CO$_2$ capture using hot K$_2$CO$_3$ solvent

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Presentation Outline

• Background

• Pilot scale experiment trials

• Concluding remarks

• Acknowledgement
Why CCS is necessary?

Three ways to CO₂ reduction

- **Efficiency improvement**
- **Renewable energy**
- **CCS**

In lowest cost scenario, **CCS contributes to 17% of total reduction** (IEA, 2013)

Without CCS, total cost for CO₂ reduction increases 70%

**CCS is necessary** for CO₂ reduction, and is **cost competitive with renewable energy technologies**

Source: IEA, 2013
Current progresses of CCS demonstration

EU: 12 demonstration projects of the “Flagship Program” are canceled or stagnated
Australia: New government attitude not positive……
North America: Demonstration goes slowly

Progress slowly, far behind planning
### What’s the key barriers for CCS?

**High cost and high energy penalty!**

<table>
<thead>
<tr>
<th></th>
<th>IGCC pre-combustion</th>
<th>Post-combustion</th>
<th>Oxygen combustion</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Unit investment, $/kW</strong></td>
<td>1400-1600</td>
<td>700-850</td>
<td>700-850</td>
</tr>
<tr>
<td>(refer. plant)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Unit investment, $/kW</strong></td>
<td>1900-2100</td>
<td>1100-1500</td>
<td>1350-1650</td>
</tr>
<tr>
<td>(capture plant)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Increase in unit</strong></td>
<td>25%-40%</td>
<td>75%-90%</td>
<td>90%-106%</td>
</tr>
<tr>
<td><strong>investment</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Increase in cost of</strong></td>
<td>35%-40%</td>
<td>70%-90%</td>
<td>90%-115%</td>
</tr>
<tr>
<td><strong>electricity</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>CO₂ capture cost, $/t</strong></td>
<td>30-70</td>
<td>50-130</td>
<td>40-100</td>
</tr>
<tr>
<td><strong>Efficiency penalty,</strong></td>
<td>6-10</td>
<td>10-15</td>
<td>10-12</td>
</tr>
<tr>
<td><strong>percentage points</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Why hot potassium carbonate solvent?

\[ CO_2 + K_2CO_3 + H_2O \leftrightarrow 2KHCO_3 \]

**Reaction (1)**

- **Low energy requirement** for regeneration due to lower heat of reaction
- **Low cost**
- **Low volatility and toxicity**
- **High capacity**
- **Co-removal of NO\textsubscript{x} and SO\textsubscript{x}**
- **Environmentally friendly**
Pilot scale experiment trials
The mechanism of unpromoted $K_2CO_3$ solvent for $CO_2$ absorption

Overall reaction

$$CO_2 + CO_3^{2-} + H_2O \Leftrightarrow 2HCO_3^-$$  \hspace{1cm} \text{Reaction (4)}

Elementary steps

$$CO_2 + H_2O \Leftrightarrow HCO_3^- + H^+$$  \hspace{1cm} \text{Reaction (5)}

$$CO_2 + OH^- \Leftrightarrow HCO_3^-$$  \hspace{1cm} \text{Reaction (6)}

$$H_2O \Leftrightarrow H^+ + OH^-$$  \hspace{1cm} \text{Reaction (7)}

Reactions (5) and (6) followed by instantaneous Reactions (8) and (9)

$$H^+ + CO_3^{2-} \Leftrightarrow HCO_3^- + CO_3^{2-}$$  \hspace{1cm} \text{Reaction (8)}

$$CO_3^{2-} + H_2O \Leftrightarrow HCO_3^- + HCO_3^-$$  \hspace{1cm} \text{Reaction (9)}

- Limiting step
- Rate based, highly dependent on partial pressure
- Low $CO_2$ partial pressure, low absorption rate
The promoted $K_2CO_3$ solvent for $CO_2$ capture

Research focus on different promoters

<table>
<thead>
<tr>
<th></th>
<th>MEA</th>
<th>Piperazine</th>
<th>Borate</th>
<th>Carbonic Anhydrase</th>
<th>Glycine</th>
<th>Proline</th>
</tr>
</thead>
<tbody>
<tr>
<td>$CO_2$ absorption rate enhance</td>
<td>0.33-2.52</td>
<td>Comparable to MEA</td>
<td>0.17-0.22</td>
<td>0.04-0.22</td>
<td>0.30-3.52</td>
<td>0.87-4.65</td>
</tr>
<tr>
<td>Cost, $/kg</td>
<td>0.8-4.5</td>
<td>-</td>
<td>1.0-7.7</td>
<td>469-9996</td>
<td>5.7-22.7</td>
<td>36-143</td>
</tr>
<tr>
<td>Low Vapour Pressure</td>
<td>X</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>√√√</td>
<td>√√√</td>
</tr>
<tr>
<td>Environment friendly</td>
<td>X</td>
<td>X</td>
<td>-</td>
<td>X</td>
<td>√√√</td>
<td>√√√</td>
</tr>
</tbody>
</table>

\[
CO_2 + NH_2CH_2COO^- \Leftrightarrow -OOCNH_2^+CH_2COO^-
\]

\[
-OOCNH_2^+CH_2COO^- + B^- \Leftrightarrow -OOCNHCH_2COO^- + HB
\]

\[
-OOCNHCH_2COO^- + H_2O \Leftrightarrow NH_2CH_2COO^- + HCO_3^-
\]

\[
+NH_3CH_2COO^- + H_2O \Leftrightarrow NH_2CH_2COO^- + H_3O^+
\]

- equilibrium based
- instantaneous rate based
Experiment setup

ANLEC RIG — UNO-MK3 process

Absorber: 4.25m, three packing, each packing 0.8m
Regenerator: 3.45m, three packing, each packing 0.765, 0.82, 0.83m
Super mini ring (SMR), 3.48sqcm/cc
Performance indicators

- Performance of the absorber

\[
CO_2 \text{ absorption rate} = \frac{V_{\text{rich}} *[K^+]_{\text{rich}} * L_{\text{rich}} - V_{\text{lean}} *[K^+]_{\text{lean}} * L_{\text{lean}}}{M_{CO_2}}
\]

- Performance of both absorber and stripper

\[
CO_2 \text{ recovery rate} = \frac{\text{mole flow rate of } CO_2 \text{ in feed gas} - \text{mole flow rate of } CO_2 \text{ in clean gas}}{\text{mole flow rate of } CO_2 \text{ in feed gas}}
\]

- Energy consumption

Heat consumption for CO\(_2\) regeneration = \[
\frac{\text{Heat duty of reboiler, MW}}{\text{mass flow rate of } CO_2 \text{ in feed gas} * CO_2 \text{ recovery rate, kg/s}}
\]
CO₂ absorption rate upgrade with promoter under different CO₂ feed concentrations

Unpromoted K₂CO₃ solvent: 5%-10% absorption rate at 10% CO₂ feed concentration

With glycine: as high as 98%
Effect of CO$_2$ feed concentrations and liquid to gas ratios

- Higher CO$_2$ partial pressure enables better absorption
- CO$_2$ recovery rate increases almost linearly with CO$_2$ feed concentrations
- Increase L/G ratio promotes CO$_2$ recovery rate
Effect of gas feed speed

Lower gas speed

- Longer residence time
- More CO$_2$ absorbed
- Higher CO$_2$ recovery rate

Feed gas flow rate, kg/hr

CO$_2$ recovery rate, %

L/G=5
40% K$_2$CO$_3$ + 10% Glycine
CO$_2$ molar concentration in feed gas=10%
CO\(_2\) recovery rate improvement potential

\[\text{CO}_2\text{ loading in lean solvent, mol-CO}_2/\text{mol-K}^+\] + \[\text{CO}_2\text{ recovery rate, }\%\] + 

\[\text{CO}_2\text{ loading in rich solvent, mol-CO}_2/\text{mol-K}^+\] +

0.45 0.50 0.55 0.60 0.65

0
10
20
30
40
50

\text{CO}_2\text{ loading in lean solvent, mol-CO}_2/\text{mol-K}^+

\text{CO}_2\text{ loading in rich solvent, mol-CO}_2/\text{mol-K}^+
**CO₂ recovery rate improvement potential**

High recovery rate over 90%

- L/G = 4
- 40% K₂CO₃ + 10% Glycine
- CO₂ molar concentration in feed gas = 10%

**CO₂ loading in lean solvent, mol-CO₂/mol-K⁺**

- L_lean = 0.34
- L_lean = 0.35
- L_lean = 0.40
- L_lean = 0.45

**CO₂ recovery rate**
Energy reduction potential — Reducing heat loss

Simulation results hint a lot of heat losses from the stripper.

Well insulation enables low energy consumption.

CO₂ loading in lean solvent is around 0.3 (0.9 in rich loading), 2.5 GJ/ton.

Energy reduction potential based on simulation analysis.
K$_2$CO$_3$ precipitating/crystallization process

Slurry with less water is sent to regeneration column
Particle size: 150-200 μm (stable operation)

40 wt% K$_2$CO$_3$ + 10% Glycine (Malvern Mastersizer 2000)
CO\textsubscript{2} regeneration heat consumption

Crystallization process, CO\textsubscript{2} regeneration heat consumption will be reduced by 40\%-50\%
Conclusions

• Compared to the unpromoted K$_2$CO$_3$ solvents, the solvents with the new promoter can significantly promote the CO$_2$ absorption rate in the absorber from around 5%-9% to as high as 98% when CO$_2$ concentration in feed gas is 10%. While, due to the upper pressure limit of the stripper, the CO$_2$ recovery rate in the new promoted K$_2$CO$_3$ solvent can only be enhanced by 2-3 times than that in the solution without promoters.

• CO$_2$ concentration or partial pressure in the feed gas will significantly influence the CO$_2$ recovery rate and energy consumption. It is shown that CO$_2$ recovery rate will be improved from around 15% to around 40% by increasing CO$_2$ concentration in feed gas from 10% to 30%.

• Improving L/G also enhances the CO$_2$ recovery rate and thereby decreases the heat consumption for CO$_2$ regeneration.

• At high gas speed 20-30 kg/h, decreasing the gas speed of the feed gas can improve the CO$_2$ loadings in rich solvent slightly and thereby the CO$_2$ recovery rate. At low gas speed 10-20 kg/h, low gas speed enables much better CO$_2$ recovery rate.
Conclusions

• Solvent analysis shows that the temperature of the regenerator at current operations (~127 °C) is not enough to get enough, as expected, lean solvents, and thereby the higher CO₂ recovery rate and lower energy consumption for CO₂ regeneration cannot be obtained.

• It is not a problem to get 90% CO₂ recovery rate for post-combustion CO₂ capture using the new promoted K₂CO₃ solvents. It can be inferred from current data that if CO₂ loadings in rich and lean solvents could be 0.50-0.65 and 0.30-0.35, the CO₂ recovery rate of 90% could be obtained.

• Crystal formation was observed using 45 wt% potassium carbonate solvents with 10% promoters or at high CO₂ concentrations in feed gas (around 25%). With the use of precipitating process developed by The University of Melbourne, the energy consumption for CO₂ regeneration can be reduced to around 2 GJ/ton-CO₂ for CO₂ capture from the flue gas of the power plant, which is around 40%-50% lower than that using the traditional amine based solvents.
Acknowledgement

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Future considerations

• The decomposition temperature of the potassium carbonate solvents with the new promoter is higher than that was expected (~127 °C). New design of the reboiler is needed to get the stable higher temperature of the regenerator. Reboilers with multiple or continuous stages and new stripper resistant to higher pressure are recommended.

• New packing of both the absorber and regenerator with higher specific surface area can be tested to make the absorption and stripper more efficiently and thereby reduces the size of equipment.

• There are large amount of heat losses of current heater and stripper. Better insulation is needed to reduce the heat consumption.

• The precipitation performance of KHCO₃ needs further tests and investigations to decrease the energy consumption of the CO₂ regeneration.