Recent Research on CO_2 Separation from Flue Gas

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Global CO_2 Emissions

Country	CO_2 Emission ($MtCO_2$)			
	1990	2003	2004	2010
USA	4,989	5,800	5,923	6,156
China	***2,241***	***3,898***	***4,707***	***6,432***
Russia	2,334	1,602	1,685	1,840
Japan	1,015	1,244	1,262	1,260
World	21,246	25,508	26,922	30,670

Source: Energy Information Administration/International Energy Outlook 2004 with High Oil Price Case

CO_2 Emission in China

Year	Total	Coal		Petroleum		Natural Gas	
	Mt CO_2	Mtc	%	Mtc	%	Mtc	%
1990	2,241	1,886	84.2	325	14.5	30	1.34
2003	3,898	3,117	80.0	711	18.2	70	1.80
2004	4,707	3,809	80.9	816	17.3	83	1.76
2010	6,432	5,103	79.3	1,151	17.9	178	2.76
2015	7,376	5,946	80.6	1,184	16.1	246	3.33

Source: Energy Information Administration/International Energy Outlook 2004 with High Oil Price Case.

Recent Research on CO_2 Separation Technology

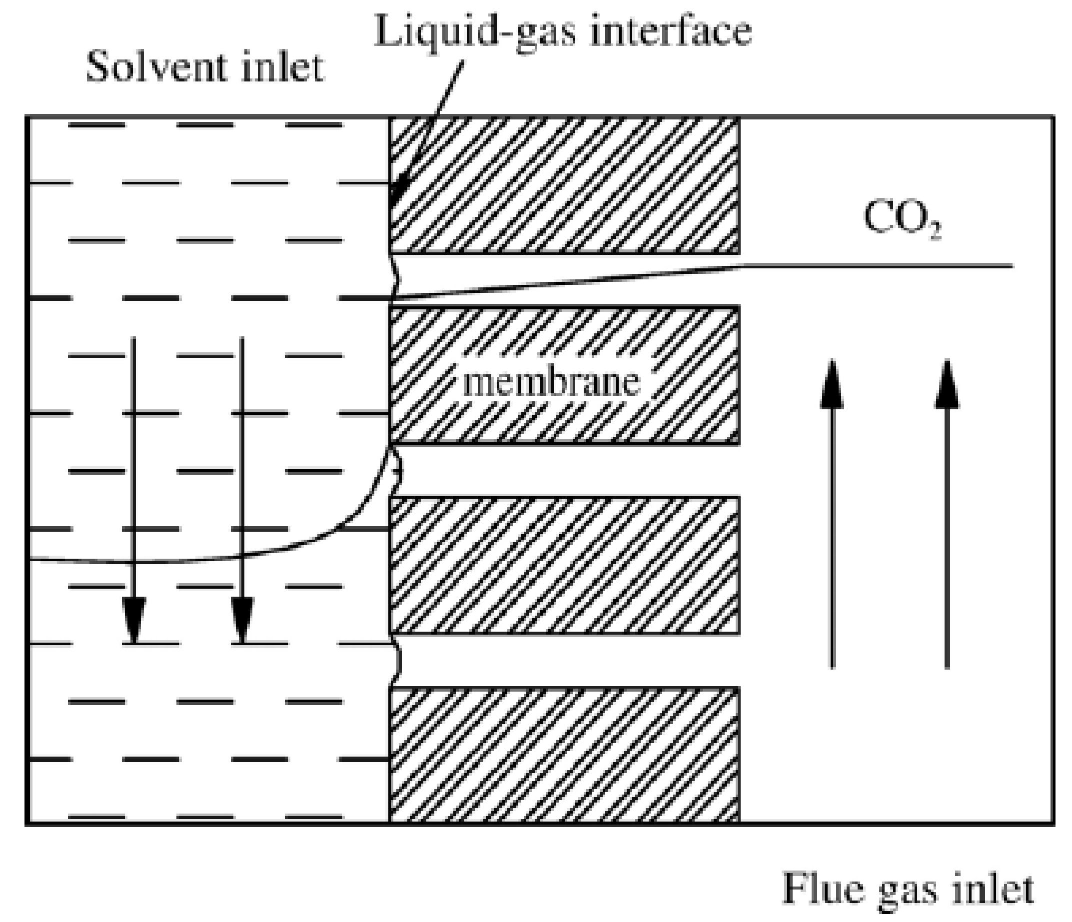
- **Membrane gas absorption technology**

Using hollow fiber membrane contactors to absorb CO_2 from flue gas into solvent.

- **Chemical absorption technology**

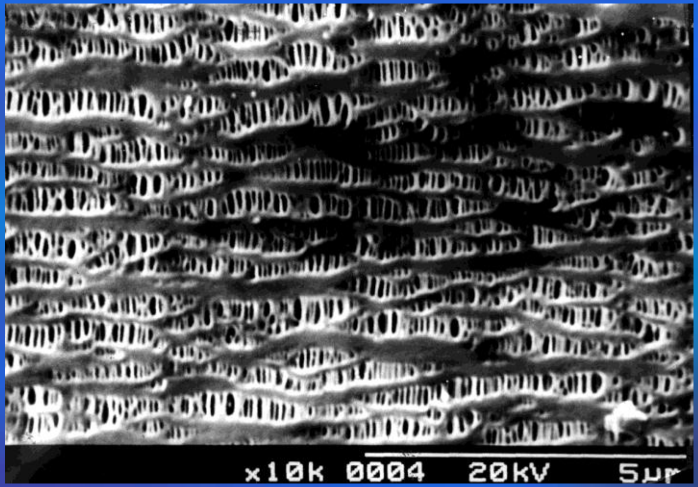
Using random or structured packed columns to capture CO_2 from flue gas into solvent.

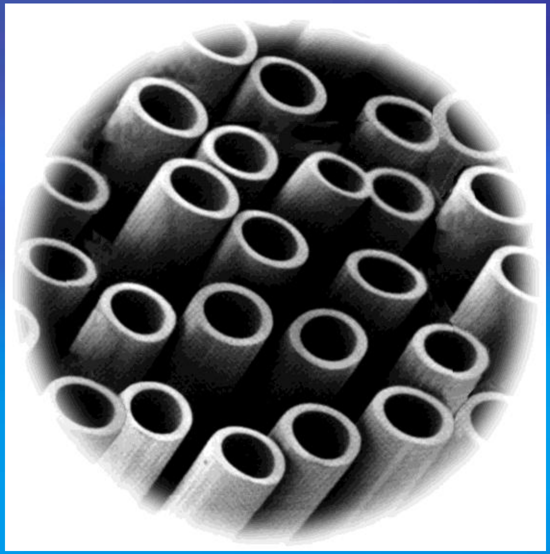
CO_2 Membrane Gas Absorption Technology

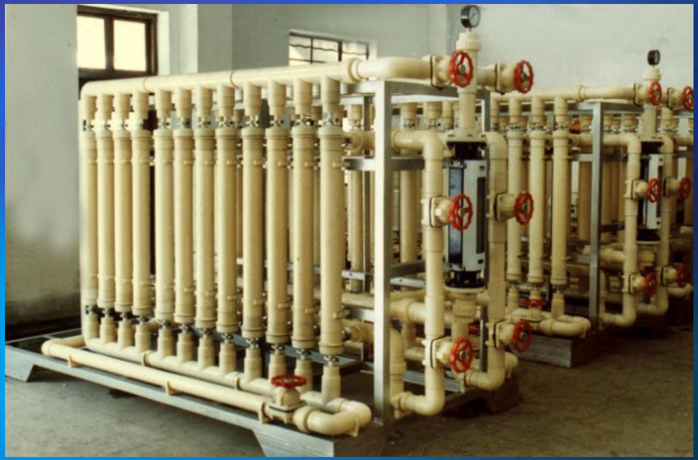


- Hydrophobic microporous membranes are used to form a permeable barrier between the liquid and gas phases;
- Absorbent liquid offers the CO_2 selectivity;
- Liquid phase and gas phase are not directly contacted;
- Main driving force is the differential concentration of CO_2 between gas phase and liquid phase;
- Membrane pores must be completely filled by gas.

Shape and Structure of the Polypropylene Hollow Fiber Membrane







Advantages of Membrane Gas Absorption

- ***Operational flexibility.***

  - Liquid phase and gas phase are not directly contacted

  - Avoid the conventional problems such as flooding, foaming, channeling and entrainment in packed column.

- ***More economic.***

  -Membrane device has larger contact area

  - Reduction over 70% in size and 66% in weight compared with conventional columns.

- ***Linear scale-up.***
  The modularity of membrane modules makes the design simple and easy to be scaled up linearly.

- ***Easier prediction.***
  The interfacial area is known and constant. It does not depend on the operating conditions such as temperature and liquid flowrate. As a result, it is easier to predict the performance of a membrane contactor.

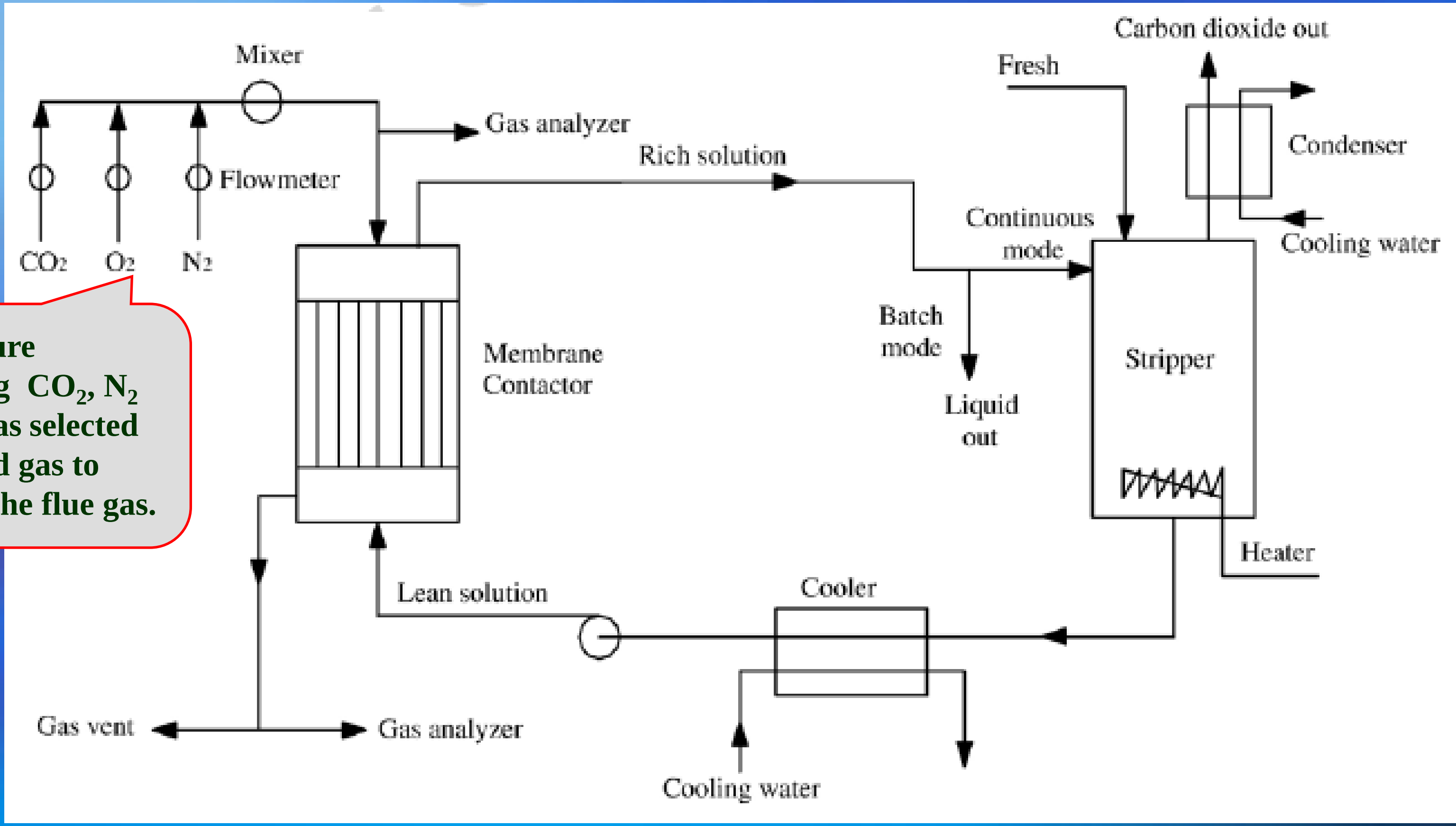
Potential Problems of Membrane Gas Absorption

Main puzzle: How to prevent the membrane wetting in the long-term operations?

- *Using hydrophobic membranes*
- *Surface modification of membrane*
- *Composite membrane*
- *Selection of denser hollow fiber membrane*
- *Selection of liquids with suitable surface tension*
  - *High surface tension*
  - *High reactivity with CO_2*
  - *Chemical compatibility with membrane material*
  - *Easiness of regeneration*
- *Optimizing operation conditions*

An amino acid salt, Potassium Glycinate (PG) is our studying focus.

Pilot-Scale Experimental Membrane Contactor

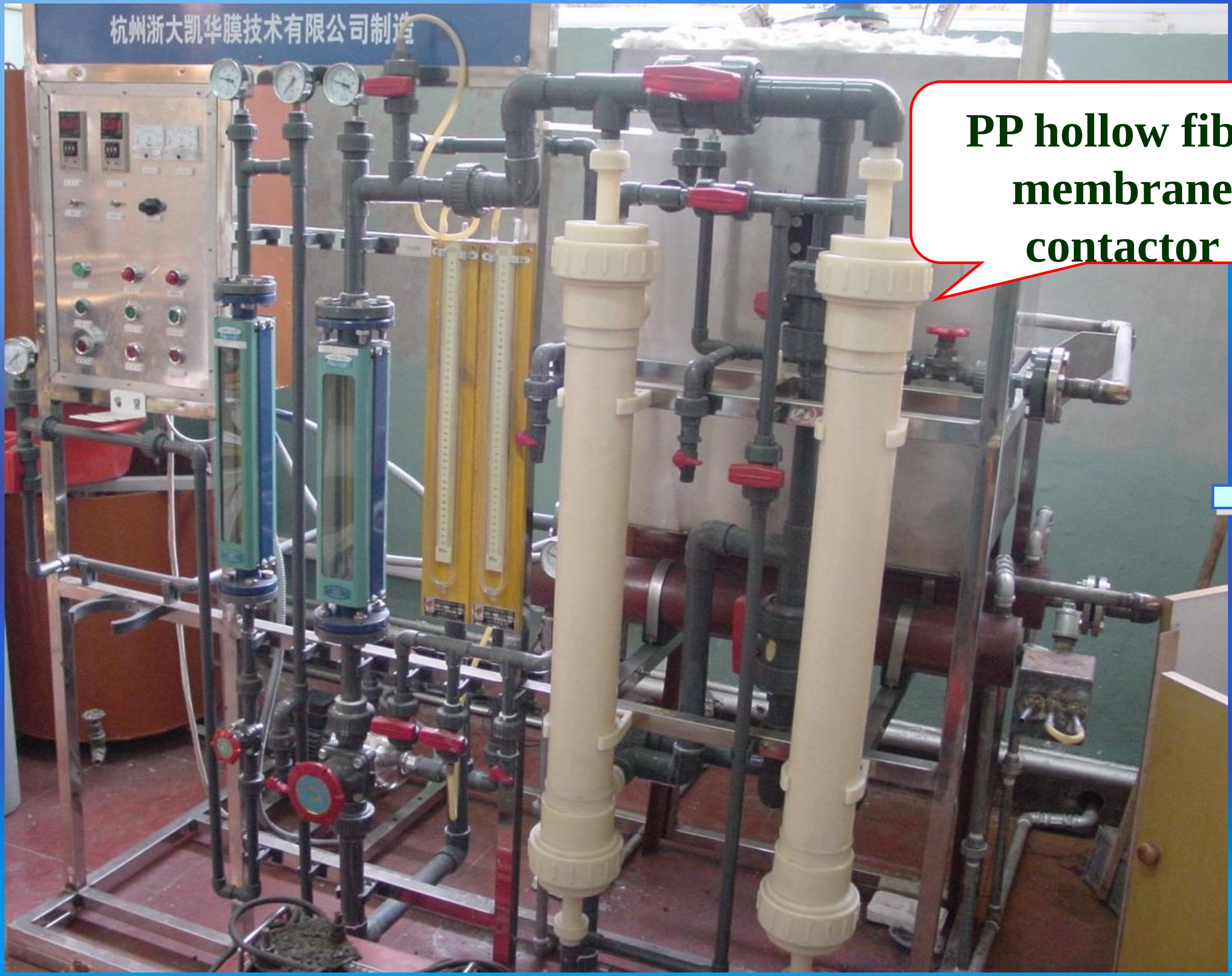


Gas mixture containing CO_2, N_2 and O_2 was selected as the feed gas to simulate the flue gas.

Experimental setup of CO_2 absorption in a membrane contactor

All results were printed in Fuel Processing Technology 88 (2007) 501-511.

Pilot-Scale Experimental Membrane Contactor

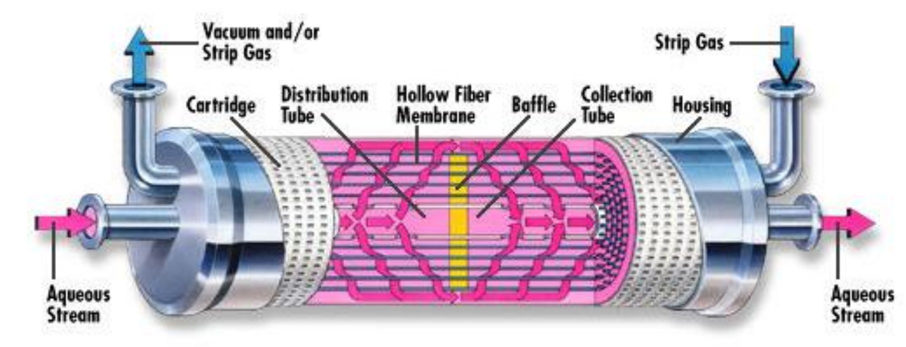


PP hollow fiber membrane contactor

Supported by Hi-Tech Research and Development Program of China (863)(No.2002AA529190)

Pilot-scale experimental test bench: 5 Nm^3/h

Characteristics of Hollow Fiber and Membrane Contactor



Module I.D. (m)	0.08
Fiber O.D. (µm)	442
Fiber I.D. (µm)	344
Fiber length (m)	0.8
Module length (m)	1.0
No. of fibers	7000
Average pore size (µm)	0.02 × 0.2
Fiber porosity (%)	>45
Packing density (%)	21.4
Contactor area (inner, m^2)	6.05

Absorbent Liquids

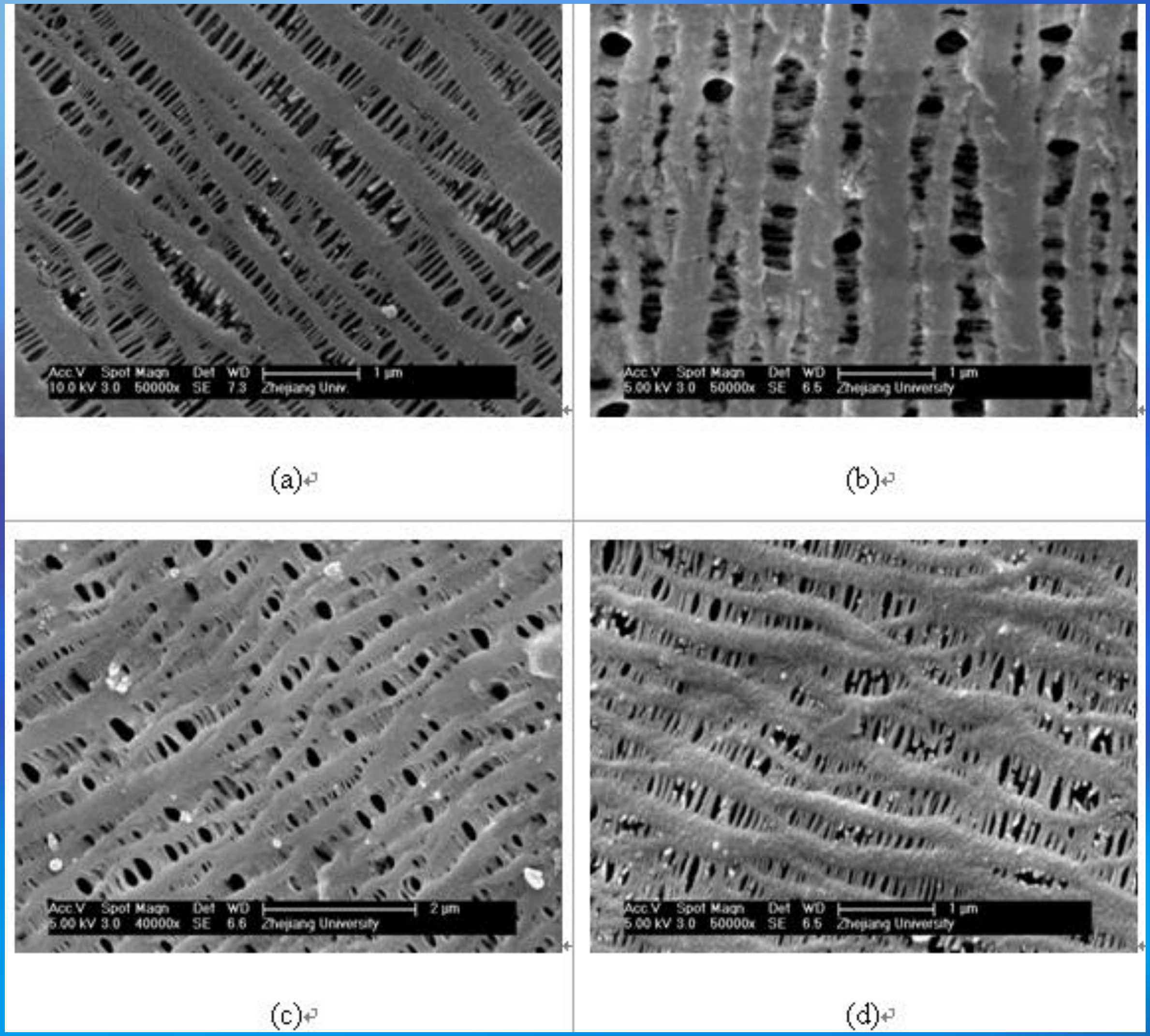
- ***Conventional absorbents, Monoethanolamine (MEA) and Methyldiethanolamine (MDEA).***

MEA and MDEA were dissolved in deionized water to make aqueous 0.5-3 kmol/m^3 solutions.

- ***Potassium Glycinate (PG)***

Potassium glycinate (PG) was prepared by neutralizing glycine with an equimolar amount of potassium hydroxide (KOH).

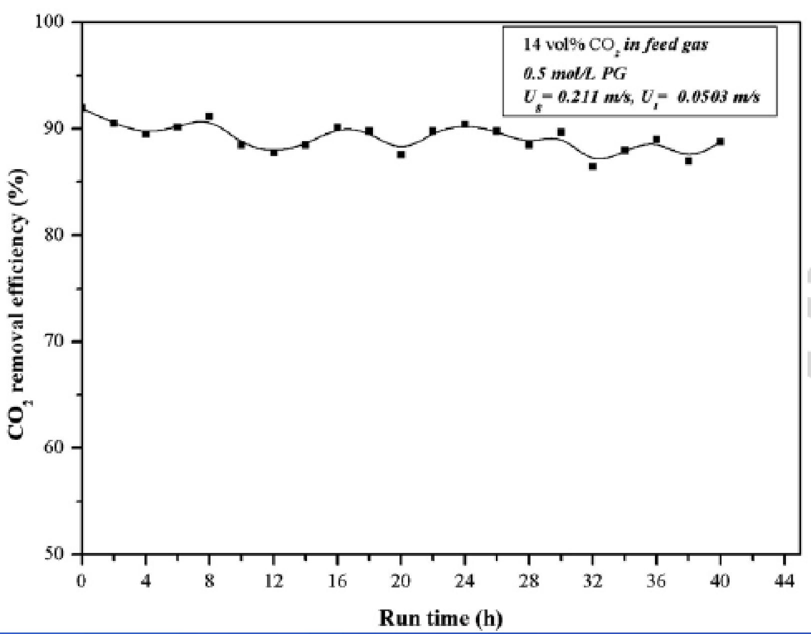
Membrane Wetting



SEM images of PP hollow fiber membranes wo/w immersing in aqueous 1 mol/L MEA solution with different CO_2-loading for about 35 days (magnification: ×50,000). (a) Blank, non-immersing; (b) 1 mol/L MEA (0.22 mol/mol CO_2-loading); (c) 1 mol/L MEA (0.35 mol/mol CO_2-loading); (d) 1 mol/L MEA (0.50 mol/mol CO_2-loading).

The long-term contact between PP membranes and aqueous MEA solution will alter the hydrophobic characteristic of membranes and increase the membrane wetting potential

Wetting Qualities of Aqueous PG solution for PP membrane



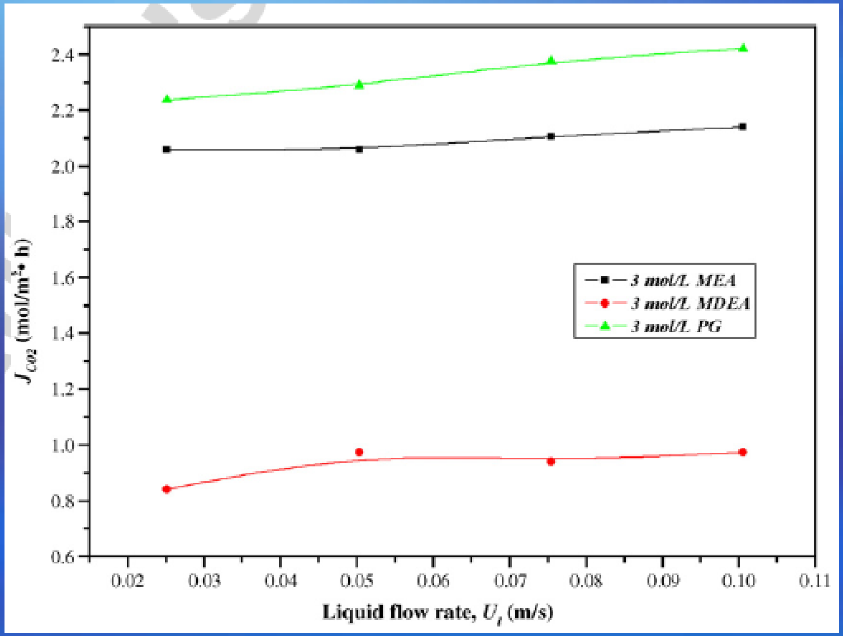
Long-term performance of PP hollow fiber membrane contactor over 40 h.

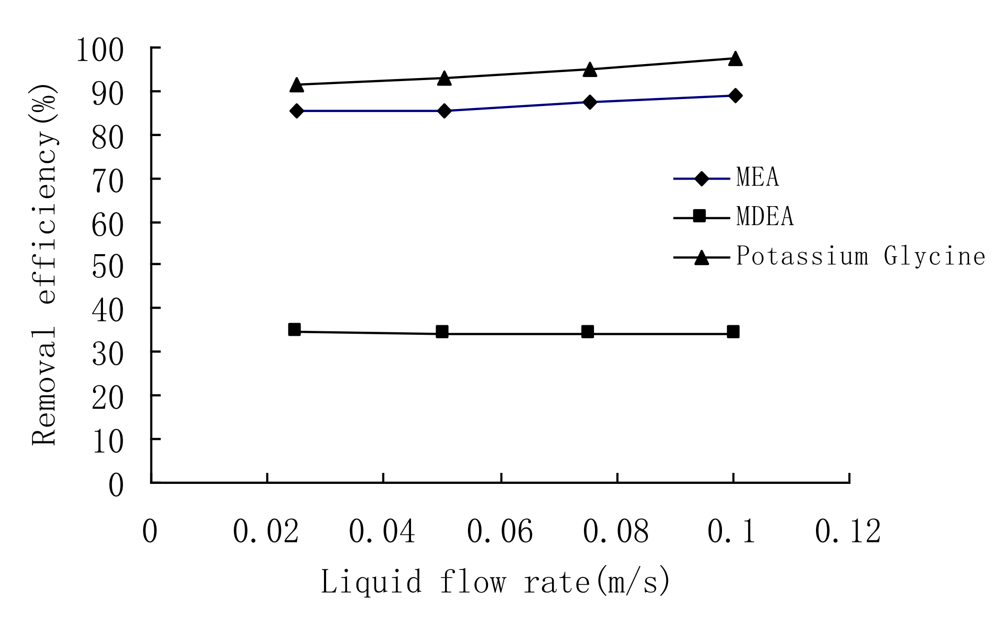
- The long-term operation result shows that aqueous PG solution **can not wet the PP membrane** in the long-term operation of about 40 h at a relatively lower concentration, 0.5 mol/L because of the relatively stable CO_2 removal efficiency.

- It can be deduced that **increasing the concentration of PG will decrease the potential to wet the PP membrane**, due to the fact that the surface tension of aqueous PG solution increases with the PG concentration.

Compared with the conventional absorbent liquids, aqueous PG solution has the **good adaptability** to the PP membrane, and perhaps can be used to replace these absorbents.

Effect of Liquid Flow Rate

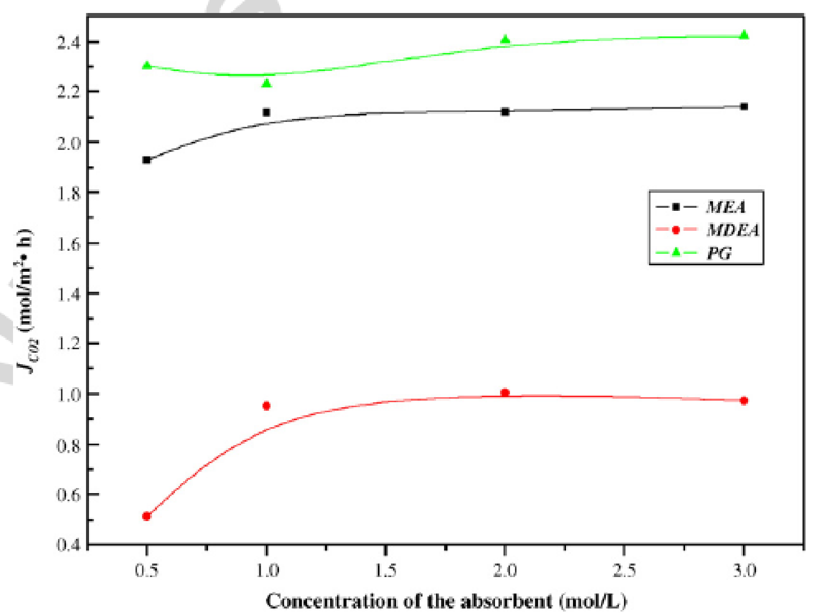




Influence of liquid flow rate on the mass transfer rate of CO_2 (U_g=0.211 m/s; T_g=298 K; CO_2 Conc. = 14%; T_l=308 K)

Influence of liquid flow rate on removal efficiency of CO2 (Ug=0.211 m/s; Tg=298 K; CO2 Conc. = 14%; Tl=308 K)

Effect of Absorbent Concentration

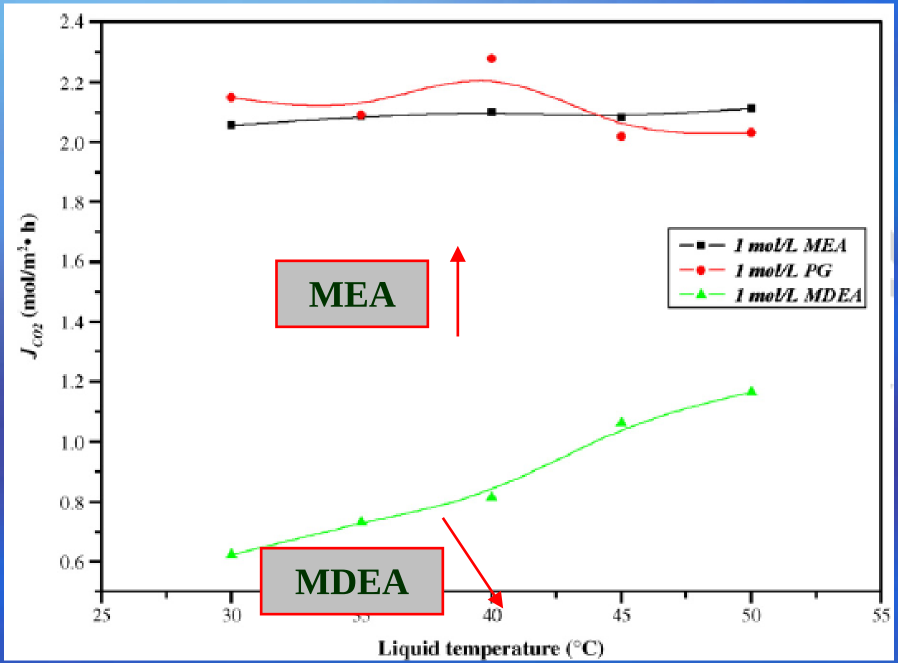


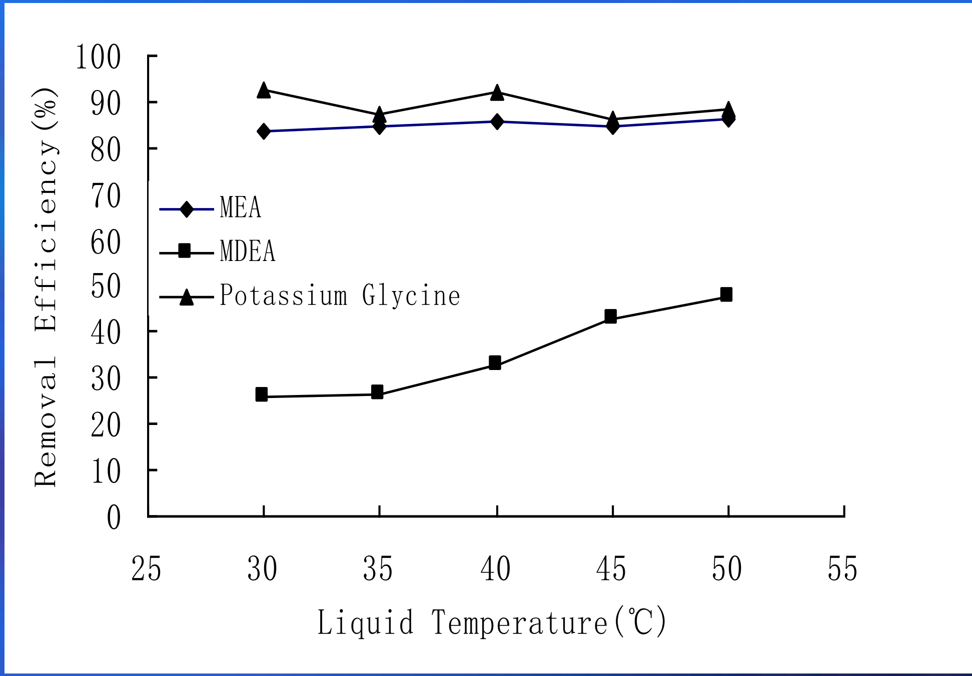
Influence of absorbent concentration (U_g=0.211 m/s; T_g=298 K; CO_2 Conc. = 14%; U_l=0.101 m/s; T_l=308 K)

- It is clearly shown that the mass transfer rate generally increases with the absorbent concentration and aqueous PG solution performs better than MEA and MDEA.

- A compromise has to be taken among the higher CO_2 absorption, wetting potential and crystallization prevention when using PG as absorbent.

Effect of Liquid Temperature

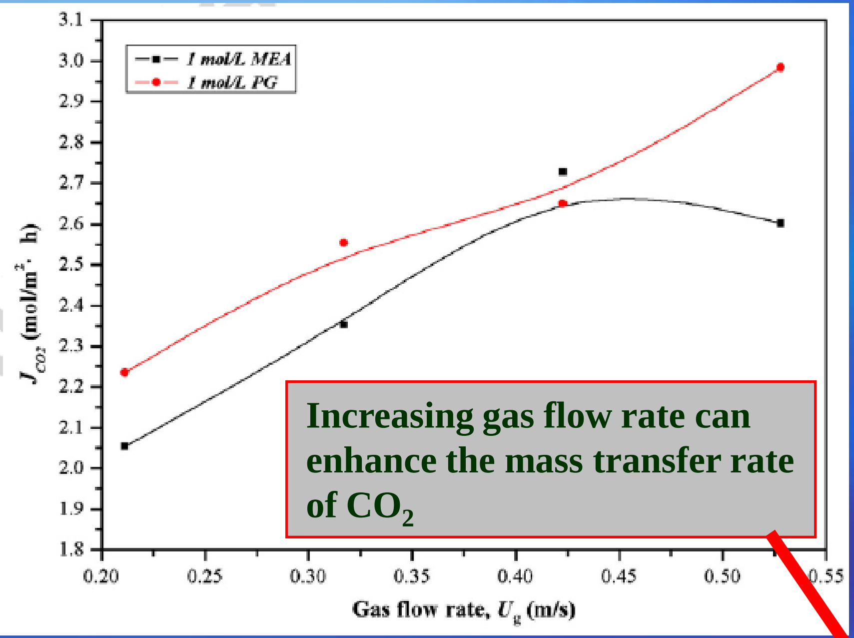




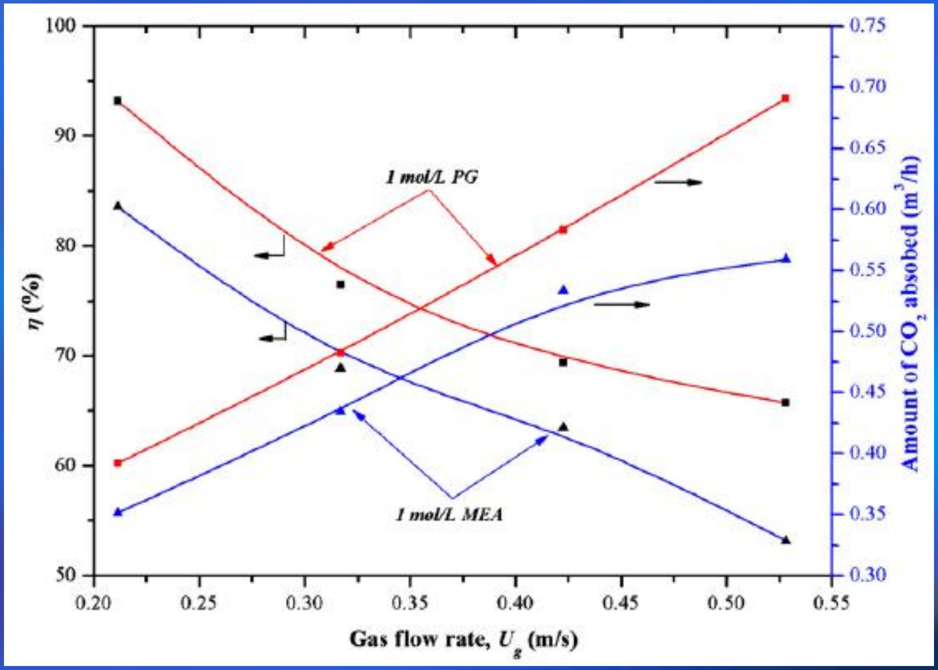
Influence of liquid temperature (U_g=0.211 m/s; T_g=298 K; CO_2 Conc. = 14%; U_l=0.0503 m/s;)

- **So, *a relatively lower temperature* operation was seemingly more favorable to CO_2 removal when using PG.**

Effect of Gas Flow rate



Increasing gas flow rate can enhance the mass transfer rate of CO_2

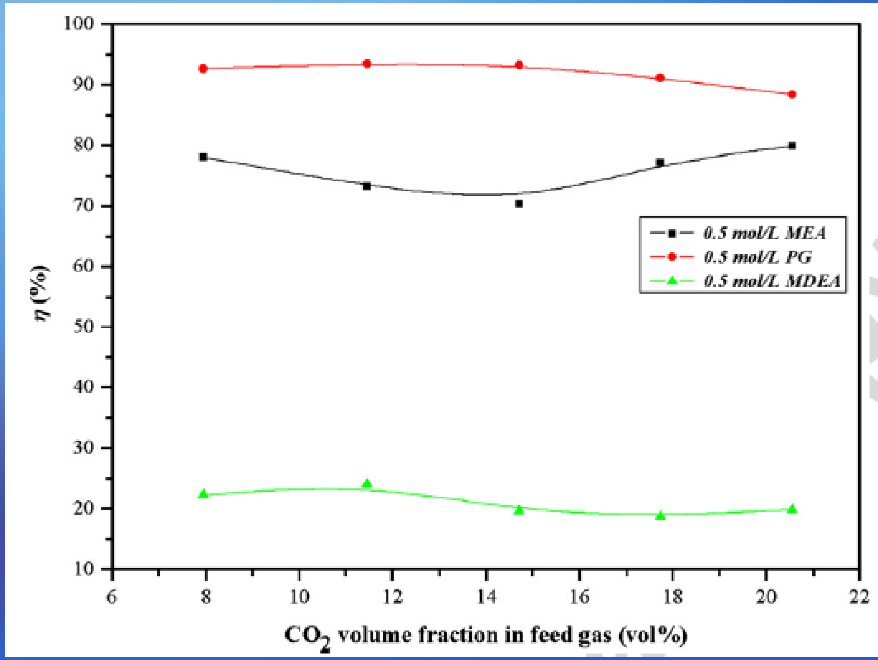


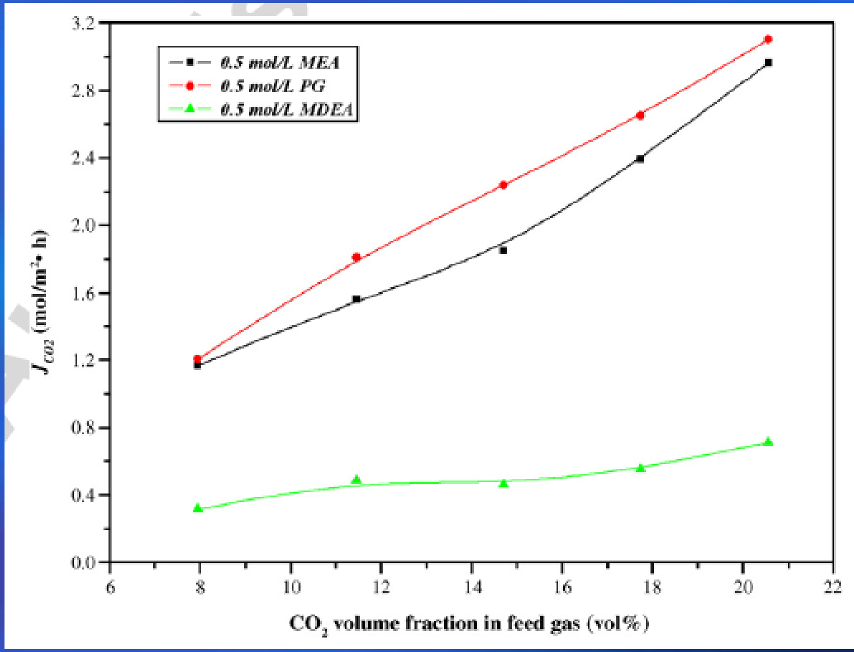
Influence of gas flow rate (T_g=298 K; CO_2 Conc.=14%; U_l=0.0503 m/s; T_l=308 K)

- **The mass transfer rate and removal efficiency using PG are higher than MEA. So, *PG is more suitable to absorb CO_2 when gas velocity is frequently changed.***

- **When increasing the gas flow rate, the CO_2 removal efficiency will reduce, but the amount of CO_2 absorbed by liquid increases, thus leading to the increase of mass transfer rate.**

Effect of CO_2 Volume Fraction in Feed Gas

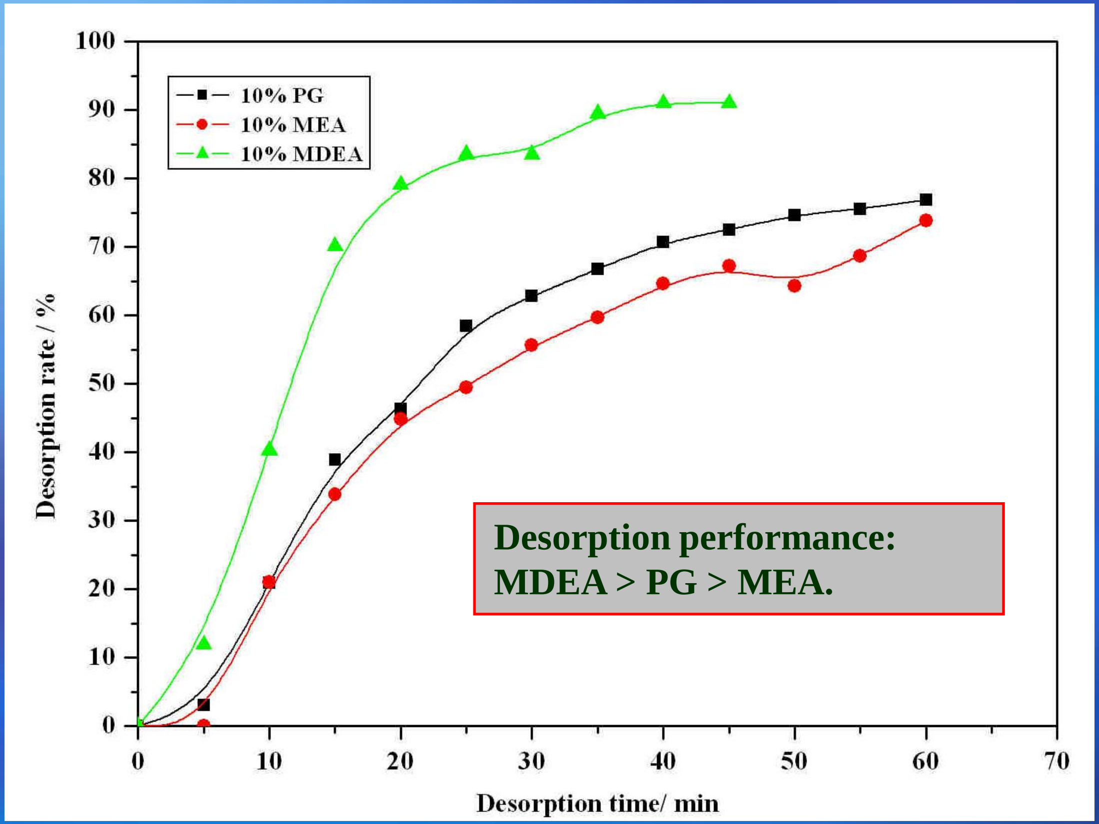




• Effect of CO_2 volume fraction in feed gas

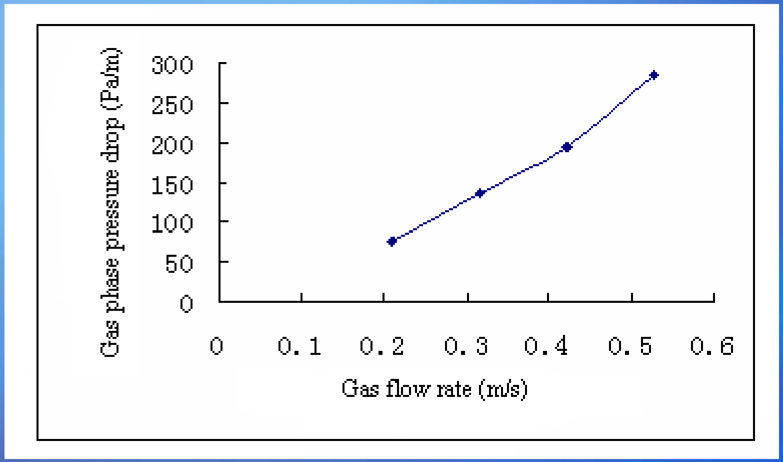
• It proves that the system in combination with PP hollow fiber membrane contactors and aqueous PG solution could be applied into various kinds of coal-fired power plants in CO_2 separation.

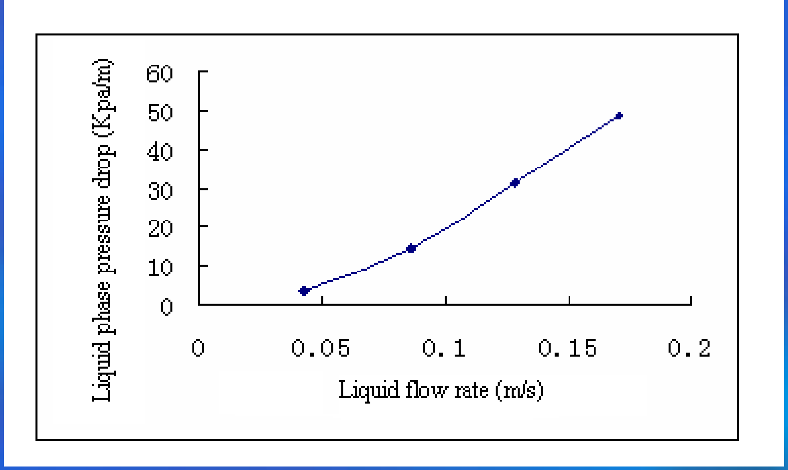
Desorption Characteristic of Aqueous PG Solution



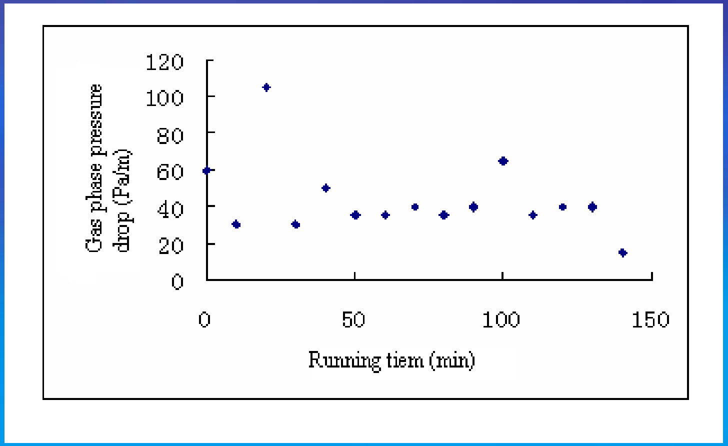
• If only CO_2 absorption performance, desorption performance and wetting potential are considered, aqueous PG solution perhaps could be alternative to MEA. But some more problems such as how to select the liquid temperature, how to select a suitable PG concentration, how to decrease the PG price and so on need to be emphasized in the next research step.

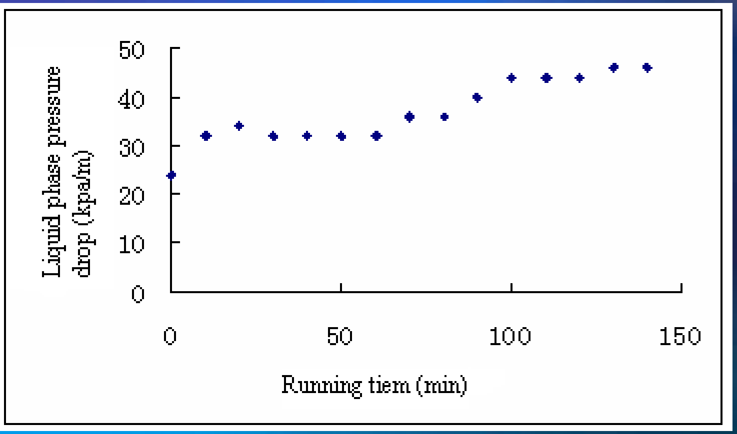
Pressure Drop





The pressure drop at semi-batch operation



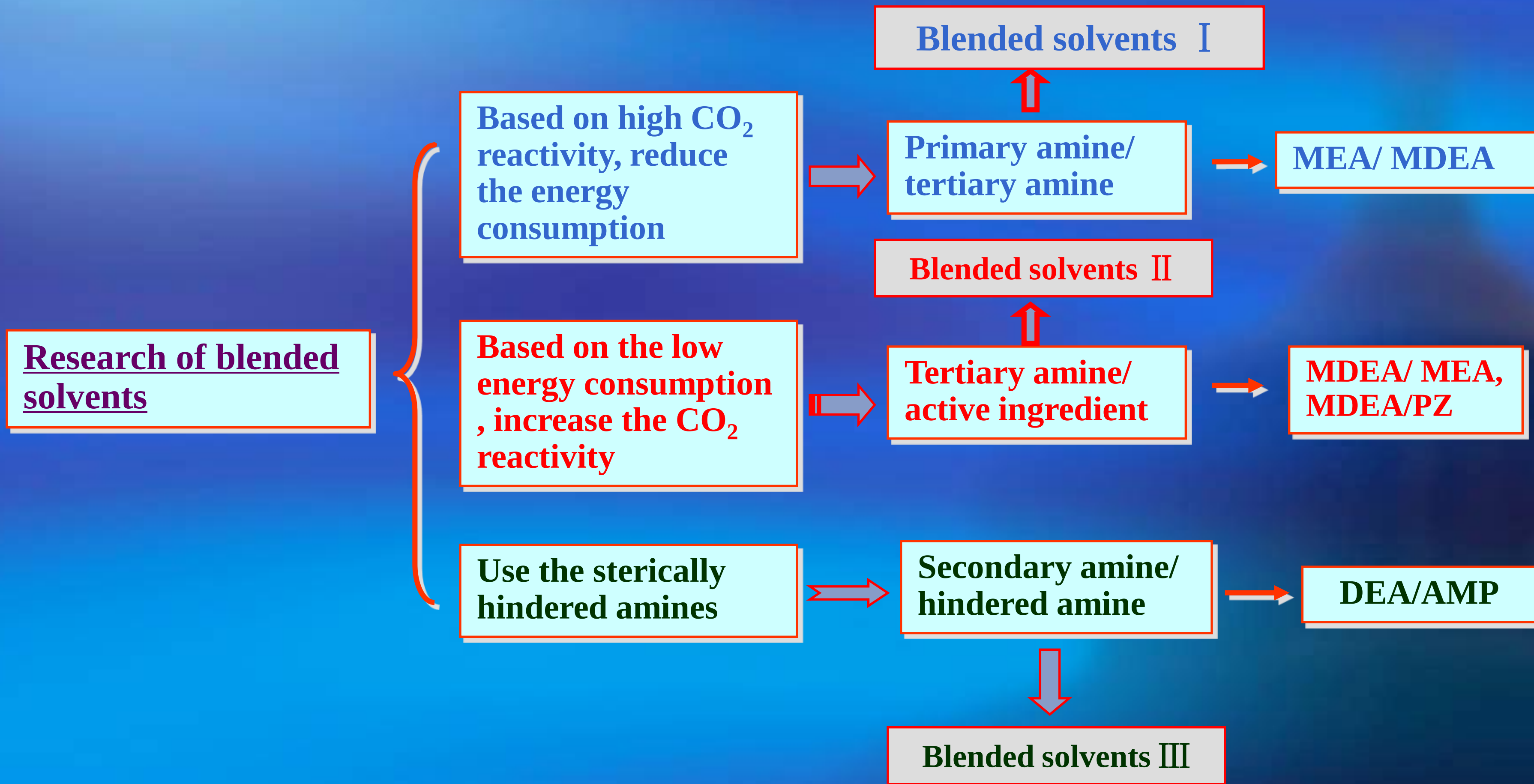


The pressure drop at continuous operation

Principle of Blended Solvents Research

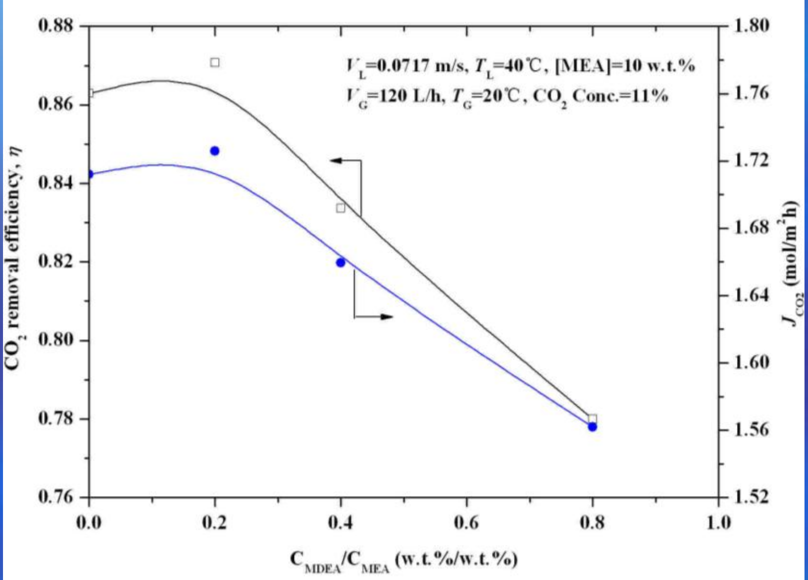
- ***Principle***

In combination with *high reactivity with CO_2* and *low regeneration energy consumption*.

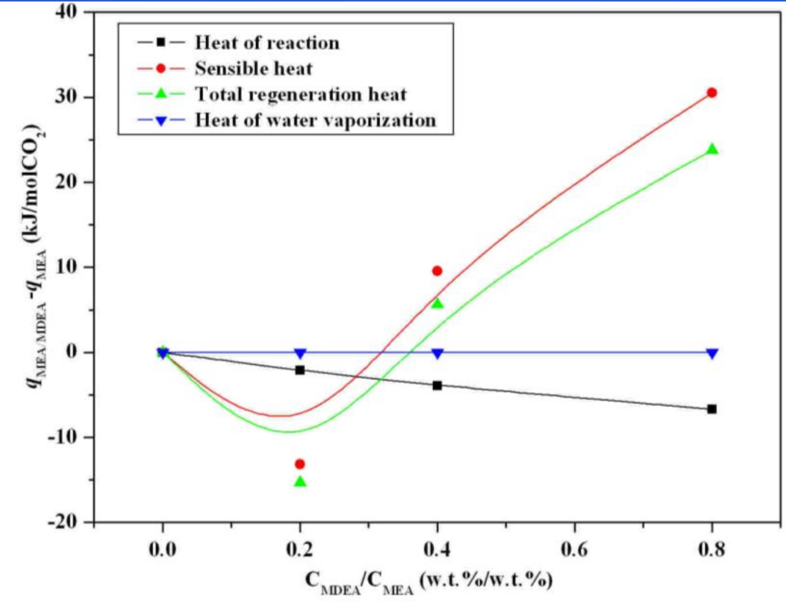


Blended Solvents Research Ⅰ

• ***What optimal concentration of additives is added?***



Effect of MDEA concentration in the blended solvents on mass transfer rate of CO_2.

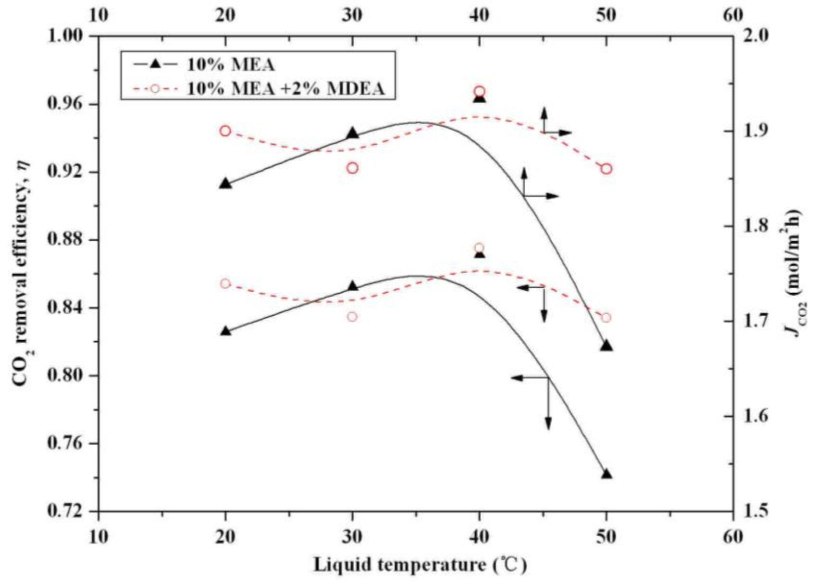


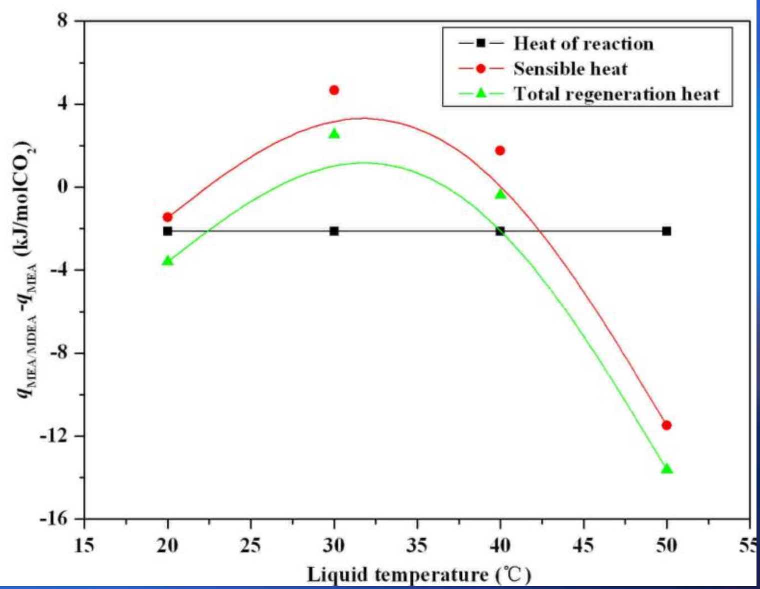
Effect of MDEA concentration in the blended solvents on regeneration energy consumption.

When CO_2 absorption performance and energy consumption are taken into consideration, the optimal relative concentration of MDEA added into aqueous MEA solution is recommended to *a small amount*, for example, MDEA/MEA=1:0.2.

Blended Solvents Research Ⅰ

• *The CO_2 absorption performance of blended solvents Ⅰ.*

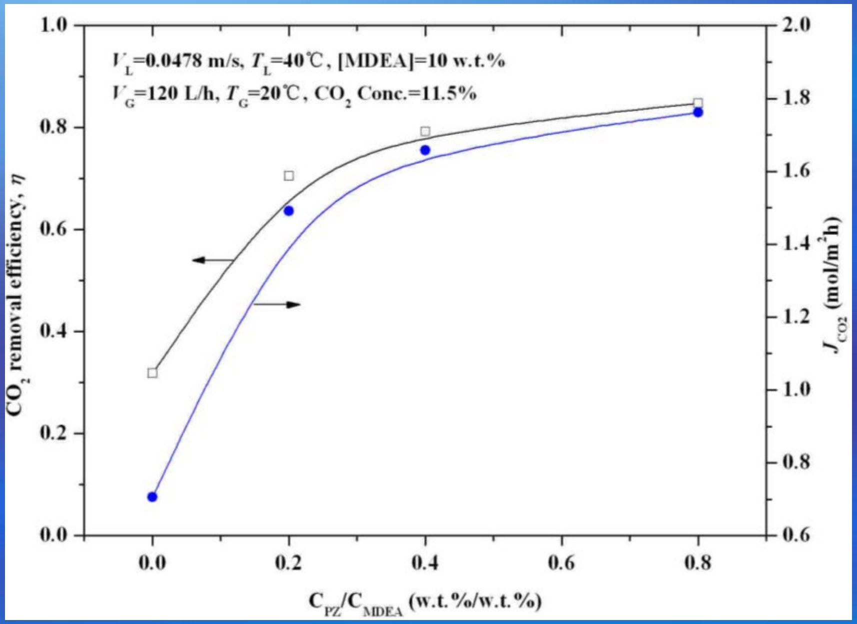


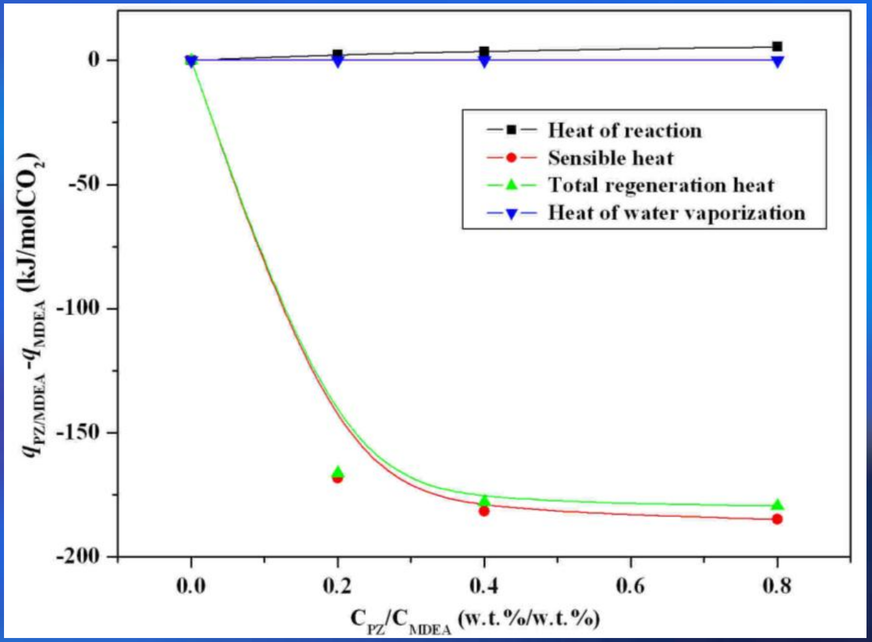


• **Effect of liquid temperature.**

When the small amount of MDEA is added into aqueous MEA solution, although the positive effect of MDEA on CO_2 absorption performance is not significant, the regeneration energy consumption can be reduced in some degree.

Blended Solvents Research Ⅱ





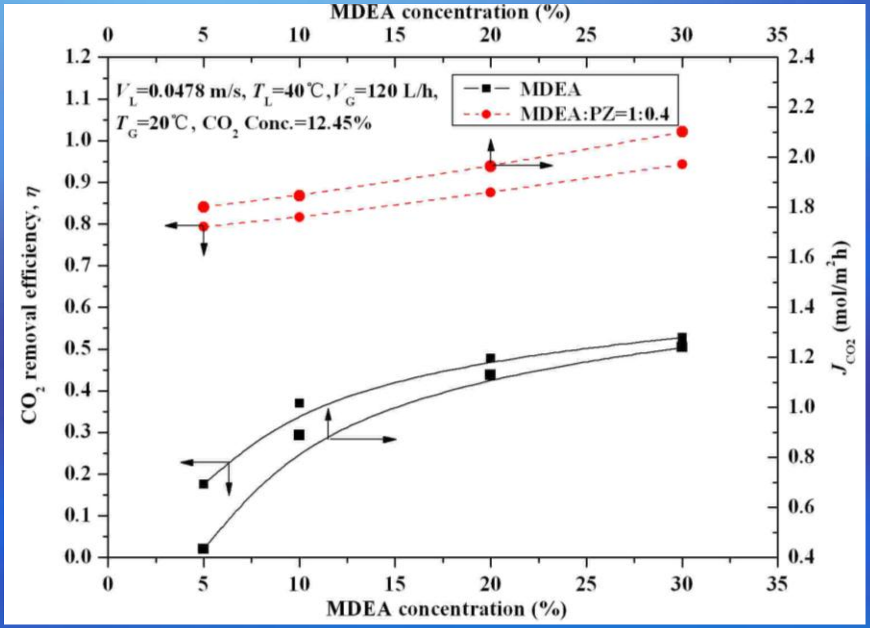
Effect of PZ concentration in the blended solvents on CO_2 removal efficiency.

Effect of PZ concentration in the blended solvents on regeneration energy consumption.

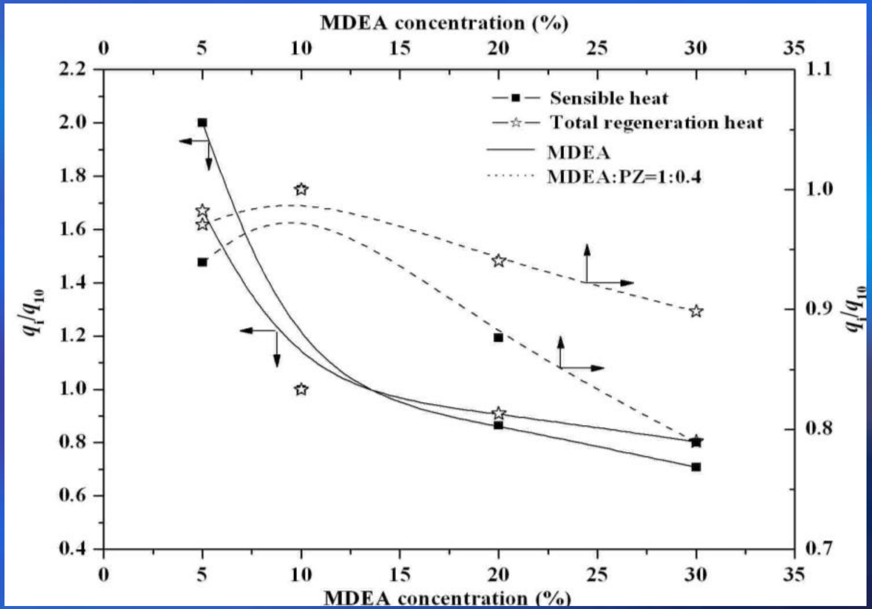
When CO_2 absorption performance and regeneration energy consumption are taken into consideration, the optimal relative concentration of PZ added into aqueous MEA solution is recommended to *a moderate amount*, for example, MDEA/PZ=1:0.4.

Blended Solvents Research Ⅱ

- ***The CO_2 absorption performance of blended solvents Ⅱ***



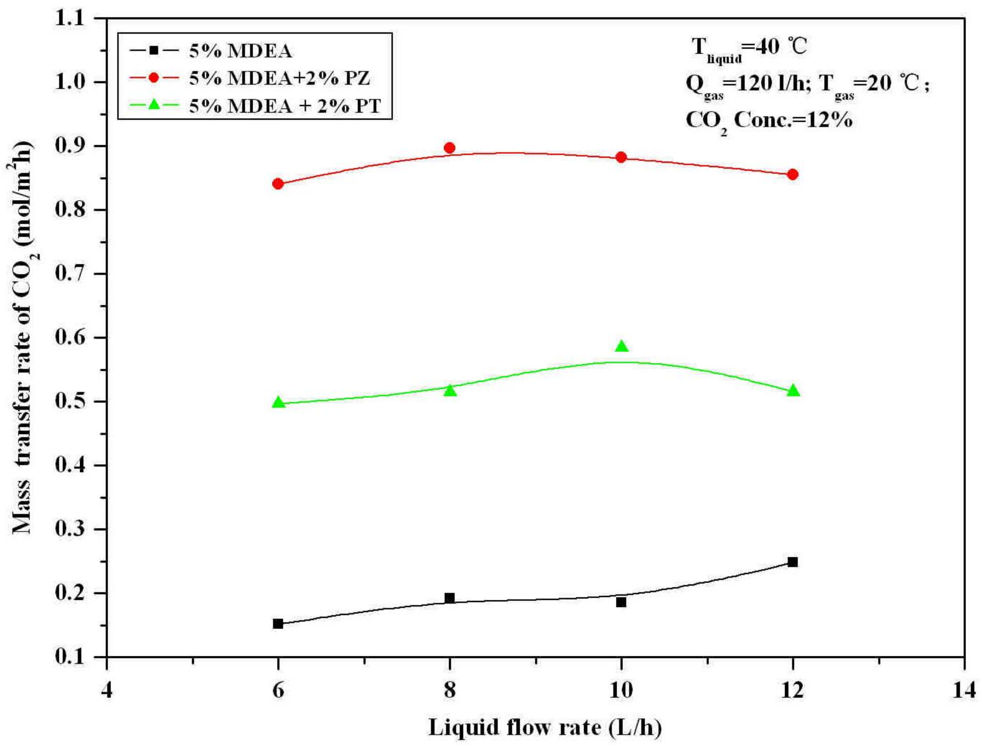
Effect of absorbent concentration in the blended solvents on CO_2 removal efficiency.



Effect of absorbent concentration in the blended solvents on regeneration energy consumption.

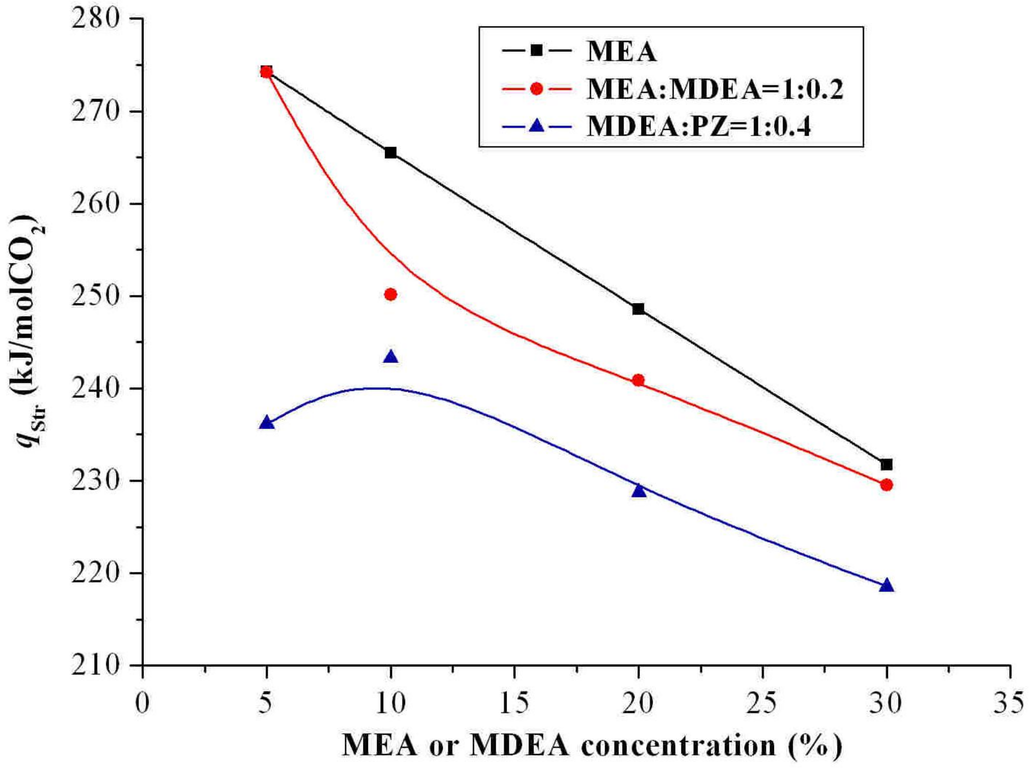
Blended Solvents Research Ⅱ

- ***The CO_2 absorption performance of blended solvents Ⅱ.***



- **Effect of liquid flow rate.**

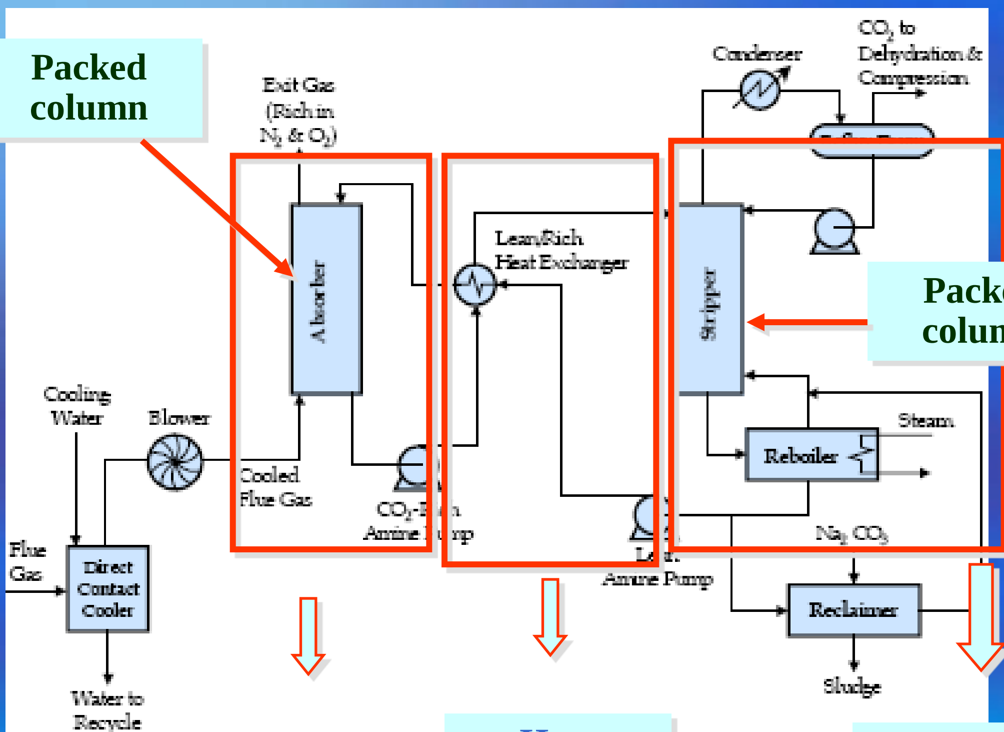
Some Useful Results about Three Blended Solvents



- When the small amount of MDEA is added into aqueous MEA solution, **the regeneration energy consumption can be reduced by about 1~6%.**
- When the moderate amount of PZ is added into aqueous MDEA solution, the regeneration energy consumption can be reduced by **about 5~14%.**

CO_2 Chemical Absorption Technology

CO$_2$ Capture by Chemical absorption Method



Packed column

Packed column

Absorption system

Heat exchange system

Desorption system

The CO$_2$ absorption process generally consists of (1) an absorption unit where CO$_2$ is recovered from a gas phase into a liquid solvent and (2) a heat exchange system where rich solution is heated by lean solution before being pumped into desorption unit, and lean solution is cooled to a specific temperature value before being pumped into absorption unit; (3) a desorption unit where the absorption capability of the used solvent is recovered before being reintroduced to the absorption unit.

Typical amine absorption process for CO$_2$ recovery from flue gas

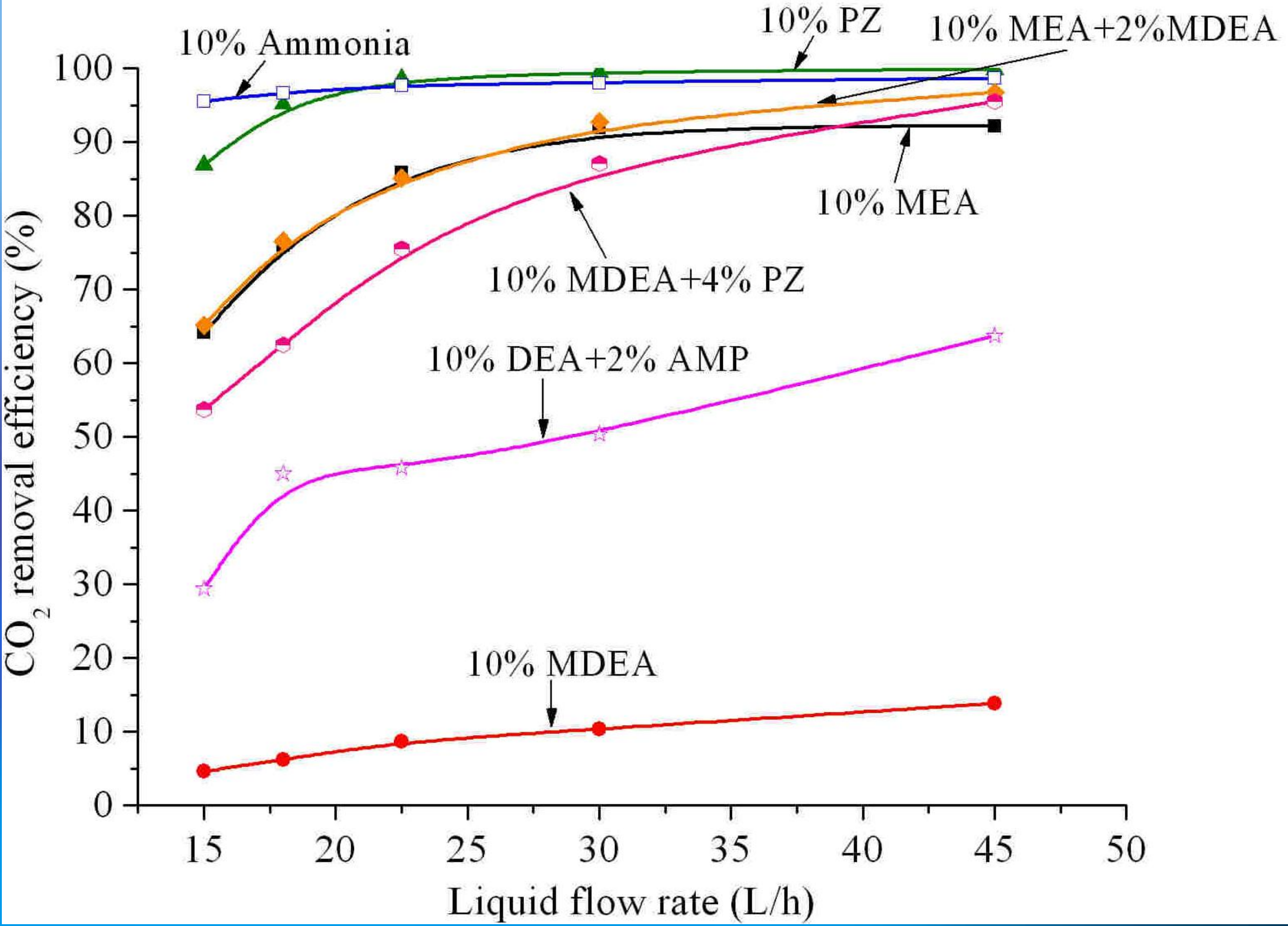
Experimental Setup

Structured packed column: perspex glass

Stainless steel silk screen packing

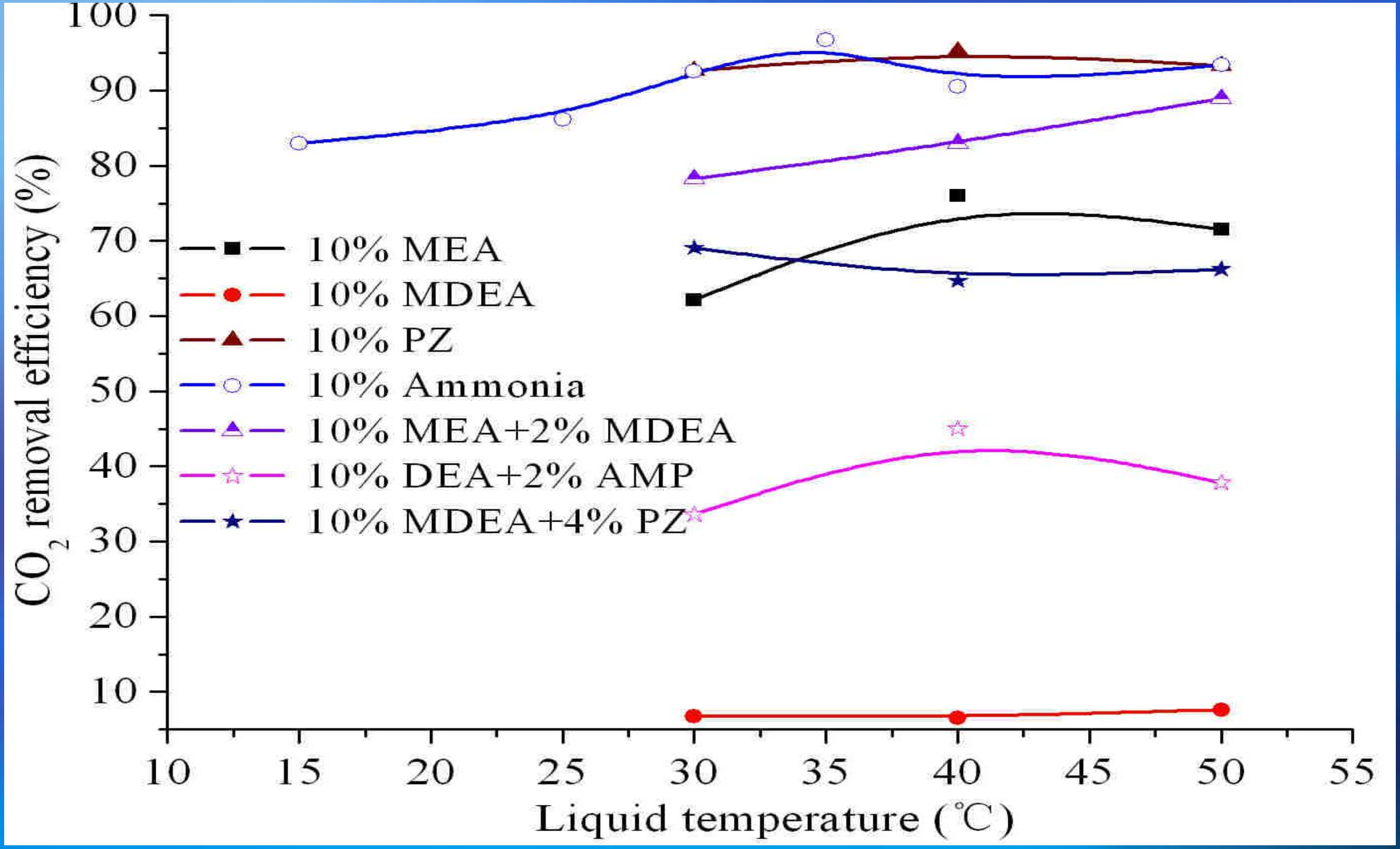
Structured packing was placed with each layer rotated with 90° with respect to the previous one.

Effect of liquid flow rate



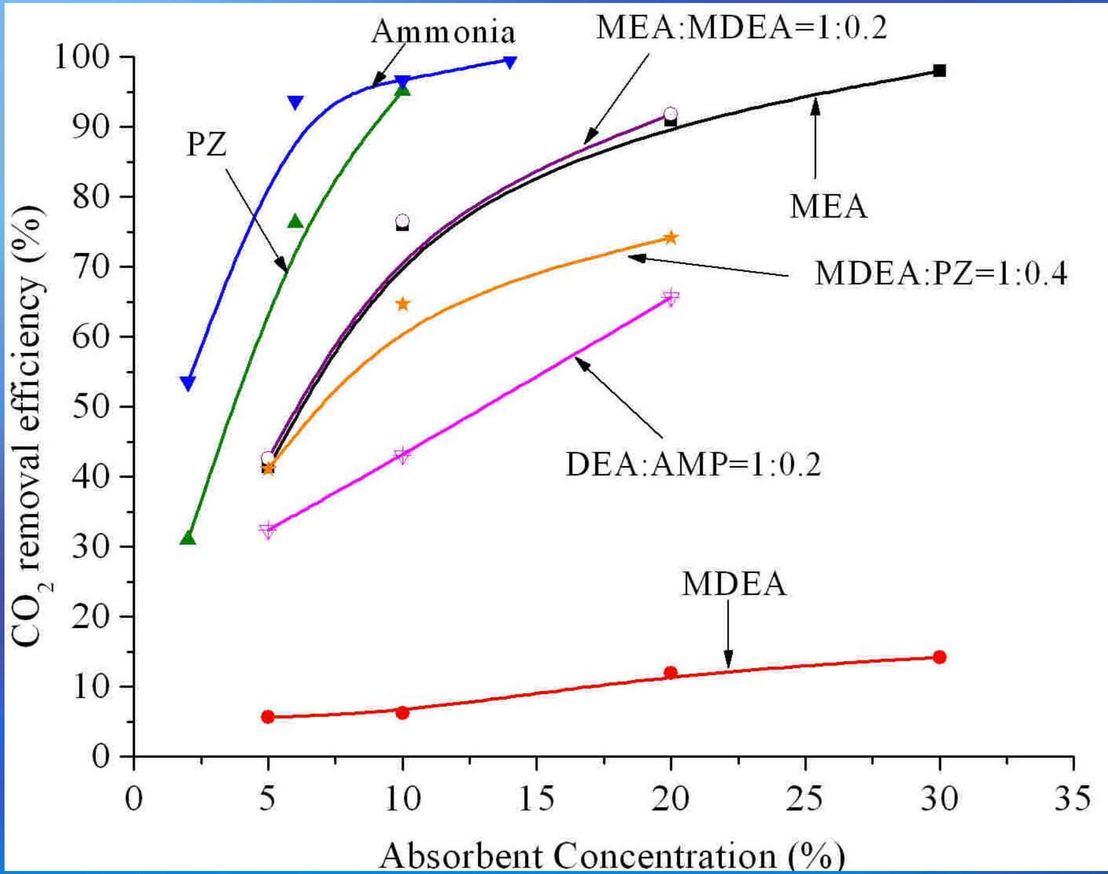
Effect of liquid flow rate on CO_2 removal efficiency

Effect of liquid temperature



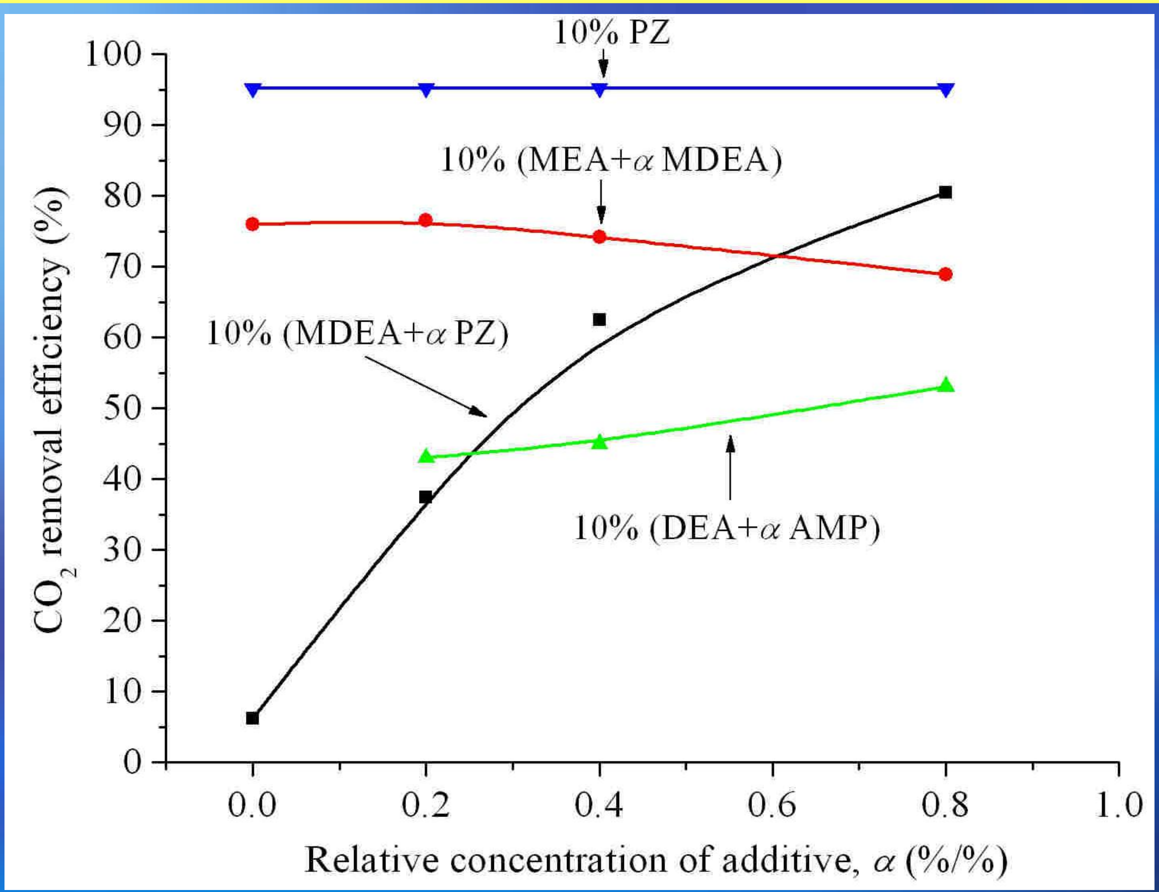
Effect of liquid temperature on CO_2 removal efficiency

Effect of absorbent concentration



- **CO_2 removal efficiency increases with absorbent concentration;**
- **Ammonia and PZ have the highest CO_2 removal efficiency;**
- **MEA/MDEA (1:0.2) has the slightly larger CO2 removal efficiency than the single MEA in all the experimented absorbent concentration ranges.**

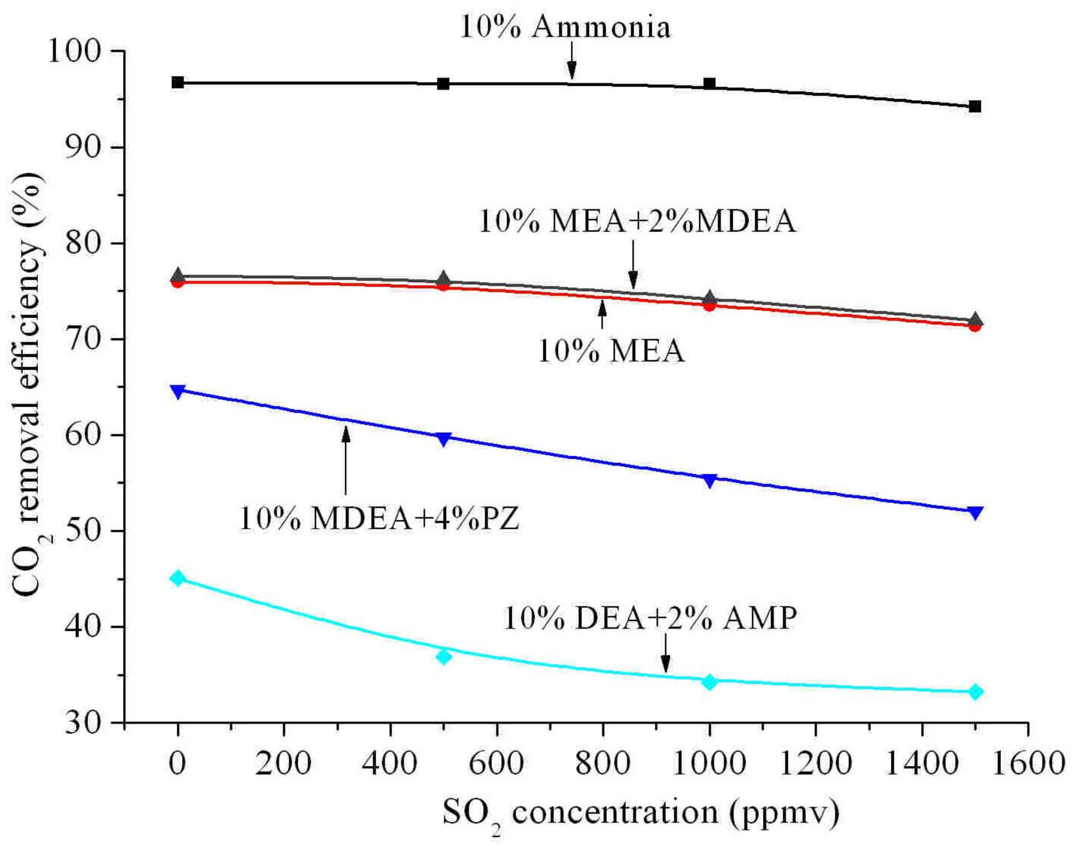
Effect of additive concentration



- **MEA/MDEA solvent: CO_2 removal efficiency firstly increases and then decreases with the increase of MDEA concentration. When the small amount of MDEA was added into MEA, the removal efficiency is slightly increased.**

- **MDEA/PZ solvent: CO_2 removal efficiency increases with the PZ concentration because of the higher CO_2 reaction rate of PZ.**

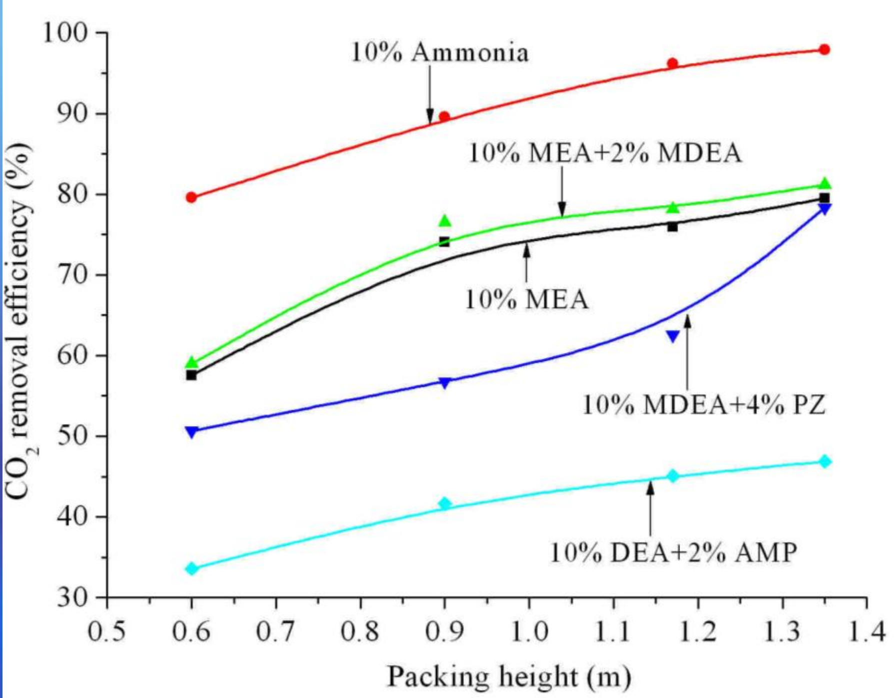
Effect of SO_2

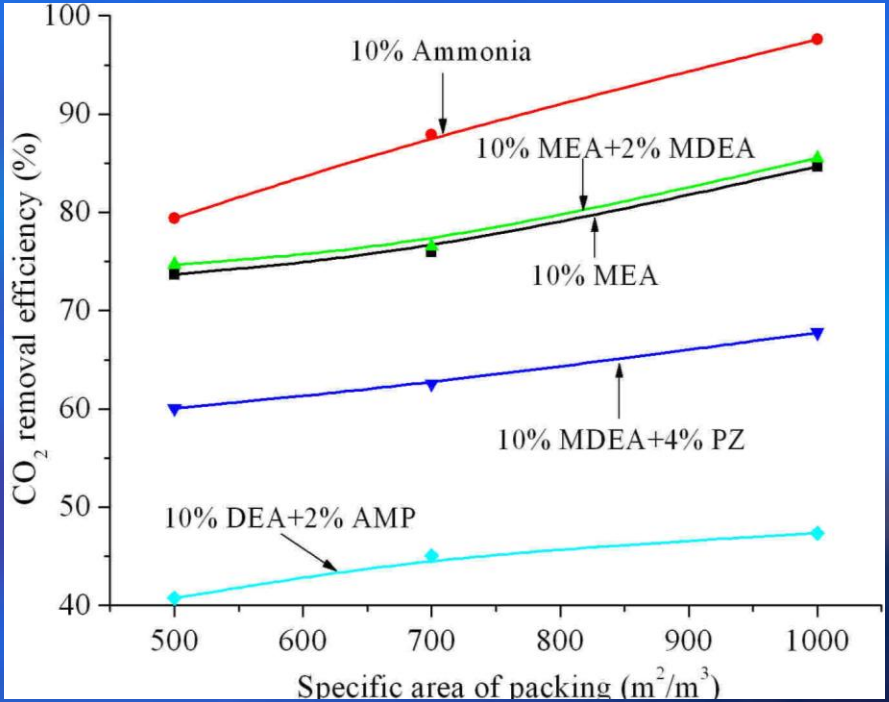


• **Results:** **The effect of SO_2 on CO_2 removal efficiency is negative due to the competitive reaction between absorbent and SO_2 or CO_2. (Reaction rate between SO_2 and absorbent is higher than that between CO_2 and absorbent)**

• **Tendency:** **The extent of negative effect of SO_2 on CO_2 removal increases with the decrease of reaction rate between absorbent and CO_2. For example, the negative effect of SO_2 on DEA/AMP>MDEA/PZ>MEA>MEA/MDEA>Ammonia.**

Effect of other operating factors





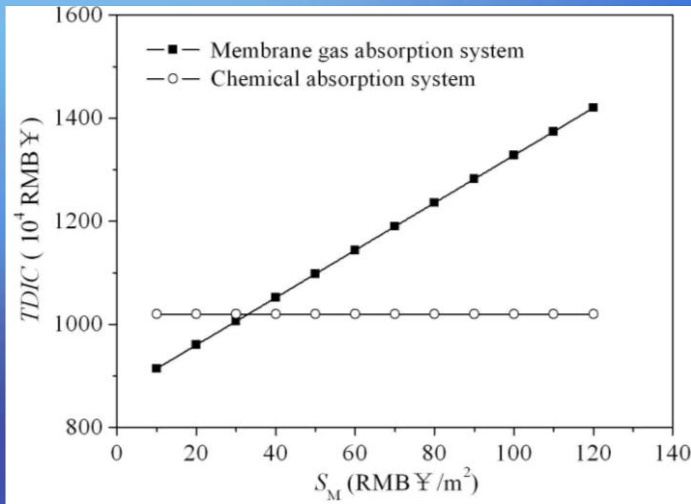
Effect of packing height on CO_2 removal efficiency.

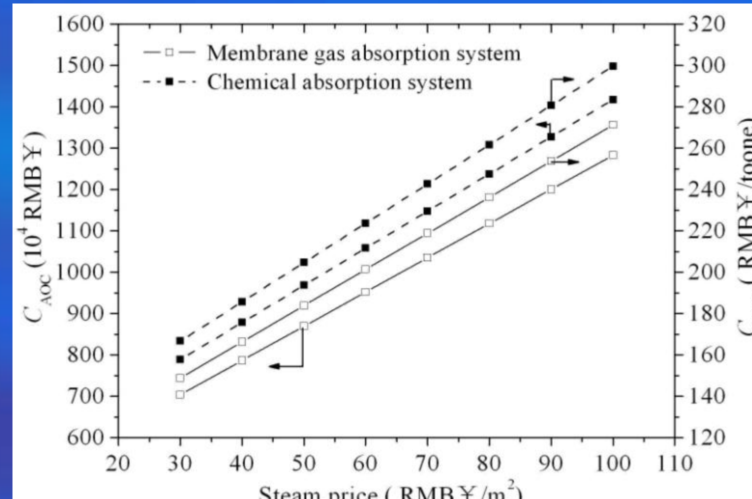
Effect of specific area of packing on CO_2 removal efficiency.

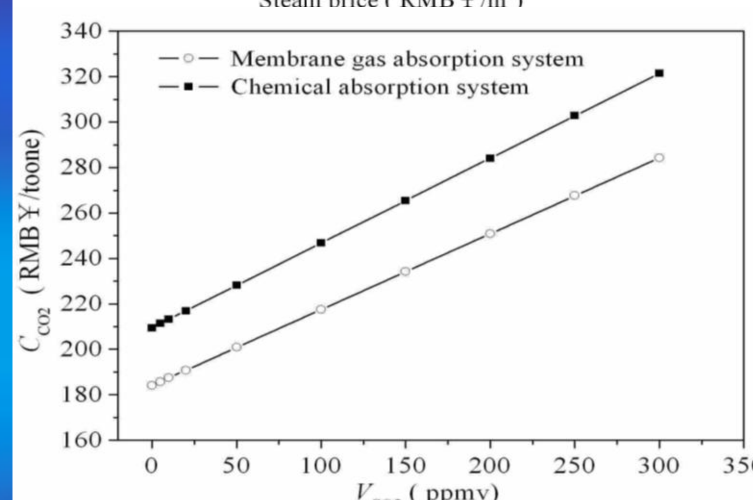
Comparative Analysis of CO_2 Separation from Flue Gas Using Membrane Absorption System (MAS) and Chemical Absorption System (CAS)

Economic analysis between MAS and CAS

- ***Influencing factors***



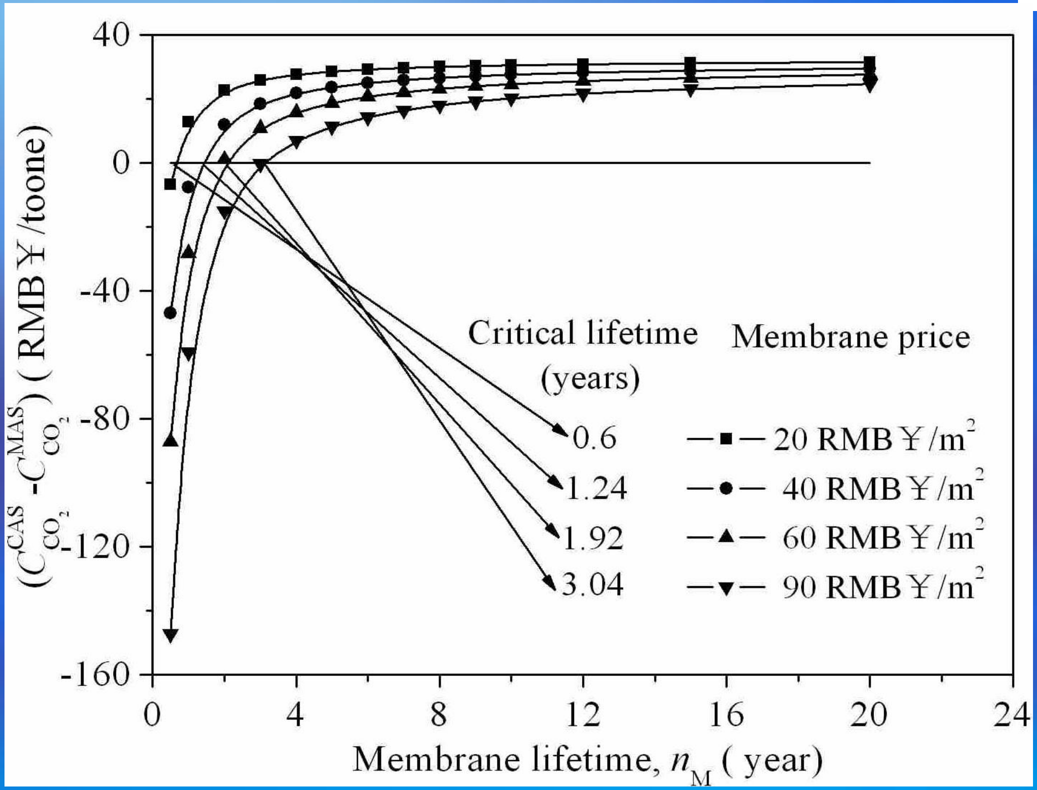




- **In terms of CO_2 captured cost, it also can be seen that MAS performs better than CAS in all range of steam price and SO_2 concentration when membrane price and lifetime are kept to reach a proper value**

Economic analysis between MAS and CAS

- ***Critical membrane lifetime***



- **When the real operational time of membrane modules is reduced to less than the critical value decided by membrane price, the cost of CO_2 captured of MAS will be inversely higher than that of CAS.**

The real operational time of membrane modules decides whether MAS performs better than CAS or not.

Conclusion

- **CO_2 separation by membrane absorption has advantage of operation flexibility, be easy to be scale up and economical, but membrane wetting is big challenge. PG solution looks very suitable.**
- **Chemical absorption technology is one of very potential technology for CO_2 separation. Suitable absorption liquid and optimal operation parameters seems to realize high efficiency and low energy penalty in which ammonia and some mixing absorbent looks very promising.**
- **Membrane absorption system looks superior to chemical absorption system unless serious membrane pore-wetting and pore-plugging happened. Research on how to reduce the membrane price and how to prolong the membrane lifetime is very important in the future.**

Thank you for your attention!