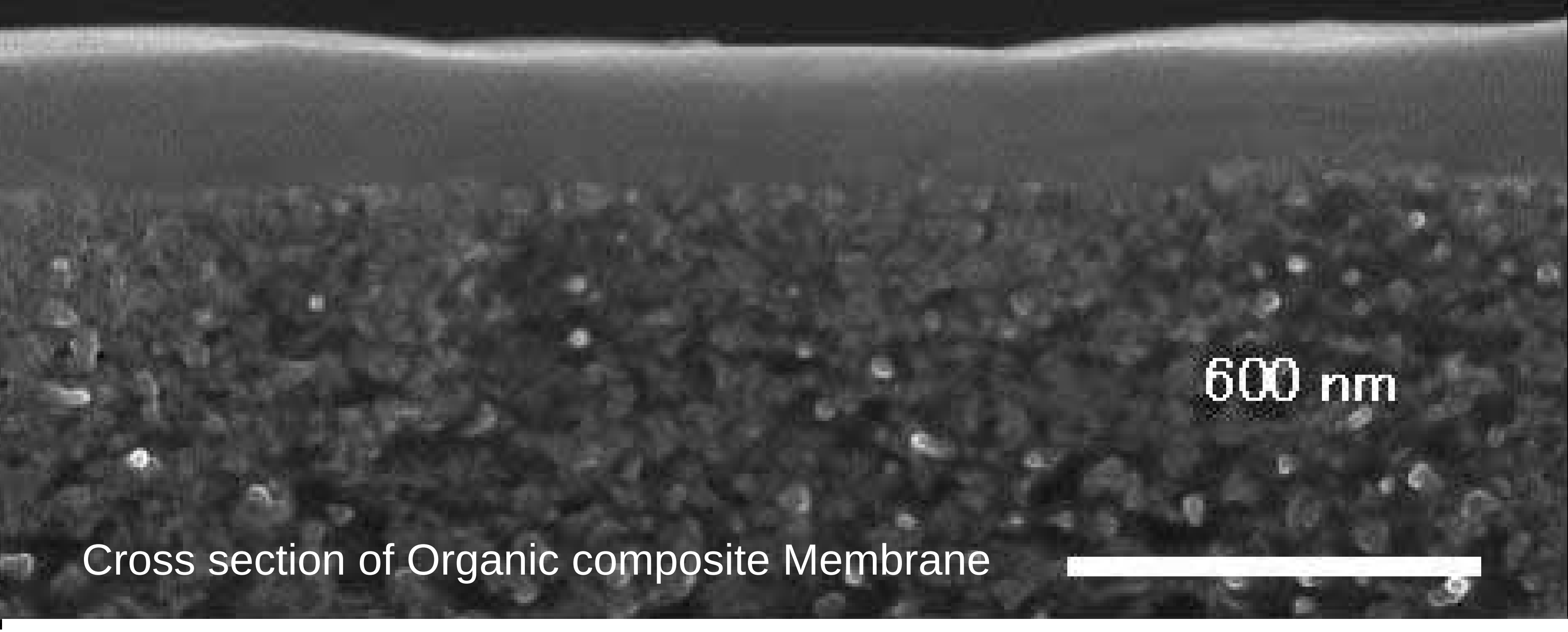
CCS Workshop 2007
15th, February , 2007
The Keihanna Plaza in Kyoto

CO2 separation and capture technology: Present and future



Cross section of Organic composite Membrane

Y. Fujioka

Research Institute of Innovative Technology for the Earth

Outline

1. Measures against global warming

2. Introduction of CO_2 capture technology for CCS

3. Development of CO_2 capture technology in RITE

4. Progress of organic membrane separation

DNE 21 Model

Measures against global warming

1. Energy management

- Energy Saving
- Fuel Switching

2. Renewable Energy

- Biomass
- Solar cell
- Wind Power
- Hydro & Geoth.

3. Nuclear Power

- Nuclear Power

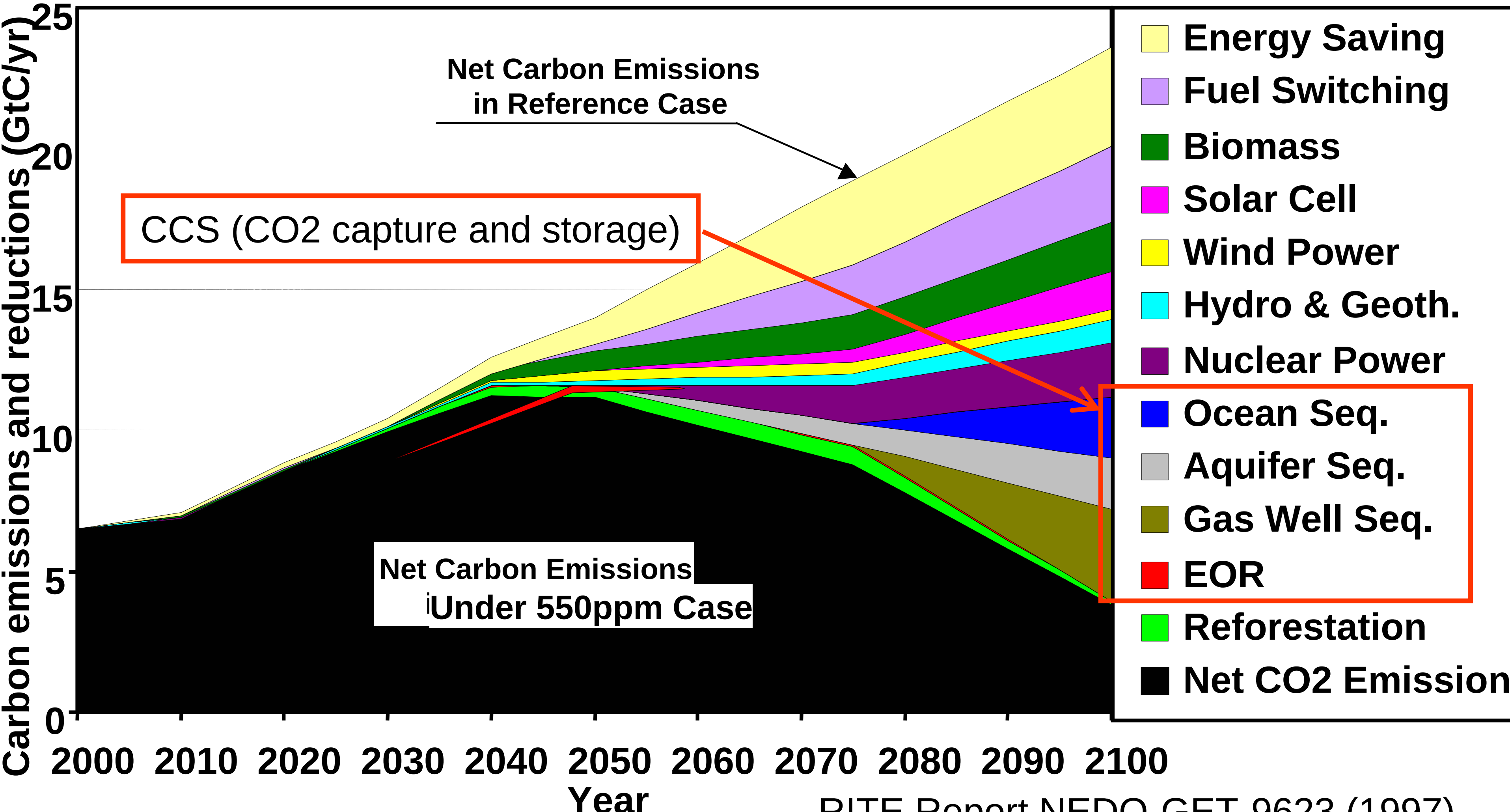
4. CO_2 capture and Storage

- Ocean Seq.
- Aquifer Seq.
- Gas Well Seq.
- EOR

5. Enlargement of CO2 sink

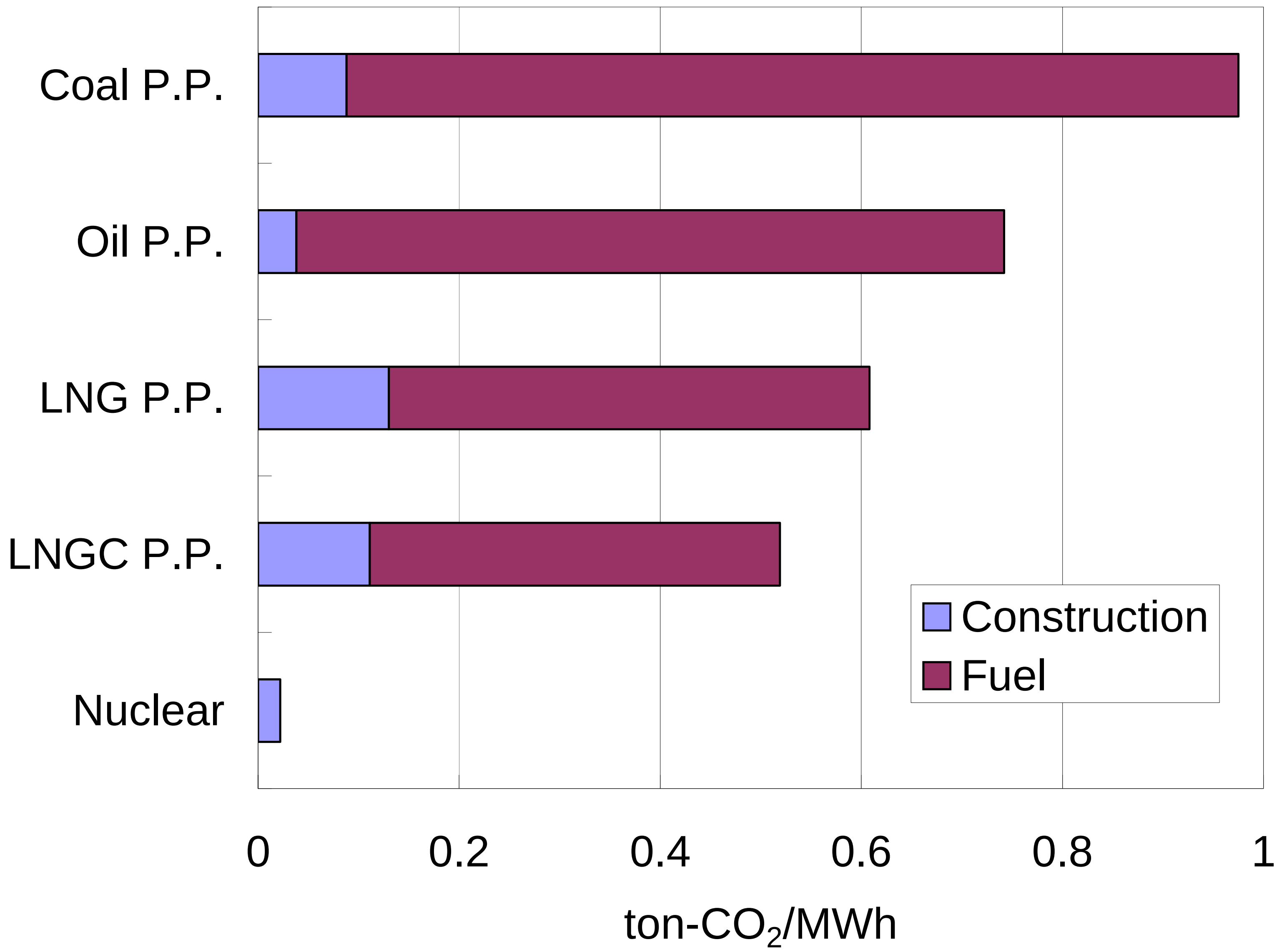
- Reforestation

Technological Options for 550 ppmv Stabilization

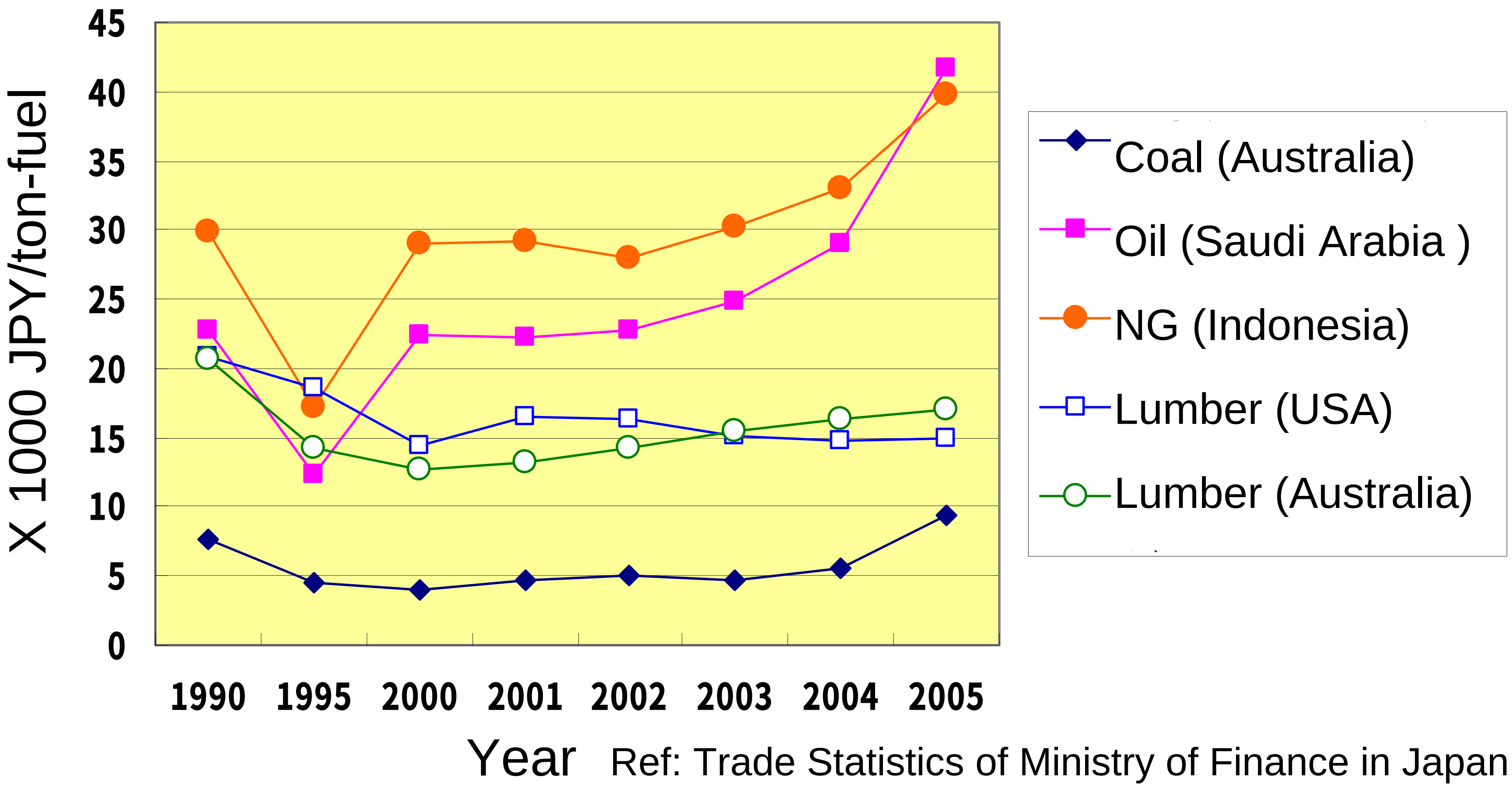


RITE Report NEDO-GET-9623 (1997)

CO_2 emission without CO_2 Capture



Trend of energy cost in Japan

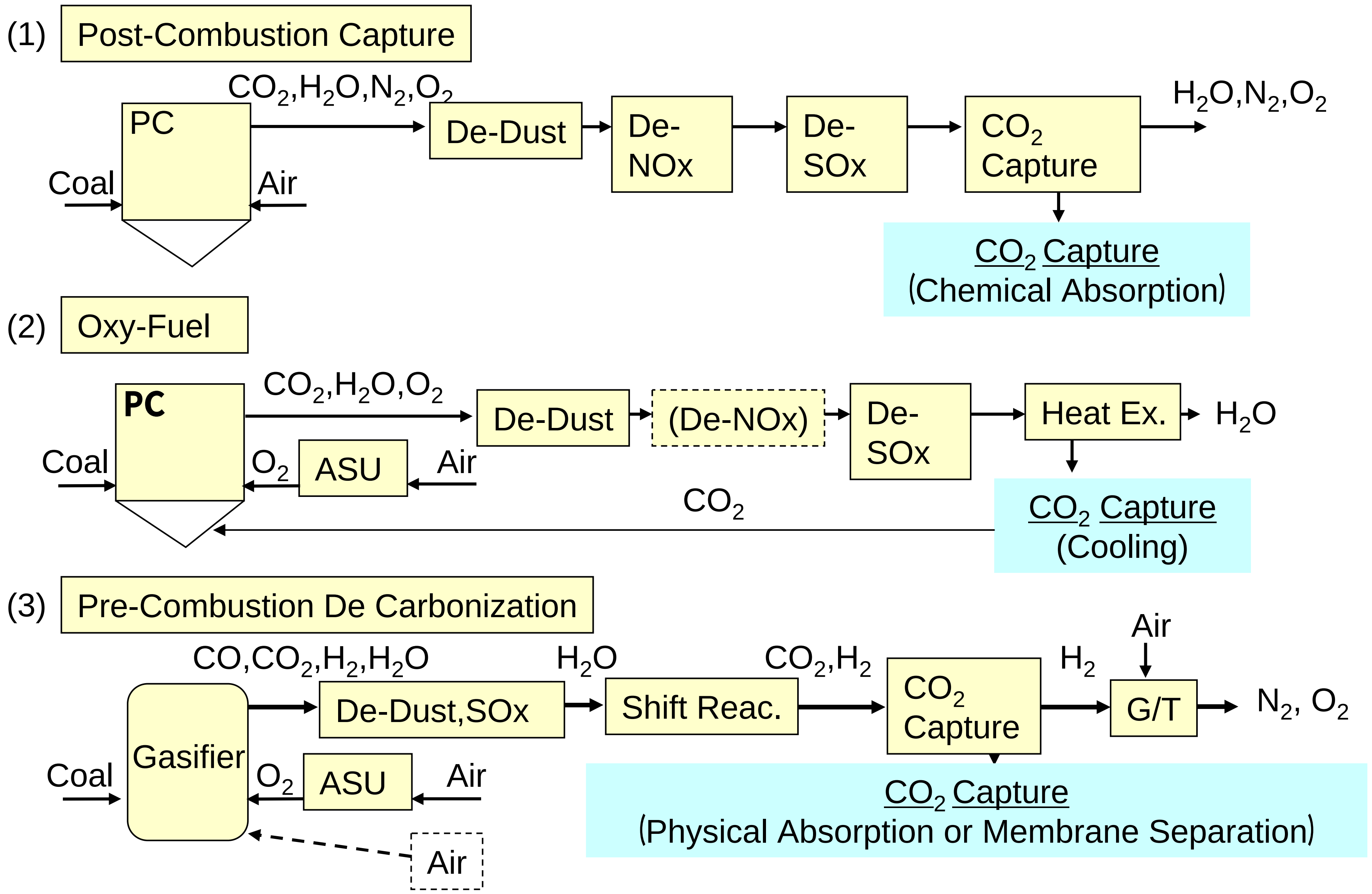


Ref: Trade Statistics of Ministry of Finance in Japan

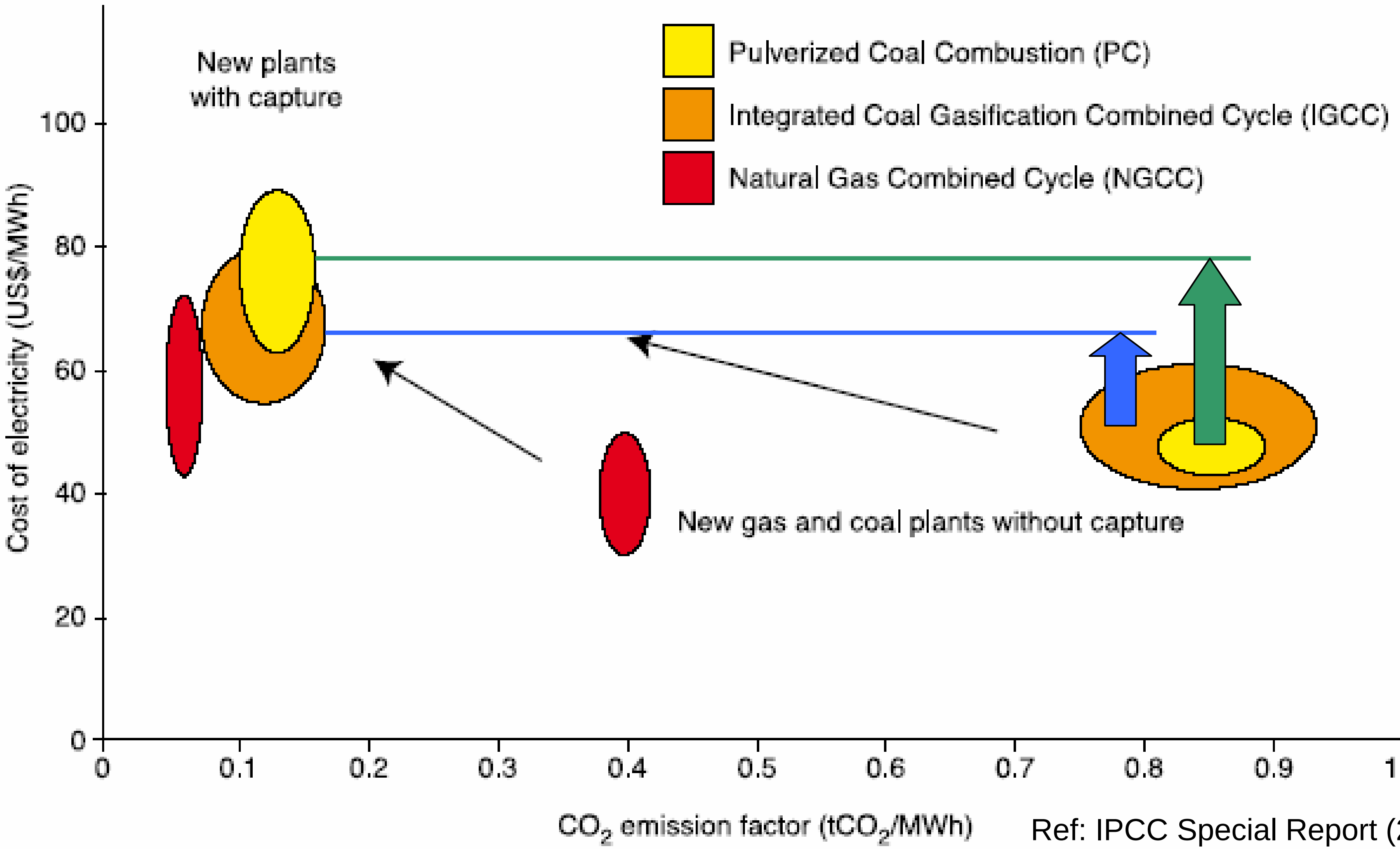
Comparison of fuel cost (% / MJ) in Japan

Oil : NG : Coal : Lumber = 300 : 300 : 100 : 500

Coal Conversion & CO_2 Capture



Electricity Cost with & without CO_2 Capture



Ref: IPCC Special Report (2005)

CO_2 Separation Cost

System	Minimum	Maximum	Average
	[US$/t on-$CO_2$ avoided]		
Existing PC + Chemical Absorption	45	73	59
New Designed PC + Chemical Absorption	29	51	41
NGCC + Chemical Absorption	37	74	53
IGCC + Physical Absorption	13	37	28
Oxyfuel (PC)	14	72	40

Ref; IPCC Special Report (2005)

CO_2 Separation Energy

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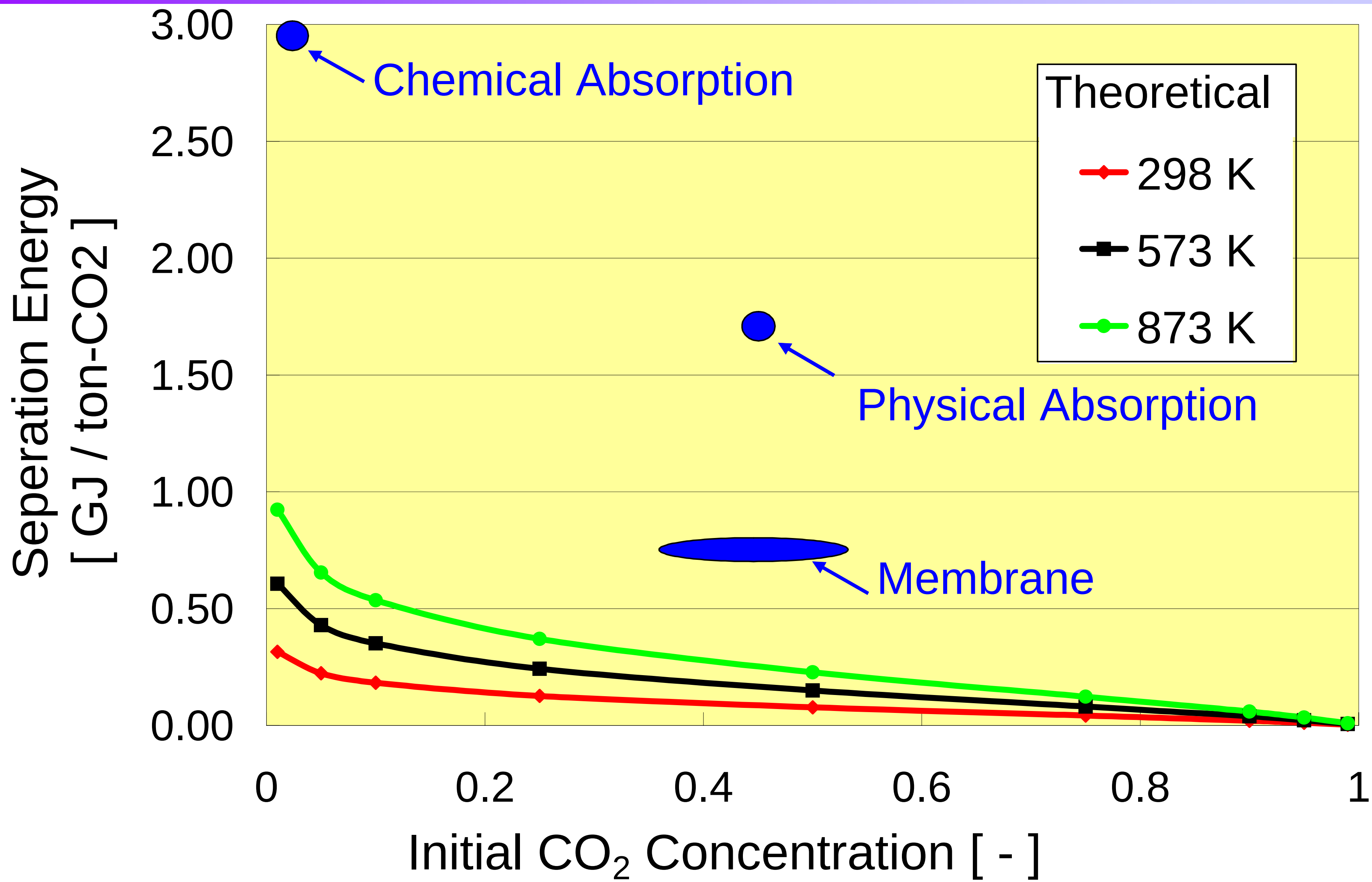
Capture Method	Separation Energy [GJ/ton-CO_2]	CO_2 Source	Experimental Scale
Rotational TSA	3.1	PC	Bench
PTSA	6.5	PC	Bench
TSA	4.2	PC	Bench
Chemical Absorption (MEA)	4.0	PC	Pilot
Chemical Absorption (KS solution)	2.9	NG Boiler	Pilot
Physical Absorption	1.7	IGCC	Commercial
Cooling	2.5	Oxy-fuel (Coal)	Bench
Membrane	0.7	IGCC	Beaker

Separation Energy



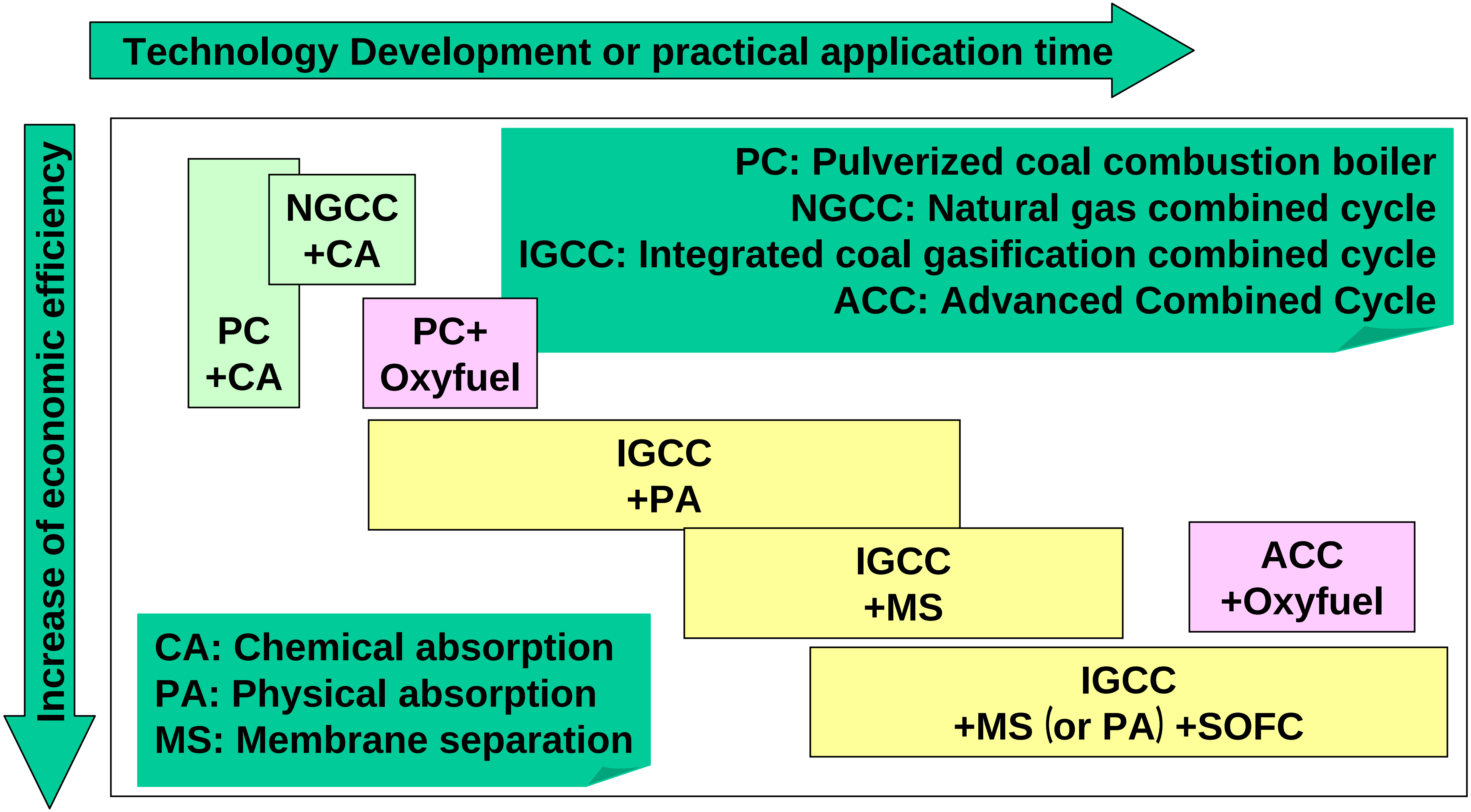
Oxyfuel

- Increase of energy in Oxyfuel

a.	ASU (Air Separation Unit) Δ	2.1 GJ/ton-CO_2
b.	CO_2 Recirculation fun Δ	0.3
c.	Cooling Water Δ	0.1
d.	Total	2.5

- ASU Energy Ratio
  - ✓ Practical/Theoretical Energy = 4
    - ✖ It is difficult to reduce Oxyfuel energy.

Vision of power plant and CO_2 capture



CO_2 Capture technology in RITE

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1. Chemical Absorption
   - ✓ Improvement of absorbent for CO_2 for low separation energy
2. Inorganic Membrane
   - ✓ Membrane reactor for water-gas shift reaction at high temperature
3. Organic Membrane
   - ✓ Membrane with high CO_2/N_2 and CO_2/H_2 selectivity.

COCS project (Cost Saving CO_2 Capture System)

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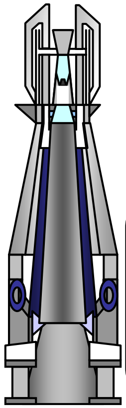
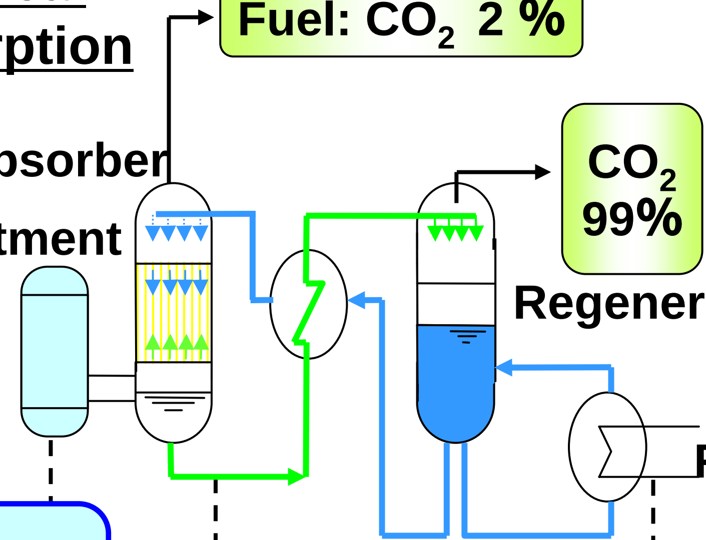
Steel Works



Blust Furnace Gas
CO_2 22%
(CO,H_2 etc.)

Chemical Absorption



Improvement of Pre-treatment

New Absorbent

Utilize of Low Grade Waste heat in Steel Works

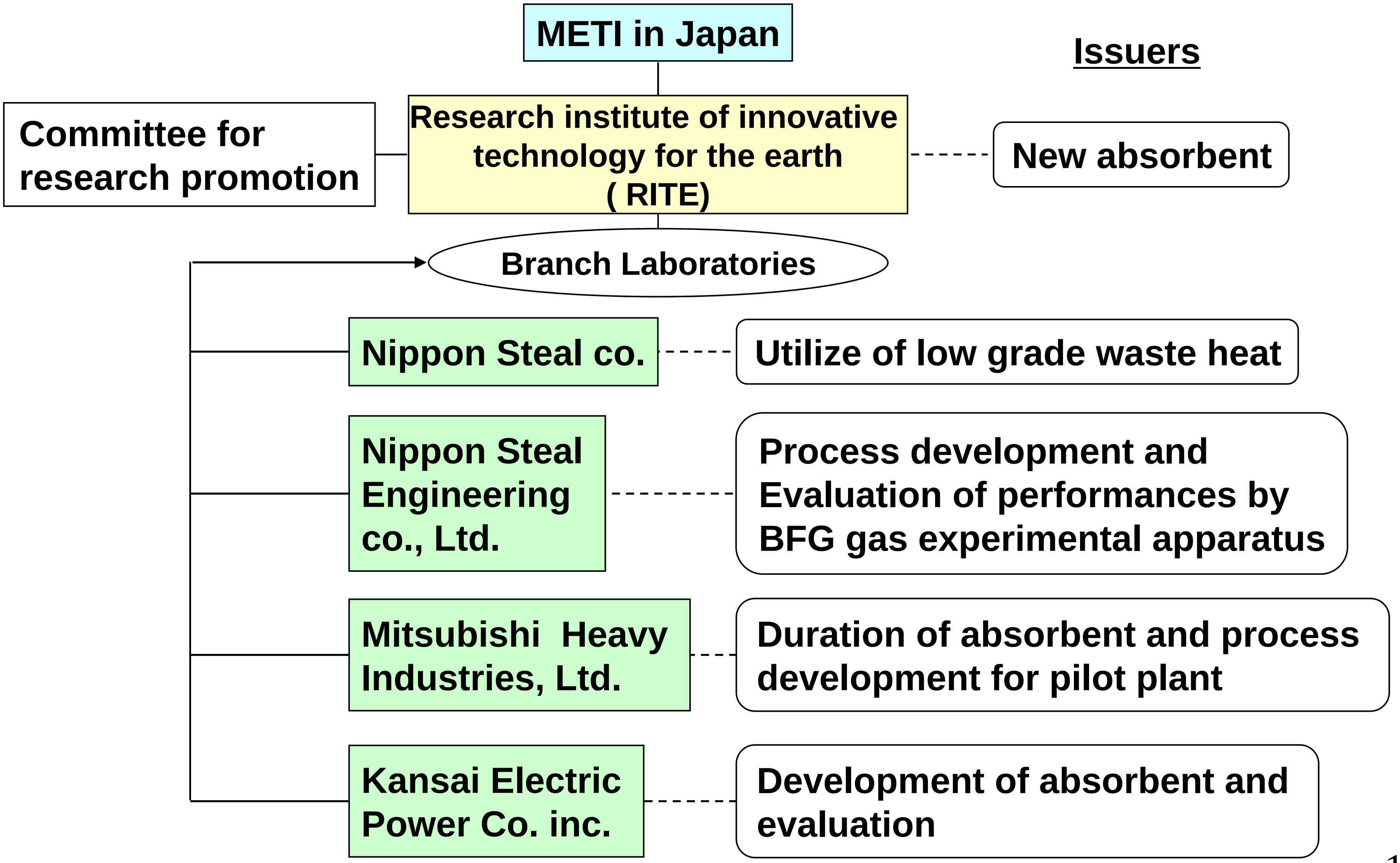
Low Cost of CO_2 absorption System

Project Target : 2.5 GJ/t-CO_2
Future Target : 1.8 GJ/t-CO_2

Objectives

Reduce CO_2 Capture Cost by half and Evaluate New Technology

Development organization and issuers



Development of New Absorbents

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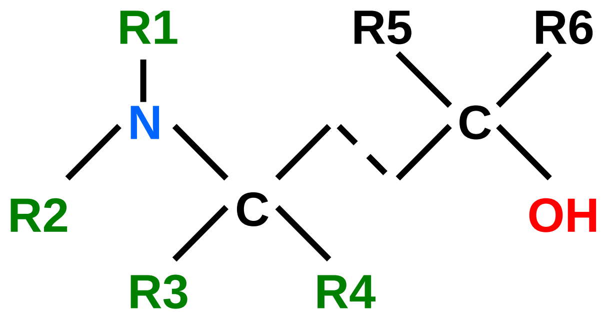
Steric Hindered Group：R1, R2, R3, R4
- Control of Carbamate Formation
- Increase CO_2 Desorption
- Reduce Heat of Reaction

Hydroxyl Group: OH
- Electron Acceptor (Activation of Amino Group)
- Hydrophilic（Increase in Solubility to water）
- Formation of Hydrogen Bond（Elevation of Boiling Point, Control of Volatility）



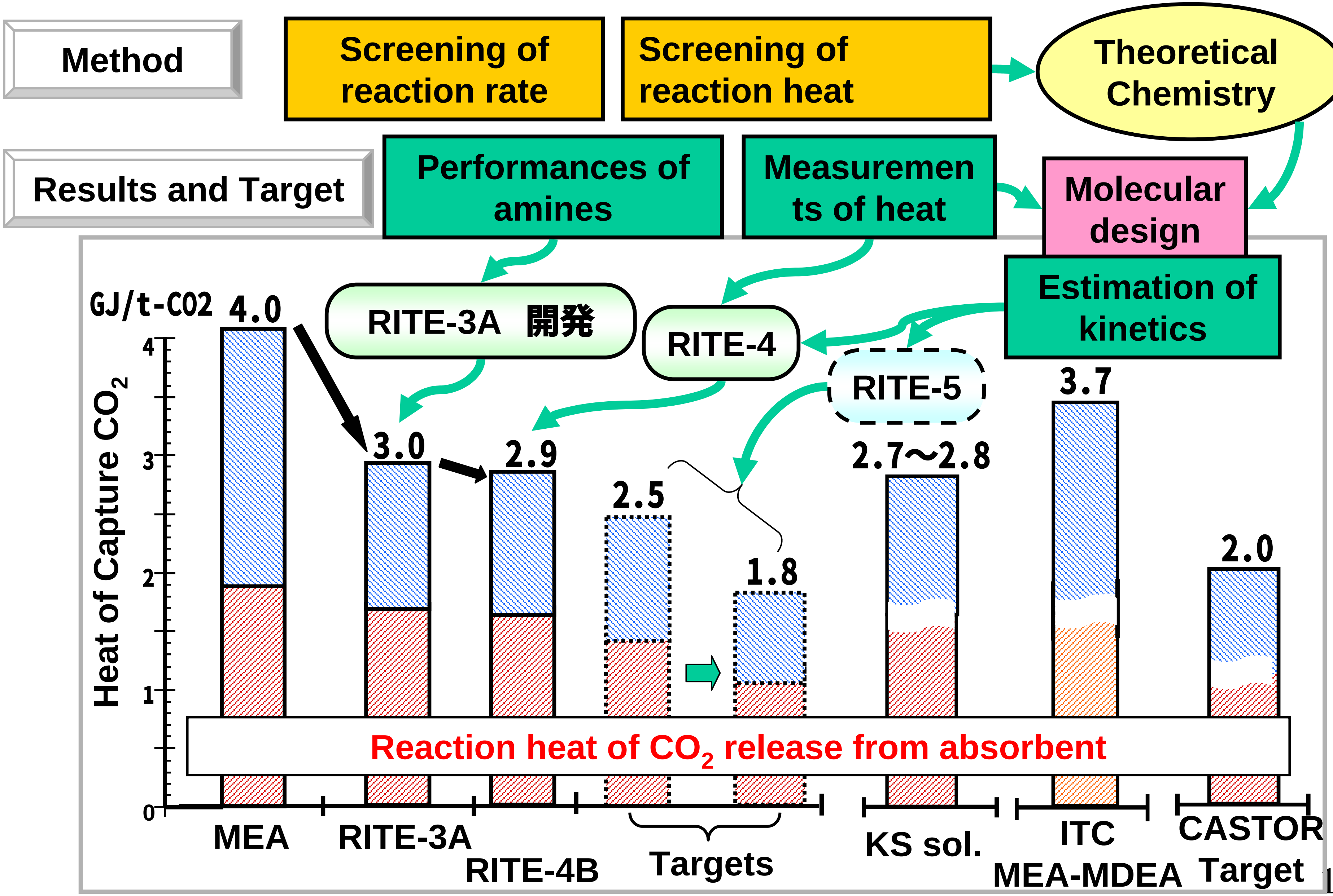
Example of Amine Molecule

First Step
- Screening Commercial Amine
- Formulate Amine Compound

Second Step
- Design and Synthesize New Amine

Amino Group: N
- Electron Donor
- Bond with CO_2（Formation of Carbamate or HCO_3^- Anion）
- Proton Acceptor（Formation of Protonated Cation）
- Primary, Secondary, Tretiary Amine、Number of Amine Group

Decreasing reaction energy by new absorbent



Bench scale apparatus using BFG gas

CO_2 Lord:1 t-CO_2/d

- Location： Kimitsu iron works of Nippon Steal co.
- Absorber： Diameter 150 mm, Height 3600 mm (Fixed bed 1000mm x 2)
- Regenerator： Diameter 200mm, Height 3720 mm (Fixed bed 1000mm×2)
- Input (BFG)： 100 m^3(STP)/h

NIPPON STEEL ENGINEERING

Inorganic Membrane Reactor

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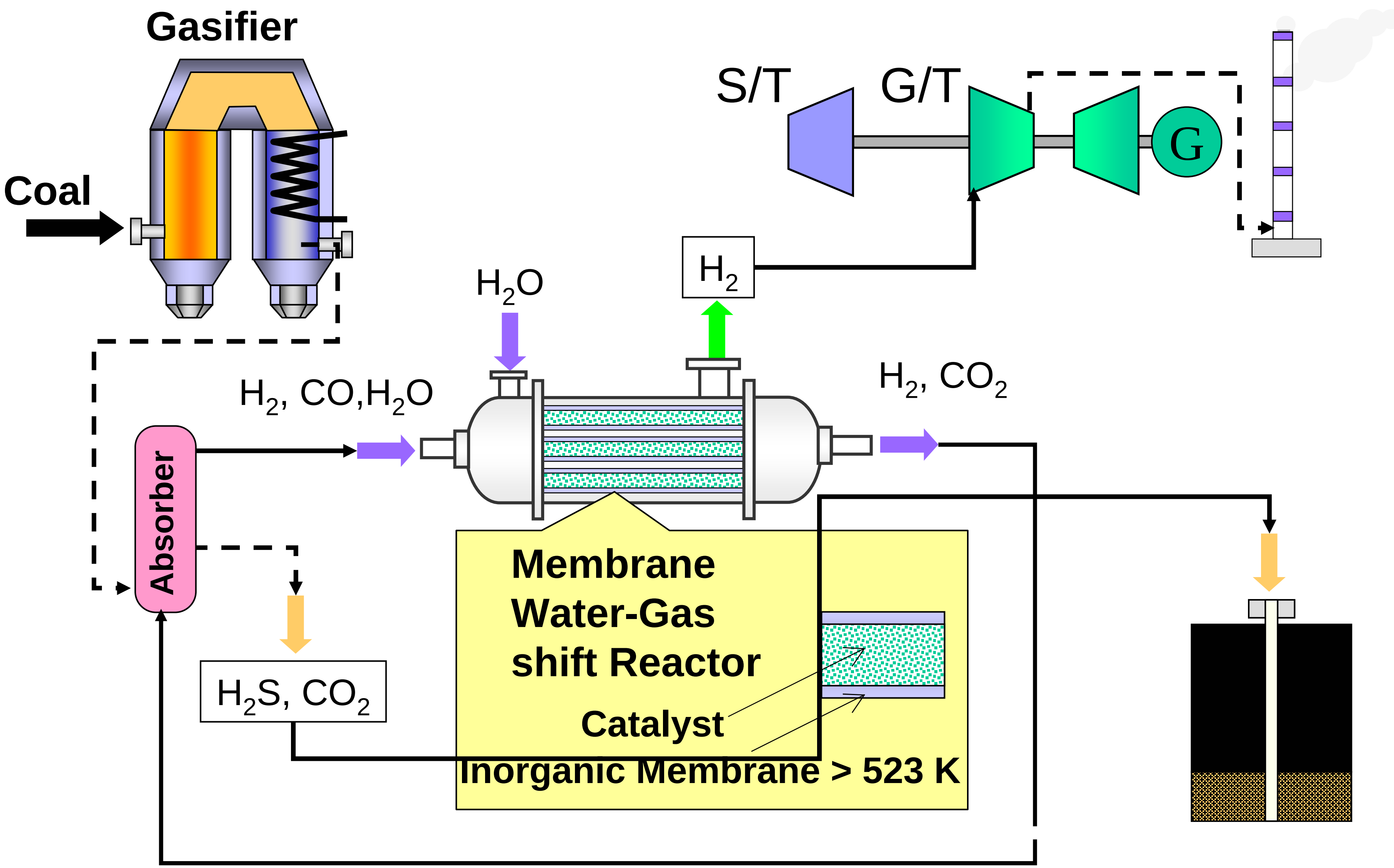

Hydrogen separation membrane with Pd nano particles within mesopores

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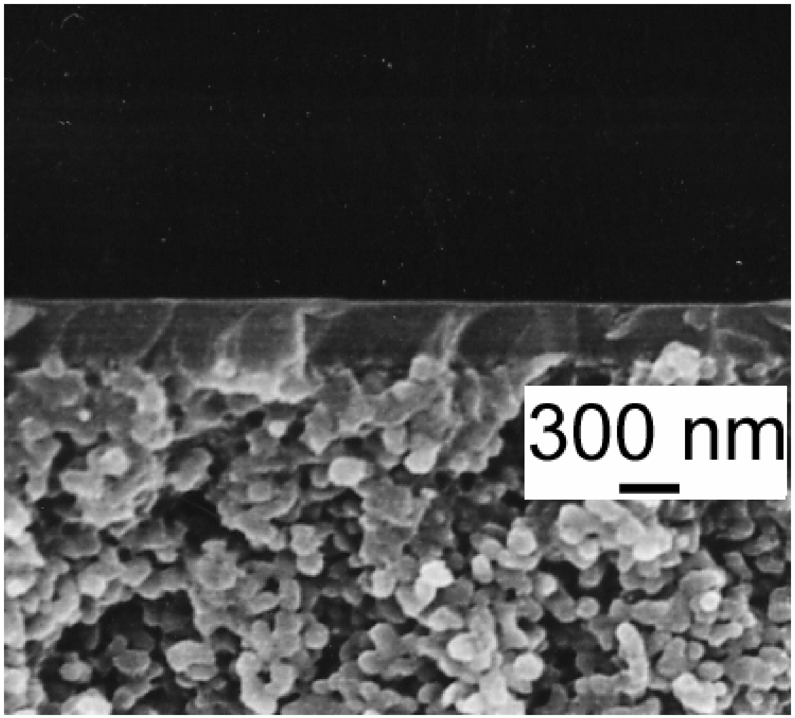
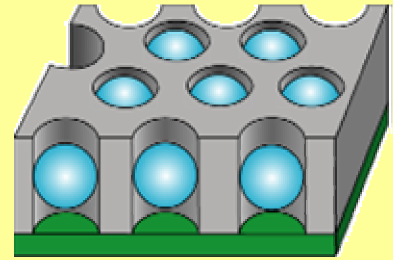
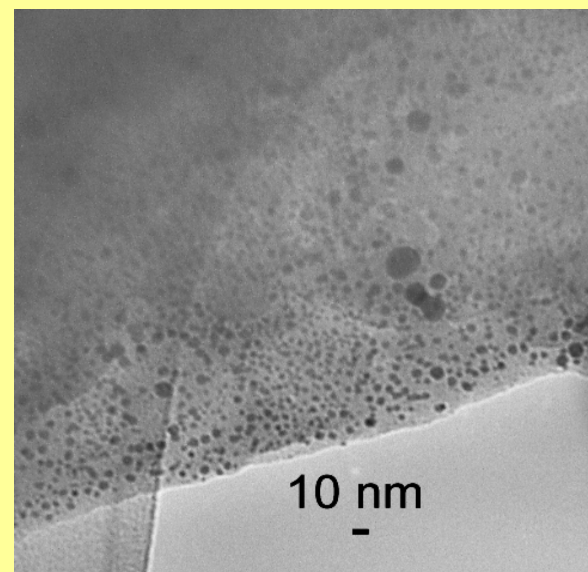


Cross sectional view: Mesoporous silica membrane prepared on porous alumina substrate

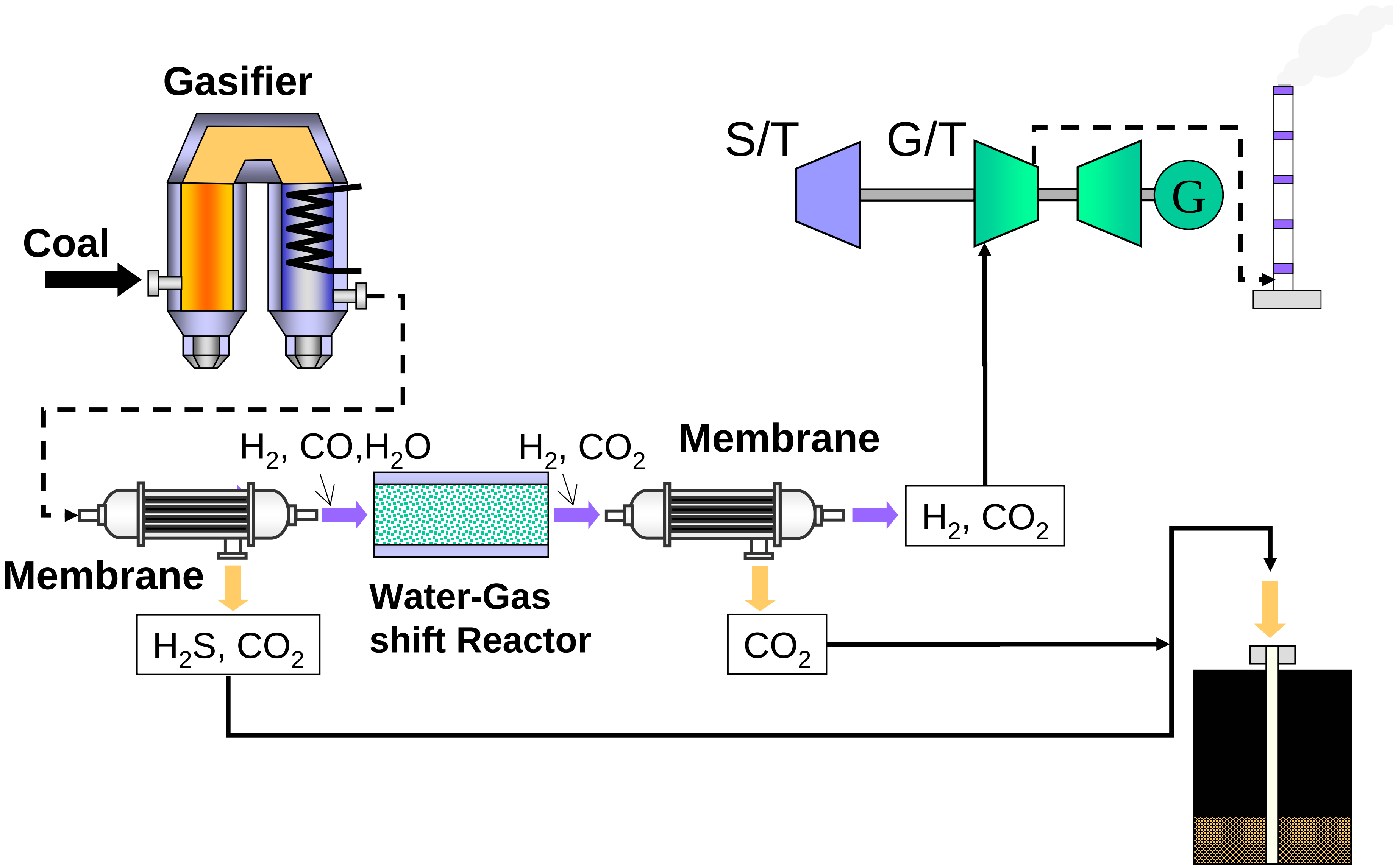


Schematic images



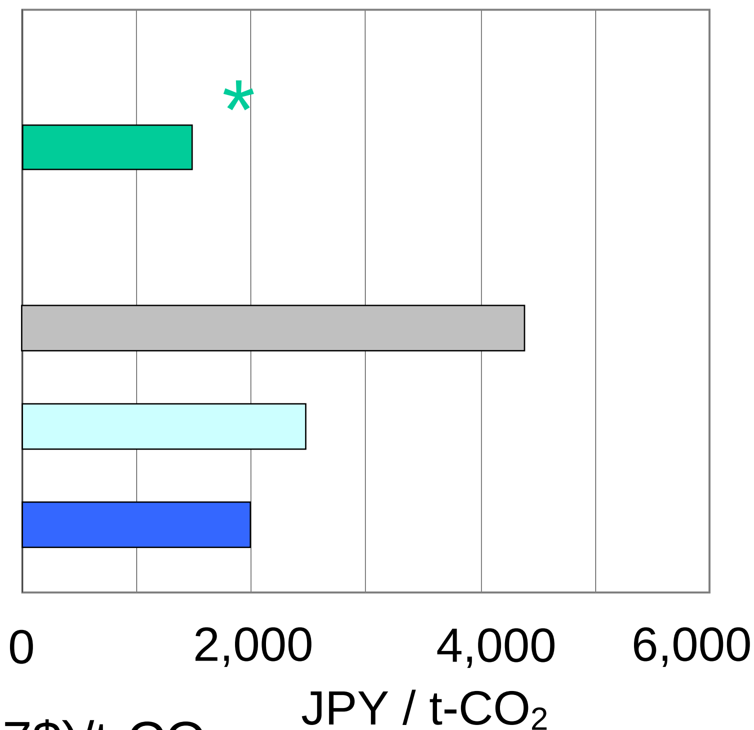
TEM image

Organic Membrane



Cost target of CO_2 Capture Development

CO_2 Capture	Gas Pres.	Gas Comp.	Membrane Performance (Target)
Membrane IGCC	4MPa	CO_2:40% H_2, H_2O	QCO_2 :1×10^{-9} ($m^3\ m^{-2}\ s^{-1}\ Pa^{-1}$) $\alpha CO_2/H_2$: 500
Chemical Absorption		Current (KS solution)	
Flue gas Atmospheric pressure		2010 Target(New Solvent)	
		2013 Target(New Solvent)	

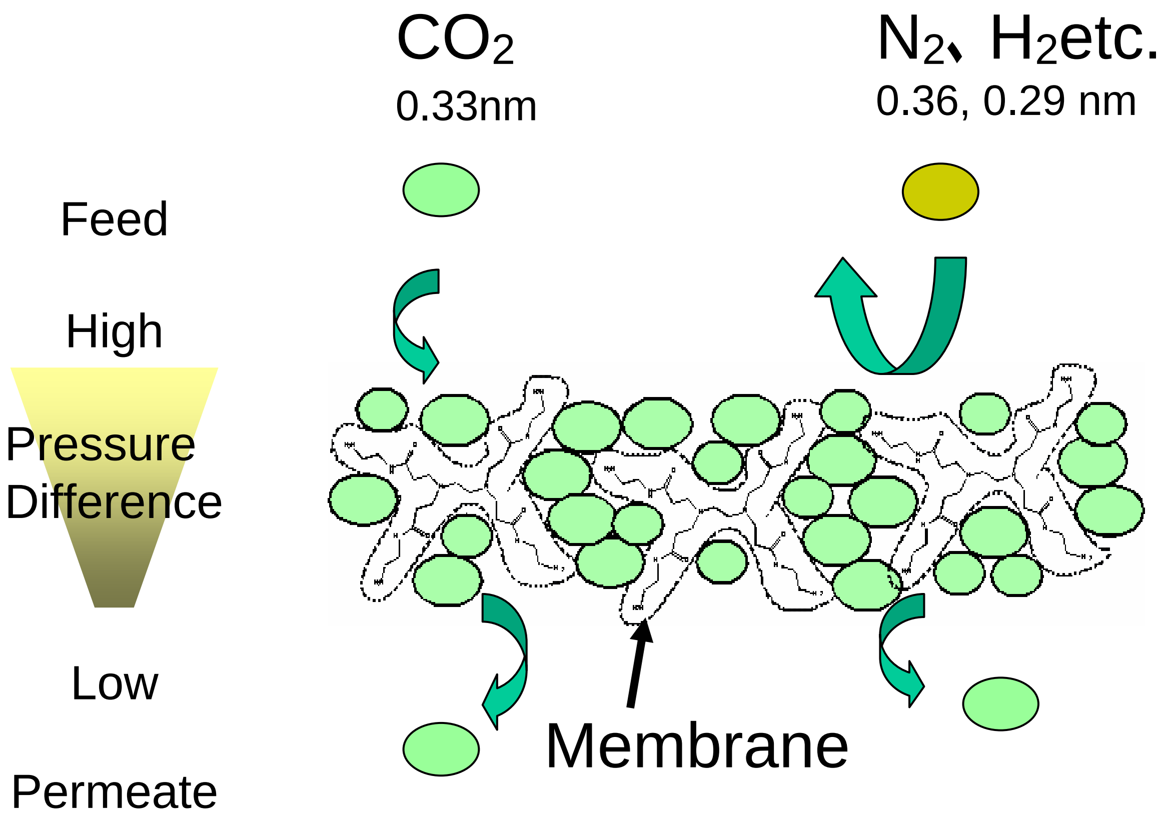


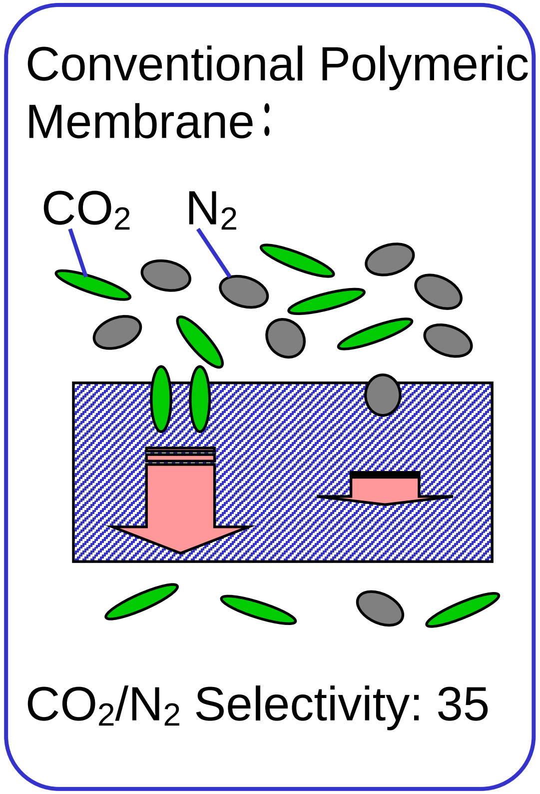
Physical Absorption 1,600 ~4,400 JPY(13 ~ 37$)/t-$CO_2$

* Duration period Facility:15 years Membrane:5 years

Membrane Cost: 50,000 JPY/m^2 = 420 $ / m^2

Concept of CO_2 Molecular Gate Membrane





Excellent CO_2 / H_2 , CO_2 / N_2 selectivity>500

Improvement of Dendrimer

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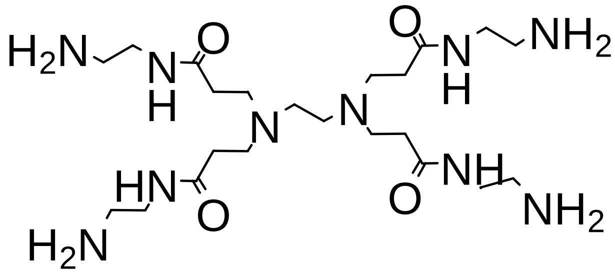
Dendrimer 1



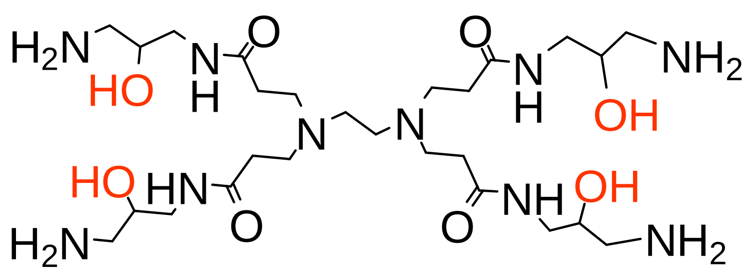
CO_2/N_2 separation:
A. S. Kovvali, H. Chen, and K. K. Sirkar
J. Am. Chem. Soc. 2000, 122, 7594-7595

Conventional PAMAM(Polyamidoamine) dendrimer

Optimization of chemical structure of dendrimer for CO_2 molecular gate function:

Computer simulation, Synthesis, Analysis

Dendrimer 2



Newly Synthesized

Hydroxyl PAMAM (Polyamidoamine) dendrimer

Definition of Permeance & Selectivity

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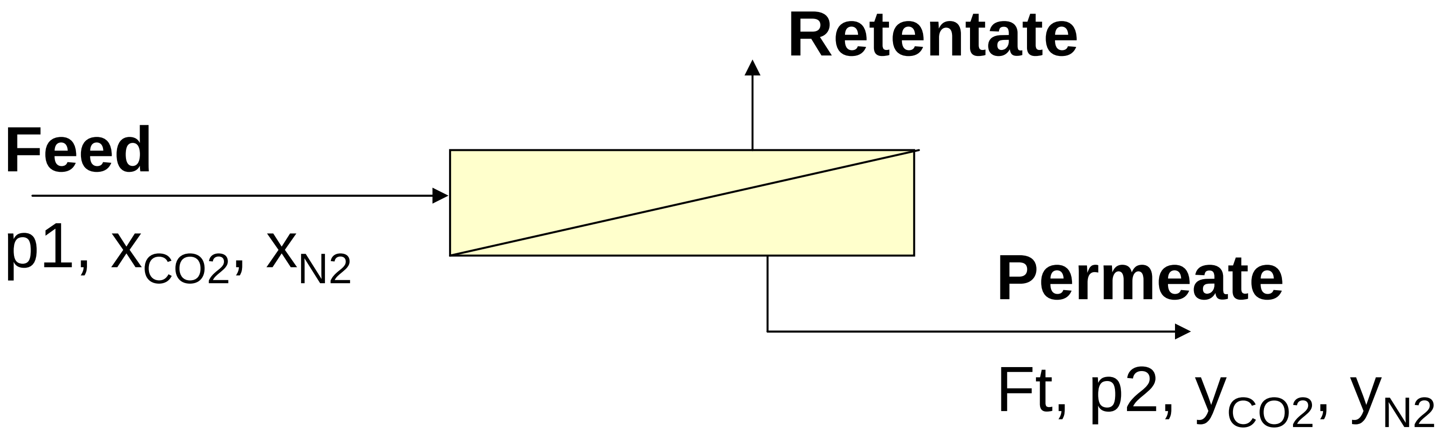


CO_2 permeance, Q_{CO2}: $Ft \cdot y_{CO2} / (p1 \cdot x_{CO2} - p2 \cdot y_{CO2}) / A$

N_2 permeance, Q_{N2}: $Ft \cdot y_{N2} / (p1 \cdot x_{N2} - p2 \cdot y_{N2}) / A$

CO_2/N_2 selectivity, $\alpha_{CO2/N2}$: Q_{CO2}/Q_{N2}

Q ($m^3\ m^{-2}\ s^{-1}\ Pa^{-1}$): permeance

x (-): molar fraction in feed, y (-): molar fraction in permeate

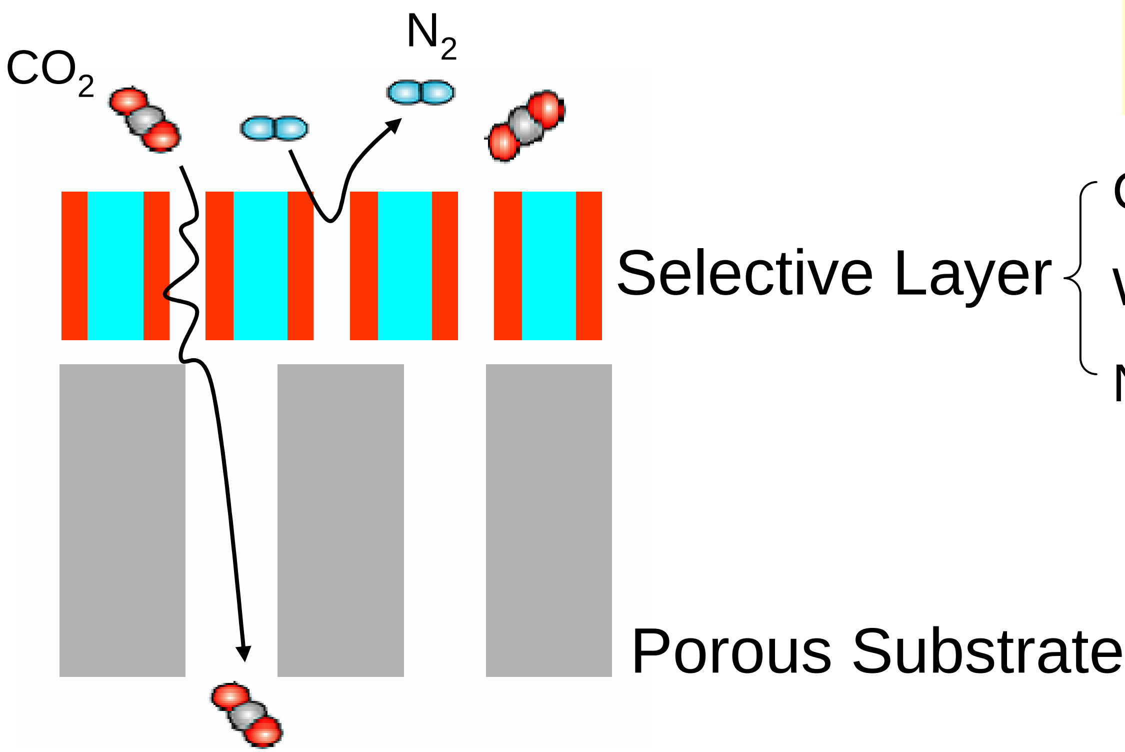
P1 (Pa): total pressure in feed, p2 (Pa): total pressure in permeate

Ft ($m^3\ s^{-1}$): total gas flux of permeate

A (m^2): membrane area

CO_2 Separation Membranes Structure

Membrane concept



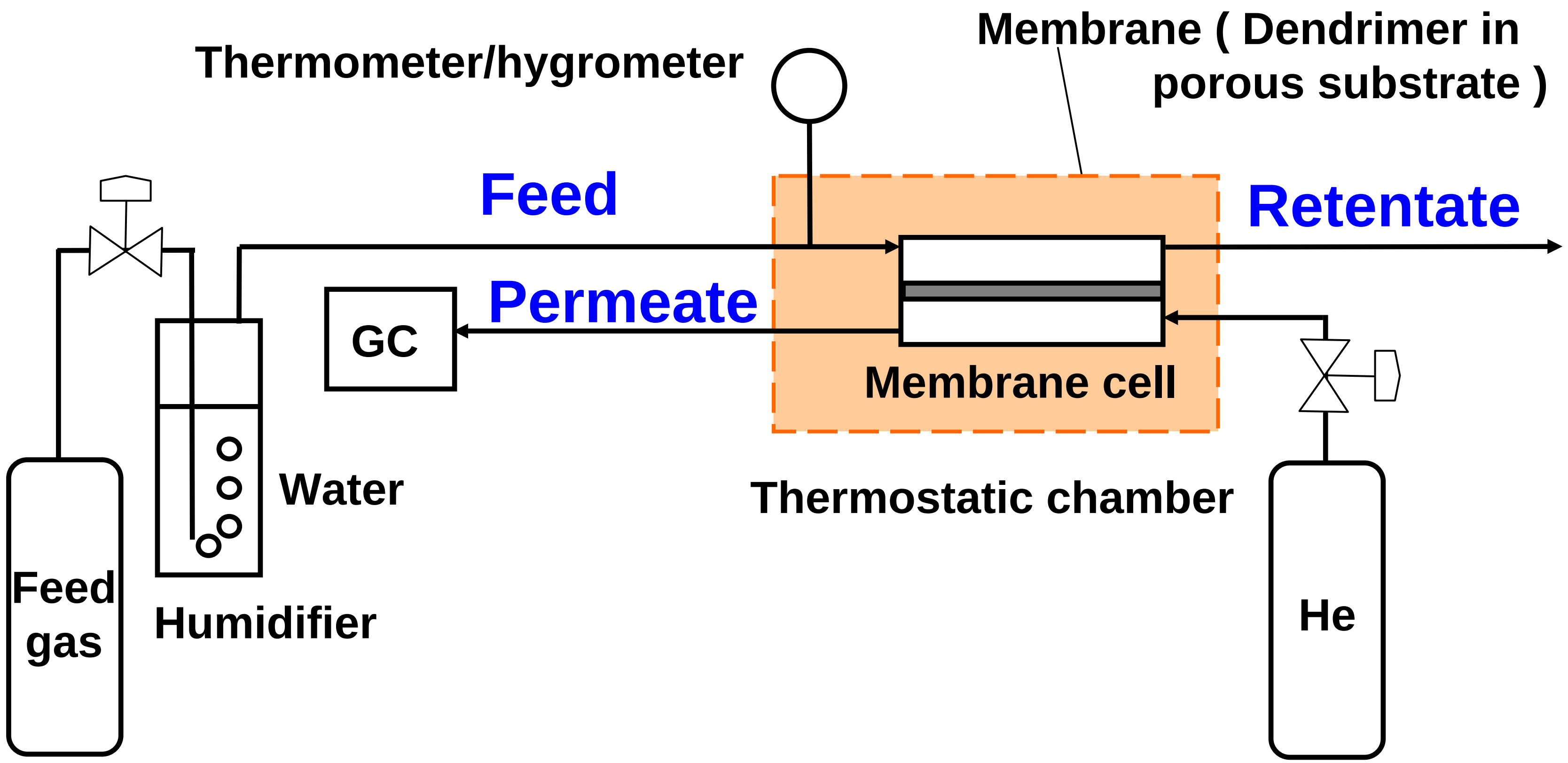
Sub-Nanoscale Materials Control

- CO_2 affinity
- Well-controlled pore diameter
- No defect structure of thin film

High CO_2 selectivity and permeability

Evaluation of performance of Selective Layer

Schematic diagram of gas permeation apparatus (sweep method)



Feed gas CO_2/H_2=5/95(v/v),
Temperature 298 K,
Sweep gas (He) flow rate, 10 mL/min,
Relative humidity (RH) 0 - 97%,
Feed gas flow rate, 100 mL/min,
Effective membrane area, 8.0 cm^2

Structure of Membrane

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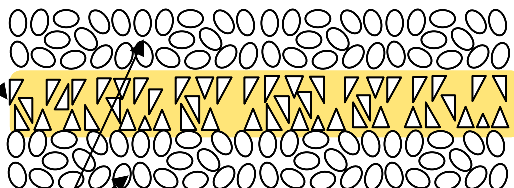
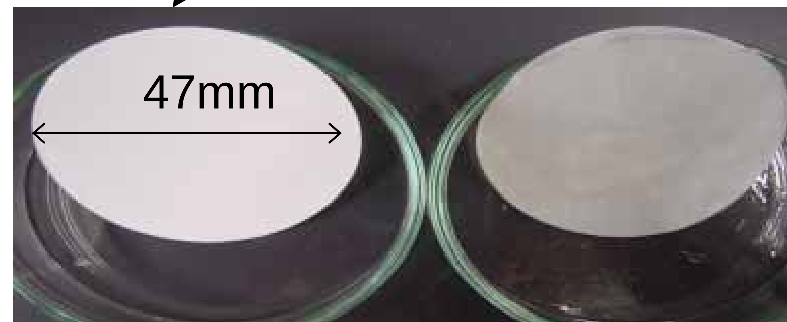
Selective Layer

(Dendrimer1 or Dendrimer 2
+Hydrophilic porous substrate)



Hydrophobic porous substrate

Hydrophilic porous substrate



After supporting Dendrimer in Hydrophilic porous substrate

Dendrimer

- Dendrimer 1 (PAMAM; Reagent by Aldrich)
- Dendrimer 2 (Hydroxyl PAMAM; Synthesized reagent by RITE)

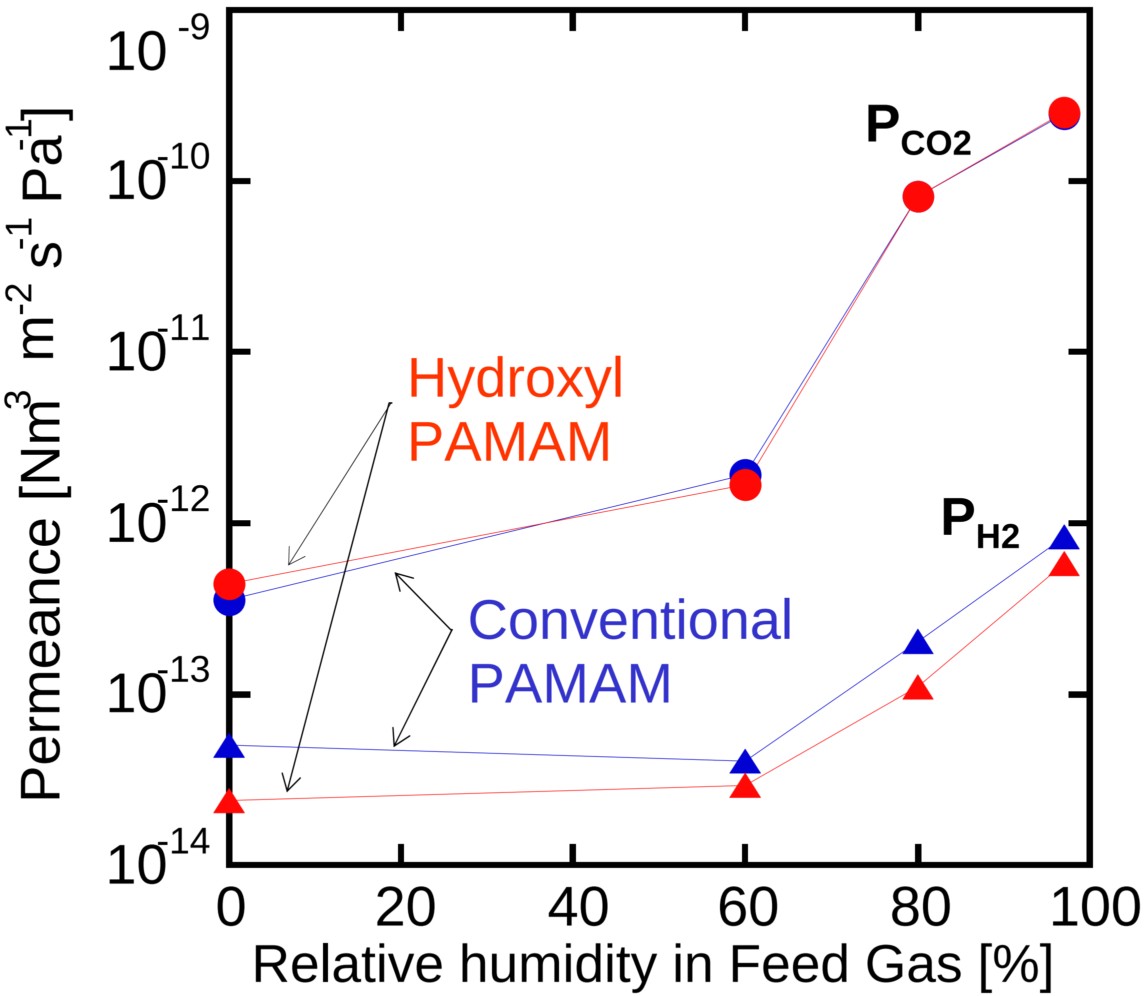
Hydrophilic porous substrate

- PVDF (pore size 0.1 μm, void volume 70%, thickness 100 μm)

Hydrophobic porous substrate

- PVDF (pore size 0.45 μm, void volume 75%, thickness 100 μm)

CO_2/H_2 Separation by Dendrimer

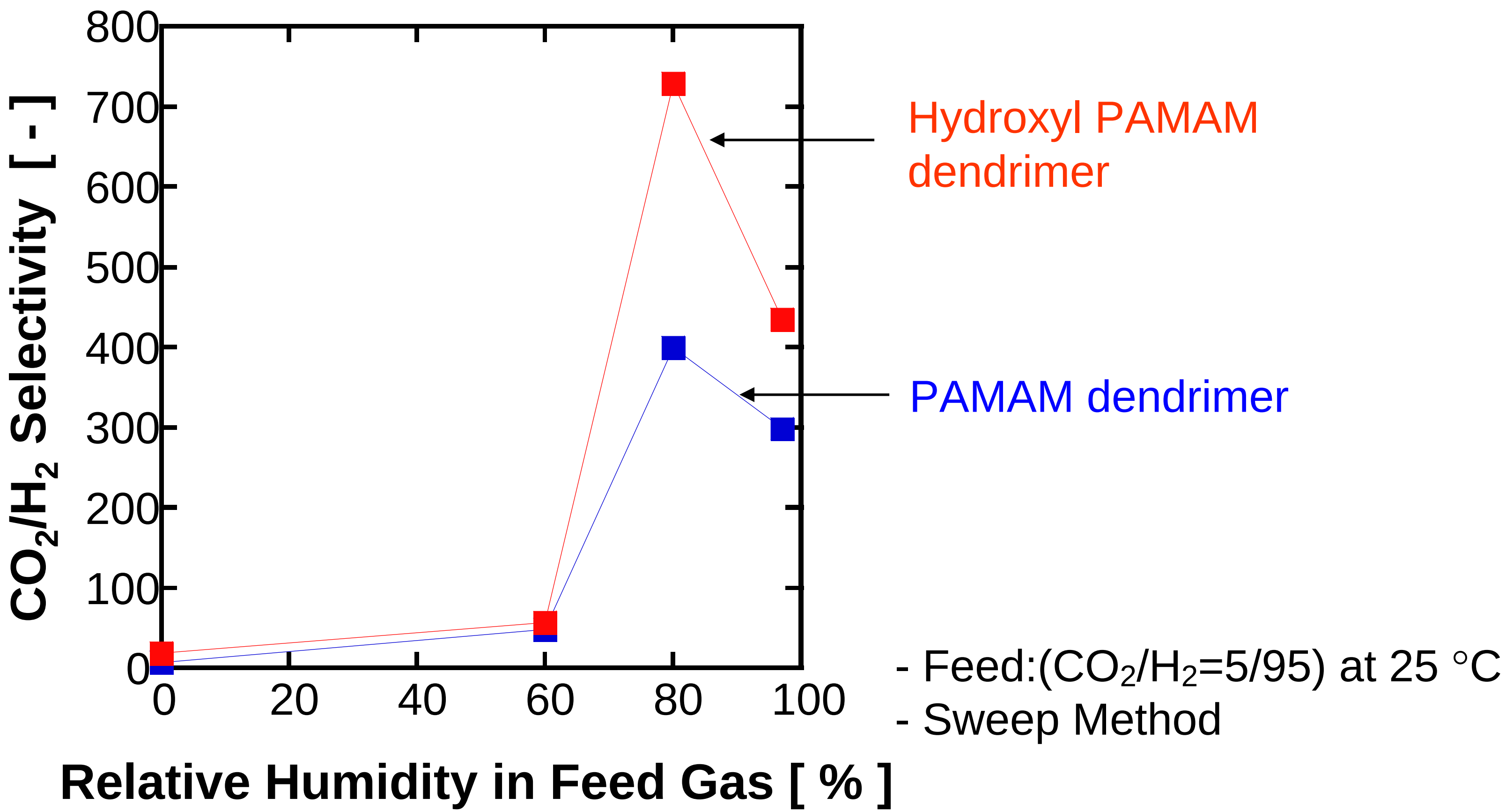


Conventional PAMAM CO_2:● H_2▲, Hydroxyl PAMAM CO_2:● H_2▲

Feed:(CO_2/H_2=5/95) at 298K (25 °C),

Δp_{CO2}=0.005MPa Δp_{H2}=0.095MPa

CO_2/H_2 Selectivity of Dendrimers



Hydroxyl PAMAM Dendrimer

P_{CO2}=8.1×10^{-11} [m^3 (STP) m^{-2} s^{-1} Pa^{-1}], $\alpha_{CO2/H2}$=730 at 80RH%

CO_2 decreases H_2 permeability

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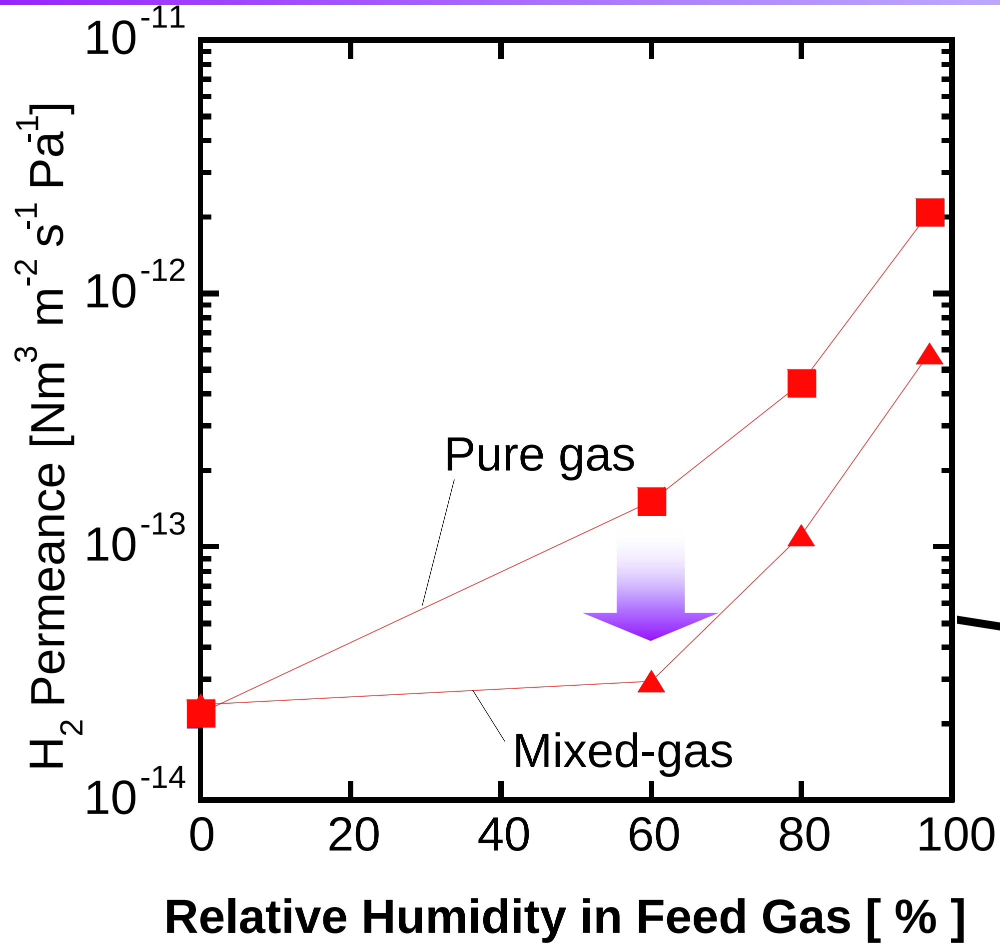
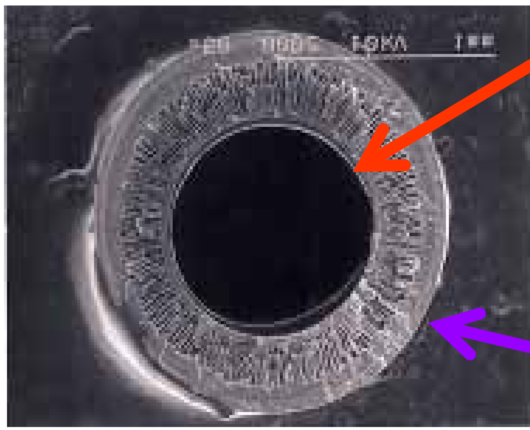


	Mixed-gas 5% CO_2	Pure gas
Dendrimer 2	▲	■

H_2 Permeability
Pure gas > Mixed-gas
(CO_2: 5 %)

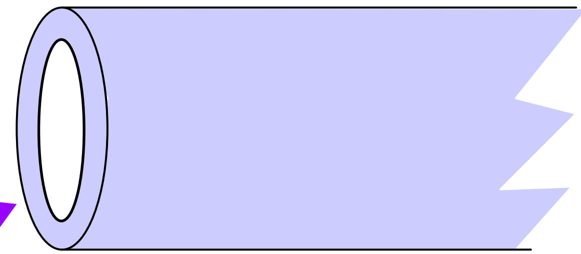
CO2 apparently obstructs H_2 permeation in Dendrimer

200mm Membrane Module



1 mm

Selective Layer ,
Chitosan + PAMAM Dendrimer



Support Substrate, PSF Hollow fiber

200 mm , ϕ3/8 inch

In-situ Module Modification Method

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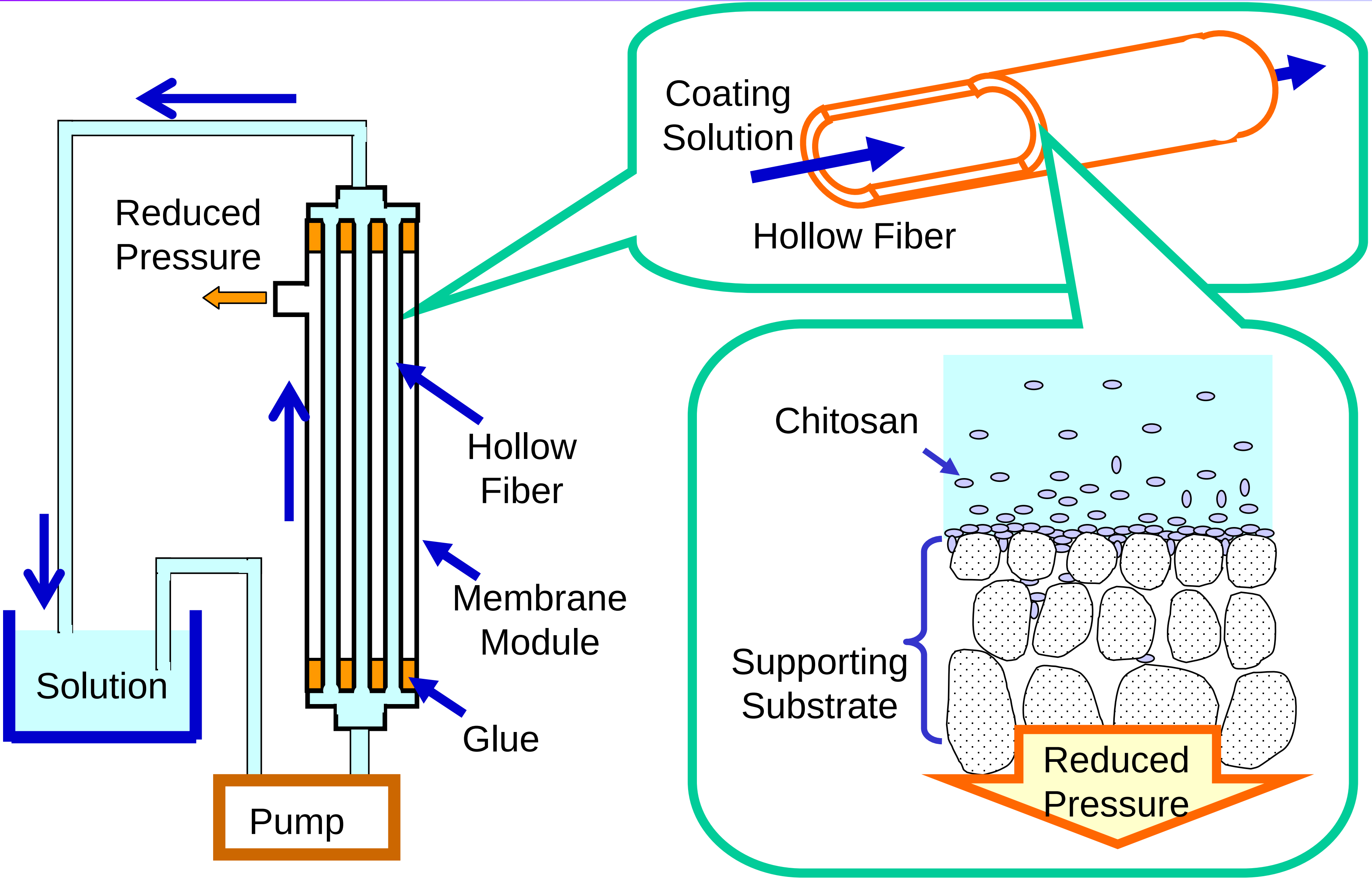

SEM Images of Selective Layer

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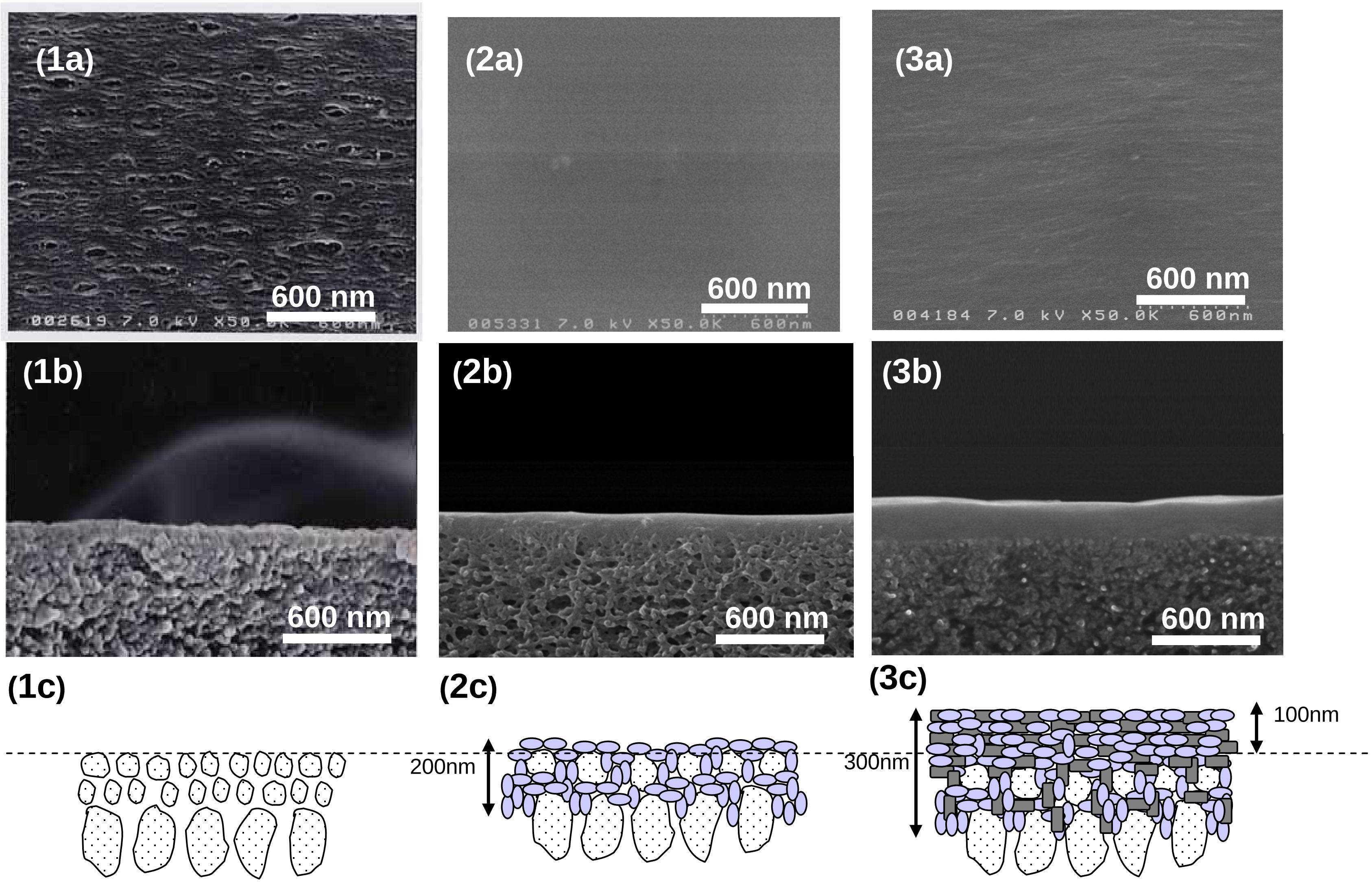

Concluding Remarks

- The combination of measures against global warming will have good effect.
- CCS is one of great measures against global warming, which is acted in advanced countries.
- Among CO_2 separation system, RITE have been developing the chemical absorbent and membrane material.
- The target of RITE absorbent is decreasing the cost by half.
- If a membrane separation method will be applicable to IGCC, CO_2 separation will become really economical.