台灣在二氧化碳回收及再利用上之研究現況

Current Research on CO_2 Recovery and Utilization in Taiwan

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二氧化碳捕捉及封存技術研討會July 18, 2006

Outline

1. Introduction
2. Preview of CO_2 recovery technologies
3. Preview of CO_2 utilization
4. Current research on CO_2 recovery and utilization in Taiwan
5. Conclusions

Humanity's Top Ten Problems for Next 50 years

Energy
Water
Food
Environment
Poverty
Terrorism & War
Disease
Education
Democracy
Population

2003	6.3	Billion People
2050	9-10	Billion People

Source: R. E. Smalley 2003
NANOTECHNOLGY, the S&T Workforce, ENERGY & Prosperity

Introduction

- 98.22 % of energy was imported in 2005.
- Energy consumed by industrial sector is about 55 %.
- CO_2 emission was about 270 million tons in 2005, ranked as the 22nd in the world.
- CO_2 emission per capita is 12.4 tons in 2005, ranked as the 3rd just behind the US and Australia.

資料來源：經濟部能源局

CO_2 Emission from Different Sectors in Taiwan

- Industry (55.2 %)
- Transportation (13.8 %)
- Residence (11.9 %)
- Commerce (6.0 %)
- Energy (4 %)
- Agriculture (2 %)
- Others (7.2 %)

資料來源：經濟部能源局

CO_2 Emission from Industries in Taiwan

- Iron and steel (27 %)
- Oil chemistry (16 %)
- Electronics (10 %)
- Textile (6 %)
- Cement (5 %)
- Paper-making (4 %)

資料來源：經濟部能源局，2005

CO_2 Emission by Fossil Fuels

- Coal (53.6 %) H/C ratio: 0.8~1.2
- Oil (38.2 %) H/C ratio: 1.8~2.0
- Natural gas (8.2 %) H/C ratio: 3~4

- Because of cost, natural gas consumption is much lower than that in USA, European nations, and Japan.

The Strategies to Reduce CO_2

- Promote energy efficiency
- Use low-carbon, new, and renewable energy
- CO_2 recovery
- CO_2 conversion and utilization
- CO_2 fixation and storage

Promote Energy Efficiency

- Energy saving
- Process improvement and innovation. (Cleaner production and sustainability)
- Material innovation and recycling
- Improvement of energy efficiency in power generation plant (CO_2 emission is 0.69 kg per kilowatt-hour in 2005)

Use Low-Carbon, New, Renewable Energy

- Oil and coal emit 53 and 84 % more CO_2 than LNG.

- Solar, wind, geothermal, and hydraulic power are clean but not stable energy sources. The efficiency of a solar cell is less than 20 %, usually 15%.

- Biofuel is an alternative energy source.

- 20 % of all energy consumption from substituted energy is not easy to achieve.

CO_2 Recovery

- Physical methods
  - Physical absorption
  - Physical adsorption
  - Cryogenic separation
  - Membrane separation
- Chemical method
  - Chemical absorption

CO_2 Conversion and Utilization

- Direct use in dry ice, food packing, carbonated soft drink, extinguisher, bactericide, propellant, solvent, ---

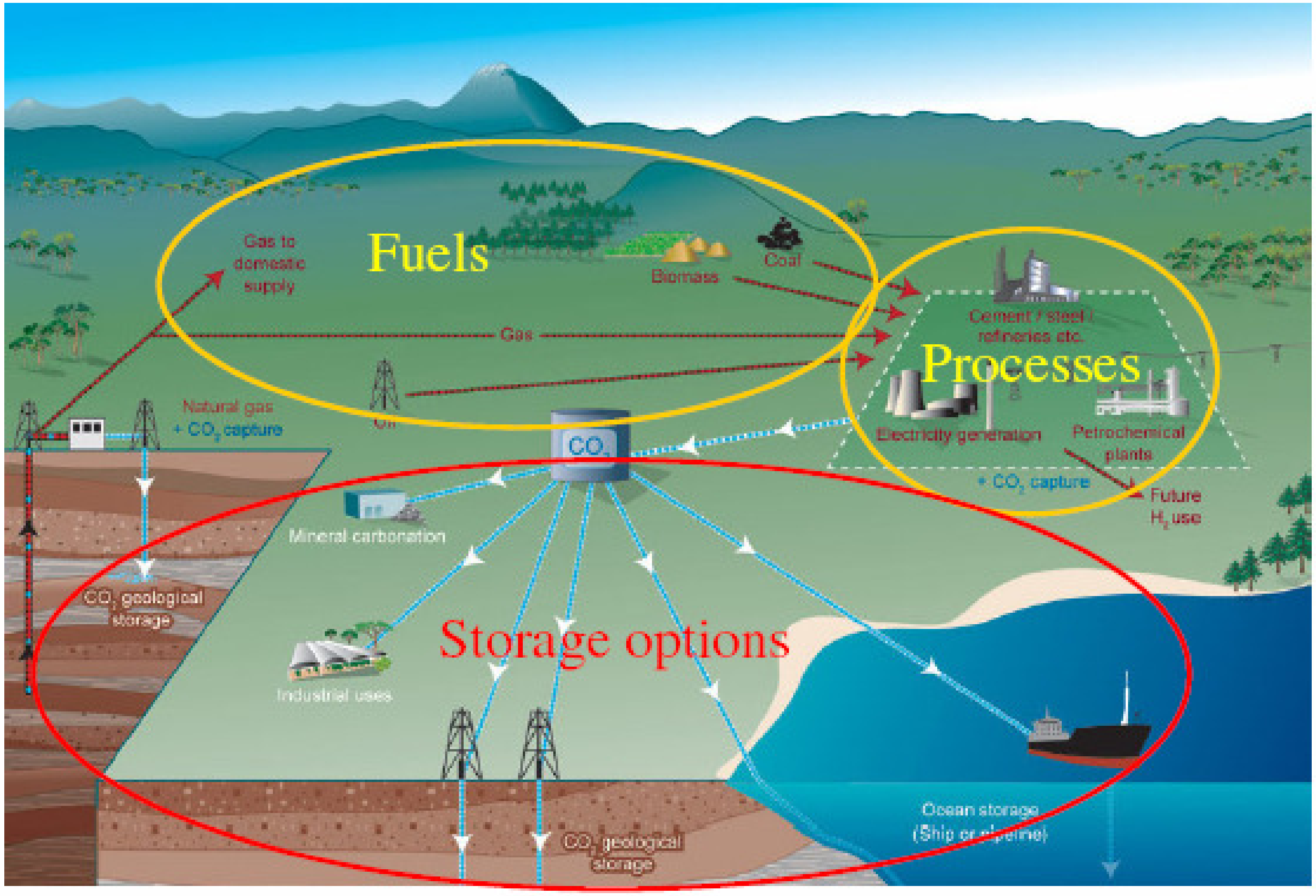
- Conversion pathways:

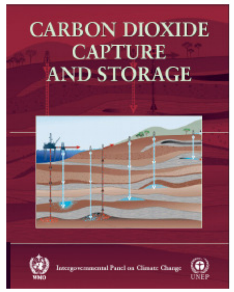
  reforming, hydrogenation, chemical synthesis, copolymerization, photo catalysis, ---

CO_2 Fixation and Storage

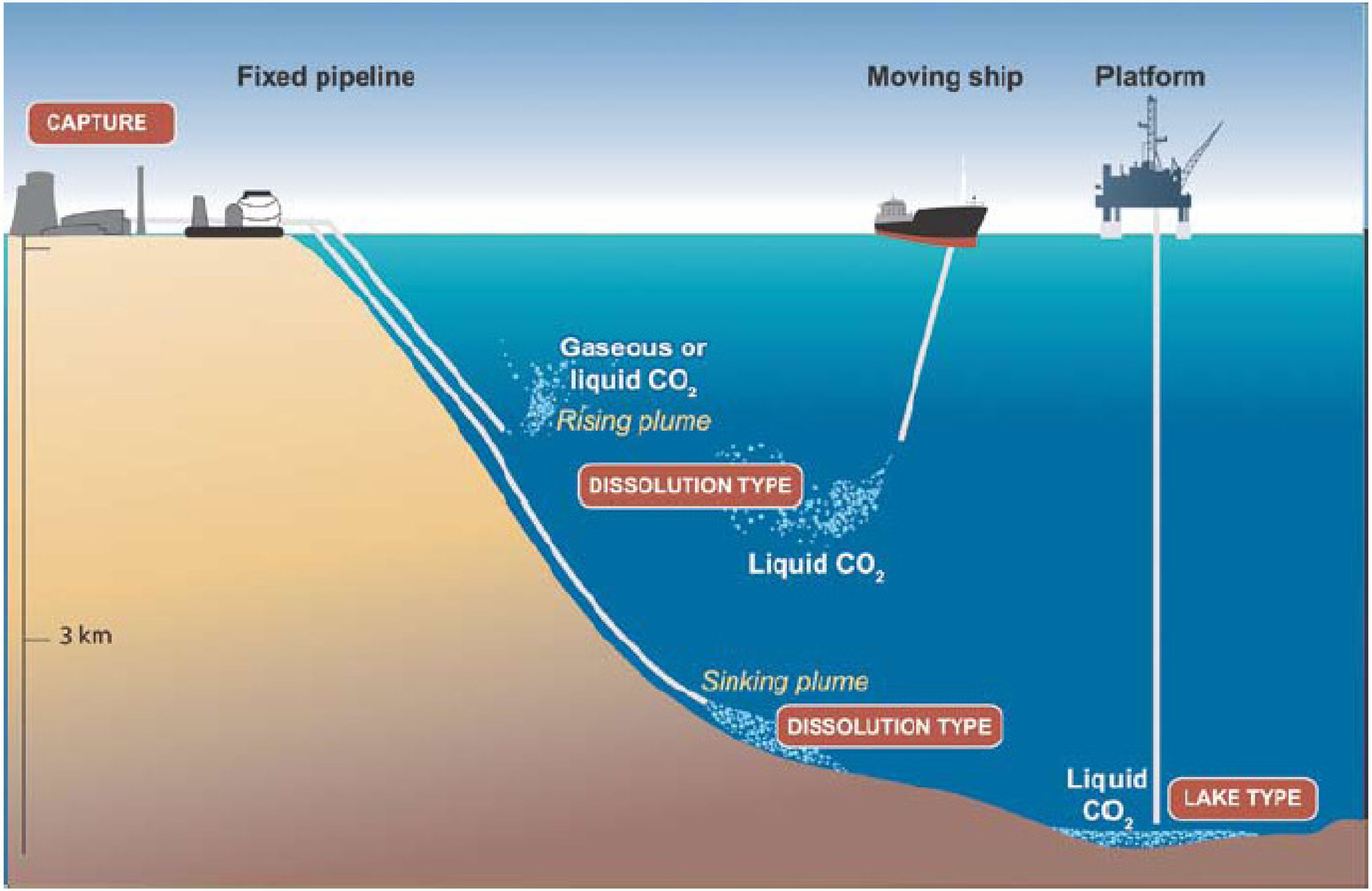
- CO_2 can be sequestered in oceans or spent gas and oil wells.
- Fixation by inorganic minerals.
- Biofixation.

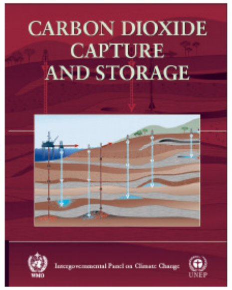
CO_2 Capture and Storage System



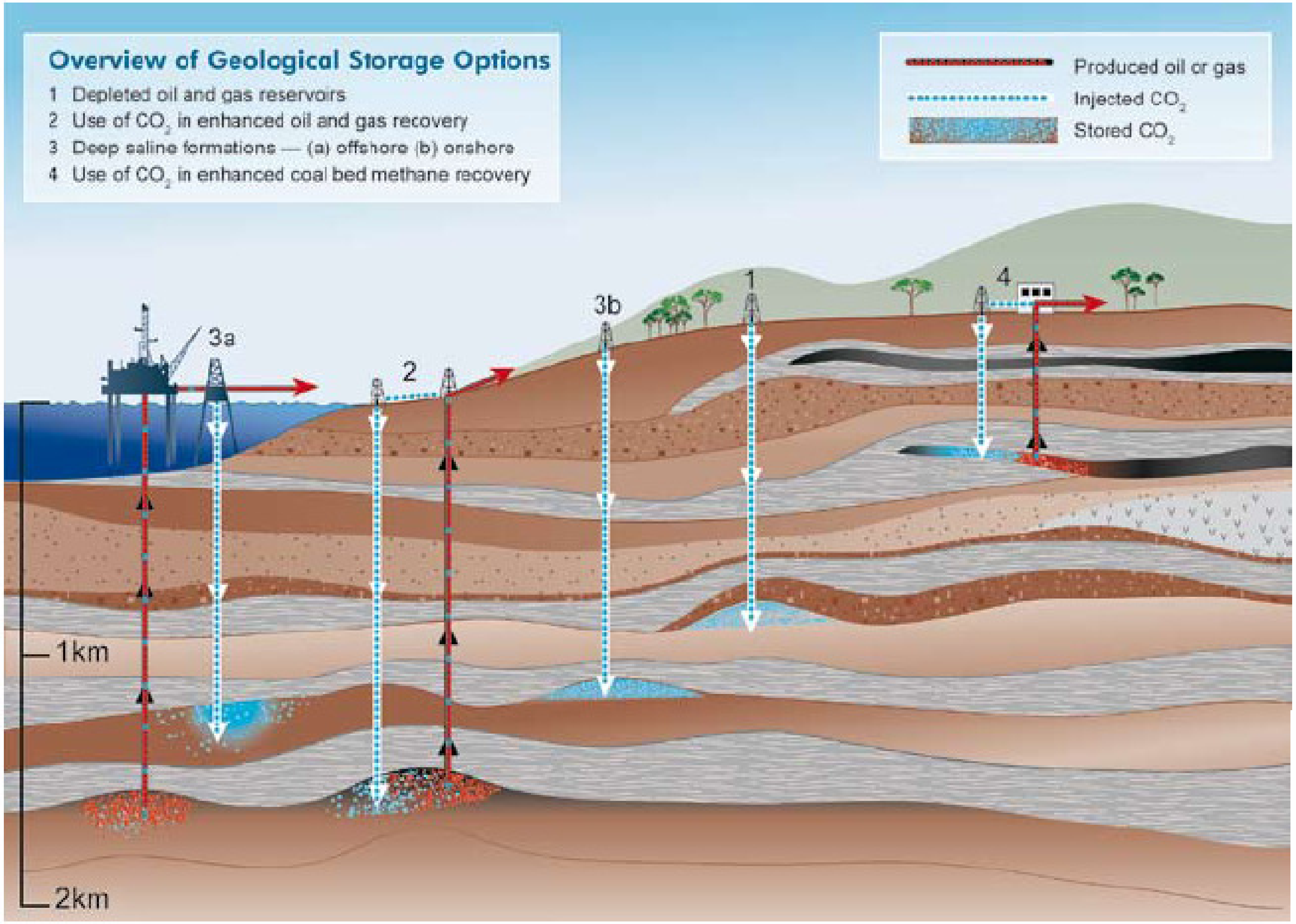


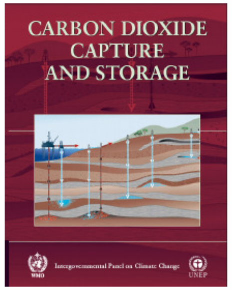
Oceanic Storage



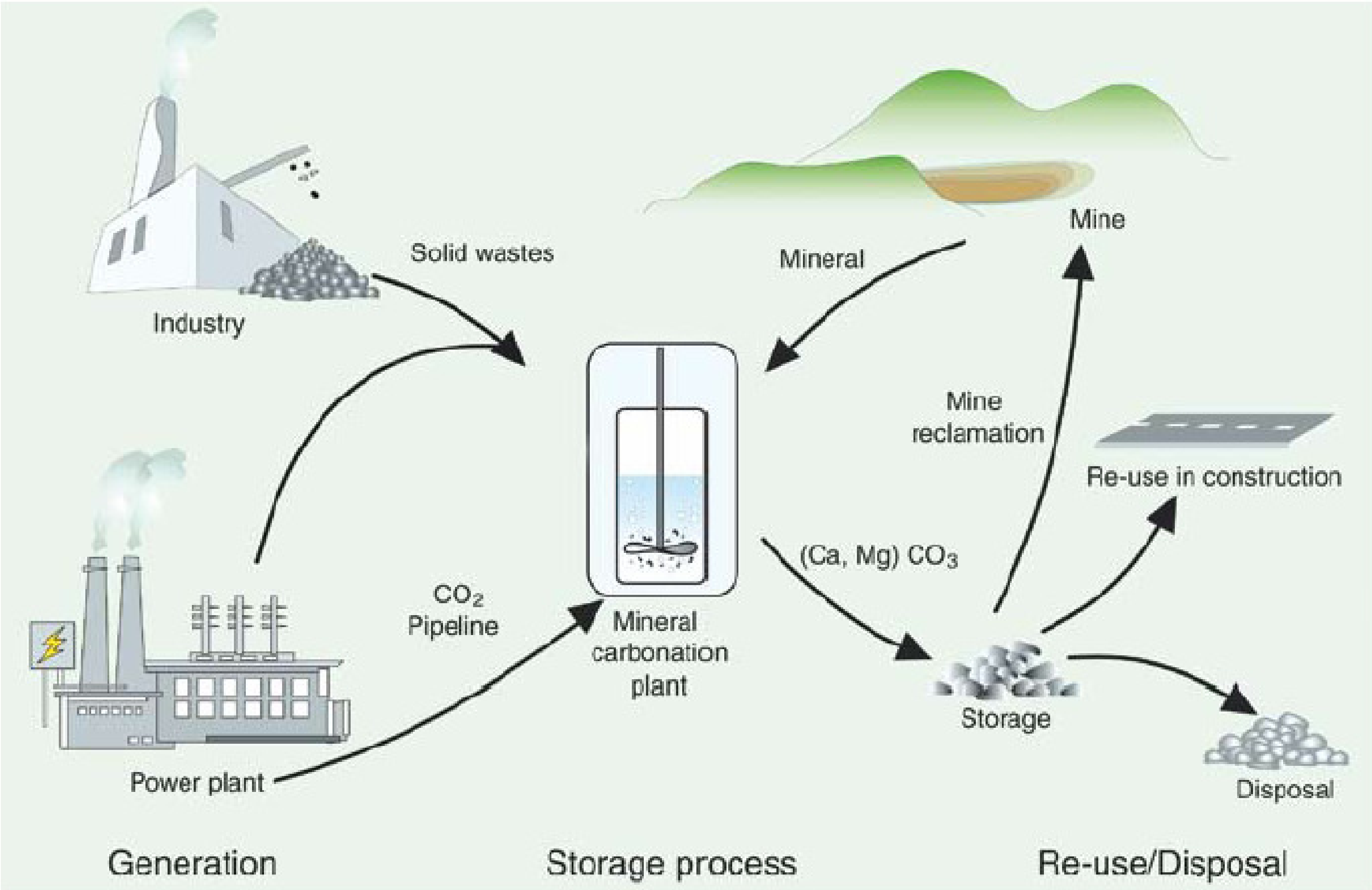


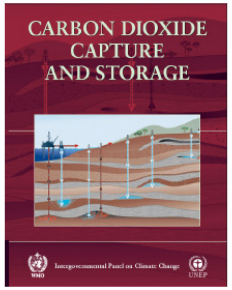
Geological Storage



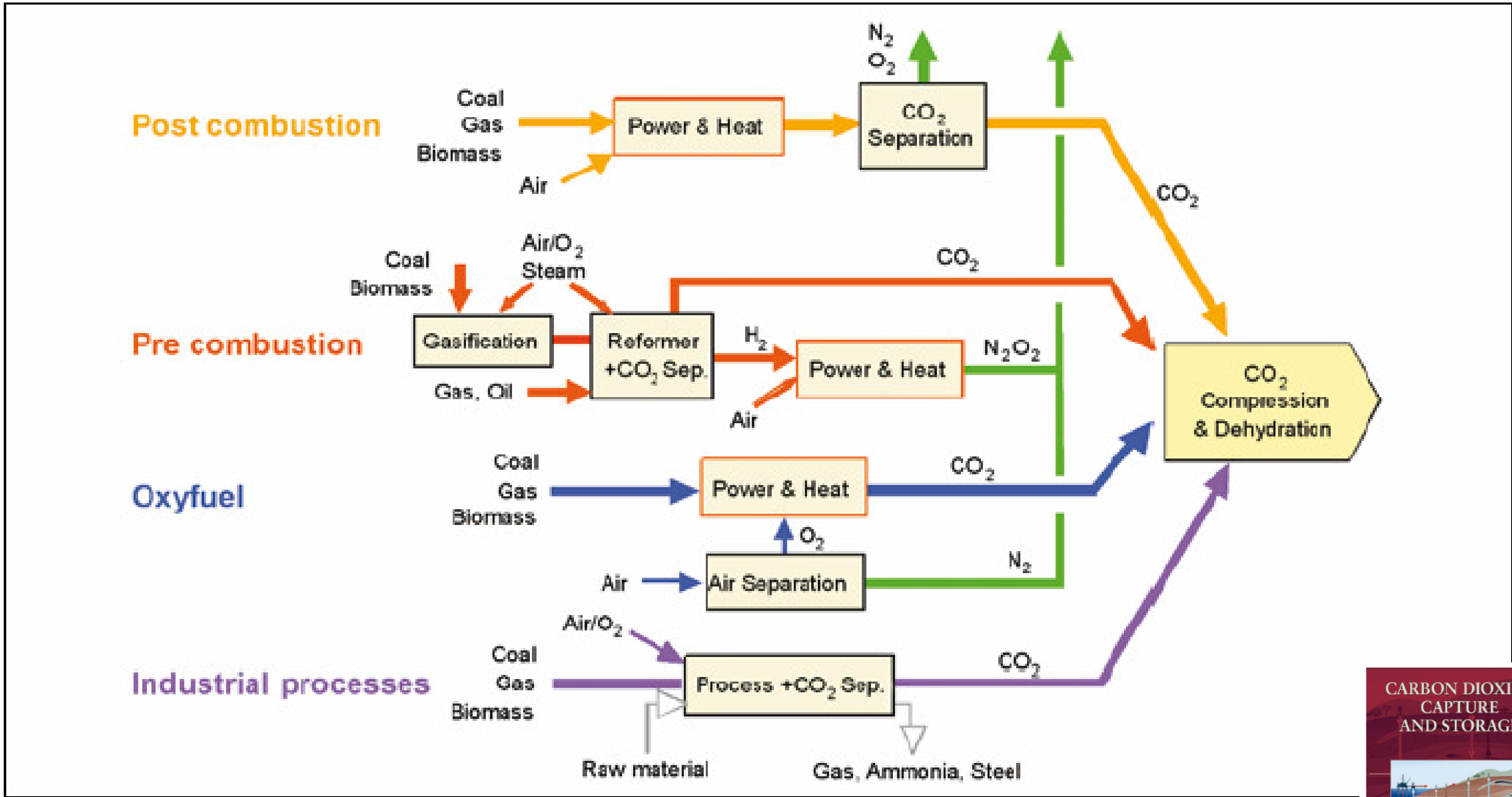


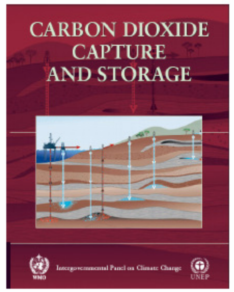
Mineral Carbonation





Preview of CO_2 Recovery Technologies





Physical Absorption

- **To treat pressurized flue gases containing high percentage of CO_2**

Technology	Solvent	Licensor
Purisol	n-Methylpyrrolodine	Lurgi
Rectisol	Methanol	Lurgi,Linde
Selexol	Dimethyl Ether of PG	Norton

Physical Adsorption

- Adsorbents: activated carbon, molecular sieve, ---

- Operations:
  - Pressure Swing Adsorption (PSA)
  - Temperature Swing Adsorption (TSA)
  - Electrical Swing Adsorption (ESA)

Cryogenic Separation

- Limitation
  - 90 % CO_2 concentration is recommended

- Disadvantages
  - High energy cost
  - Expensive cooling equipment
  - Purify gas before cooling

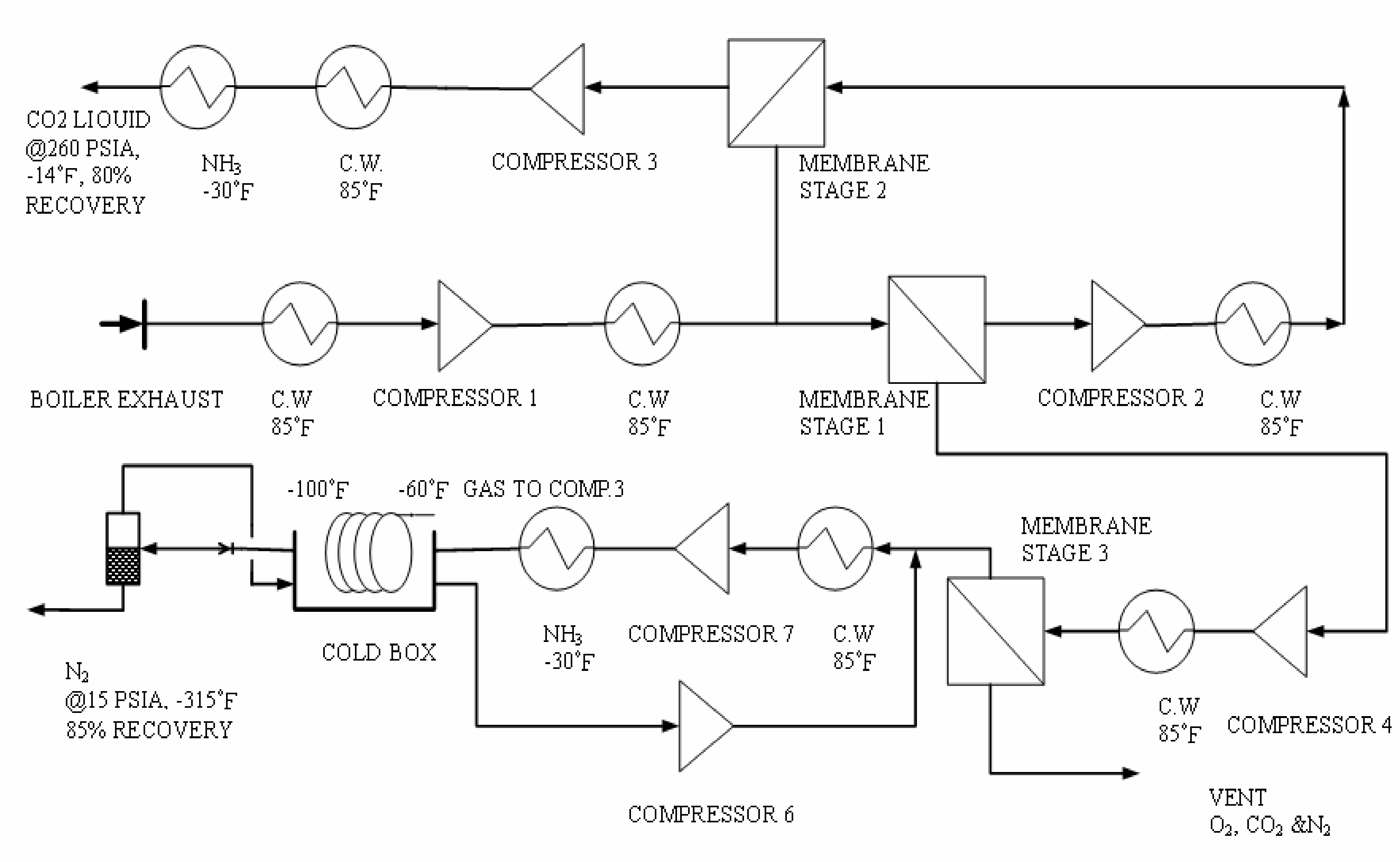
Membrane Separation

- Materials:

  Cellulose acetate, Polyimide, Alumina, Y-zeolite, Poly(ethylene oxide-co-epichlorohydrin), ---

- Operations:

  hollow fiber, spiral wound, ---



資料來源：以薄膜回收二氧化碳之技術手冊，經濟部工業局

Chemical Absorption

Technology	Solvent	Licensor
Alkanoamines	MEA,DGA,DEA,TEA, MDEA,AMP,PZ	Union Carbide Fluor, Dow, Lurgi, Shell, Texaco
Benfield	K_2CO_3 Solution	Union Carbide
Catacarb	Salt Solution + Catalyst	Eickmeyer and Associates

Absorbents

- Primary amines: monoethanolamine, diglycoamine, ---

  high reaction rate, high corrosion, carbamate formation

- Secondary amines: diethanolamine, Diisopropanolamine, ---

  medium reaction rate, carbamate formation

- Tertiary amines: triethanolamine, N-methyldiethanolamine, ---

  high capacity, low reaction rate

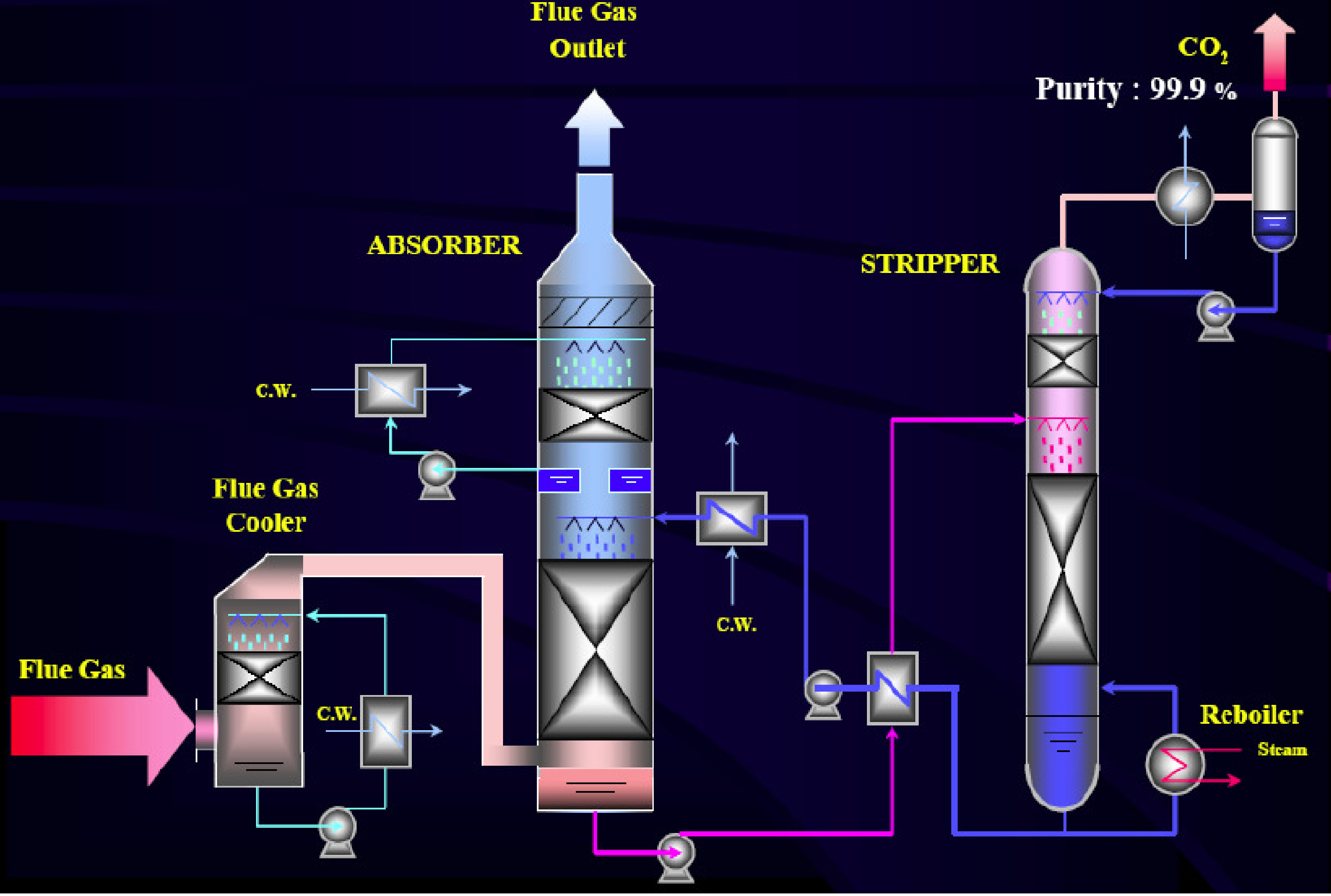
- Sterically hindered amines: 2-amino-2-methyl-1-propanol (AMP), 2-piperidineethanol (2-PE), ---

  high capacity, thermodynamic superiority

- Promoters: Piperazine (PZ)

  high reaction rate, high corrosion, limited solubility

Process Flow for Amine Absorption



The current research subjects in absorption

- synthesis of new absorbents
- absorbent formulations
- operations with high efficiency
- packing in absorption column
- reduction of corrosion and loss of absorbents
- simulation and optimization
- reduction of operation cost

Chemical Absorption + Membrane Contactor

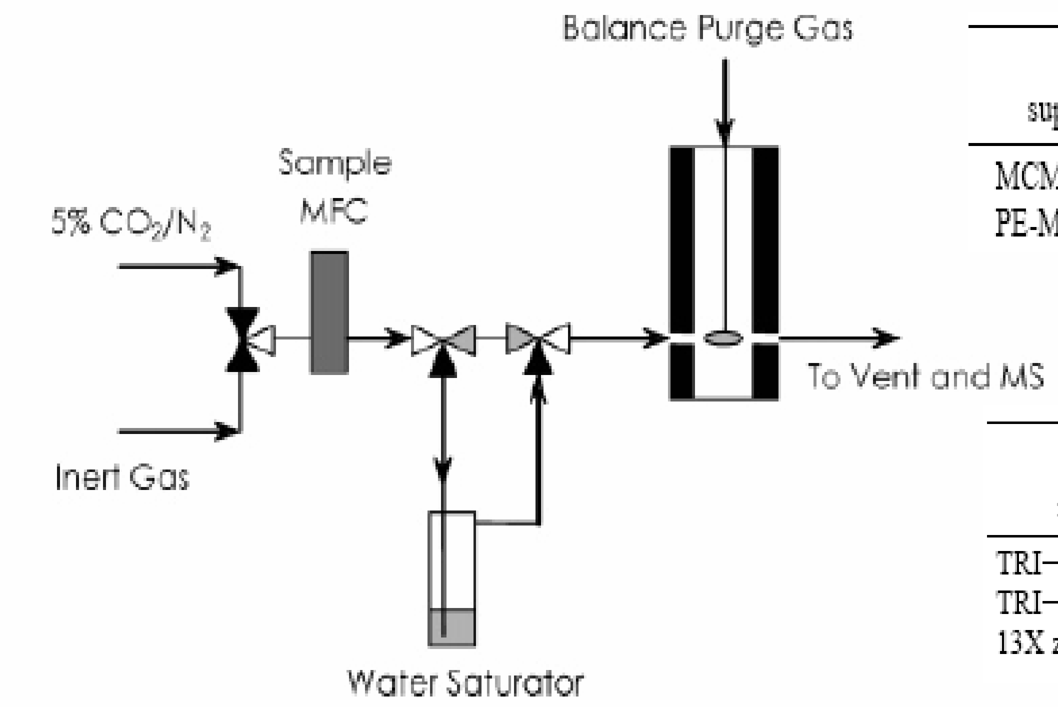
- The contact area 500-1500 m^2/m^3 is much higher than that in a traditional absorber column 100-250 m^2/m^3

- Constant contact area of liquid and gas

- Avoid foaming and flooding, and a possible horizontal arrangement

Hoff, et al., Ind. Eng. Chem. Res. 2004, 43 (16), 4908-4921.

Chemical Absorption + Physical Adsorption



support	BET surface area (m^2/g)	pore diameter (nm)	volume (cm^3/g)
MCM-41	1140	3.7	1.03
PE-MCM-41	950	10	2.2

material	amount grafted (mmol(N)/g)	Adsorption Capacity (mmol/g)		
		dry CO_2	H_2O	humid CO_2
TRI−MCM-41	5.69	0.97	2.56	1.01
TRI−PE-MCM-41	5.98	1.41	3.11	1.52
13X zeolite		2.05	15.11	0.09

Harlick and Sayari, Ind. Eng. Chem. Res., 2006, 45, 3248-3255.

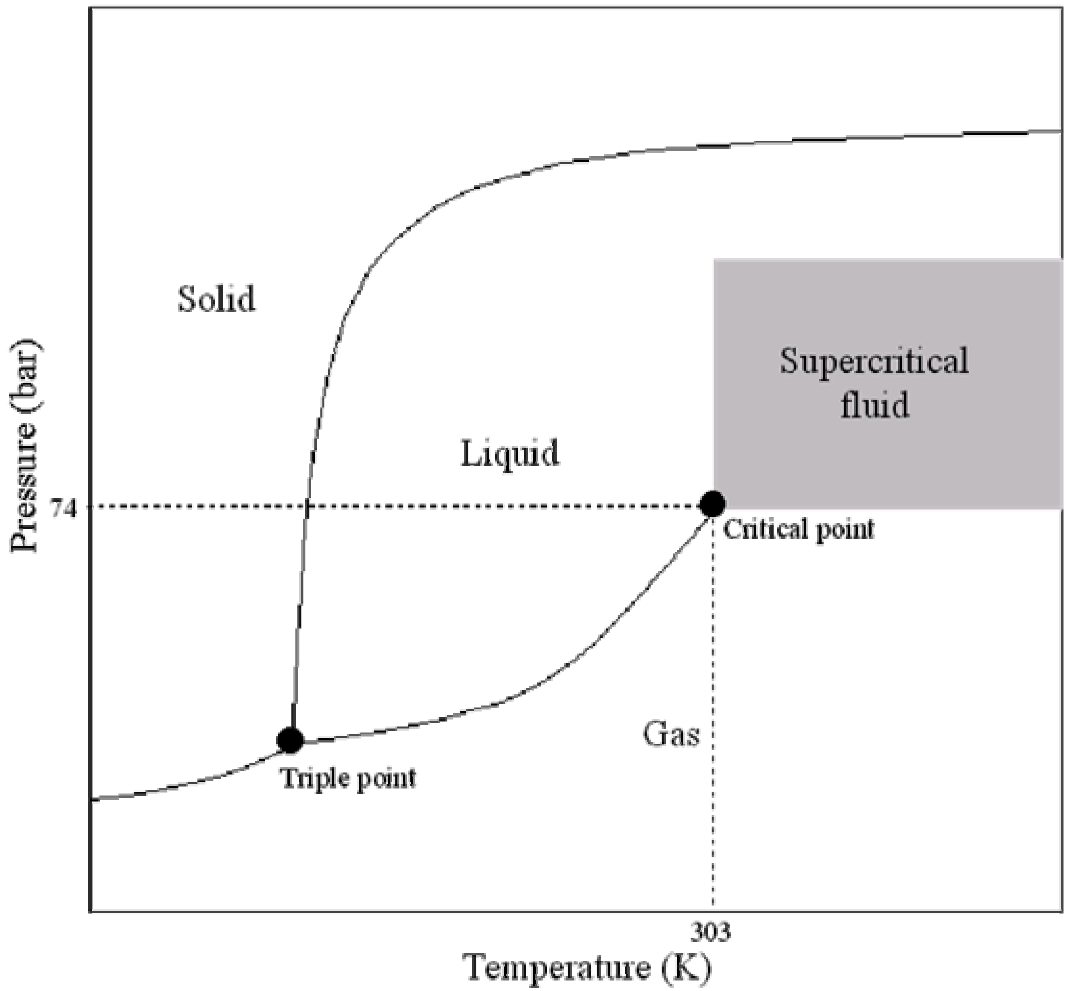
Preview of CO_2 Utilization

- Direct use in dry ice, food packing, carbonated soft drink, extinguisher, bactericide, propellant, solvent, ---

- CO_2 as the carbon source
  - Chemicals such as urea, salycilic acid, organic and inorganic carbonates, polyethercarbonate, ---
  - Energy Products such as methanol, dimethyl carbonate, dimethyl ether, ---

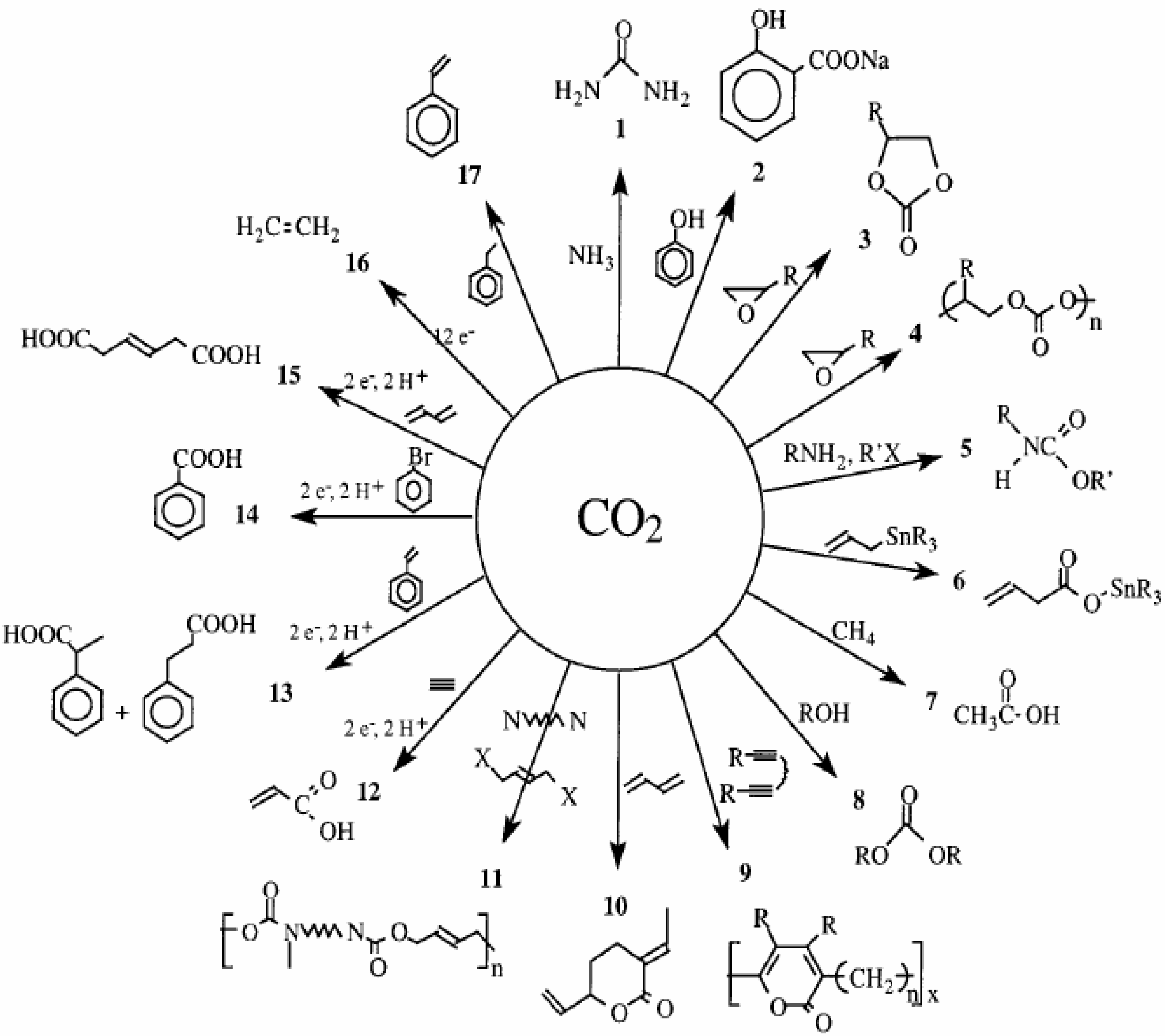
Supercritical Fluids

- Supercritical CO_2 has been regarded as the green solvent.



Solvents \ Conditions	Tc (°C)	Pc (psi)
CO_2	31.1	1072
H_2O	374.4	3208.2
Ammonia, NH_3	132.4	1646.2
Methane, CH_4	-82.4	667.2
Ethane, C_2H_6	32.2	697.6
Propane, C_3H_8	96.8	616.4
Methanol, CH_3OH	240.1	1173.4
Isopropanol, $CH_3CHOHCH_3$	235.8	690.4

Chemical Synthesis



Arakawa et al., Chem. Rev. 2001, 101, 953-996.

CO_2 as Carbon Source

- Gasification
  $$C + CO_2 + 171\ kJ \rightarrow 2CO$$

- Reforming
  $$CH_4 + CO_2 + 247\ kJ \rightarrow 2CO + 2H_2$$

- Methanol Synthesis
  $$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$

- Methanation
  $$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O + 90kJ$$

- Enhanced Photosynthesis
  $$CO_2 + H_2O \rightarrow \text{Chemicals}$$

CO_2 Copolymerization

- Polymers and Copolymers from CO_2

  CO_2 -epoxide copolymer

  CO_2 -ethyleneimine (aziridine)

  CO_2 -vinyl ether copolymer

Carnol Process

Brookhaven National Lab

- Methane decomposition:
  $CH_4 \rightarrow C + 2H_2$
- Methanol synthesis:
  $CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$
- Overall reaction
  $3CH_4 + 2CO_2 \rightarrow 2CH_3OH + 2H_2O + 3C.$

- Possibly reduce 45% of CO_2 emission in the US by replacing gasoline with methanol

Energy Source - Dimethyl Carbonate (DMC)

- Octane Number is 105.

- Replace MTBE (methyl-tert-butyl-ether) as the additive in gasoline.

- Synthesis of DMC from CO_2

$$2CH_3OH + CO_2 \rightarrow (CH_3O)_2CO + H_2$$

Energy Source - Dimethyl Ether (DME)

- Similar to Propane and Butane
- Cetane Number is 55 ~ 60, better than Diesel, 40 ~ 55
- No sulfur, avoid air pollution
- Lower explosion limit is 3.4 ~ 17 %, higher than propane, 2.1 ~ 9.4 %
- Synthesis of DME from CO_2

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$

$$H_2O + CO \rightarrow H_2 + CO_2$$

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O$$

Projects carried out on CO_2 Reduction in Taiwan

Sponsored by Industrial Development Bureau (工業局)

- In the project "Reducing greenhouse gases emission from industrial processes" (1992-1997), the technology to assess CO_2 emission (IPCC) was established and the strategies for reduction of CO_2 emission were proposed. （清大黃大仁、馬振基、談駿嵩及台科大顧洋）

- In the project " Promotion of greenhouse gases reduction technologies to chemical industry"(1997-2002), reduction technologies related to enhancement of energy efficiency were promoted to industries（清大黃大仁、馬振基、談駿嵩及台科大顧洋）

前瞻優質生活環境科技跨領域研究專案計畫

Sponsored by National Science Council (國科會工程處)

1. Recovery of CO_2 from the exhausted gases by Higee technique（清大談駿嵩）

2. Recovery of CO_2 from the exhausted gases by functionalized inorganic molecular sieve membrane（清大楊家銘）

3. Conversion of CO_2 into carbonate（台大戴怡德）

4. Conversion of CO_2 into methanol（清大凌永健）

空氣污染防制科技研發計畫

Sponsored by Sustainable Development Research Committee

1. Design and development for CO_2 photoreduction to methanol
   - 二氧化碳光催化生成甲醇之研究(中央陳郁文)。
   - 含奈米光觸媒薄膜中孔洞材料還原溫室氣體二氧化碳之研發（中研院簡淑華）。
   - 光催化還原方法減量溫室氣體CO_2（台大吳紀聖、東華林欣瑜）。

2. The technical evaluation for using minerals and alkaline solid residues on the sequestration of carbon dioxide

- 利用礦物、鹼性固廢物為吸附劑進行二氧化碳封存技術評估（台大蔣本基、北醫張怡怡）。
- 新穎二氧化碳吸收劑配方開發－吸收二氧化碳之反應動力及熱力性質量測及評估研究（中國醫藥江鴻龍、中原李夢輝）。
- 高效能二氧化碳回收用薄膜接觸式氣液反應技術之評估及開發（南亞林素霞、中原童國倫）。
- 創新型TiO2光觸媒轉化還原CO2之研究（清大王竹方、大葉柯雅雯）。

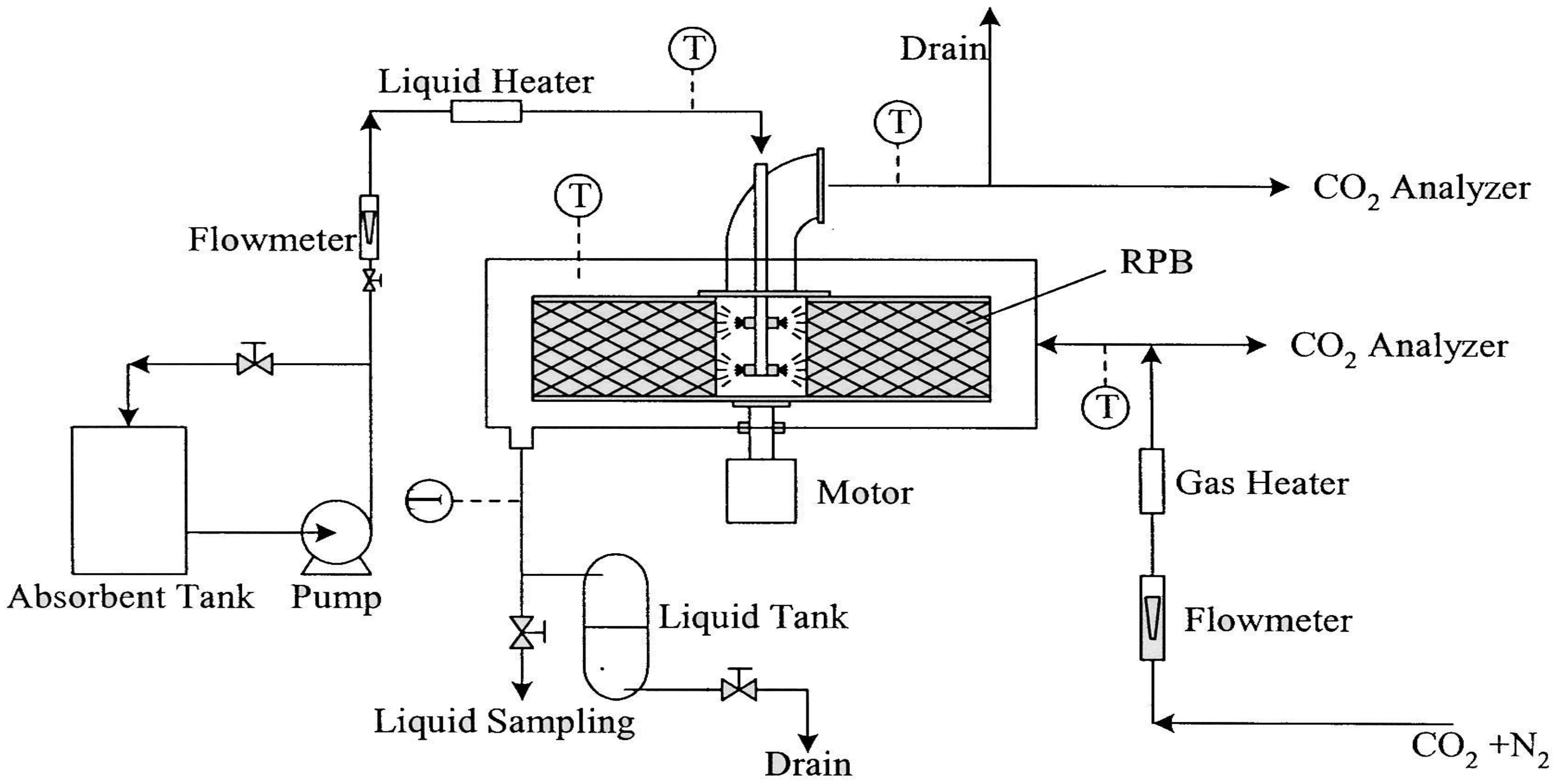
3. Removal of carbon dioxide by absorption in a cross-flow rotating packed bed（長庚林佳彰）

Research on CO_2 Recovery in Taiwan

Chemical Absorption

- Measurement of CO_2 absorption kinetics, Henry's constant, viscosity, and density of single and mixed amines (中原李夢輝)
- Simulation and optimization of CO_2 absorption from flue gases of power generation plants (淡江張煖)
- Removal of carbon dioxide by absorption in a rotating packed bed (清大談駿嵩)

Chemical Absorption + Higee



Rotating Packed Bed: I.D. 7.0 cm; O.D. 16.0 cm; Height 2.0 cm

Packed Bed: I.D. 1.9cm; Height 110cm

Lin, C. C. et al., Ind. Eng. Chem. Res. 2003, 42, 2381

Tan, C. S.; Chen, J.E., Sep. Purif. Technol. 2006, 49, 174

Comparison of the Removal Efficiency between a Rotating Packed Bed and a Packed Column

	Packed Tower	RPB
Pressure, atm	1	1
Temperature, K	297	300
Gas phase		
CO_2 concentration, mol %	9.8	10
Gas flow rate, L/min	4.9~10.4	4.4~13.1
Gas load, m3/m2/h	1044~2196	38~111
Liquid phase		
AMP concentration, kmol/m3	1.1	1
Liquid flow rate, mL/min	46	42
Liquid load, m3/m2/h	9.7	0.4
$K_G a$ (based on liquid load), 1/s	0.07	0.14

Physical Adsorption

CO_2 recovery by vacuum swing adsorption (VPSA)（中央周正堂）

Membrane

Two research teams are synthesizing nanoporous zeolite and high thermal stability polymer membranes to separate CO_2 from the flue gases of power generation plants (清華大學及中原大學)

Using supercritical CO_2 as the cleaning agent

- Five King Cereals Industry CO., Ltd.（五王糧食）is the first company in world uses supercritical CO_2 to remove insecticide from rice.

- Tex-Ray Industrial Co., Ltd.（南緯實業）has devoted to supercritical fluid applications including dyeing, cleaning, and extraction from 1997.

- Some companies have done research and development on supercritical foaming and photoresist removal from wafers.

- In the alkylation of toluene with propylene and isopropanol in supercritical carbon dioxide over CLD modified HZSM-5 Pellets, 50% more of selectivity and yield towards p-cymene were observed compared to the operations in gas（清大談駿嵩）

- Supercritical extraction of ginkgolides and ginsenosides from ginkgo and ginseng（中興張傑明）

CO_2 Utilization in Industry in Taiwan

- Oriental Union Chemical Corp. (東聯化學) produces ethylene carbonate (EC) from the reaction of CO_2 with ethylene oxide.

- Chimei-Asahi Corp. (旭美化成) is the first plant in the world to produce polycarbonate (PC) from EC. This process avoids using phosgene.

Polymer Synthesis

- Synthesis of alternating polyethercarbonate (PC) from copolymerization of CO_2 with epoxides such as propylene oxide, butene oxide, and cyclohexene oxide using a yttrium-metal coordination catalyst (清大談駿嵩)

- Synthesis of PC from block copolymerization of CO_2 with mixed epoxides using a yttrium-metal coordination catalyst (清大談駿嵩)

- To improve thermal and mechanical properties of PC, nanoparticles were infused into the base PC via sol-gel (清大談駿嵩)

Research on CO_2 Utilization in Taiwan

CO_2 – Methane Catalytic Reforming

- CO_2 reforming of methane to synthesis gas over bimetallic Ni-Cr/yttria-doped ceria catalysts（清大黃大仁）

- CO_2 reforming of methane to synthesis gas over Ni/MgO-Al_2O_3-$AlPO_4$ catalysts（中央陳郁文）

Photoreduction

- Photocatalytic reduction of carbonate in aqueous solution by UV/TiO_2 process（台科大顧洋）

- Photoreduction of CO_2 using metal-loaded titania as the catalyst（台大吳紀聖）

- Photoreduction of CO_2 to methanol using an optical-fiber photoreactor（台大吳紀聖）

Mineral Fixation

- Factors affecting wollastonite carbonation under CO_2 supercritical conditions（台大戴怡德）

Conclusions

- Most of the industrial companies in Taiwan have recognized their responsibility to reduce CO_2 emission.

- Fossil fuels will still be the major energy resources in next 20 years, so that recovery and utilization of CO_2 should be paid attention to.

- Because the technologies for CO_2 recovery and utilization are not matured yet and the technology innovation becomes fast, it is not late for industries in Taiwan to begin the research on reduction of CO_2 emission.

- If the integrated teams consisting of academia, research institute, and industry can be formed, fruitful research progress is expected.

Thanks for your attention

敬請指教