# Research Work on $CO_2$ Capture

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# Outline

- Background
- Pre-combustion $CO_2$ Capture: Sorption enhanced hydrogen production from natural gas and coal
- Post-combustion $CO_2$ Capture: $CO_2$ separation from flue gas using dry sorbent, amine and membrane
- Oxy-fuel Combustion: $O_2/CO_2$ gases production for oxy-fuel combustion
- Conclusions

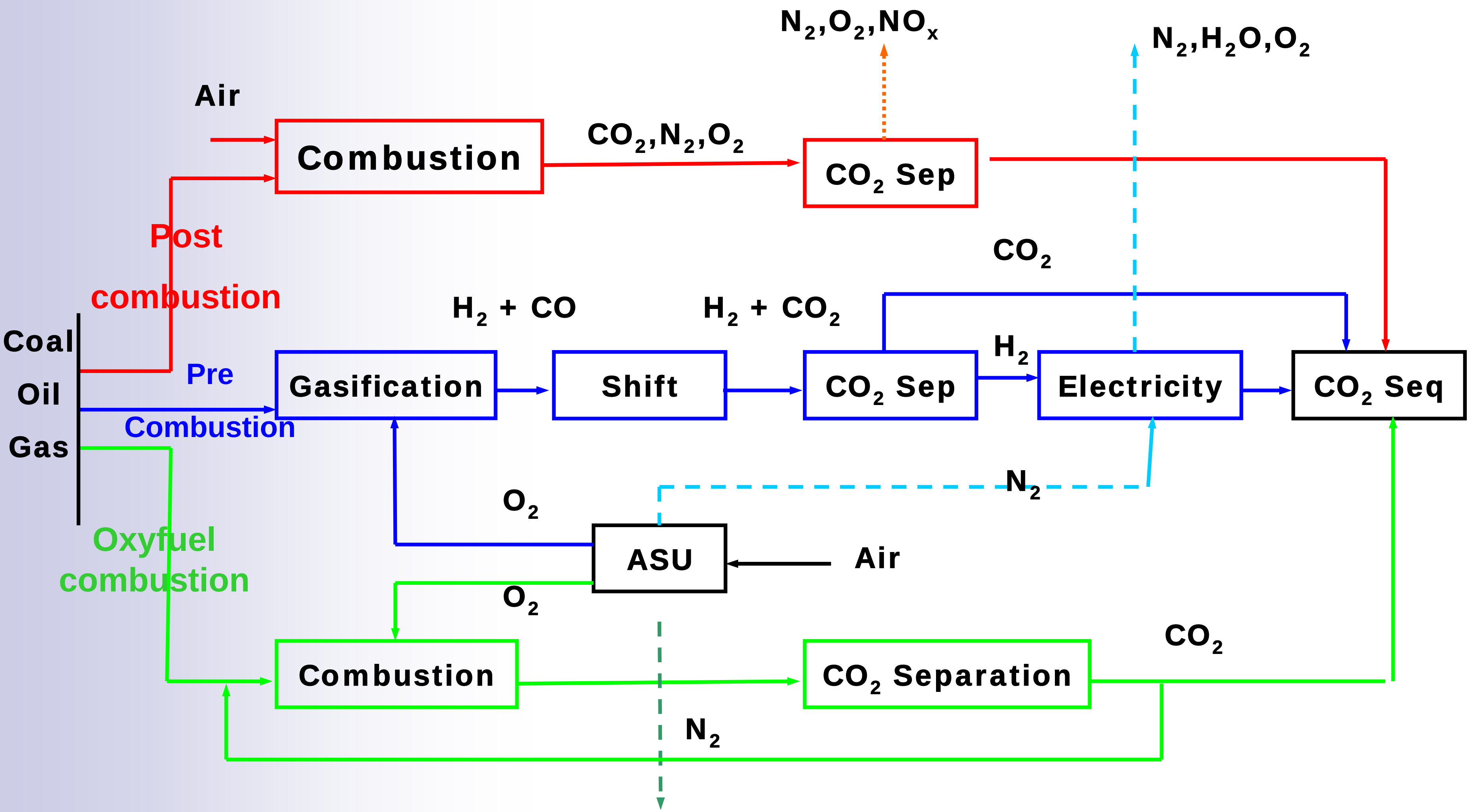
# Background

**National Basic Research Program of China (No. 2006CB705807)**

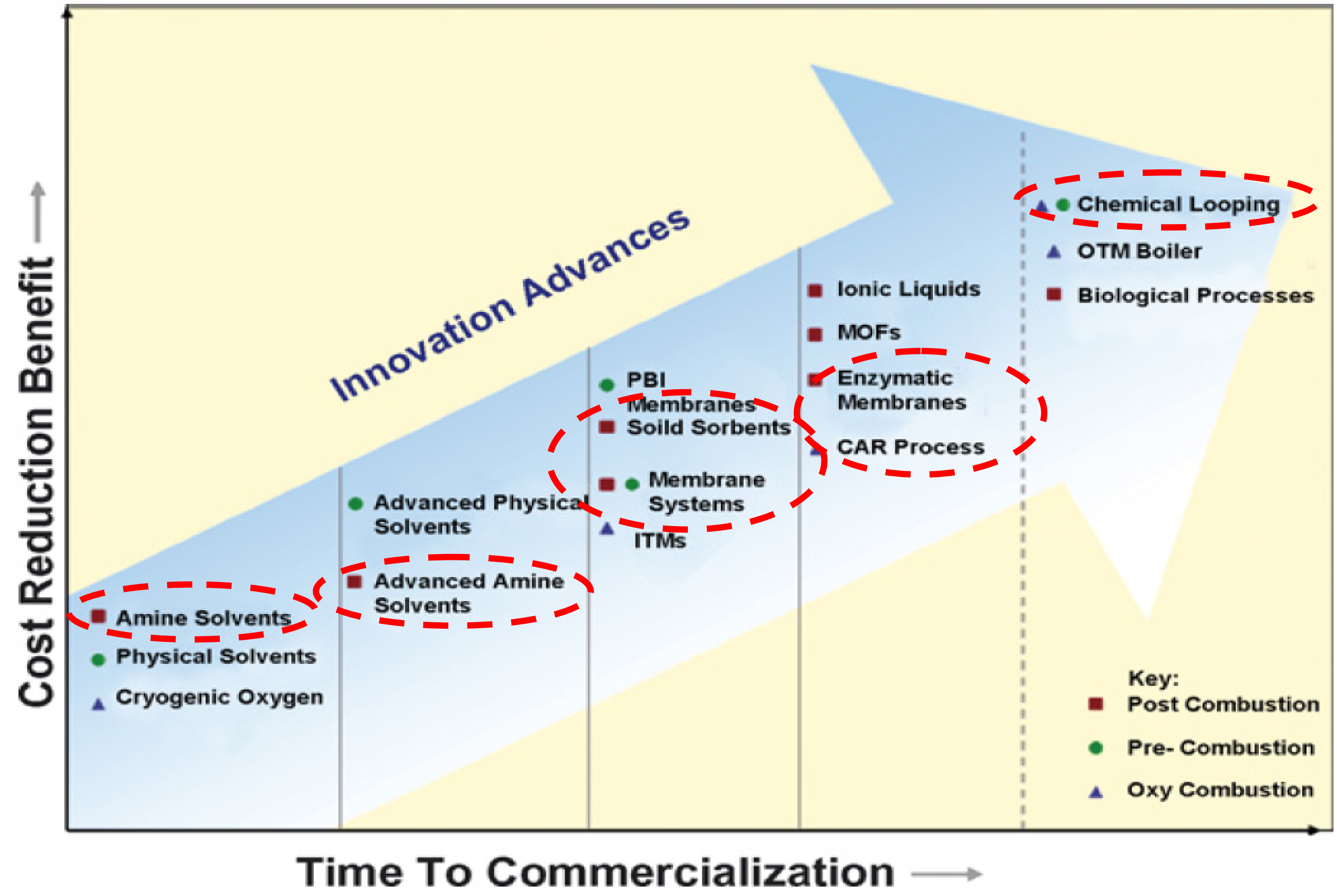
| Scientific problems | Research contents | Objectives |
| --- | --- | --- |
| **$CO_2$ Capture** | $CO_2$ capture technologies | Low cost |
| $CO_2$-Oil phases behavior | **Multiphase and multicomponent phase behavior of $CO_2$-oil system** | Improving oil recovery |
| **EOR** | Diffusion and seepage theory in EOR | Maintaining EOR stable and effective |
| $CO_2$ sequestration | Characteristic of CO2 moving front and CO2 sequestration in china | Obtaining the capacity of EOR and sequestration |

# Background

## $CO_2$ Capture Technologies



# Background




**Figueroa J. D., et al Advances in $CO_2$ capture technology**—The U.S. Department of Energy's Carbon Sequestration Program. **International Journal of Greenhouse Gas Control，2008(2), 9-20**

# Pre-combustion $CO_2$ Capture

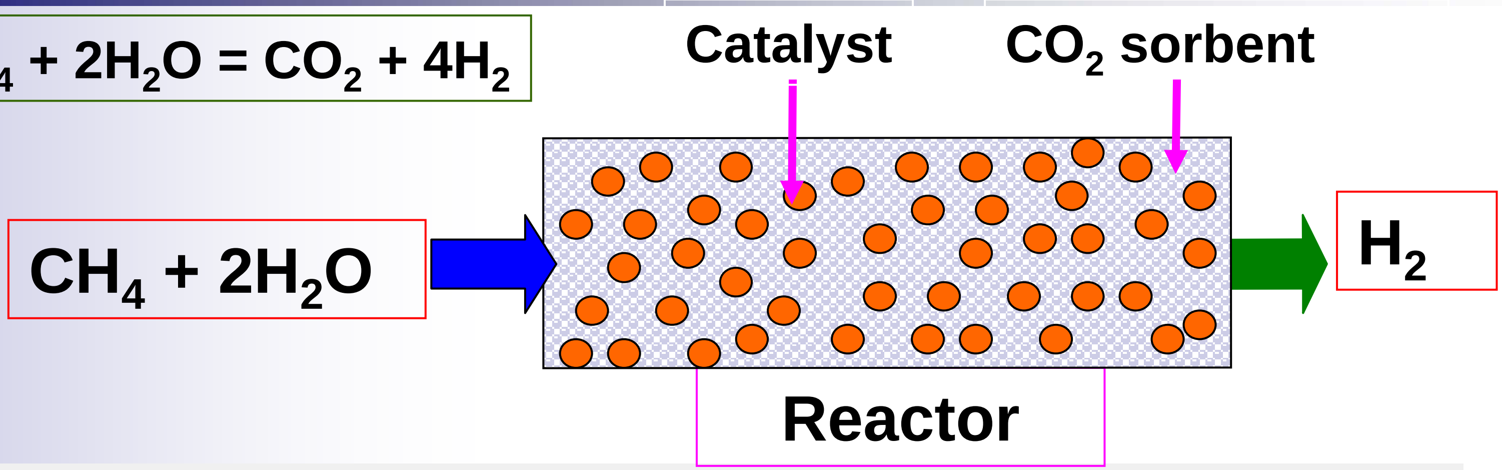
- Sorption enhanced hydrogen production

  from natural gas at THU

-Hydrogen production from coal using supercritical water at SXICC, CAS

# Sorption enhanced hydrogen production

$$CH_4 + 2H_2O = CO_2 + 4H_2$$



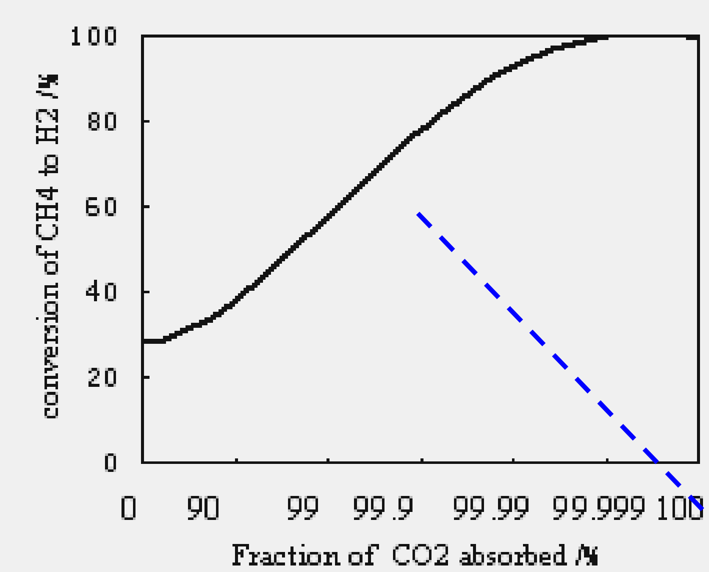




Fig.1 Equilibrium conversion of $CH_4$ to $H_2$

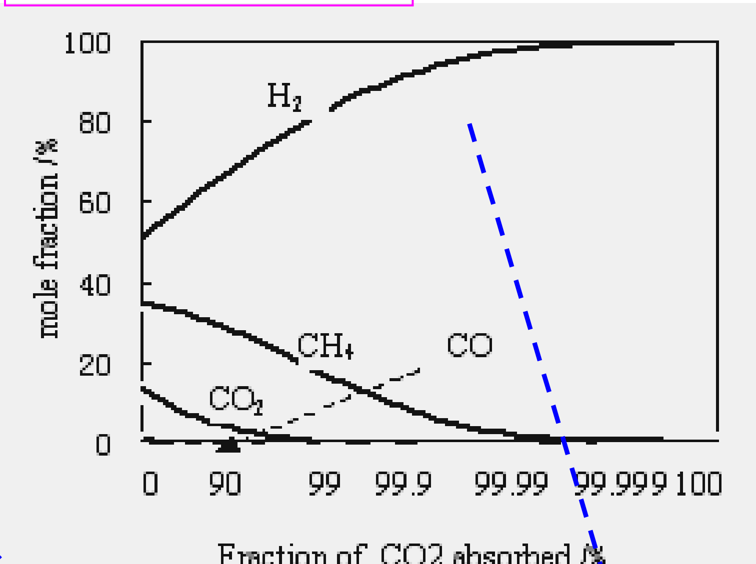
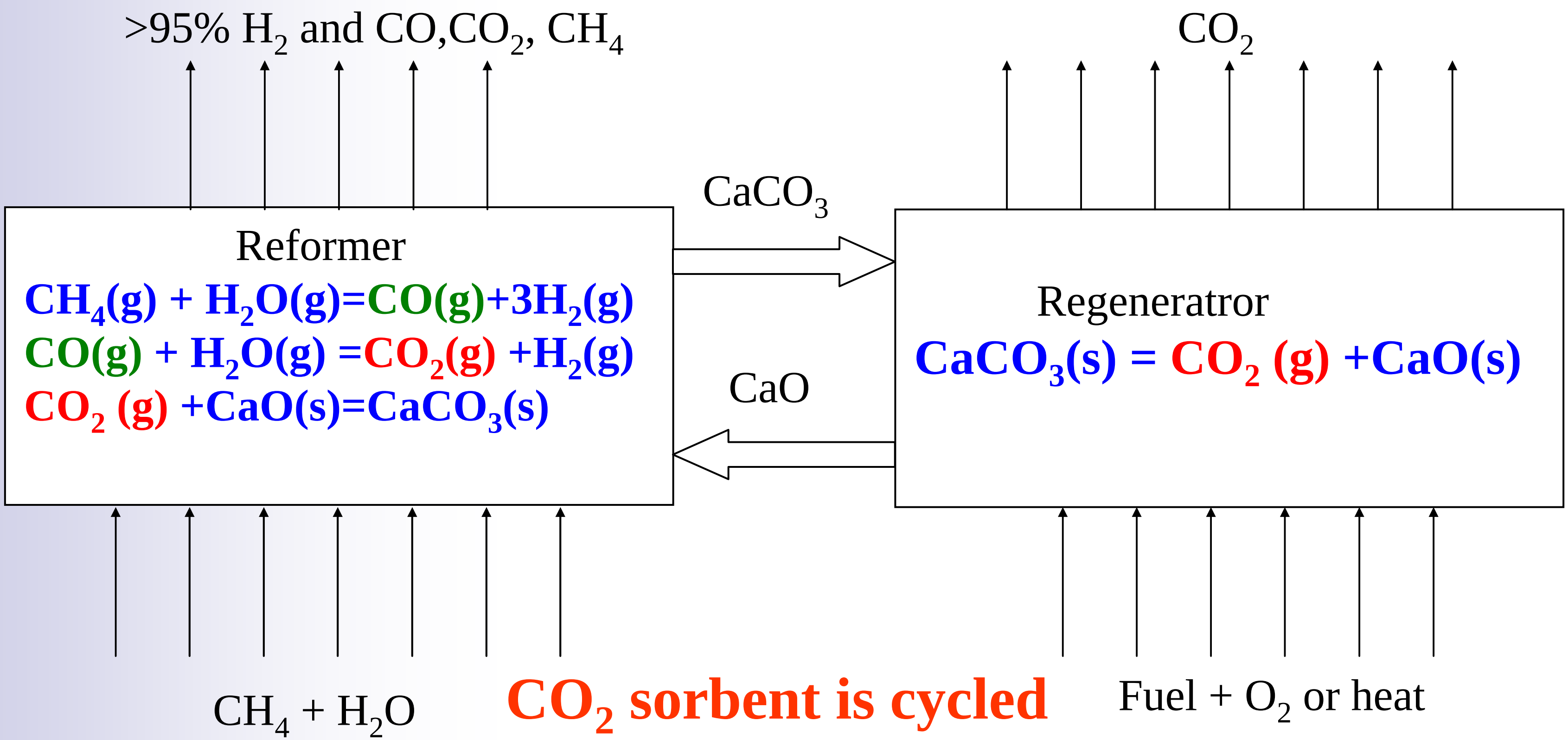



Fig.2 Equilibrium gas phase composition

**When $CO_2$ is absorbed (1)$CH_4$ conversion↑ (2)$H_2$ concentration↑**

# Sorption enhanced hydrogen production



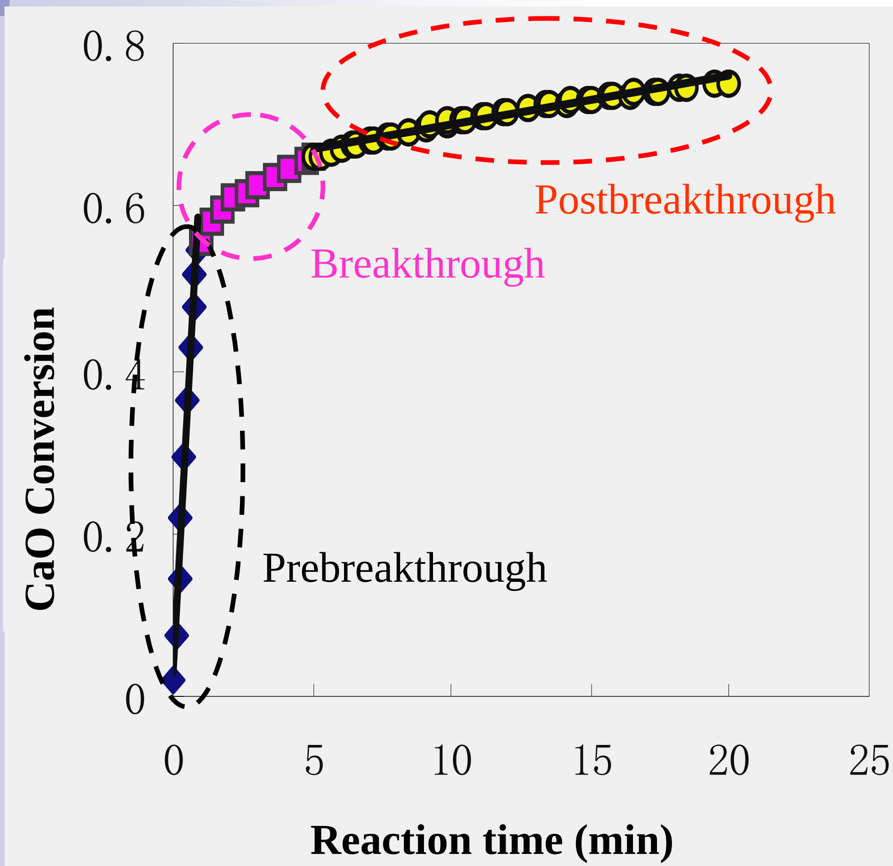

**（1）high concentration of $H_2$（95+%) in single reactor;**

**（2）No need of shift reactor;**

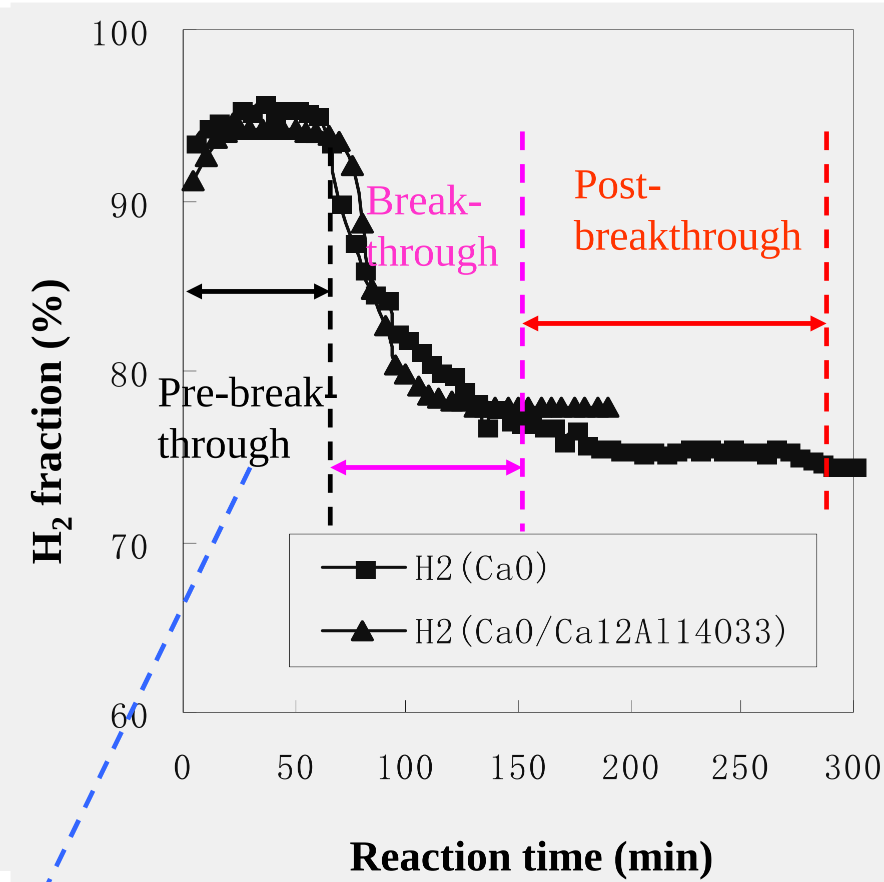
**（3）No need of other heat source;**

**（4）lowering cost.**

# Sorption enhanced hydrogen production

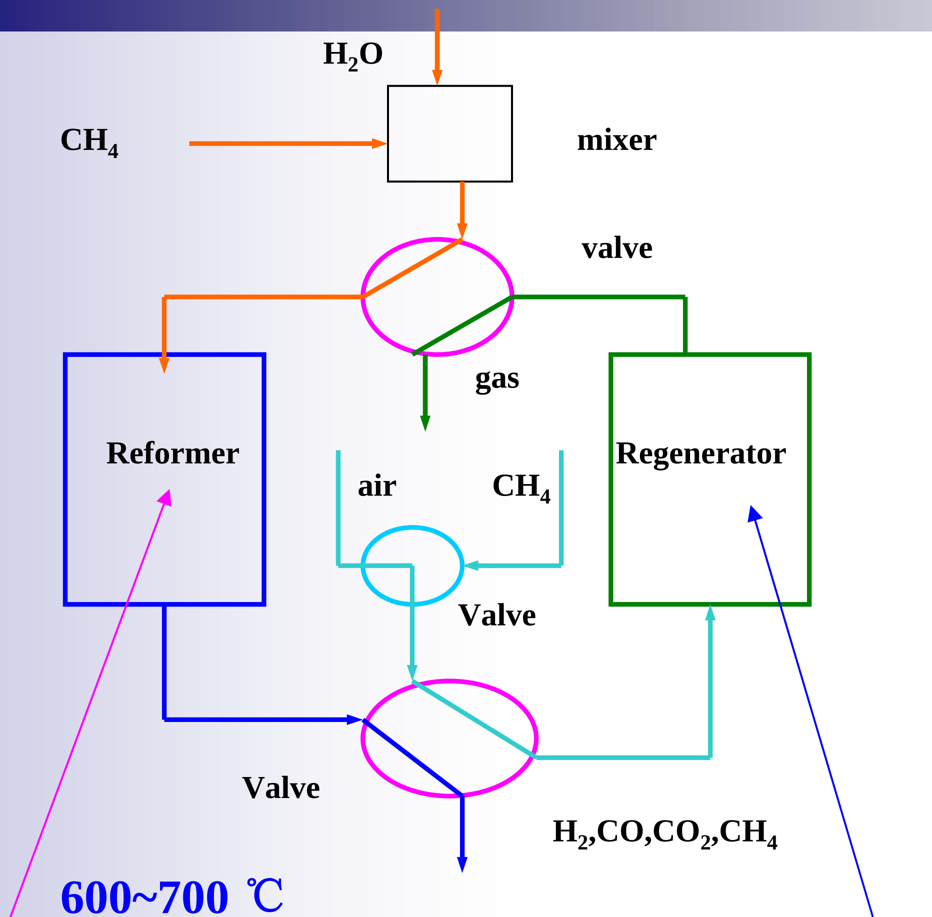



The reaction of CaO with $CO_2$




## $H_2$ Fraction>90%

# Sorption enhanced hydrogen production




600~700 ℃

$CaO + CO_2 \longrightarrow CaCO_3$

800~900 ℃

$CaCO_3 \longrightarrow CaO + CO_2$

**Reformer**

$CH_4(g) + H_2O(g) = CO(g) + 3H_2(g)$

$CO(g) + H_2O(g) = CO_2(g) + H_2(g)$

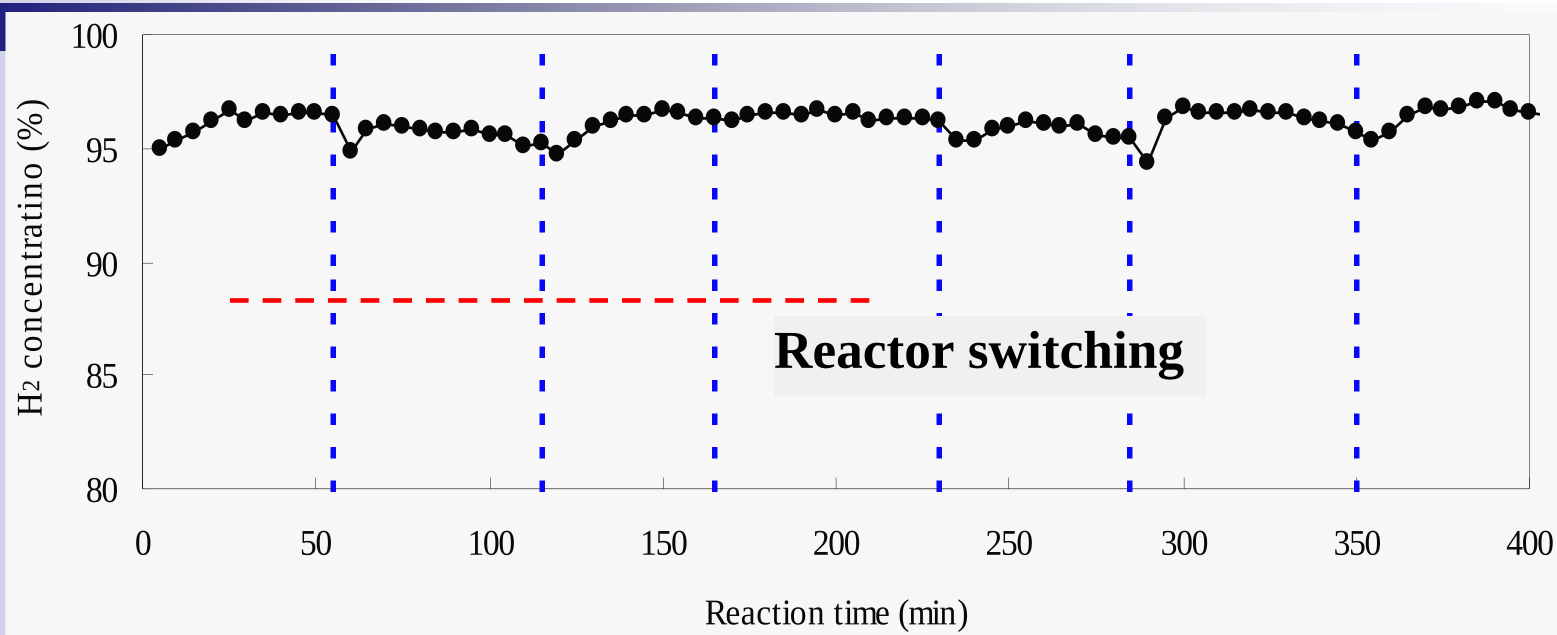
$CO_2(g) + CaO(s) = CaCO_3(s)$

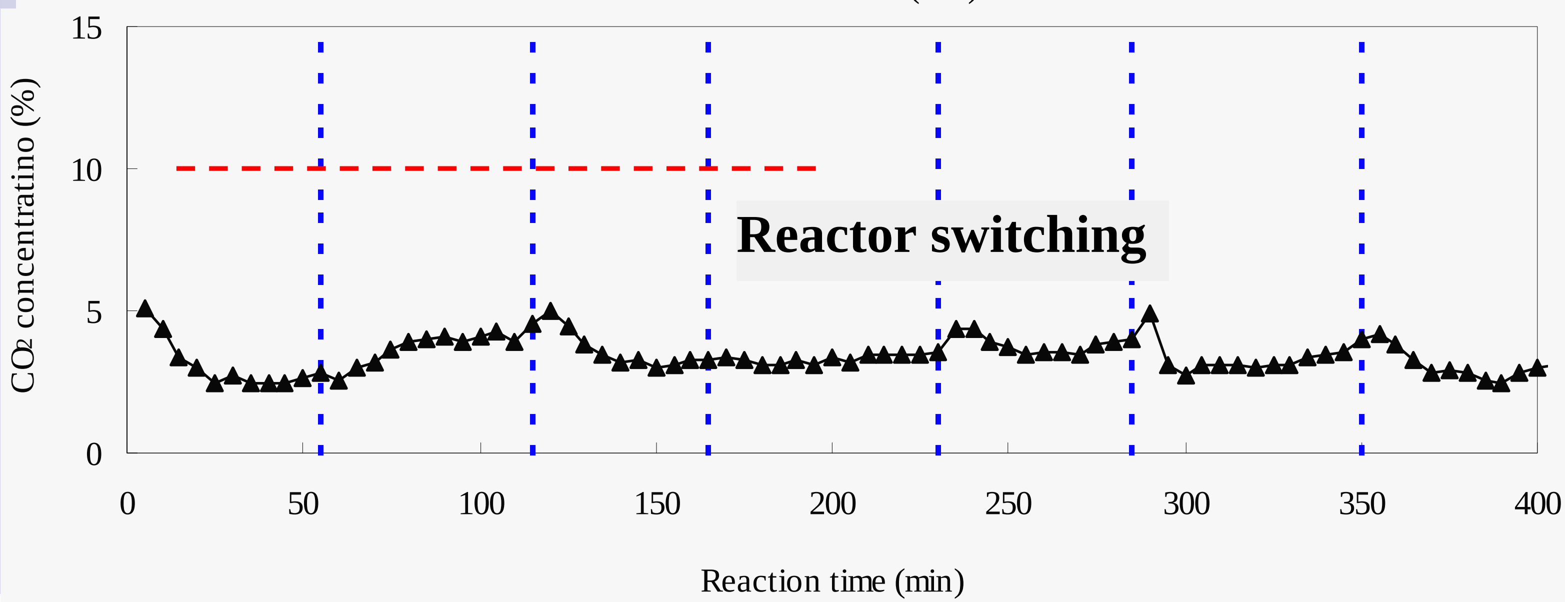
**Regenerator**

$CaCO_3(s) = CO_2(g) + CaO(s)$

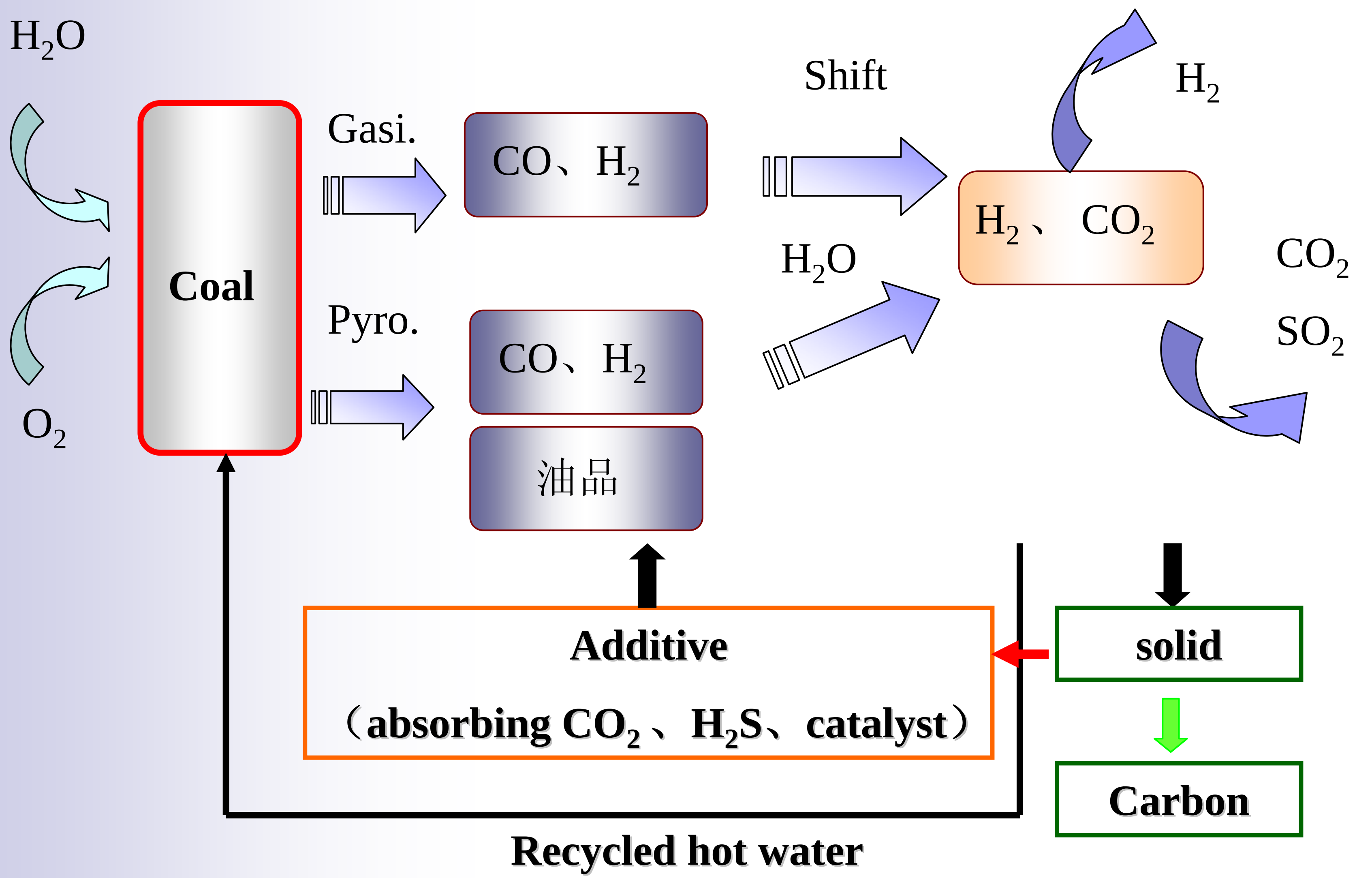
# Sorption enhanced hydrogen production

# Sorption enhanced hydrogen production



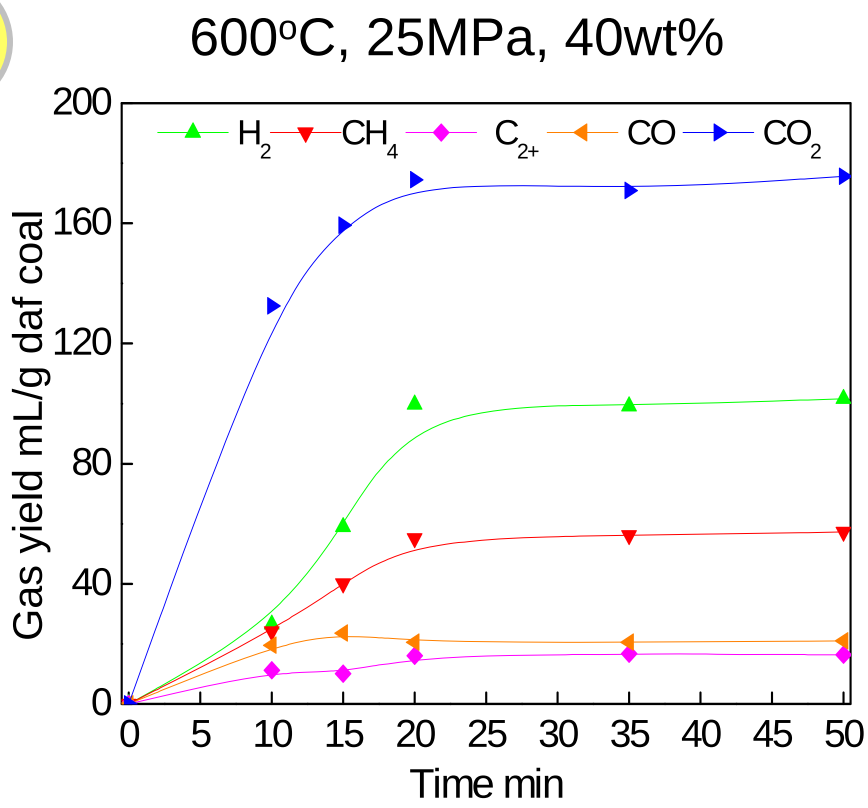



# Hydrogen production from coal using supercritical water



# Hydrogen production from coal using supercritical water

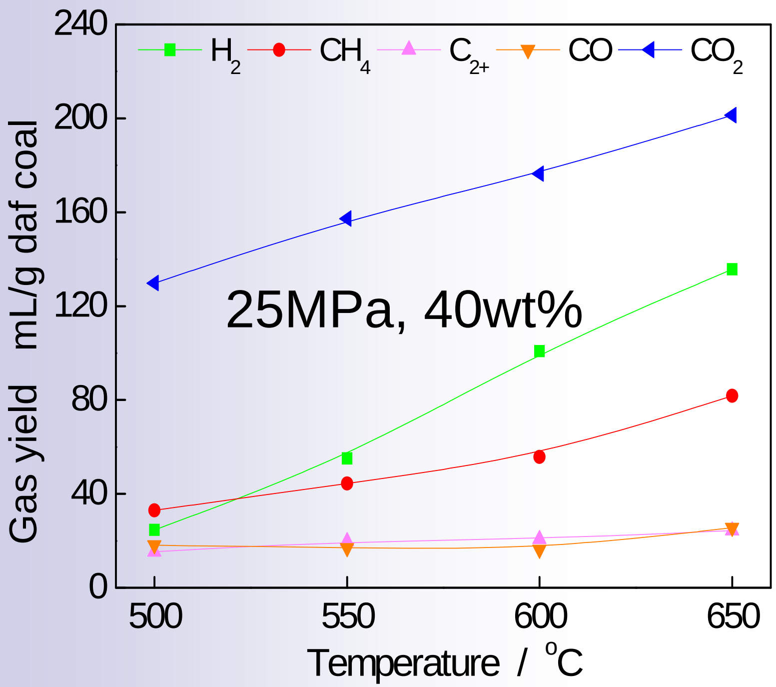
**Continuous flow reactor system using supercritical water**



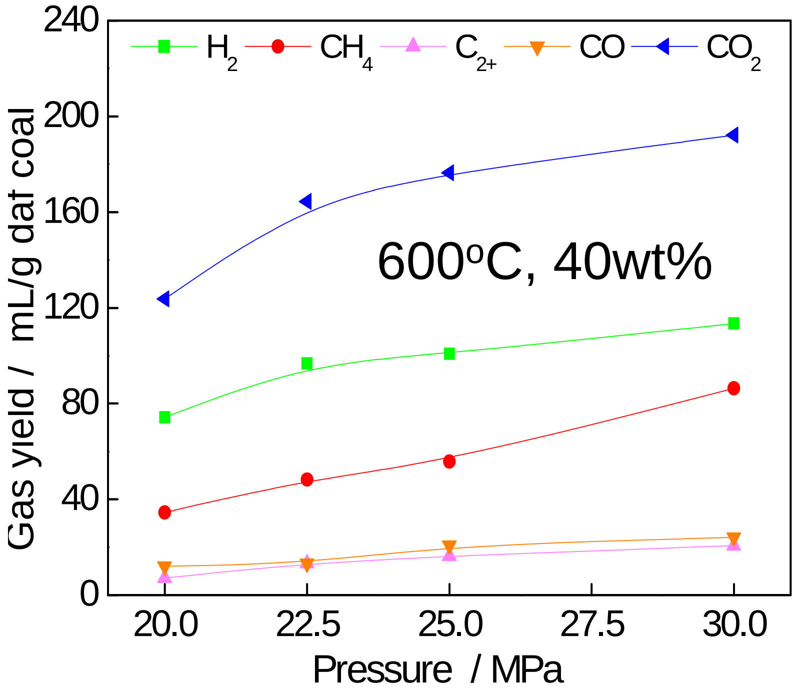

Design temperature: 700℃
Design pressure: 35MPa
Solid feeding: 2kg/h

**After 15～20min, reactor system can operate stably**

# Hydrogen production from coal using supercritical water



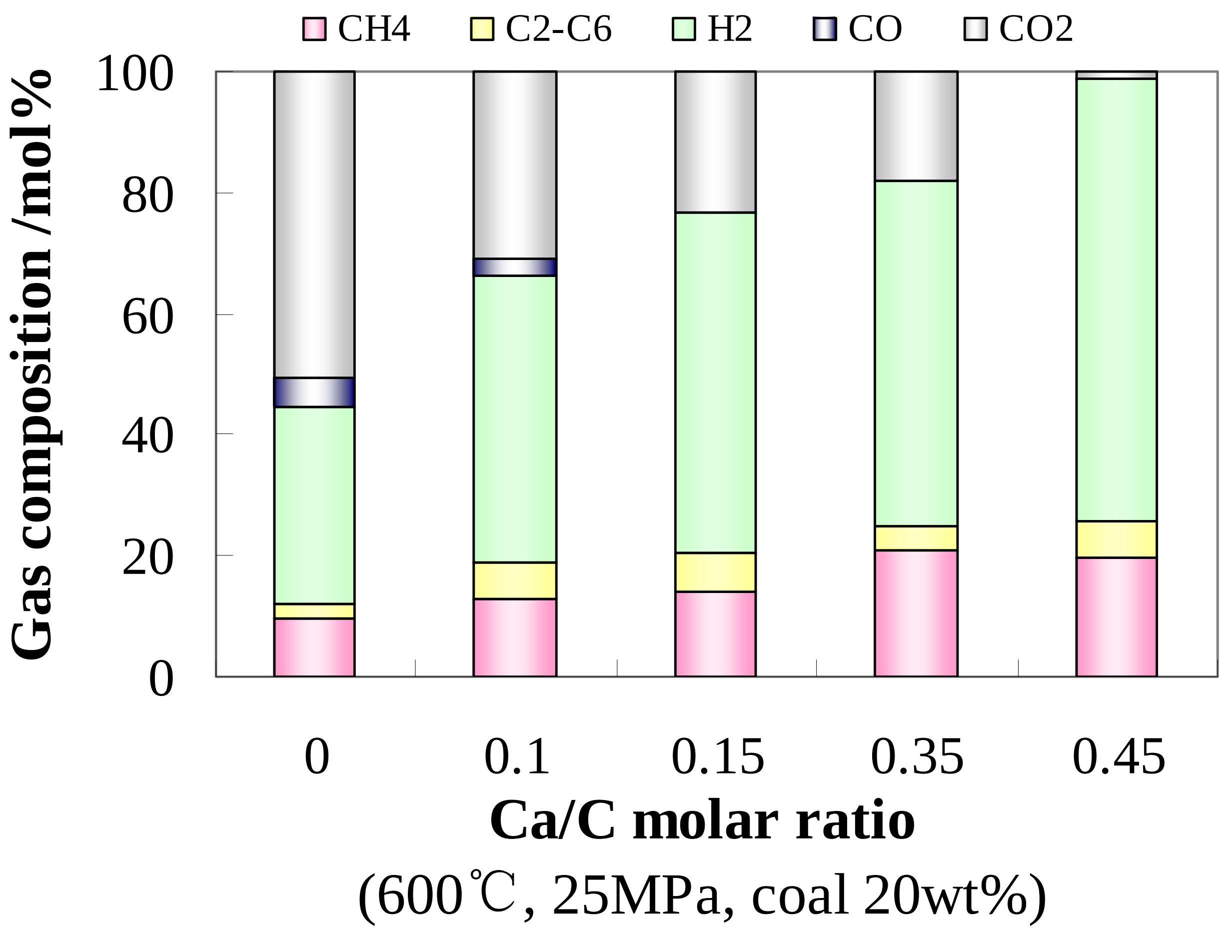

Temperature influence




Pressure influence

- Both $H_2$ amount and fraction in gas atmosphere increase with the increasing of temperature
- With the increasing of pressure, $H_2$ fraction decreases, while $CH_4$ fraction increases.

# Hydrogen production from coal using supercritical water




As the CaO/C molar ratio increases, $CO_2$ diminishes in the gaseous product with an increase in the amount of carbonate. Indicating $CO_2$ being captured by CaO.

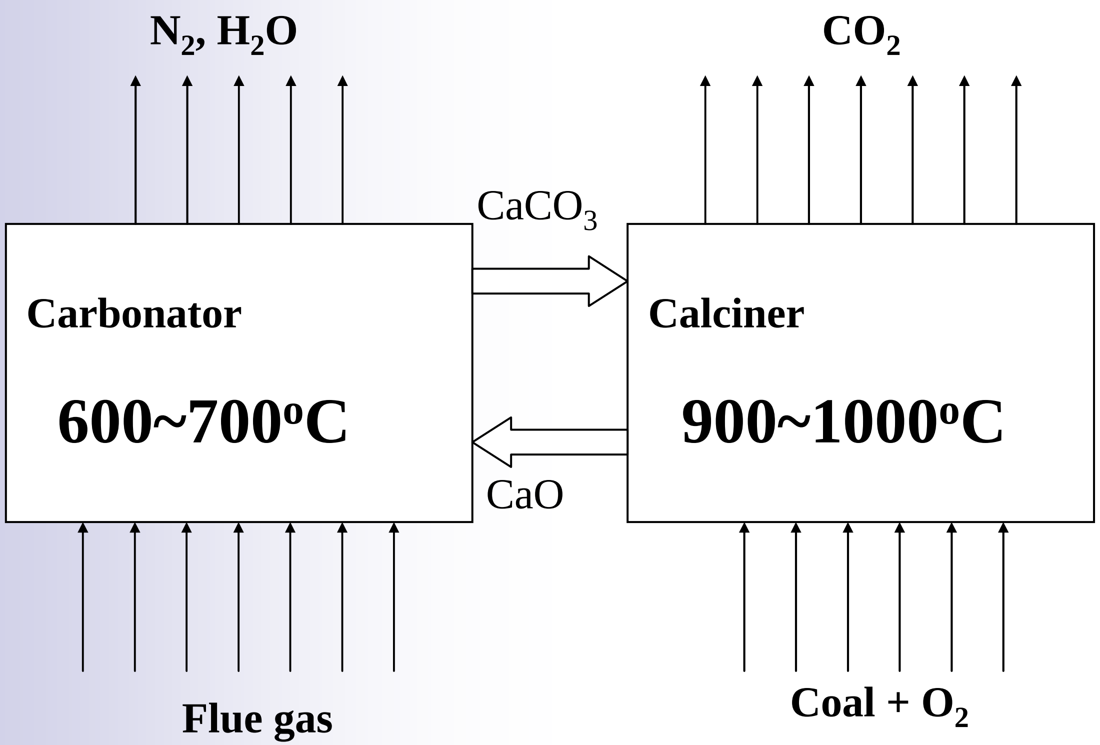
# Post-combustion $CO_2$ Capture

**-$CO_2$ Separation from Flue Gas Using Dry Solid Sorbent at THU**

**-$CO_2$ Separation from Flue Gas Using Amine and Membrane at TJU**

# Dry Solid Sorbent

## $CO_2$ Separation from Flue Gas Using $CaO$-$CaCO_3$ Cycle



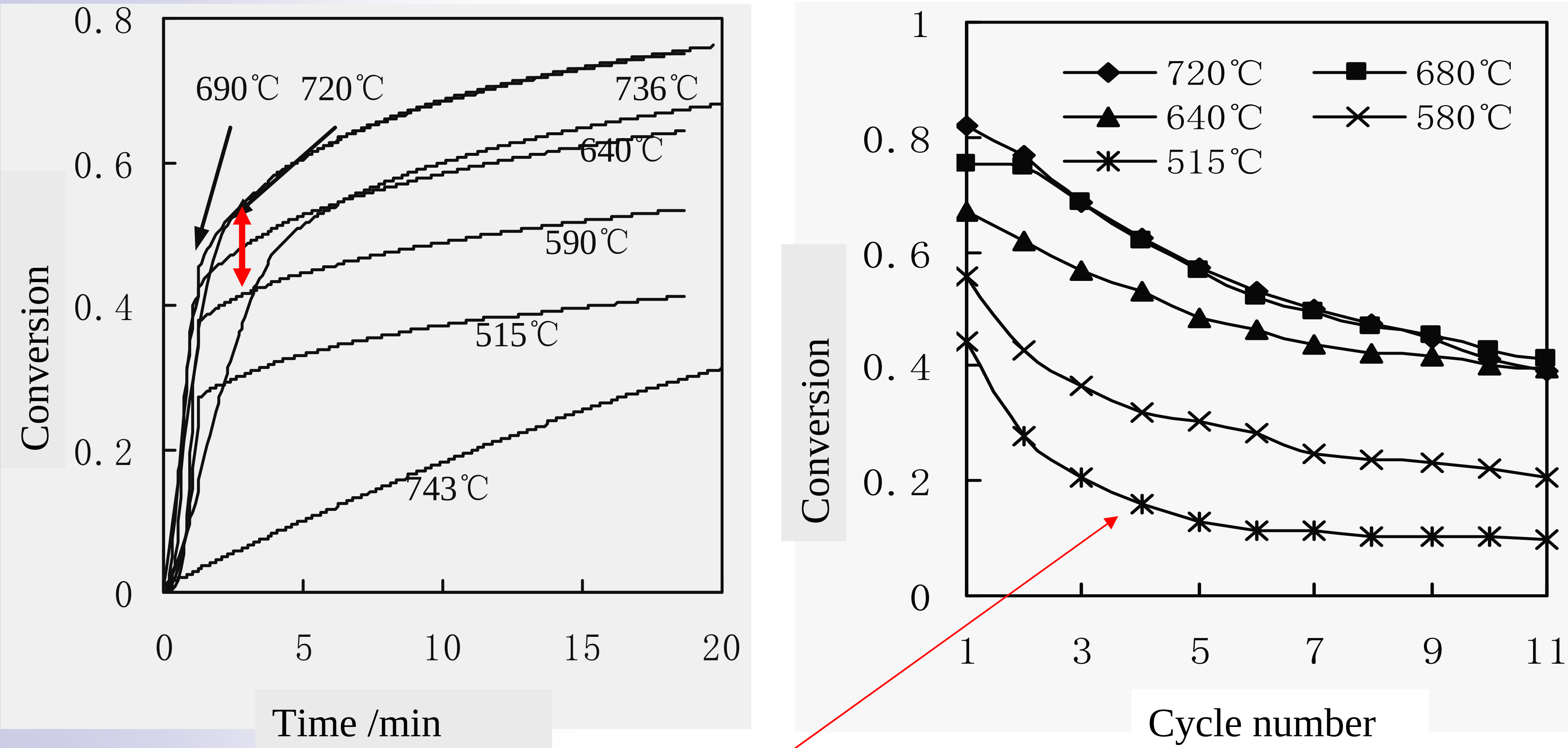

- Plentiful sorbent
- Cheap sorbent (limestone)
- $SO_2$ in flue gases

**Carbonation: $CaO + CO_2 = CaCO_3$ –178kJ/mol**

**Calcination: $CaCO_3 = CaO + CO_2$ 178kJ/mol**

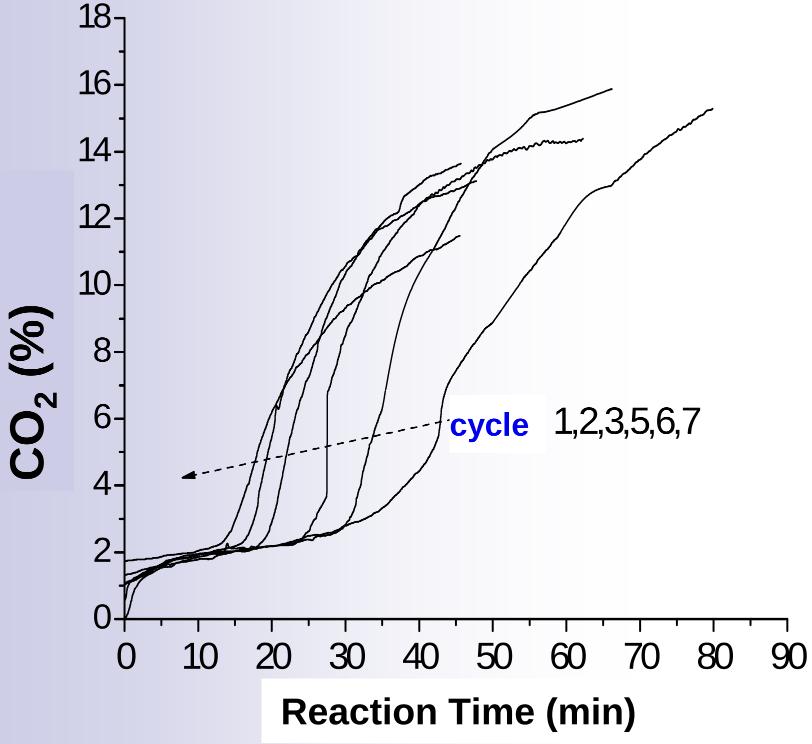
# Dry Solid Sorbent

## The reaction of CaO with $CO_2$

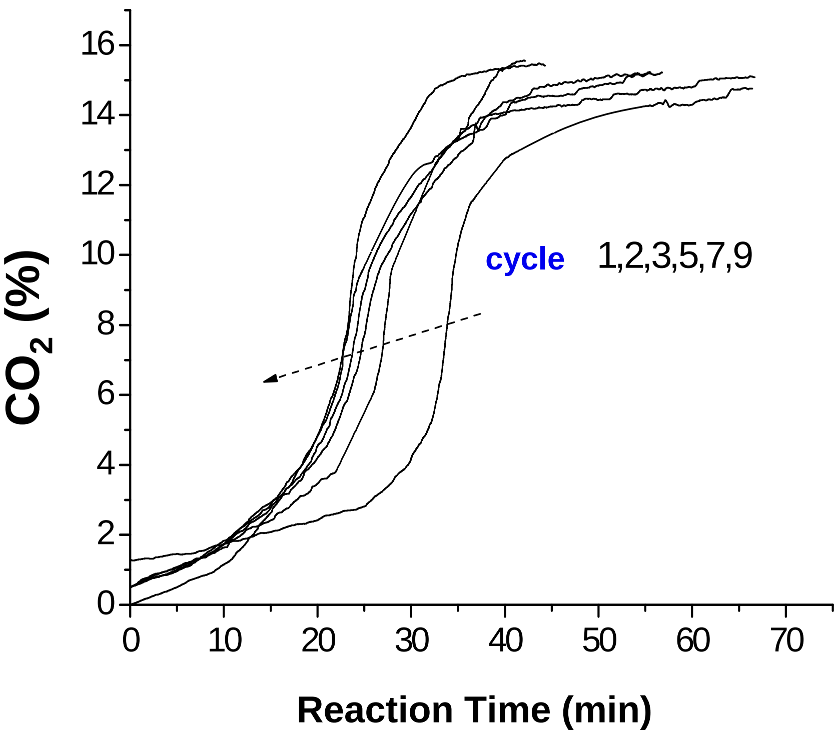



**CaO activity decreases significantly with cycle number increasing。**

# Dry Solid Sorbent



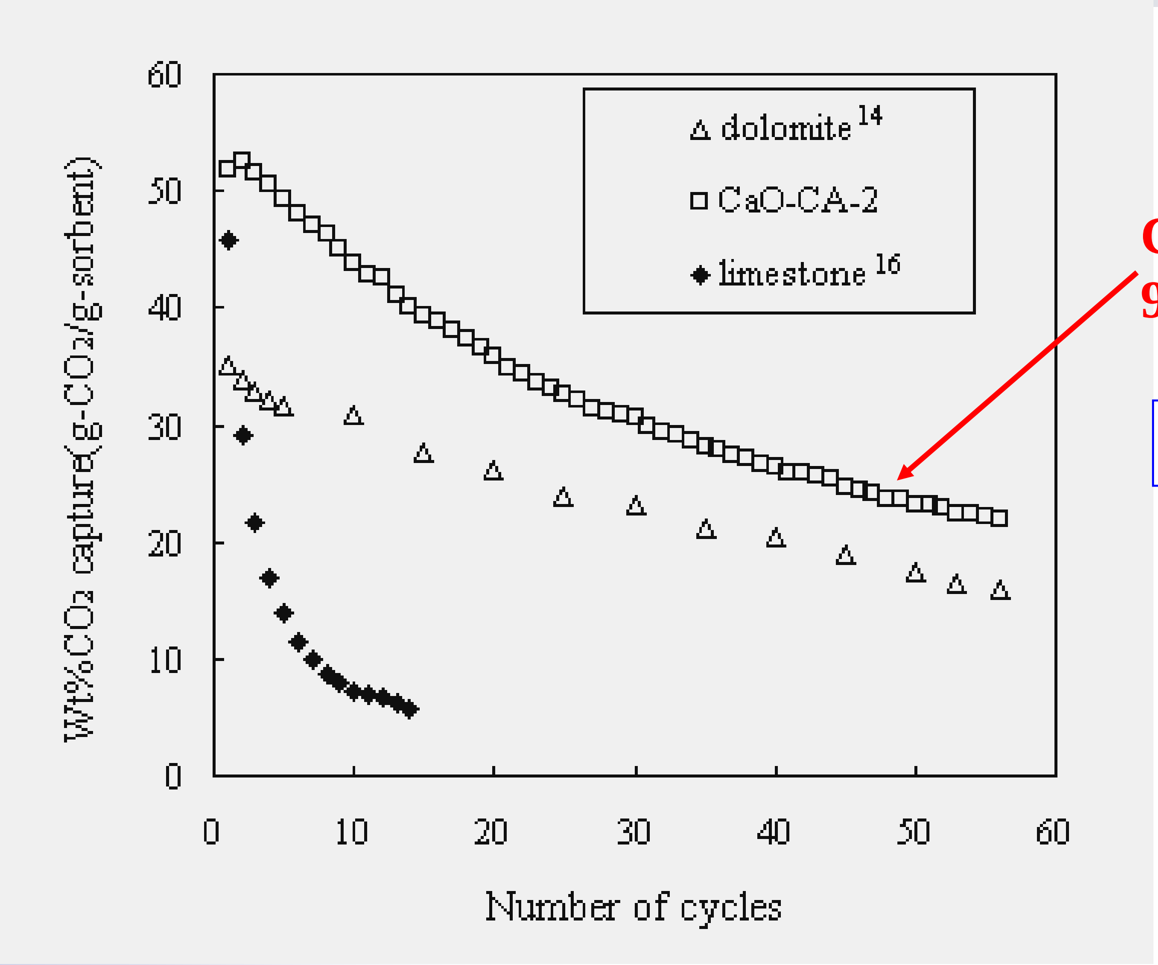

90～200μm limestone




200～450μm limestone

**Carbonation with limestone as sorbent in fluidized bed reactor**

# Dry Solid Sorbent

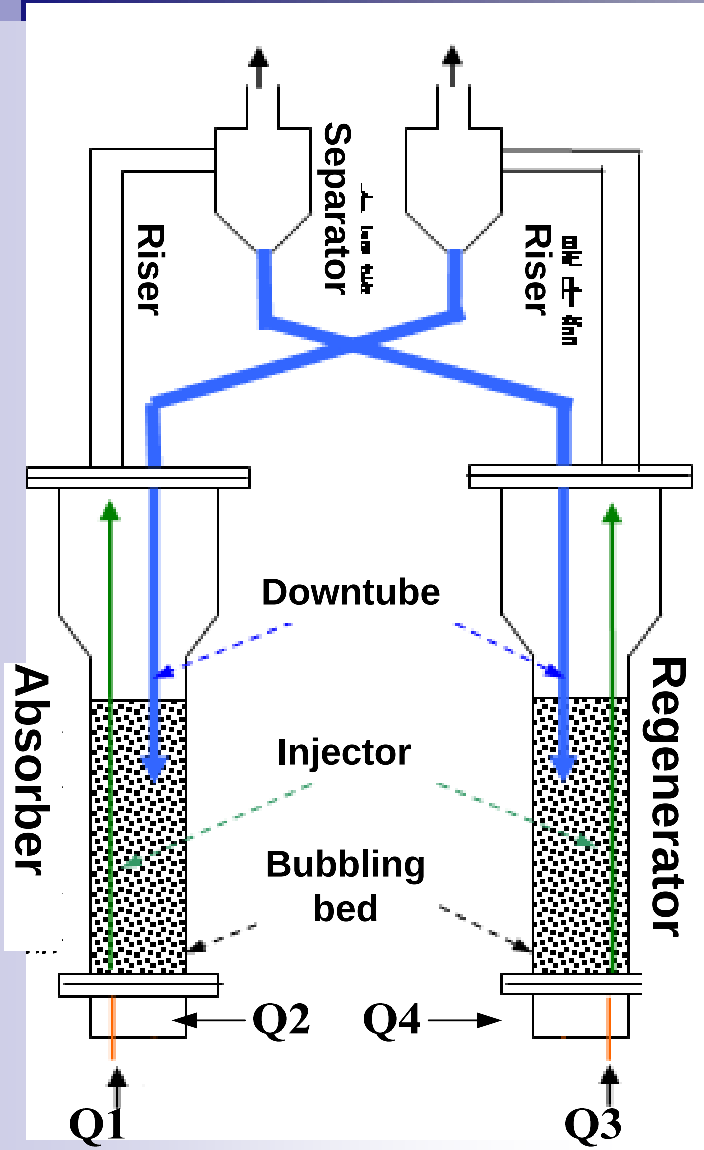



**Calcination temperature: 980 ℃**

**$CaO/Ca_{12}Al_{14}O_{33}$**

**Comparison of $CaO/Ca_{12}Al_{14}O_{33}$ with other sorbents**

# Dry Solid Sorbent




Dual bubbling fluidized beds

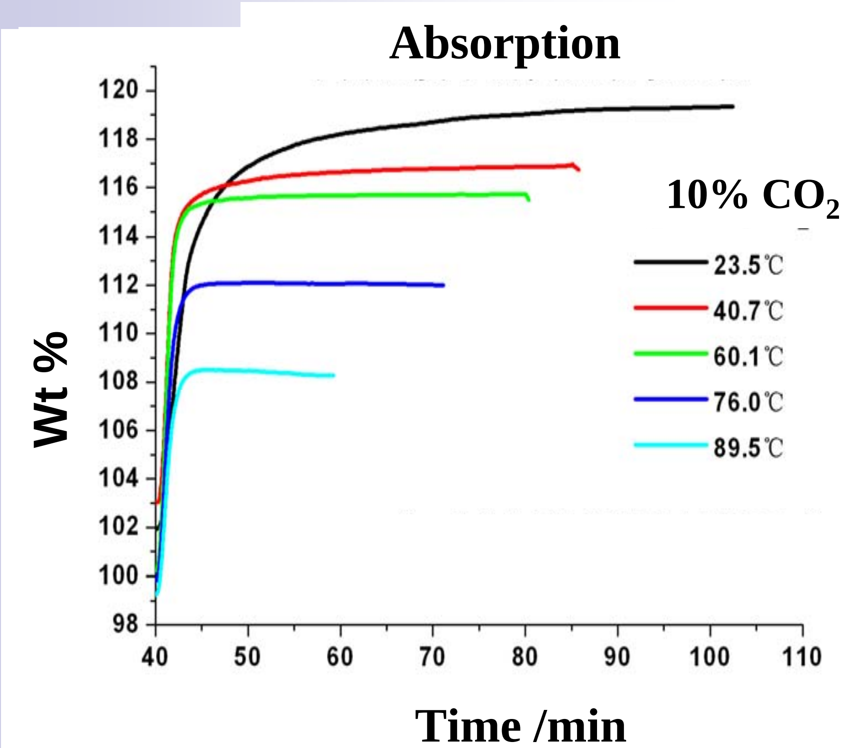
# Dry Solid Sorbent

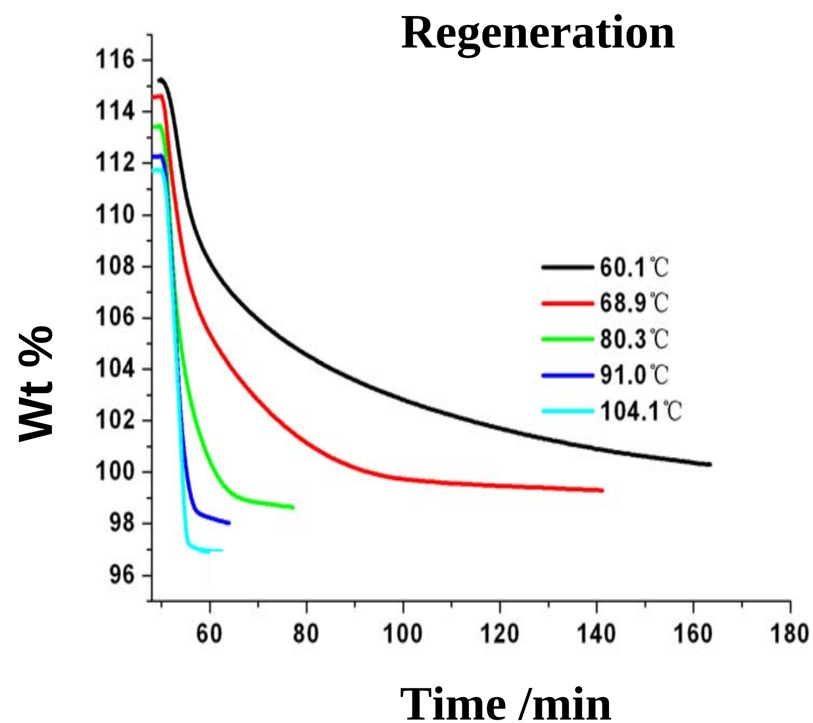
$CO_2$ capture cost：  \$/tonne $CO_2$ avoided

| | |
|---|---|
| Amine (new supercritical) | 40 – 43 |
| Oxyfuel (new supercritical) | 27 – 43 |
| IGCC | 22 – 26 |
| Calcination/Carbonation (Dolomite) | **18 - 23** ($X_{abs}$ = 0.23) ($X_{abs}$ = 0.52) |

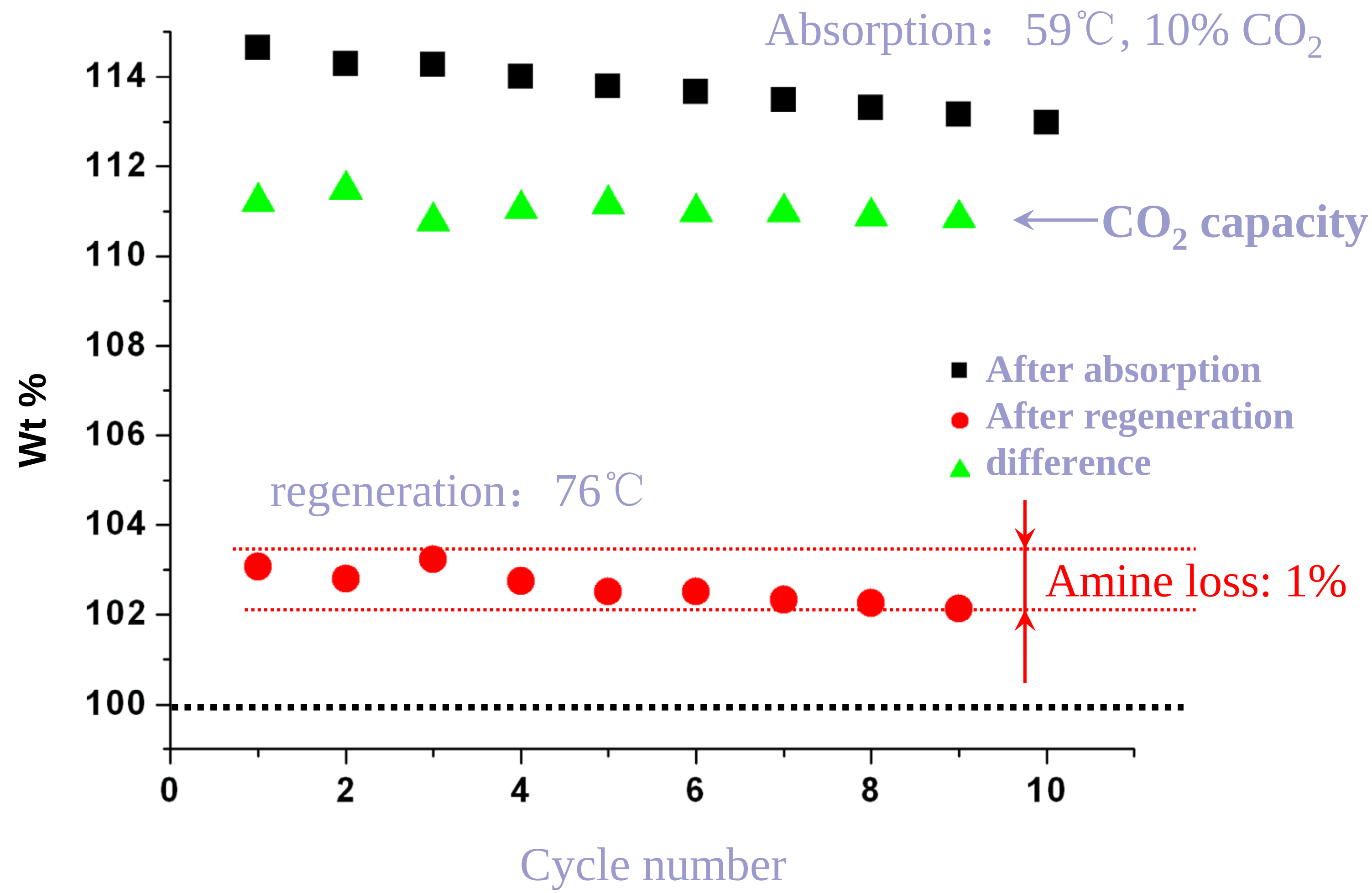
# Dry Solid Sorbent

**Low temperature solid $CO_2$ sorbent, $CO_2$ can be absorbed effectively at 20~80$^oC$, and sorbent can be easily regenerated at 60~100$^oC$.**



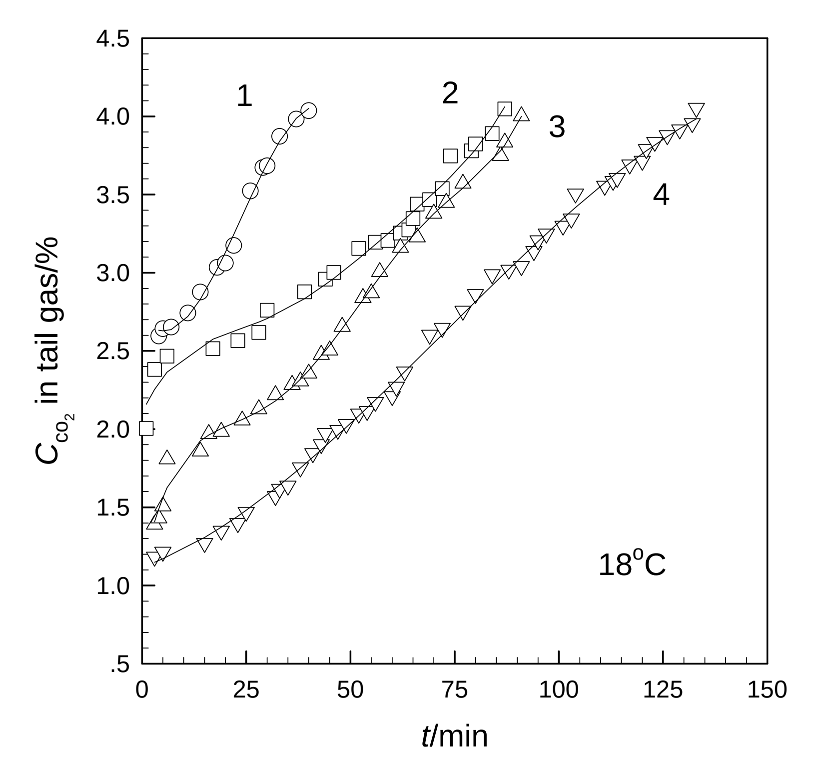
# Dry Solid Sorbent

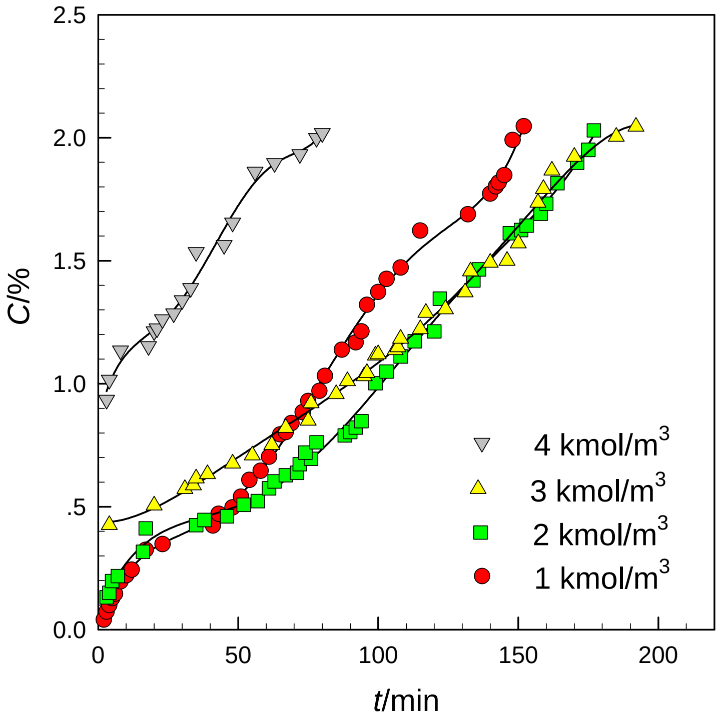



**High $CO_2$ capacity, stable cyclic reactivity**

# Amine

**MDEA + different additives**

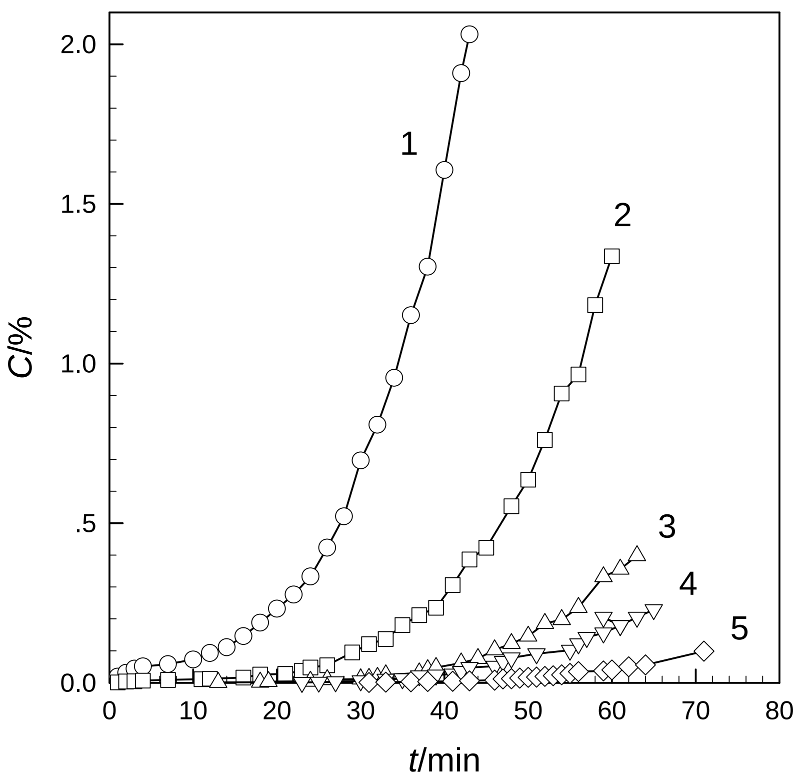


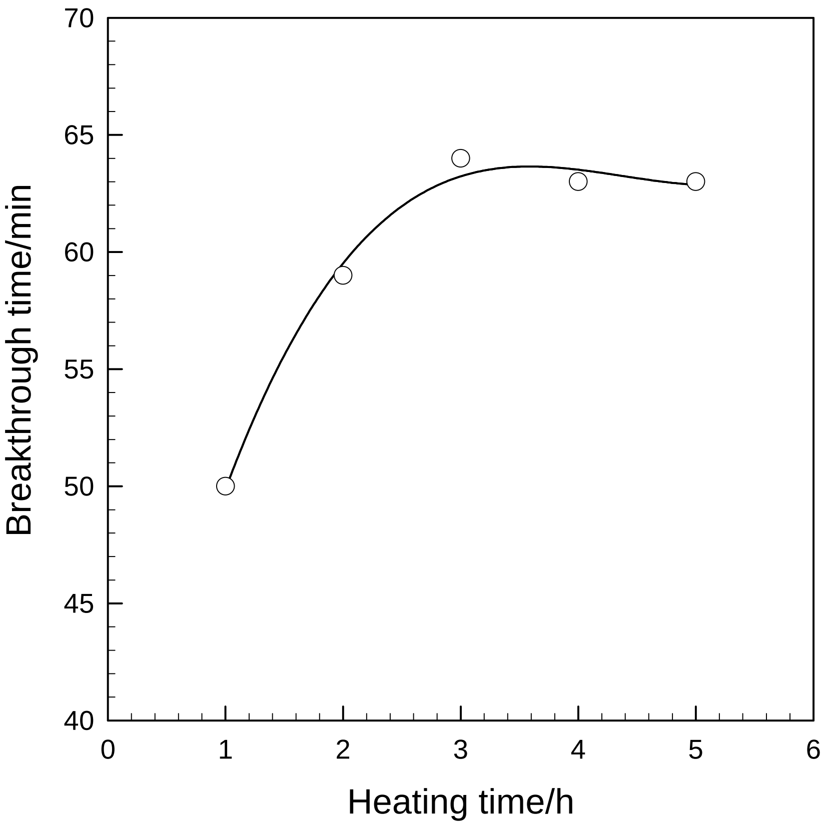




The capture ability of MDEA+PZ is the best

The optimum concentration of MDEA is 2M

# Amine




The effect of PZ concentration:

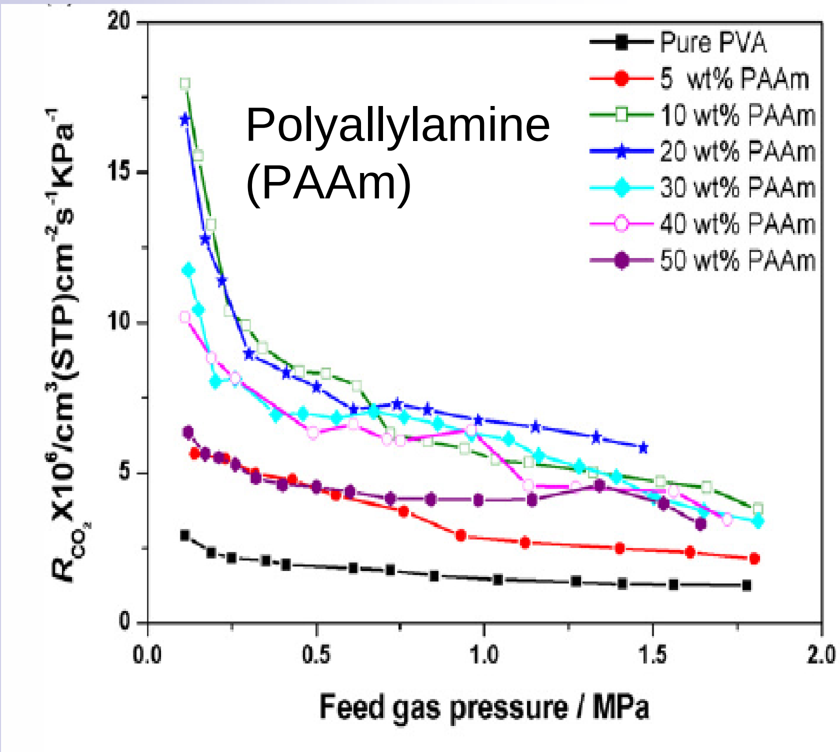
1: 0.2M; 2: 0.3M; 3: 0.4M; 4: 0.5 M; 5: 0.6 M.

--- 0.4 ~0.6M can be used

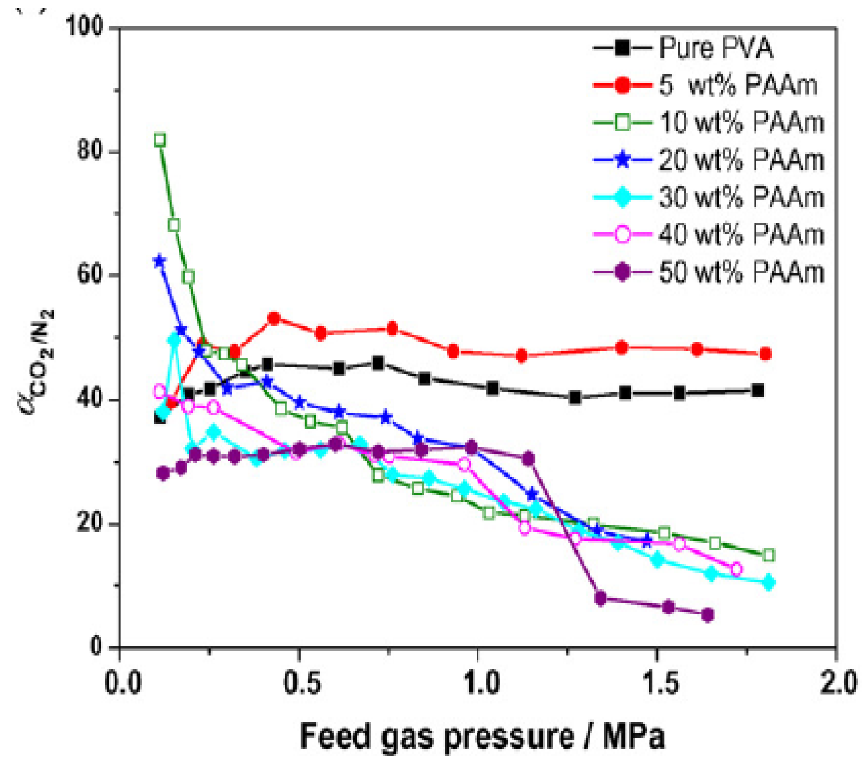
The effect of regeneration time

Sorbent can be regenerated completely within 3h

# Membrane




$CO_2$ permeance




$CO_2/N_2$ selectivity

Effect of PAAm content on gas permeance and selectivity for PAAm–PVA/PSF membranes tested with $CO_2/N_2$ gas mixture

PAAm–poly(vinyl alcohol) (PVA)

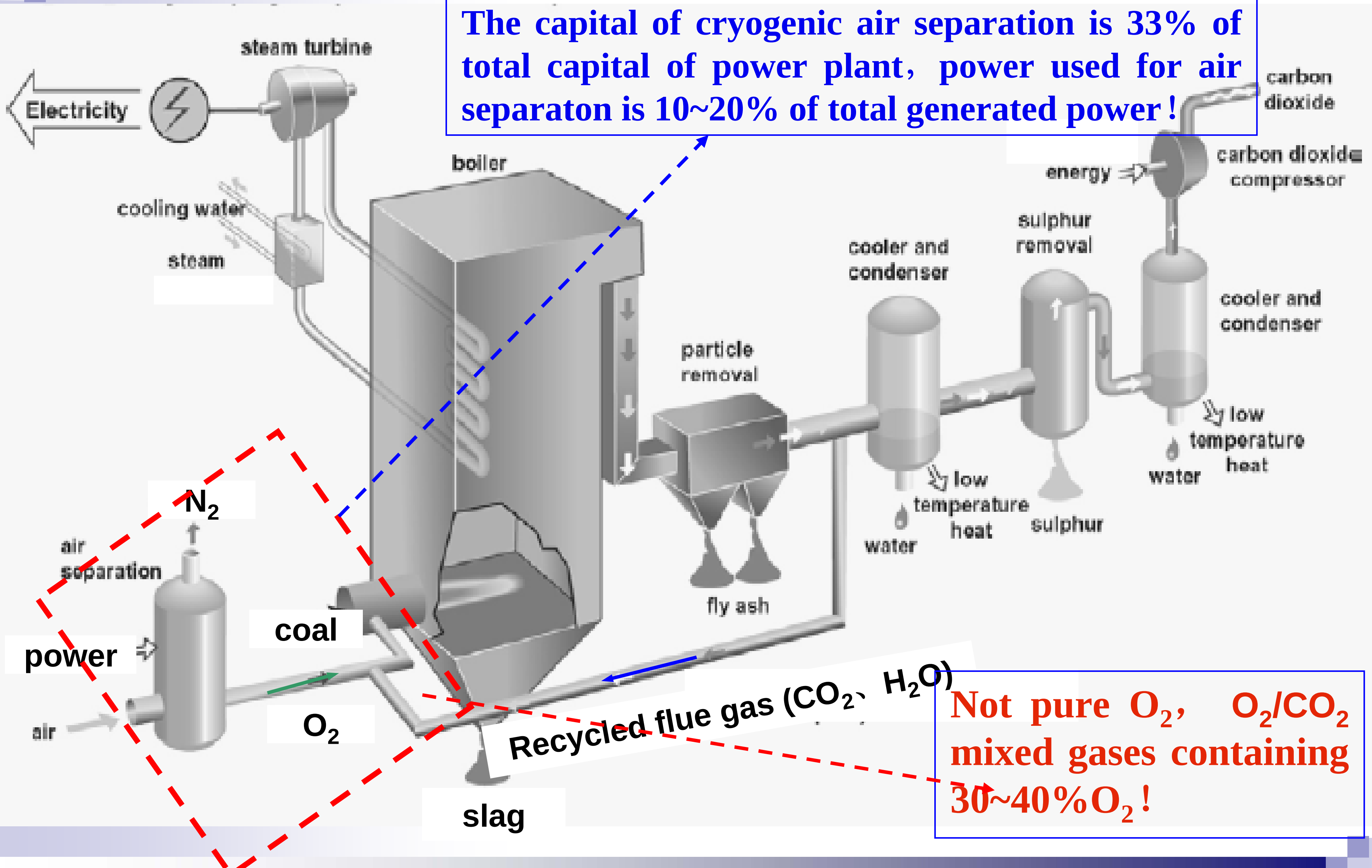
polysulfone (PSF)

# Oxy-fuel Combustion

**-$O_2$/$CO_2$ gases production for oxy-fuel combustion**

# $O_2/CO_2$ Combustion-The production of $O_2$-$CO_2$ gases

**The capital of cryogenic air separation is 33% of total capital of power plant, power used for air separaton is 10~20% of total generated power!**



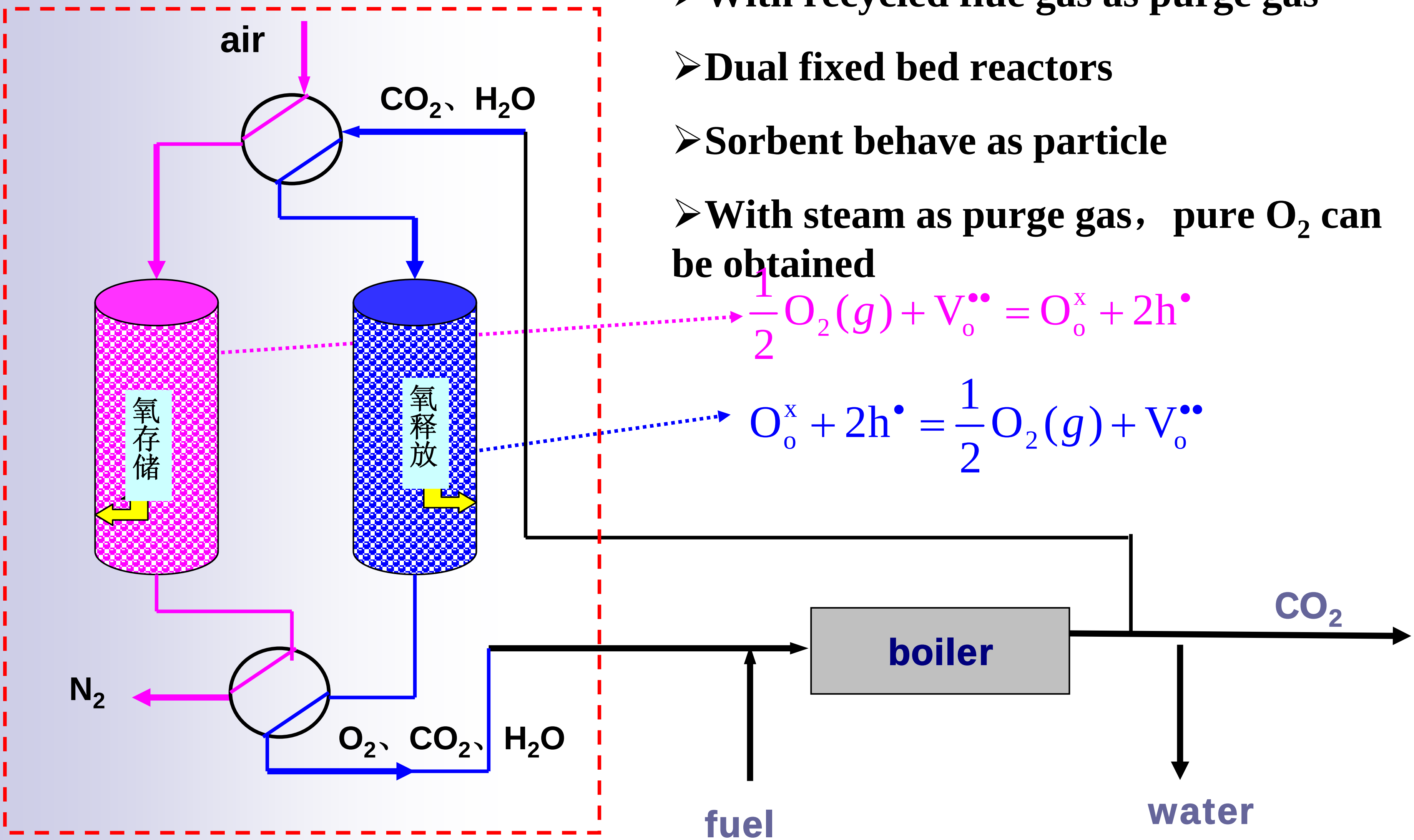

**Not pure $O_2$, $O_2/CO_2$ mixed gases containing 30~40%$O_2$!**

# $O_2/CO_2$ Combustion-The production of $O_2$-$CO_2$ gases

- **With recycled flue gas as purge gas**
- **Dual fixed bed reactors**
- **Sorbent behave as particle**
- **With steam as purge gas, pure $O_2$ can be obtained**

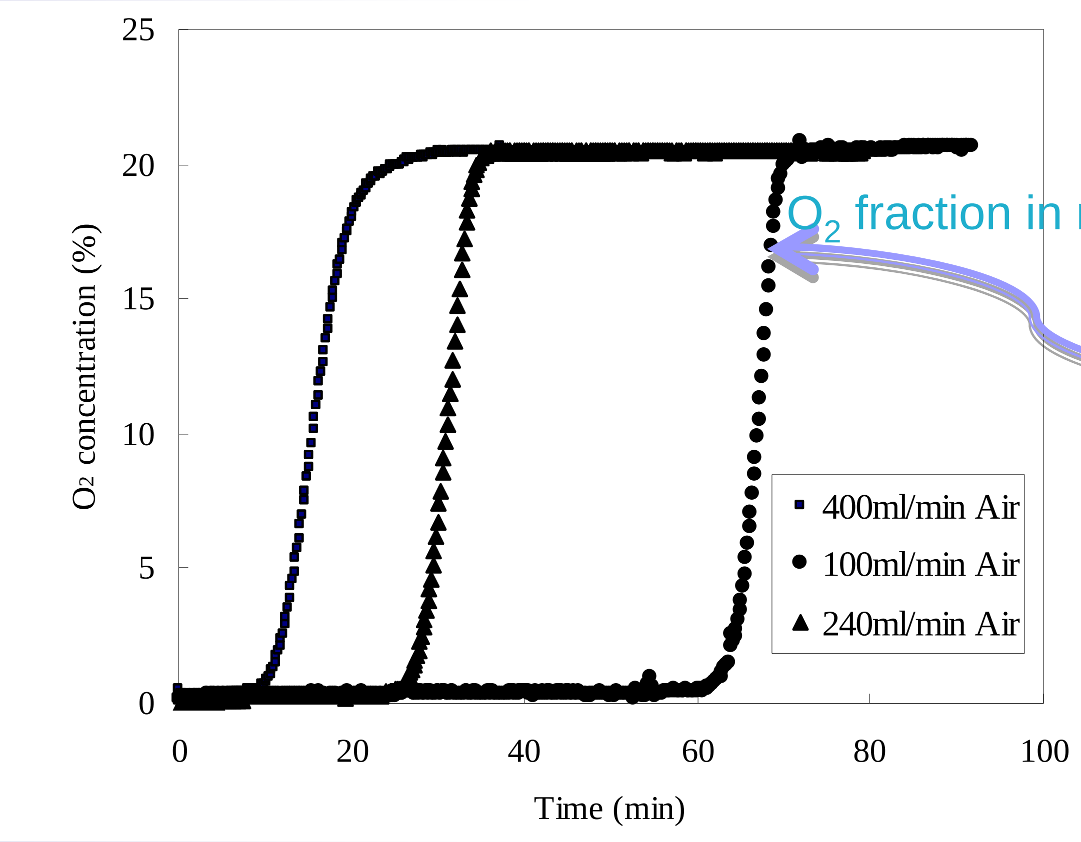
$$\frac{1}{2}O_2(g) + V_o^{\bullet\bullet} = O_o^x + 2h^{\bullet}$$

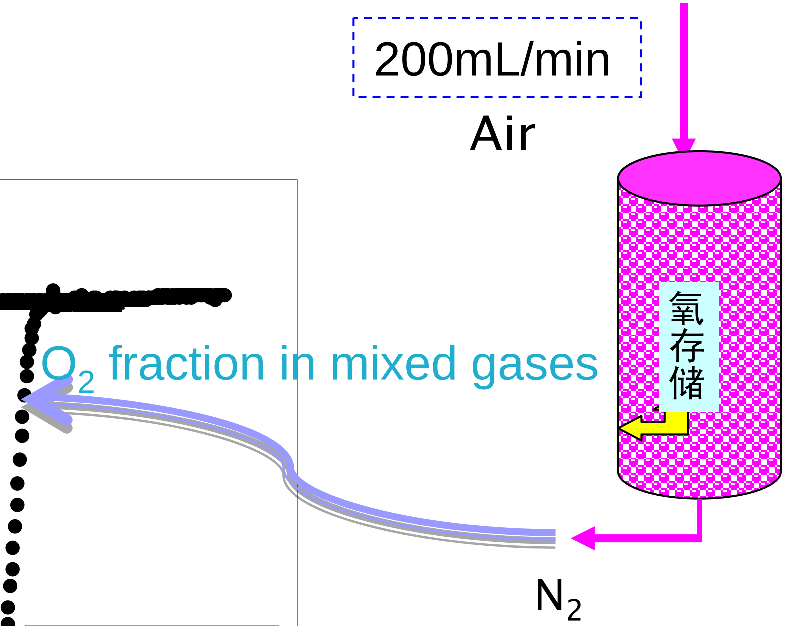
$$O_o^x + 2h^{\bullet} = \frac{1}{2}O_2(g) + V_o^{\bullet\bullet}$$



# $O_2/CO_2$ Combustion-The production of $O_2$-$CO_2$ gases

**Sorption test**

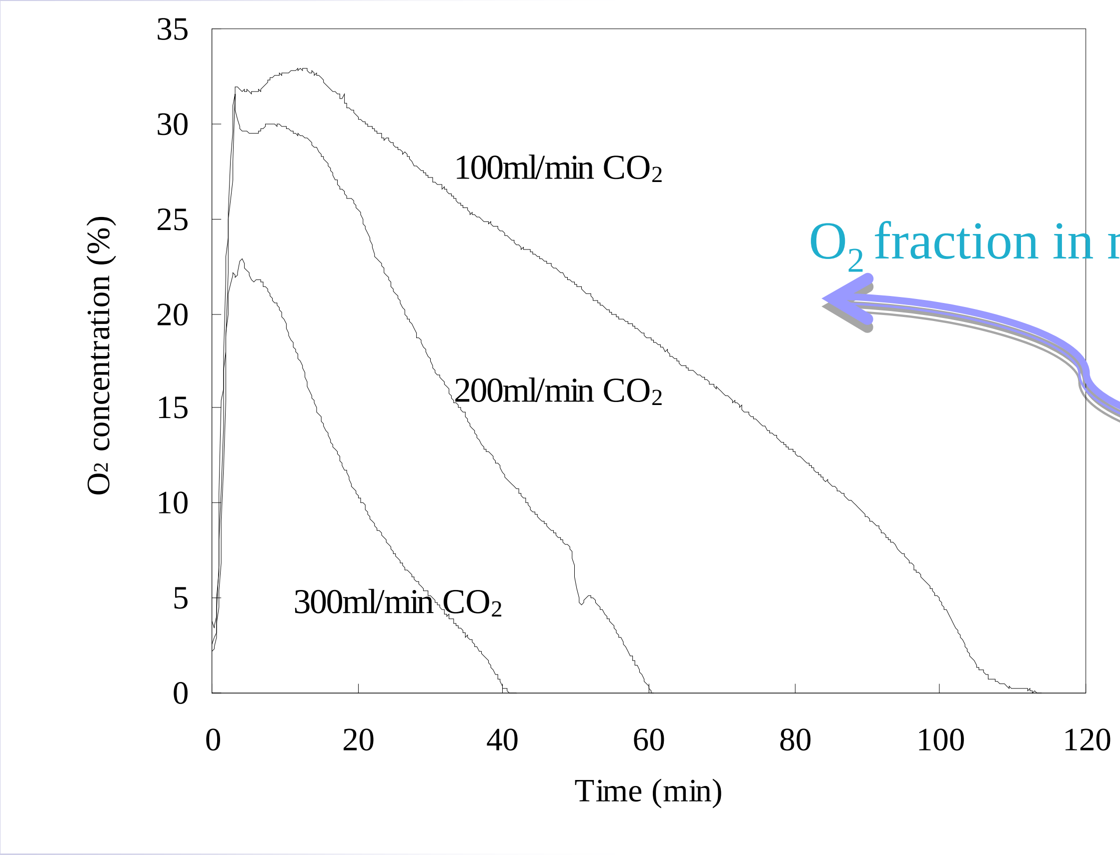


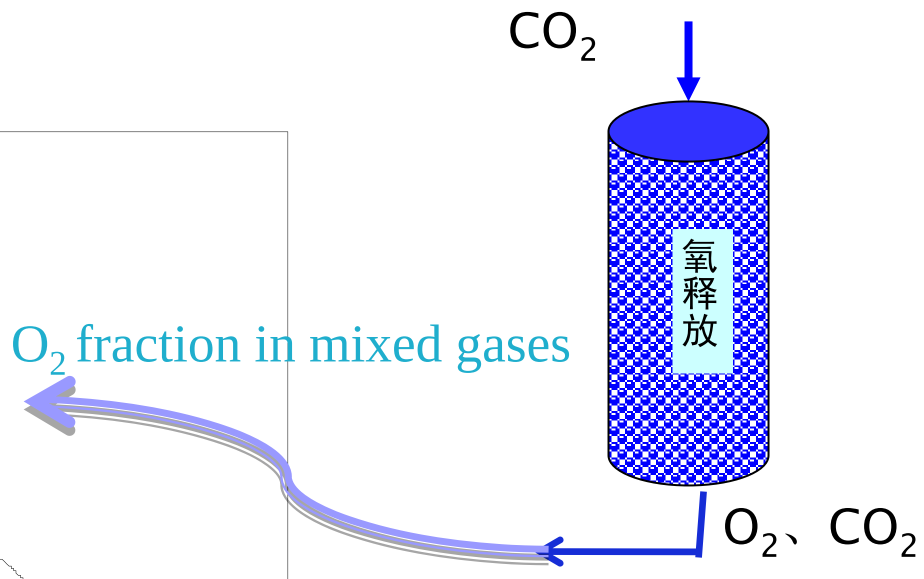




$O_2$ can be absorbed effectively by sorbent

# $O_2/CO_2$ Combustion-The production of $O_2$-$CO_2$ gases

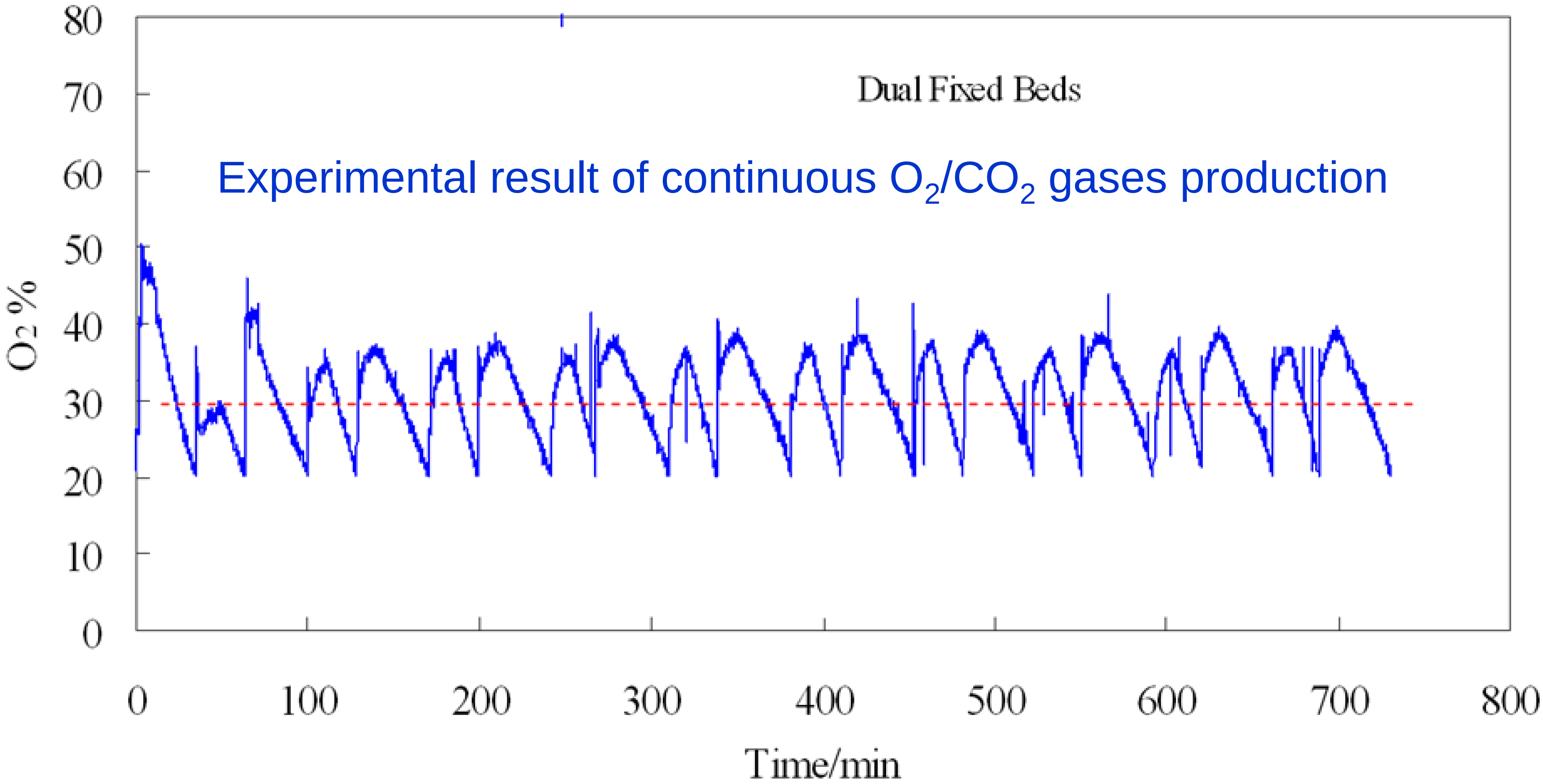
**De-sorption tests**




With $CO_2$ as purge gas, $O_2$-$CO_2$ mixed gases containing 25~35%$O_2$ can be produced。

# $O_2/CO_2$ Combustion-The production of $O_2$-$CO_2$ gases




$O_2/CO_2$ gases stream with average ~30% $O_2$ concentration for oxy-fuel combustion can be obtained based on chemical looping cycle in dual fixed beds

# Conclusions

- Continuous hydrogen stream (>90%) was obtained using two fixed bed reactor from $CO_2$ sorption enhanced hydrogen production process

- A new sorbent, $CaO/Ca_{12}Al_{14}O_{33}$, was developed and tested, results indicated that this sorbent has high cyclic reactivity and stability

- $CO_2$ separation from flue gas using $CaO$-$CaCO_3$ cycle in dual fluidized beds is progressing

- $O_2/CO_2$ mixed gases stream with ~30% $O_2$ concentration for oxy-fuel combustion can be obtained based on chemical looping cycle using recycled flue as purge gas

***Thank you for your attention !***