A Study on Re-liquefaction Process of Boil-off Gas of LCO_2 Transfer Ship

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ABSTRACT

Climate change has been becoming severe over recent several decades. Greenhouse gases are considered to cause this phenomenon. Carbon dioxide has low global warming potential (GWP, 1.0) compared to other greenhouse gases such as CH_4, HFCs. But because it occupies about 76 % of emitted greenhouse gases and is considered to be controllable through many methods, CO_2 is classified as an important greenhouse gas. Much interest has been given to CCS (Carbon dioxide Capture and Storage or Sequestration) as a step to reduce the concentration of carbon dioxide in the atmosphere. At first, carbon dioxide should be captured with many impurities from the flue gas of some large plants, such as a power plant, a steel mill etc. After that, impurities should be removed from the captured gas. Then the concentration of this purified flue gas is 99.5 mol % CO_2, and 0.5 mol% N_2. This purified flue gas is called CO_2 mixture from now on. CO_2 mixture should be delivered in critical fluid state or liquid state to reduce the transferred volume to the prepared storage place such as saline-aquifer storage, oil reservoir etc.. Then CO_2 mixture should be injected to the storage using pumps. A series of these processes is called CCS. When the distance from the start point to the storage is over 1,000 km, the transfer using a ship is reported to be more economical than the one using pipelines. Because Korea and Japan emits large amount of CO_2 compared to the small territory, and are enclosed by sea, they have to secure some oversea storage place and use the delivery system of CO_2 mixture using a ship. To be transferred by ship CO_2 mixture should be liquefied. For this liquefaction processes of CO_2 were studied. Considering the impurities in CO_2 mixture, the operating conditions for the CO_2 mixture storage tank of a ship could be summarized roughly into two cases, 8 bar, equilibrium temperature (low pressure conditions) or 20 bar, equilibrium temperature (high pressure conditions). In this study, 8 bar, equilibrium temperature was chosen as the operating conditions for LCO_2 storage tanks considering realization. A ship has 50,000 m^3 storage capacity. BOR of the storage tank could be low enough such as 0.05 vol%/day on the assumption that using of high performance polyurethane foam as insulator. The amount of boil-off gas was assumed to be about 1,000 kg/hr. Re-liquefaction system was designed considering realization and installation. The yield was about 55~75 % based on the CO_2 (not CO_2 mixture) vaporized from the storage tank. Yield was increased to over 70 % through the change of structure in a re-liquefaction process.

KEY WORDS: global warming; carbon dioxide; liquefaction; a LCO_2 ship; boil-off gas; a re-liquefaction process

INTRODUCTION

As climate change has been severe, the extent of pressure to reduce the amount of greenhouse gases in the atmosphere has been increased. Carbon dioxide has been classified as an important greenhouse gas because the amount of gas can be controlled and reduced through human efforts. Many attempts to reduce and convert carbon dioxide have been tried. CCS is one of these trials. CCS is expected to cover 19% of the CO_2 reduction amount by 2050. CCS mainly consists of three procedures. One is the capturing procedure of carbon dioxide from massive CO_2 production system, like power generation plants. Another is the transporting procedure of carbon dioxide through pipeline or a ship from capturing place to storage place. The last one is injecting and surveying procedures of carbon dioxide. When the distance from a capturing place to a storage place is over 1,100 km, the transportation through a ship has been reported to be more economical than through a pipe line.

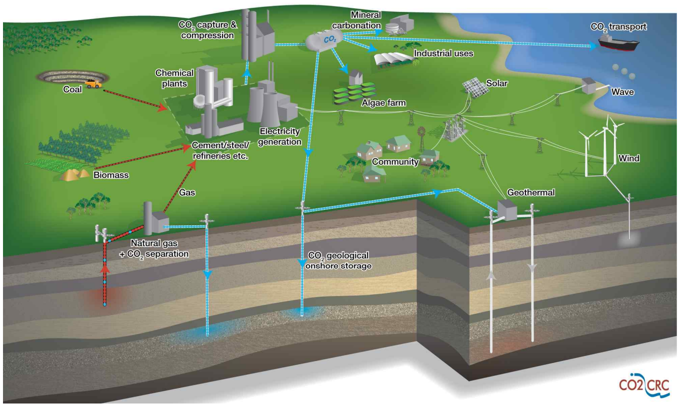

Fig. 1. Basic concept of CCS [source: CO2CRC]

In case of South Korea or Japan, countries that produce much more amount of carbon dioxide compared to its territory size, transportation of carbon dioxide through a ship will become very important in the near future. When it comes to ship transportation, the liquefaction of carbon dioxide cannot be overlooked. By now the concern of CCS has been focused only on the capturing process and comparatively minor concern has given to the development of a new liquefaction process and constructing the facilities for transportation of carbon dioxide through a ship. These phenomena are partly due to the countries that have led these researches. They have been countries having huge territory like Canada, Norway, and America. They have many storage places and they use carbon dioxide to enhance the production of oil and gas in their own land. But to develop more general and more applicable CCS system, more and more endeavor has to be made in the fields of liquefaction process and ship transportation. The research about those parts has been accomplished and the results have been summarized in this paper. To do this the liquefaction process of pure carbon dioxide was studied. Based on these results, the research about the re-liquefaction process for a LCO_2 (liquefied carbon dioxide) transfer ship was performed.

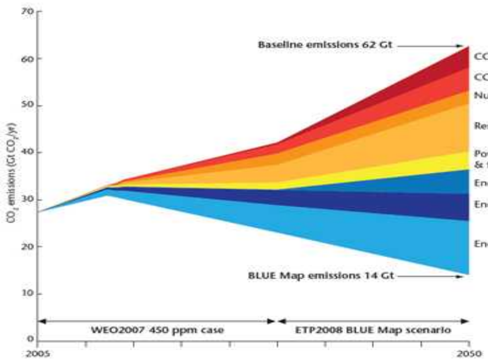

Fig. 2. CO_2 reduction scenario [source: IEA 2010 report]

LIQUEFACTION PROCESS OF CARBON DIOXIDE

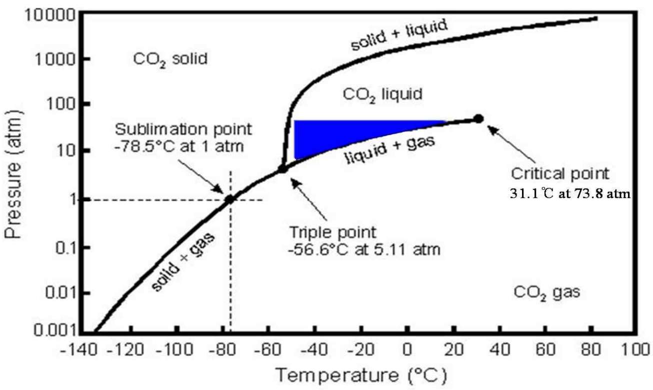

Fig. 3.Phase diagram of carbon dioxide and possible operating conditions for a LCO_2 ship (blue colored area)

Carbon dioxide has to be liquefied in order to be transported through a ship. After being liquefied, LCO_2 should be loaded into tanks of a ship. Considering the phase equilibrium conditions of carbon dioxide and operating margin, the possible operating conditions of the tank should be selected in range of 6~20 bar, -50~20 °C. For reference the triple point of carbon dioxide is -56.6 °C, 5.2 bar and the critical point is 31.1 °C, 73.8 bar. Cogent operating conditions of a LCO_2 tank for a ship are 6~8 bar, equilibrium temperature or 15~20 bar, equilibrium temperature. In this research 8 bar, equilibrium temperature was chosen as operating conditions of a LCO_2 tank in a ship.

First of all, a liquefaction process of pure carbon dioxide was studied. Feed gas was assumed to be 1,000 kg/hr of pure carbon dioxide at 40 °C, 1 bar. Liquefaction processes based on Brayton-JT cycle were studied in this paper.

Feed gas consisting of pure CO_2 is compressed to about 70~120 bar and cooled by cooling water. But temperature can't become low enough to be liquefied after being expanded. The feed gas has to be cooled by another refrigerant like propane, ammonia, or carbon dioxide which comprises another cycle like in Fig 4. Each refrigerant is chosen considering its boiling temperature, and easiness to be supplied etc.

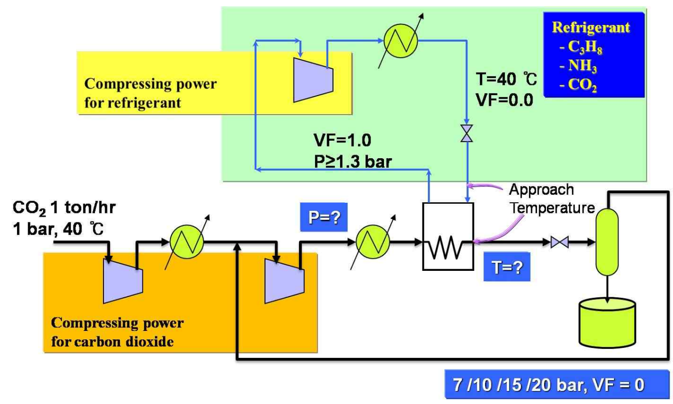

Fig. 4. Flow diagram of carbon dioxide liquefaction process

Basis of Simulation

Equations: Peng-Robinson (EOS) / Lee-Kesler (enthalpy) / COSTALD (density)
Ambient temperature: 35 °C
Feed conditions: pure CO_2 1,000 kg/hr at 40 °C, 1 bar
Product conditions: 7 / 10 / 15 / 20 bar, vapor/liquid equilibrium
Simulator: Aspen HYSYS
Compressors:
- 75% adiabatic efficiency
- compressing ratio: 1.6~2.0 for CO_2, 2.0~2.9 for C_3H_8, NH_3

Heat exchanger:
- approach temperature: 5 °C
- type: shell & tube
- shell side: a cold stream, zero pressure drop
- tube side: a hot stream, 25 kPa pressure drop

Case Study of C_3H_8, NH_3 refrigerant cycle

Simulations on liquefaction process of carbon dioxide with C_3H_8 or NH_3 refrigerant cycle were performed considering basic constraints. Temperature after compressors should be lower than 90 °C and the approach temperature of heat exchanger should be 5 °C. In case of 7 bar LCO_2 storage tank pressure, the power requirement was 141.0 kW. In this liquefaction system the high pressure after the last-compressing, the temperature after the heat exchanger, and the LCO_2 storage tank pressure could be controlled to make the power requirement needed to run the CO_2 compressors and the refrigerant compressors as low as possible. Through case studies the minimum power requirement for operating ranges are summarized as follows:

- high pressure after the last-compressing: 70~160 bar, 5 bar increment
- CO_2 temperature after the heat exchanger: -30~30 °C, 5 °C increment
- pressure of LCO_2 storage tank: 7 / 10 / 15 / 20 bar

The simulation results are summarized in Table 1 and 2. As the pressure of LCO_2 tank increased, the total power to run all compressors decreased.

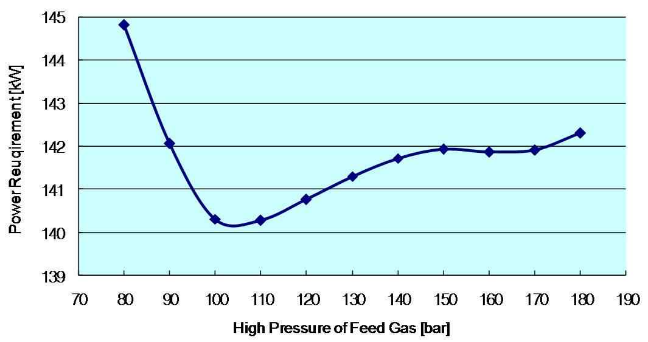

Fig. 5. Case study of 7 bar storage pressure of LCO_2 tank with C_3H_8 refrigerant cycle.

Table 1. Case study: optimization results of CO_2 liquefaction with C_3H_8 refrigerant cycle

Storage Press. [bar]	Raised Press.1# [bar]	Low Temperature* [°C]	Amt. of Refrigerant [kg/hr]	Total Power Req.♠ [kW]
7	110	-5	627	140.3
10	100	5	581	133.7
15	100	5	539	124.6
20	100	10	468	120.8

#: pressure after the last-compressing of the feed gas

*: feed gas temperature after heat transfer with C_3H_8 refrigerant

♠: power needed to run the refrigerant compressors and the CO_2 compressors

Table 2. Case study: optimization results of CO_2 liquefaction with NH_3 refrigerant cycle

Storage Press. [bar]	Raised Press.1 [bar]	Low Temperature [°C]	Amt. of Refrigerant [kg/hr]	Total Power Req. [kW]
7	100	-5	167	138.9
10	100	0	150	132.8
15	100	5	132	124.1
20	100	10	117	120.4

Case Study of CO_2 refrigerant cycle

Simulation on liquefaction process of carbon dioxide with CO_2 refrigerant cycle was performed considering basic constraints. CO_2 shows low COP at high heat rejection temperature compared to other common refrigerants. But CO2 is environmentally natural refrigerants and shows low GWP and zero ODP. It causes no safety problem because of its non-flammable and non-toxic properties. Additionally supplementation of refrigerant is very easy in case of CCS application. But in CO_2 refrigerant cycle CO_2 flow after being compressed and cooled the state of CO_2 may be critical fluid. Temperature and pressure are independent of each other in critical state. So the pressure of the CO_2 refrigerant becomes a new variable.

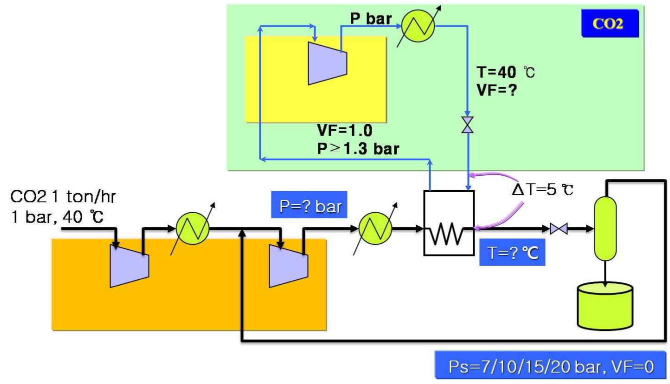

Fig. 6. Flow diagram of carbon dioxide liquefaction process with a CO_2 refrigerant cycle

Through case studies the minimum power requirement for various storage pressure of LCO_2 tank was calculated and the results are summarized in Table 3.

Table 3. Case study: optimization results of CO_2 liquefaction with CO_2 refrigerant cycle

Storage Press. [bar]	Raised Press.1 [bar]	Raised Press.2♣ [bar]	Low Temp. [°C]	Amt. of Refrig. [kg/hr]	Total Power Req. [kW]
7	120	140	5	901	149.0
10	120	140	5	850	141.8
15	100	120	15	971	131.8
20	100	120	20	879	126.6

♣: refrigerant pressure after the last-compressing in the refrigerant cycle

From the optimization results through case studies the higher the LCO_2 storage pressure, the lesser the power requirement. The optimum high pressure of the feed gas is in range of 100~120 bar. But these conclusions are obtained in views of only operating conditions. Considering the material and the structure for LCO_2 tank, different conclusions could be conducted.

RE-LIQUEFACTION PROCESS FOR BOIL-OFF GAS OF LIQUEFIED CARBON DIOXIDE MIXTURE

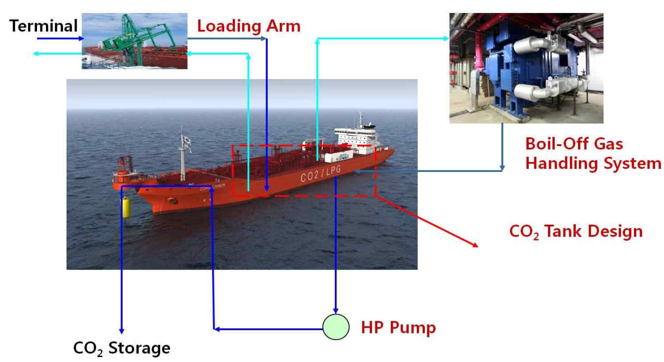

Fig. 7. Main facilities for a LCO2 transfer ship

A LCO_2 transfer ship mainly consists of three important facilities, LCO_2 storage tanks, cargo handling system including boil-off gas facilities, and high pressure pumps to transfer or inject carbon dioxide into storage place. If sailing period is short such as three to four days, an adsorber tower can be a solution. But if sailing period is long, over one week, another solution like re-liquefaction system of boil-off gas may be needed. Much concentration was given to the latter in this paper. In this case the composition of boil-off gas should be similar to real one. There are three main categories in capturing carbon dioxide from a massive production plant, that is, pre-combustion, post-combustion, and oxy-combustion CO_2 capture. Captured gas composition of each case is summarized in Table 4. In liquefaction process many impurities should be removed from the captured gas and the purity of carbon dioxide increases. The composition of LCO_2 was assumed to be 99.5 mol % CO_2, and 0.5 mol% N_2. The pressure of LCO_2 tank and the amount of boil-off gas (BOG) from LCO_2 tank were assumed to be 8 bar and 1,000 kg/m^3 respectively.

Table 4. Captured gas composition [vol%]

component	Pre-combustion	Post-combustion	oxy-combustion
CO_2	95.60	99.79	90.00
N_2	0.35	0.17	3.54
NO_x	0.00	0.01	0.15
SO_x	0.00	0.00	1.50
Others	4.05	0.03	4.81

Basis of Simulation

Equations: Peng-Robinson (EOS) / Lee-Kesler (enthalpy) / Costald (density)
Ambient temperature: 35 °C
LCO_2 composition: CO_2 99.5 mol%, N_2 0.5 mol%
BOG amount: 1,000 kg/hr (736.1 kg/hr CO_2, 263.9 kg/hr N_2)
Operating conditions of LCO_2 tank: 8 bar, vapor/liquid equilibrium
Simulator: Aspen HYSYS
Compressor:
- 75% adiabatic efficiency
- compressing ratio: 1.6~2.0 for CO_2

Heat exchanger:
- approach temperature: 3 °C
- type: plate fin
- pressure drop: 0.25 kPa for cold and hot streams

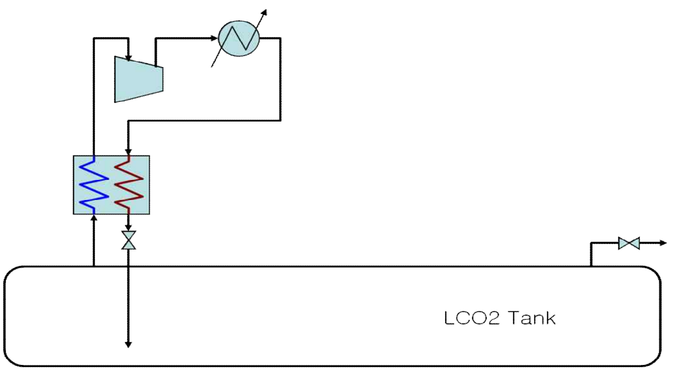

Fig. 8. Re-liquefaction system with recovery of cold heat (Case 1)

Re-liquefaction system should be simple to be installed on a ship. Re-liquefaction systems using another refrigerant cycle weren't tried and only simple re-liquefaction systems were studied in this paper. The simple re-liquefaction system is shown in Fig. 8. Required power per re-liquefied product (the specific power) was calculated to be 0.254 kW/(liquid product 1 kg/hr) and the CO_2 recover fraction to be 0.470. Only less than half amount of boil-off CO_2 was recovered. These performance were enhanced by recovering the cold heat from the vented gas.

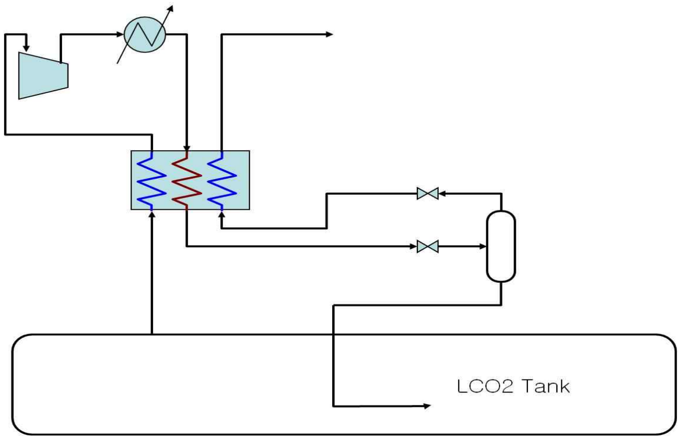

Fig. 9. Re-liquefaction system with cold heat recovery and a separator (Case 2)

The cold heat from the vented gas can be recovered in the system of Fig. 9. The specific power was calculated to be 0.192 kW/(kg/hr) and the CO_2 recover fraction 0.624. The recovered amount of CO_2 from the BOG was increased from 346.3 kg/hr to 459.2 kg/hr without additional power. Although much enhancement the CO_2 recover fraction was 0.624 and wasn't over 0.700.

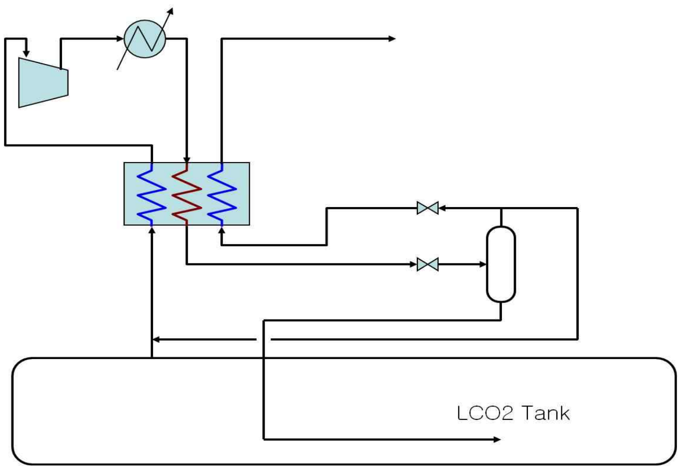

Fig. 10. Re-liquefaction system with cold heat recovery and a separator (Case 3)

To increase the CO2 recover fraction some portion of BOG was recycled. In this case the recovered amount of CO_2 was increased to 512.4 kg/hr and the recover fraction was 0.692. This system seemed to be efficient but the power consumption was increased by 40% from 88.4 kW to 123.4 kW. The energy inefficiency was shown from the specific power, 0.241 kw/(kg/hr).

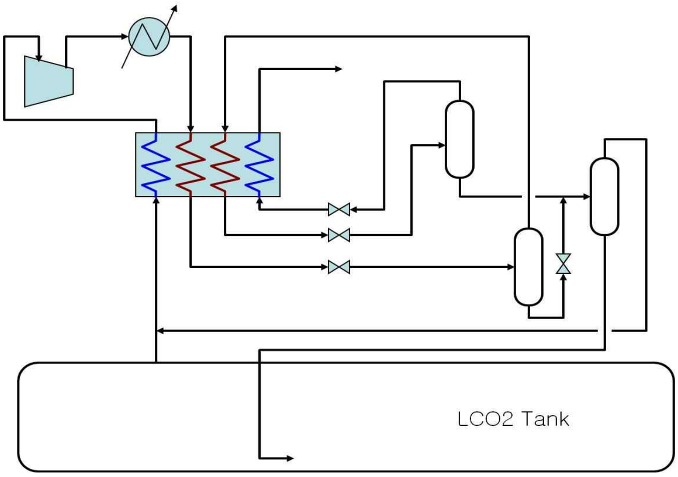

Fig. 11. Re-liquefaction system with cold heat recovery and three separators (Case 4)

In order to enhance the recover fraction without severe increase of power consumption the system was developed to decrease the recycled vent gas and to increase the cold heat recover from the vent gas like in Fig. 11. The CO_2 recover fraction was 0.743 and the power consumption 99.6 kW. The energy efficiency was also enhanced from 0.241 to 0.181 kW/(kg/hr).

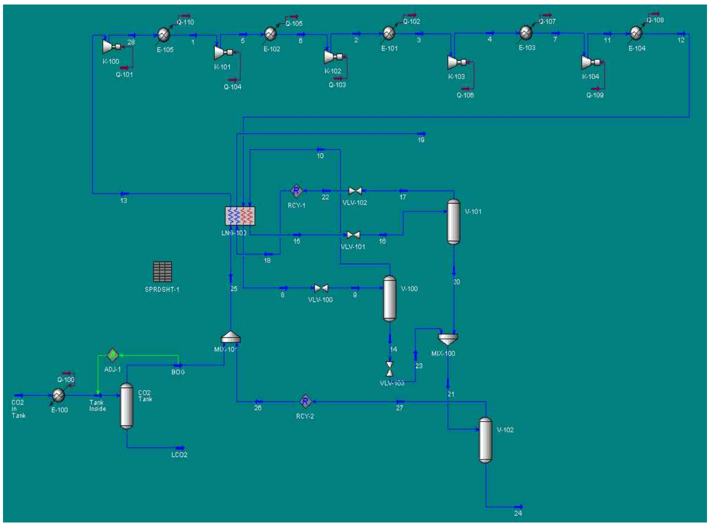

Fig. 12. HYSYS PFD for Case 4.

Table 5. Summary of performance of each case

Item	Case 1	Case 2	Case 3	Case 4
High pressure# [bar]	260	260	260	260
BOG amount (CO_2) [kg/hr]	1,000 (736.1)	1,000 (736.1)	1,000 (736.1)	1,000 (736.1)
Liquid product (CO_2) [kg/hr]	347.9 (346.3)	461.6 (459.2)	512.4 (509.6)	548.3 (546.8)
Liquefied fraction	0.348	0.462	0.512	0.548
CO_2 recover frac.	0.470	0.624	0.692	0.743
Total power [kW]	88.4	88.4	123.4	99.6
Specific power [kW/(kg/hr)]	0.254	0.192	0.241	0.181

#: the pressure of the boil-off gas after the last compressing

CONCLUSIONS

To liquefy carbon dioxide effectively another refrigerant cycle should be used. The higher is the pressure of LCO_2 storage tank, the less is the needed power to run all the compressors. To re-liquefy boil-off gas effectively the cold heat from the BOG and the vent gas has to be recovered.

ACKNOWLEDGEMENTS

This work was supported by the Industrial Strategic technology development program, 10038671, "Development of Cargo Tank, Gas Dome Design, and Loading/Unloading System for CO2 Carrier" and funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea).

REFERENCES

A. Aspelund, M. J. Molnviket, G. De Koeijer (2006) "Ship Transport of CO_2 Technical Solutions and Analysis of Costs, Energy Utilization, Exergy Efficiency and CO_2 Emissions", *Chemical Engineering Research and Design,* 84(A9), pp 847-855

A. Omata (2011) "Preliminary Feasibility Study on CO2 Carrier for Ship-based CCS", Final Report of Chiyoda Corporation, supported by Global CCS Institute, pp 4-29

James Murphy, Ron Munson, Connie Zaresmsky, John Marano, Justin Strock (2011) "DOE/NETL Advanced Carbon Dioxide Capture R&D Program: Technology Update", *U.S. Department of Energy, NETL*, pp 14-17

M. Barrio, A. Aspelund, T. Weydahl, T.E. Sandvik, L.R. Wongraven, H. Krogstad, R. Henningsen, M. Molnvik, S.I. Eide (2004) "Ship-based transport of CO_2", *7th International Conference on GHGT-7*,

Man-Hoe Kim, Jostein Pettersen, Clark W. Bullard (2004) "Fundamental Process and System Design Issued in CO2 Vapor Compression Systems", *Progress in Energy and Science*, 30, pp 119-174

Richard Doctor, Andrew Palmer (2005) "Transport of CO2", *IPCC Special Report on Carbon dioxide Capture and Storage*, pp 182-193

Stephen A. Rackley, *Carbon Capture and Storage*, Elsevier Inc., pp 19-28