深冷分離法を用いたCO_2/N_2分離のプロセスシミュレーション

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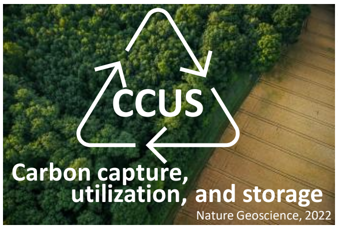
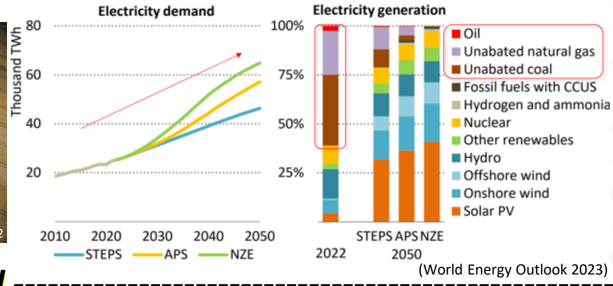
Keywords：CO_2/N_2 separation, cryogenic separation, process simulation

--Background





(World Energy Outlook 2023)

CO_2 separation methods

・Amine absorption　・Solvent absorption ← CO_2 gas separated
・Adsorption　・Membrane
・**Cryogenic separation**
→**no chemical waste, low energy consumption, low CCS cost due to CO_2 liquefication**

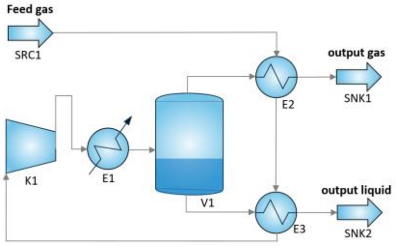
★Purpose of this study

Detailed investigation of **change in energy cost** calculation under different feed gas condition (composition, pressure, temperature)

--Calculation method

<Process model>

drawn by AVEVA™ Process Simulation



K1 : compressor　E2,E3: heat exchanger
E1 : chiller　V1 : cryogenic tower

<Condition>

Feed gas:
30 °C, 0.1 MPa,
CO_2/N_2 = 20/80, 40/60, 60/40

Compressor:
3, 4, 5 MPa (α = 75 %)

Chiller:
－30, －40, －55 °C (COP = 1.3)

→ Energy cost calculation

Output gas: 25°C (for pipeline)

Output liquid: －20 °C (for storage)

<Equation of state>

Peng－Robinson equation[1]

$$P_\mathrm{m} = \frac{RT}{v_\mathrm{m} - b_\mathrm{m}} - \frac{a_\mathrm{m}}{v_\mathrm{m}(v_\mathrm{m} + b_\mathrm{m}) + b_\mathrm{m}(v_\mathrm{m} - b_\mathrm{m})}$$

P_m: total pressure [Pa]
R : gas constant (8.314 [J/K・mol])
T : temperature [K]
v_m: molar volume [m^3/mol]
a_m, b_m: attractive and repulsive parameter

Calculated using molar fraction, critical temperature/pressure, acentric factor, and interaction parameter (-0.017)

$Z = P_m v_m/RT$: compressibility factor

$$Z^3 - (1 - B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0$$

$A = a_m P_m/R^2T^2$
$B = b_m P_m/RT$

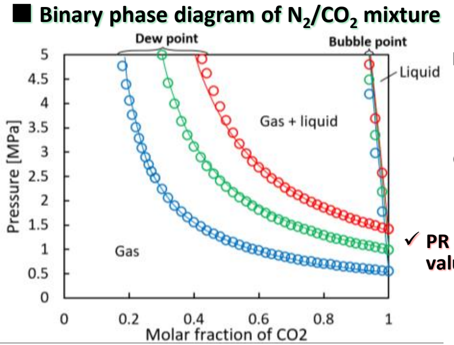
$$\ln\frac{f}{p} = \int_0^P \left(\frac{v}{RT} - \frac{1}{P}\right) dP$$

$$\ln\frac{f_\mathrm{k}^{\mathrm{G\,or\,L}}}{x_k P_\mathrm{m}} = \frac{b_\mathrm{k}}{b_\mathrm{m}}(Z^{\mathrm{G\,or\,L}} - 1) - \ln(Z^{\mathrm{G\,or\,L}} - B) - \frac{\mathrm{A}}{2\sqrt{2}B}\left(\frac{2\sum_i x_i a_{ik}}{a_\mathrm{m}} - \frac{b_k}{b_\mathrm{m}}\right)\ln\left(\frac{Z^{\mathrm{G\,or\,L}} + 2.414B}{Z^{\mathrm{G\,or\,L}} - 0.414B}\right)$$

f_k^P: fugacity of component k (phase P)
x_k: molar fraction
Z^G: the smallest Z (gas phase)
Z^L : the largest Z (liquid phase)

--Results and discussion

■ Binary phase diagram of N_2/CO_2 mixture



Legend
－30 °C
－40 °C
－55 °C
〇…calculated by PR eq.
－…literature value [2]

✓ PR equation traces literature value well.

■ Changes in output flows, CO_2 recovery rate, and energy cost under different compression pressures and temperatures

Compression pressure [MPa]	Cooling temperature [°C]	Output gas Flow [Nm³ h⁻¹]	Output gas CO_2/N_2	Output liquid Flow [kg h⁻¹]	Output liquid CO_2/N_2	CO_2 recovery rate [%]	Energy cost [kWh kg-CO_2^{-1}]
3	−30	916	56.7/43.3	163	96.6/3.4	13.4	1.28
	−40	721	46.3/53.7	538	95.4/4.6	44.3	0.445
	−55	631	40.3/59.7	708	93.6/6.4	57.6	0.368
4	−30	667	41.7/58.3	646	96.3/3.7	53.7	0.288
	−40	574	34.1/65.9	821	94.9/5.1	67.4	0.248
	−55	525	30.0/70.0	910	93.1/6.9	73.8	0.235
5	−30	503	24.4/75.6	962	96.0/4.0	79.6	0.255
	−40	464	20.3/79.7	1030	94.3/5.7	84.3	0.267
	−55	439	18.4/81.6	1070	92.6/7.4	86.5	0.273

Feed gas condition is 30 °C, 0.1 MPa, 1000 Nm³ h⁻¹, and CO_2/N_2 = 60/40 (mol/mol)

Feed composition CO_2/N_2	Output gas Flow [Nm³ h⁻¹]	Output liquid Flow [kg h⁻¹]	CO_2 recovery rate [%]	Energy cost [kWh kg-CO_2^{-1}]
20/80	978	41.8	10.0	5.67
40/60	709	556	67.4	0.474
60/40	439	1070	86.5	0.273

Feed gas condition is 30 °C, 0.1 MPa, and 1000 Nm³ h⁻¹. Compression pressure is 5 MPa, and cooling temperature is −55 °C.

✓ **The maximum recovery rate was 86.5 % (5 MPa, －55 ℃)**
✓ **The lowest energy cost was 0.235 kWh/kg-CO_2 (4 MPa, －55 ℃)**
✓ **Recovery rate and energy cost of CO_2 = 60 % was 8.7-fold higher and 21-fold lower than those of CO_2 = 20%**

■ Comparison with other techniques

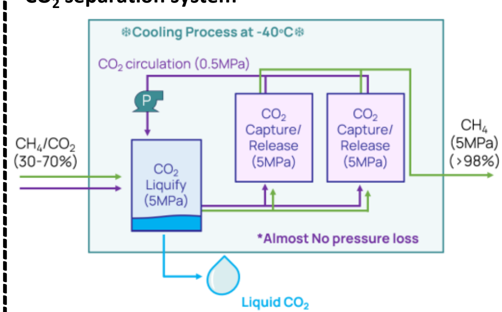
Method	Material	CO_2 composition of feed gas [%]	Phase of recovered CO_2	Energy cost [kWh kg-CO_2^{-1}]	Ref
Cryogenic separation	-	**60**	**Liquid**	**0.235**	**This work**
Chemical absorption	Amine group	-† 15	Gas	1.111 0.751	Gao *et al.*, 2020 Seonggon *et al.*, 2023
Physical absorption	Propylene carbonate, methanol	-†† 32	Gas	0.325 0.522	Mohammed *et al.*, 2014 Ma *et al.*, 2021
Adsorption	Activated carbon, zeolite, MOF	10 30	Gas	0.957 0.295	Subraveti *et al.*, 2019 Akdag *et al.*, 2022
Membrane separation	Zeolite, polymer	12 13	Gas	0.278 0.374	Hussain *et al.*, 2015 Arias *et al.*, 2016

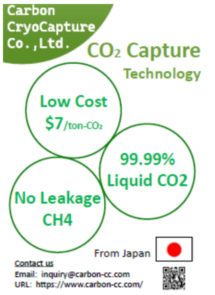
†Post combustion from fuel gas (CO_2~15%). ††Integrated gasification coal combined gas (CO_2~3%)

✓ **Cryogenic separation is applied for separation of high-content CO_2 gas.**
✓ **The energy cost is 21～83 % of other techniques**

■Practical work in JST－START project

CO_2 separation system

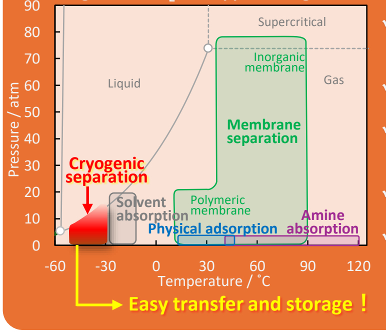




✓ **We are demonstrating CO_2 recovery system using 6 Nm³/h of feed gas.**
✓ **We aim to form an ecosystem that includes the separation and recovery of CO_2 to its utilization.**

Conclusion

Phase diagram of CO_2 and applied range of techniques



→ Easy transfer and storage！

✓ CO_2/N_2 phase diagram was evaluated using Peng－Robinson equation.
✓ Cryogenic CO_2/N_2 separation model was simulated.
✓ The case of 5 MPa/－55 ℃ showed the highest recovery rate of 86.5 %.
✓ 4 MPa/－55 ℃ was the lowest cost of 0.235 kWh/kg-CO_2.
✓ In case of high content CO_2 gas, cryogenic separation is promising for CCUS.

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