlook. U.S. Government. 61-71.

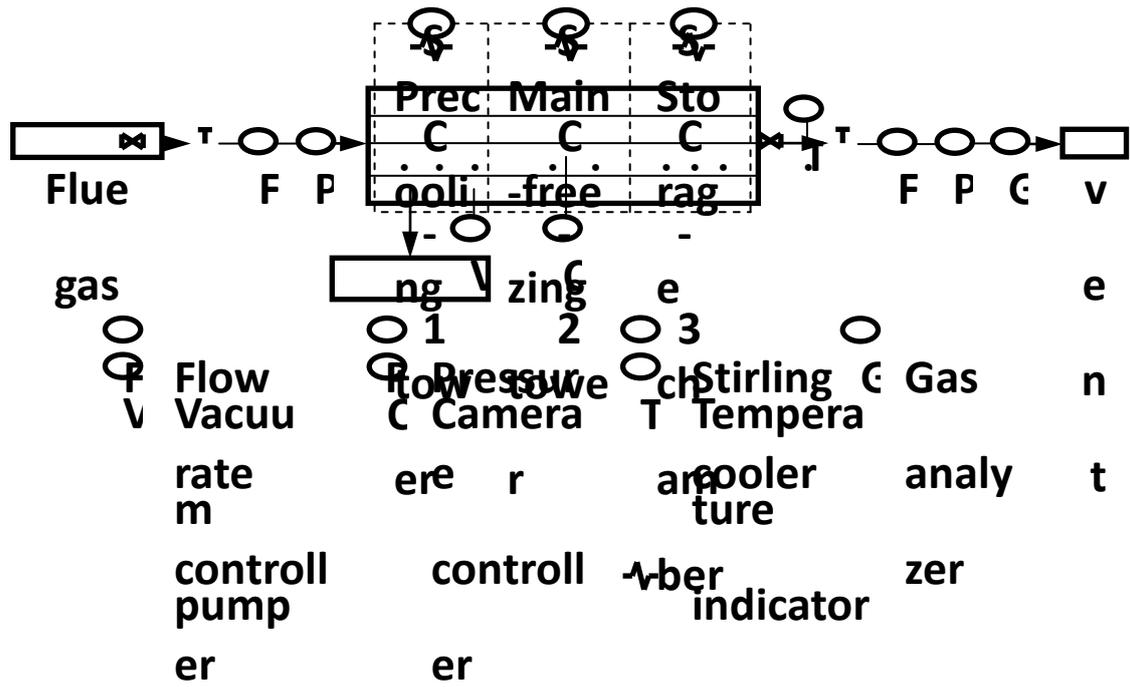


Fig. 1 Process of cryogenic CO<sub>2</sub> capture based on Stirling cooler system

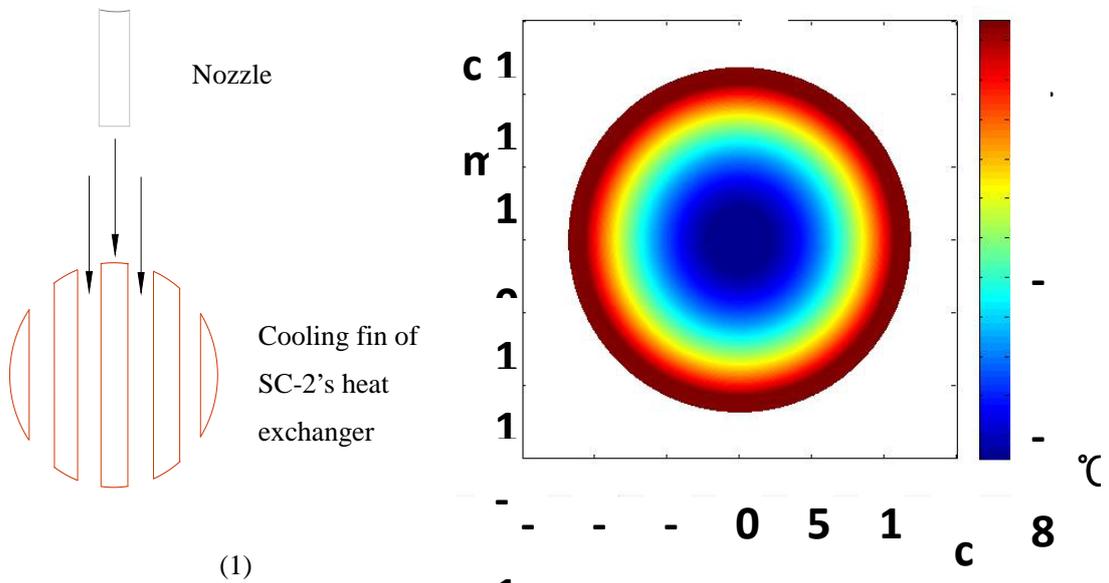


Fig. 2 The structure of cooling fin of SC-2's heat exchanger (1) and the temperature distribution of airflow in main freezing tower (2)



Fig. 3 The structure of cryogenic CO<sub>2</sub> capture system

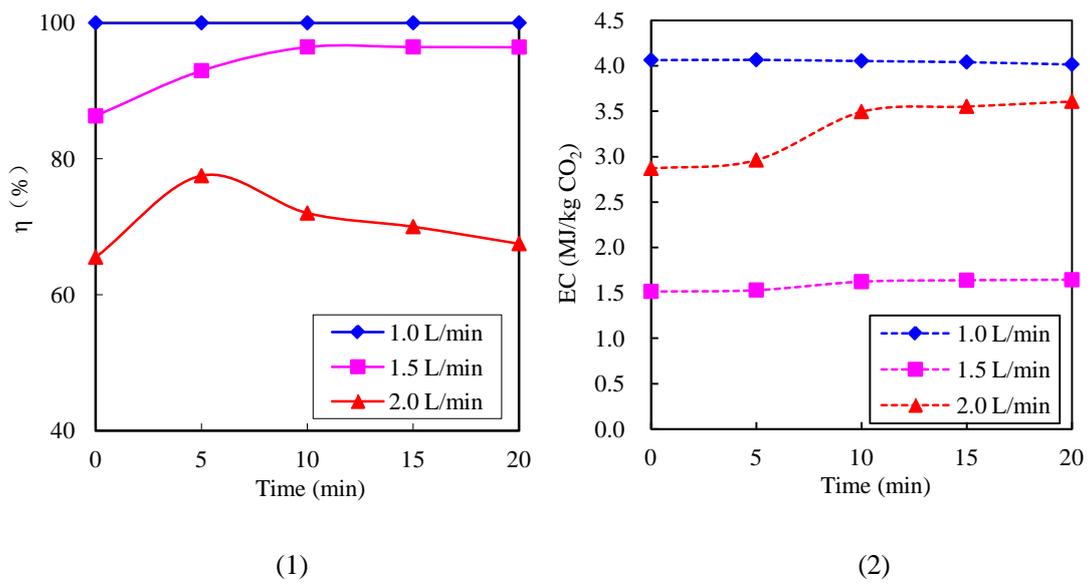


Fig. 4 Effect of flow rate ( $v$ ) of gas stream on CO<sub>2</sub> recovery ( $\eta$ ) and energy consumption (EC)

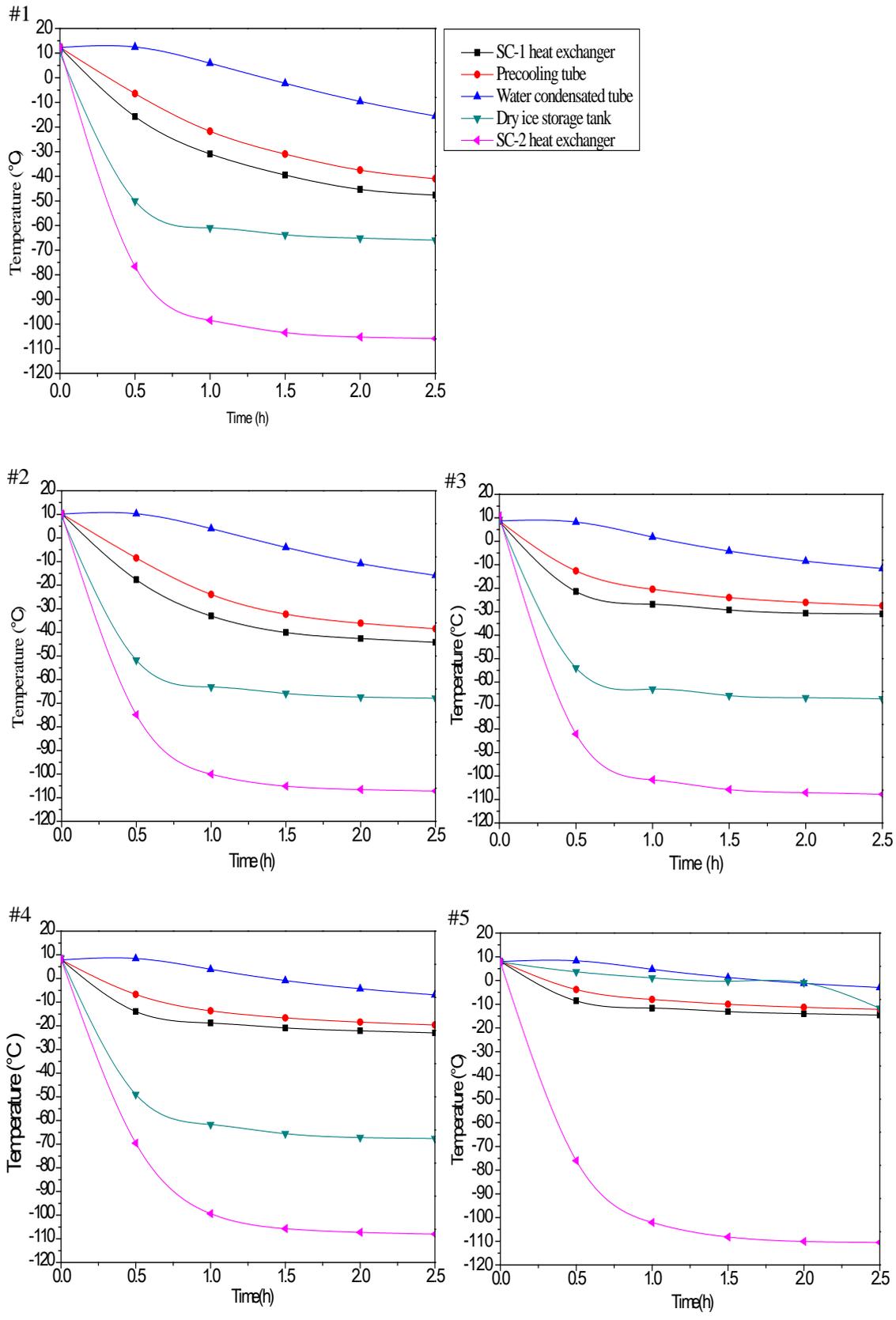


Fig. 5 Effect of SC-1 on the tendency of temperature variation of system (before gas mixture inflow)

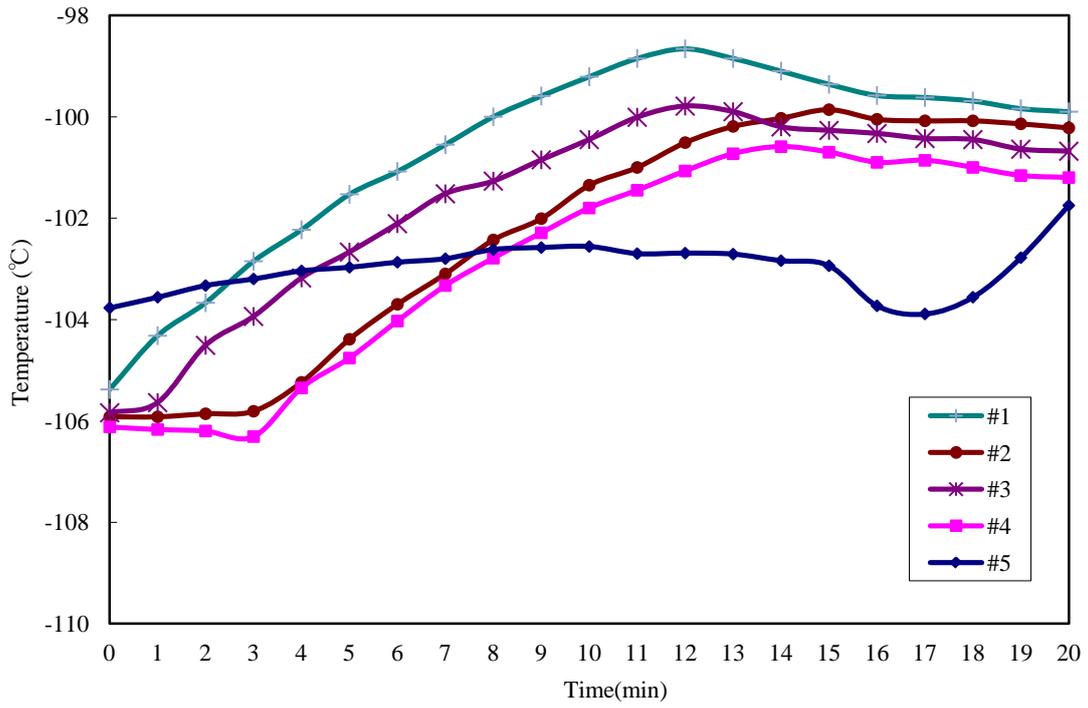


Fig. 6 The temperature variation curve of SC-2 heat exchanger in the process of CO<sub>2</sub> gas solidified (under different temperature threshold of SC-1)

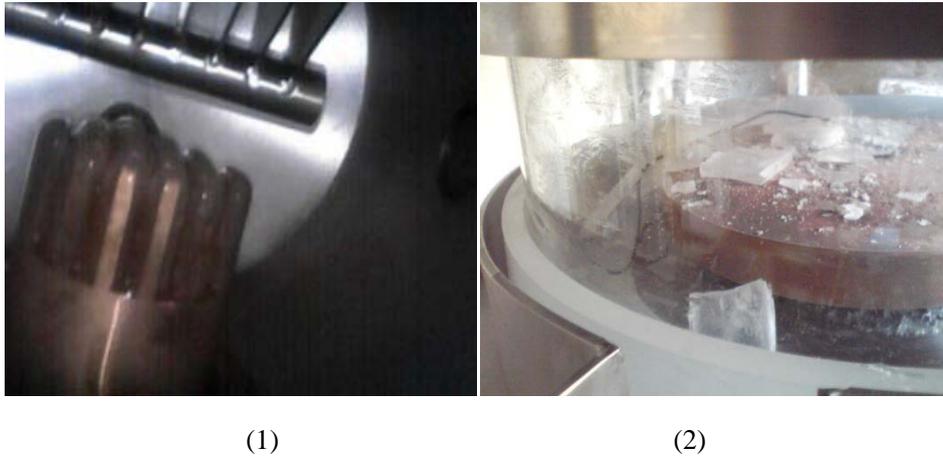
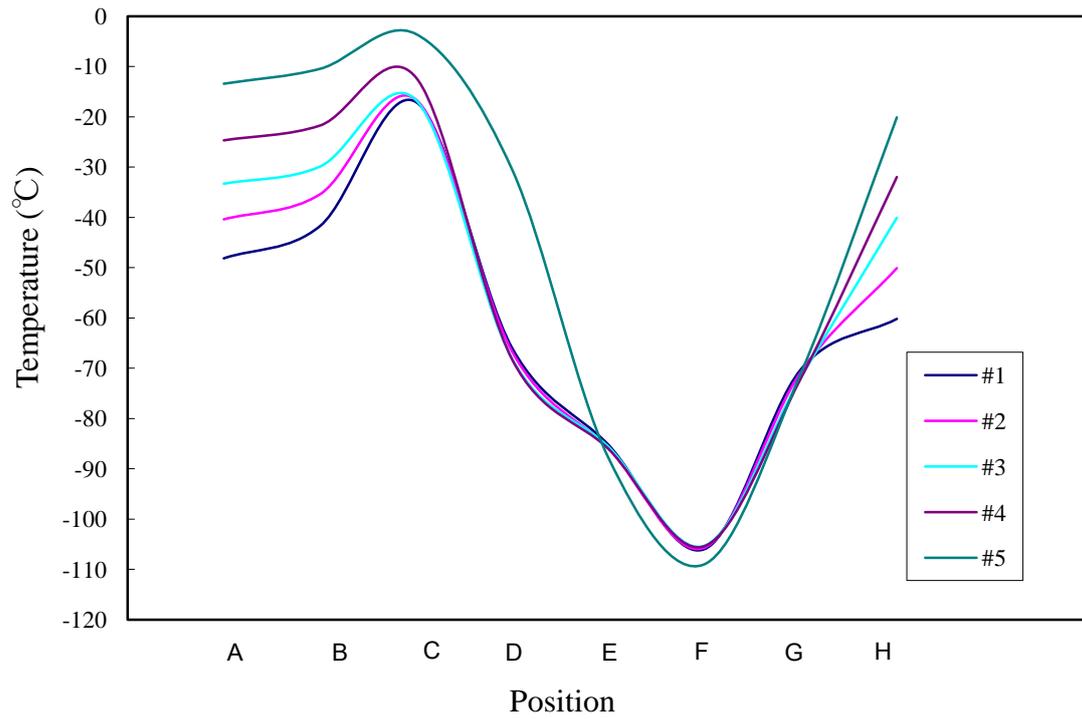


Fig. 7 The frost layer of CO<sub>2</sub> onto the cooling fin of SC-2's heat exchanger (1) and deposition in the storage column (2)



A SC-1 heat exchanger      B Precooling tube      C Water condensate tube  
 D Dry ice storage tank      E SC-2 heat exchanger      F SC-2      G SC-3      H SC-1

Fig. 8 Temperature variation of key parts in cryogenic capture system (under different temperature threshold of SC-1)

**Table 1**

Composition and condition of feed gas and ambient.

N <sub>2</sub> (vol.%)	82
CO <sub>2</sub> (vol.%)	13
H <sub>2</sub> O (vol.%)	5
Gas flow rate (L/min)	1~2
Gas temperature (°C)	24~25
Ambient temperature (°C)	24~26

Ambient humidity (%)	50~70
Ambient pressure (Pa)	$1.01 \times 10^5$

---

**Table 2**

Experimental conditions of flow rate ( $v$ ).

Experiments	#1	#2	#3
$v$ (L/min)	1	1.5	2

---

<sup>a</sup> The temperatures of SC-1, 2 and 3 are  $-120^\circ\text{C}$ ,  $-120^\circ\text{C}$  and  $-90^\circ\text{C}$ , respectively.

**Table 3**

Experimental conditions of temperature of SC-1.

Experiment	#1	#2	#3	#4	#5
Temperature of SC-1 ( $^\circ\text{C}$ )	-60	-50	-40	-30	-20

---

<sup>a</sup> Flow rate is 1.5L/min.

<sup>b</sup> The temperatures of SC-2 and 3 are  $-120^\circ\text{C}$  and  $-90^\circ\text{C}$ , respectively.

**Table 4**Comparison among the different CO<sub>2</sub> capture technologies.

Technologies	MEA (Ho et al., 2011)	Membrane (Hussain and Hägg, 2010)	Cryogenic (The present work)
Power output (MWe)	500	–	$5 \times 10^{-4}$
Total efficiency (%LHV)	39	–	–
Flue gases mass flow (kg/s)	630	284	$4.95 \times 10^{-5}$
Temperature (°C)	110	40	30

Pressure (Pa)	$1.01 \times 10^5$	$1.01 \times 10^5$	$1.01 \times 10^5$
Flue gases composition			
N <sub>2</sub>	75 (mol.%)	80 (vol.%)	82 (vol.%)
CO <sub>2</sub>	13	10	13
O <sub>2</sub>	5	5	–
H <sub>2</sub> O	7	5	5
CO <sub>2</sub> capture efficiency (%)	>85	>90	96
Energy penalty (MJ power /kg CO <sub>2</sub> )	1.6	3~4	1.5

**Table 5**

Comparison among the mentioned cryogenic capture processes.

Cryogenic processes	Advantages	Disadvantages
Clodic et al., 2004b	The fusion latent heat of CO <sub>2</sub> defrosting is recovered.	<ol style="list-style-type: none"> <li>1) The water content in the flue gas should be removed before capture process, which step would increase the capital cost or energy consumption;</li> <li>2) The frost layer of solid CO<sub>2</sub> onto the cold head surface will adversely affect the heat transfer and reduce the overall</li> </ol>

efficiency;

3) The costly heat exchangers have to be used for resisting the impact of temperature and mechanical stress.

Tuinier et al., 2011	The CO <sub>2</sub> , N <sub>2</sub> and H <sub>2</sub> O can be separated in different parts of the process, avoiding the phenomenon of plugging and pressure drop.	Due to the low coefficient of performance (COP) of the refrigerator (about 0.5 at -140°C), above 3.6 MJ electric energy was required for per unit CO <sub>2</sub> capture.
The present work	The separation among CO <sub>2</sub> , N <sub>2</sub> and H <sub>2</sub> O can be achieved.	<ol style="list-style-type: none"><li>1) It takes a long time for the whole system to reach the required cryogenic condition;</li><li>2) There is some heat loss in the capture at the junction of heat exchangers and tower;</li><li>3) The frost layer of solid CO<sub>2</sub> onto the heat exchanger surface will adversely affect the heat transfer and reduce the overall efficiency;</li><li>4) The costly heat exchangers have to be used for resisting the impact of temperature variation;</li><li>5) The oscillation of Stirling coolers would lead to a certain amount of energy loss.</li></ol>

---