Research on CO$_2$
Condensation Technology

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## Global CO₂ Emission

<table>
<thead>
<tr>
<th>Country</th>
<th>CO₂ Emission (Mtc)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>1990</td>
</tr>
<tr>
<td>USA</td>
<td>1345</td>
</tr>
<tr>
<td>China</td>
<td>620</td>
</tr>
<tr>
<td>Former USSR</td>
<td>1034</td>
</tr>
<tr>
<td>Japan</td>
<td>274</td>
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<tr>
<td>World</td>
<td>5836</td>
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</table>

# CO₂ Emission in China

<table>
<thead>
<tr>
<th></th>
<th>Total</th>
<th>Coal</th>
<th>Petroleum</th>
<th>Natural Gas</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Mtc</td>
<td>Mtc</td>
<td>%</td>
<td>Mtc</td>
</tr>
<tr>
<td>1990</td>
<td>620</td>
<td>514</td>
<td>82.9</td>
<td>98</td>
</tr>
<tr>
<td>1996</td>
<td>801</td>
<td>625</td>
<td>81.4</td>
<td>138</td>
</tr>
<tr>
<td>1997</td>
<td>822</td>
<td>661</td>
<td>80.4</td>
<td>148</td>
</tr>
<tr>
<td>2001</td>
<td>832</td>
<td>668</td>
<td>80.3</td>
<td>151</td>
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<tr>
<td>2010</td>
<td>1,109</td>
<td>1,115</td>
<td>76.5</td>
<td>277</td>
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CO$_2$ Condensation

- CO$_2$ Separation from Flue Gas
- O$_2$/CO$_2$ Combustion
- IGCC
- PGCC
Part 1
Research on CO$_2$
Separation
CO$_2$ Capture

- Adsorption of the gas by use of molecular sieves
- Physical absorption
- Chemical absorption
- Low temperature (cryogenic) processes
- Membranes
PF+FGD
Adsorption

Typical layout of a carbon dioxide (adsorption) capture plant.
Membranes

Principles of gas separation and gas absorption utilizing membranes
Physical absorption using Selexol is the most appropriate technique to remove $\text{CO}_2$ – $\text{CO}_2$ Wheel
Chemical absorption

CO₂ Capture using Amine Based Systems
Removal CO2 by NH3 Scrubbing for Urea Production

\[ \text{NH}_3(\text{l}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4\text{HCO}_3(\text{s}) \]

- US DOE—Win-WIN Scheme for CO2 Sequestration via Aqua Ammonia Scrubbing—28% Amonia capture 97% CO2
- SETRC of China and Tsinghua University make experimental research.
Removal CO2 by NH3 Scrubbing for Urea Production

1. N2 Cylinder
2. CO2 Cylinder
3. NH3 Cylinder
4. Mass flow Controller
5. Electronic Heater
6. Temperature Controller
7. Reaction Column
8. Gas Analyzer

Fig. 1. Schematic diagram of CO2 by ammonia solution scrubbing.
Integration of CO2 sequestration through NH4HCO3 Production

\[
2\text{CO}_2 + \text{N}_2 + 3\text{H}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{NH}_4\text{HCO}_3 \downarrow \quad \Delta_r G^\circ = -86.18 \text{ kJ/mol}
\]

\[
\text{CO}_2 + \text{N}_2 + 3\text{H}_2 \rightarrow (\text{NH}_2)_2\text{CO} \downarrow + \text{H}_2\text{O} \quad \Delta_r G^\circ = 31.34 \text{ kJ/mol}
\]
Cryogenic Processes--Frosting

Cryogenic methods for CO₂ capture options – Ecole de Mine de Paris, France
Scheme of CO$_2$ Sequestration by Membrane Contactor
10NM³/H Test Facility
Shape and Structure of the Polypropylene Hollow Fiber Membrane
Characteristics of Membrane

- Average diameter of micropores: $0.02 \times 0.2\mu m$
- Porosity: 35-50%
- Longitudinal tensile strength: $> 120\text{MPa}$
- Rapture strength: $> 1.0\text{MPa}$
- Gas permeation rate: $2.0 \times 10^{-2}\text{cm}^3(\text{STP})/\text{cm}^2\cdot \text{s} \cdot \text{cmHg}$
CO2 Sequestration Process

Hollow Fiber Membrane Contactor

Gas

Absorption Liquid

Absorption

Liquid

Flue Gas
Effect of Absorption Liquid Temp. on CO2 Sequestration Eff.
Effect of Absorption Liquid Concentration on CO2 Sequestration Eff.
Effect of Flue Gas Velocity on CO2 Sequestration Eff.

- 1mol/L of MEA
- 2mol/L of MEA

Removal Eff. (%) vs. Flue Gas Velocity (m/s)
Pressure Drop

Flue Gas Velocity (m/s)

Pressure Drop (Pa)
CO₂ Removal From Conventional PCF Power Plant
Part 2

O₂/CO₂ combustion system
Advantages of Oxygen Rich Combustion

- Using O$_2$/CO$_2$ mixture in combustion system, raising CO$_2$ content to 95%
- Not necessary to separate CO$_2$ from flue gas
- Improvement in boiler efficiency
- Reduction SOx, NO$_x$ emission
- Simplification of flue gas treatment
O₂/CO₂ Combustion Process

- Pulverized Coal
- Air Separation
- Boiler
- Flue Gas Recycling
- Ash Removal
- CO₂ Recovery
Test Facility

流化床
Combustion Efficiency
SO\textsubscript{2} Emission

- **SO\textsubscript{2} Removal Eff. (%)**
  - Air-FB
  - O\textsubscript{2}/C\textsubscript{O}\textsubscript{2}-FB
  - Air-CFB

- **Ca/S molar rate**

- **u (m/s)**

Graphs showing the relationship between SO\textsubscript{2} removal efficiency and Ca/S molar rate, as well as the effect of air velocity on SO\textsubscript{2} removal for different fluidization methods.
Nox Emission

- Bed Temperature (K)
- NOx (ppm)
- Air-FB
- O2/CO2-FB
- Air-CFB

- Primary/Total Flow Rate
- NOx (ppm)
- Air-FB
- O2/CO2-FB
- Air-CFB
75t/H Oxygen Enriched Combustion CFB Boiler
Part 3

IGCC
IGCC2

1. **Waste Water Treatment**
2. **Gasifier**
3. **Gas Cleanup**
4. **Expander**
5. **Combustion Chamber**
6. **Heat Recovery Steam Generation**
7. **Steam Turbine**
8. **Stack Gas**

**Process Flow**
- **Coal** to **Gasifier**
- **Raw Fuel Gas** to **Gas Cleanup**
- **Clean Fuel Gas** to **Expander**
- **G** to **Combustion Chamber**
- **CO₂** from **Heat Recovery Steam Generation**
- **Steam** from **Steam Turbine**
- **Stack Gas**

**Materials and Components**
- **Water**
- **Nitrogen**
- **Oxygen**
- **Slag**
- **Moisture**
- **Air Separation Unit**
- **Compressor**
- **Gas Turbine**
- **Heat Recovery Steam Generation**

Part 4
PGCC
Gasification

**Oxygen**

Coal

Gasifier → Hot Gas → Heat Exchanger, Clean System → Clear Gas

Gas Turbine → Generator

Flue Gas

Semicoke

Steam

Gasifier → Semicoke → Combustor → Steam

Steam Turbine

Steam

Generator

Clear System
Part 5

Near–zero Emission or Chemical Looping Gasification
Near zero emissions coal utilization technology with combined gasification and combustion

Chemical Looping Gasification (CLG)
Near zero emissions coal utilization technology with combined gasification and combustion
CFB Gasifier:

CO₂ acceptor gasification process (~25bar)

Main reactions in gasifier:

\[ \text{C+H}_2\text{O}=\text{CO+H}_2-131.6\text{kJ/mol} \]
\[ \text{CH}_4+\text{H}_2\text{O}=\text{CO+3H}_2-206.3\text{kJ/mol} \]
\[ \text{CO+H}_2\text{O}=\text{CO}_2+\text{H}_2+41.5\text{kJ/mol} \]
\[ \text{CaO+CO}_2=\text{CaCO}_3+178.1\text{kJ/mol} \]
\[ \text{H}_2\text{S+CaO}=\text{CaS+H}_2\text{O} \]
CFB Combustor

Char combustion
CaCO₃ calcination
Hydrogen combustion

Main reactions in CFB combustor:

\[
\text{CaCO}_3 = \text{CaO} + \text{CO}_2 - 178.1 \text{kJ/mol}
\]
\[
\text{C} + \text{O}_2 = \text{CO}_2 + 393.791 \text{kJ/mol}
\]
\[
\text{H}_2 + \frac{1}{2}\text{O}_2 = \text{H}_2\text{O} + 286 \text{kJ/mol}
\]
Advances:

- Reduce the requirements on gasification. Only part of coal with high activity is gasified and the char with lower activity is burned in CFB combustor.

- Realize Anaerobic Hydrogen Production with CO2 acceptor gasification and high concentration CO2 for disposal in combustor

- Realize near zero emission: few NH3 generating during gasification may be removed easily, H2S is captured by CaO in gasifier and transformed into CaSO4 in the combustor. Other pollution gas may be disposal together with CO2 gas stream.
Advances:

- System is simplified by applying two circulating fluidized bed reactors.
- Lower operation pressure (20~30 bar) reduce the difficulties and cost.
- High efficiency with applying SOFC.
**Efficiency calculation for a sample**

- **Power generation:** 400MW
- **Coal gasification ratio:** 0.7
- **Operation Pressure:** 25bar

<table>
<thead>
<tr>
<th>Proximate analysis/w%, ar</th>
<th>Ultimate analysis/w%, ar</th>
<th>Heat value/MJ/kg, Q_{dw}</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>V</td>
<td>A</td>
</tr>
<tr>
<td>2.7</td>
<td>25.17</td>
<td>21.62</td>
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<tr>
<td>Item</td>
<td>Calculation</td>
<td></td>
</tr>
<tr>
<td>-------------------------------------------------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>Coal feed rate (kg/s)</td>
<td>18.35</td>
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<tr>
<td><strong>Operation Pressure (bar)</strong></td>
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<tr>
<td>Temperature in the gasifier (K)</td>
<td>1205</td>
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<tr>
<td>Heat loss of the gasifier (kJ/s)</td>
<td>3120.93</td>
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<td><strong>Coal gasification ratio</strong></td>
<td>0.7</td>
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<tr>
<td>Hydrogen production rate (kmol/s)</td>
<td>1.42</td>
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<td><strong>Pressure in combustor (bar)</strong></td>
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<tr>
<td>Temperature in the combustor (K)</td>
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<td>Heat loss of the combustor (kJ/s)</td>
<td>1482.44</td>
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<td>Excess oxygen ratio</td>
<td>1.1</td>
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<td>Limestone supplement (kg/s)</td>
<td>4.25</td>
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<tr>
<td>Fuel utilization ratio in the SOFC (%)</td>
<td>85</td>
<td></td>
</tr>
<tr>
<td>Oxygen utilization ratio in the SOFC (%)</td>
<td>51</td>
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<tr>
<td>Power generation from the SOFC (kW)</td>
<td>269208.48</td>
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<tr>
<td>Efficiency of gas turbine cycle (%)</td>
<td>59</td>
<td></td>
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<tr>
<td>Power generation from the gas turbine (kW)</td>
<td>152115.31</td>
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<td>Efficiency of steam turbine cycle (%)</td>
<td>28</td>
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<td>Power generation from the steam turbine cycle,kw</td>
<td>3956.7</td>
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<td>Power consumption of the air separation (kW)</td>
<td>25955</td>
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<td>Power consumption of the air compressor, kw</td>
<td>99821.12</td>
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<tr>
<td><strong>Net Power generation (kW)</strong></td>
<td>413538.88</td>
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<tr>
<td><strong>System efficiency (%)</strong></td>
<td>66.52</td>
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Effect of gasification ratio and operation pressure

![Graph showing the effect of gasification ratio and operation pressure on system efficiency.](image)
Experiments on char combustion in an atmosphere Fluidized bed combustor
Char combustion in different reaction atmosphere.

- O₂/CO₂ = 61/39%
- O₂/CO₂ = 45/55
- O₂/CO₂ = 31/69
- Air: O₂/CO₂ = 11/89

The graph shows the carbon conversion rate over time for each reaction atmosphere.
## GE Current Options

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<thead>
<tr>
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<th>IGCC</th>
<th>SCPC</th>
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<tbody>
<tr>
<td><strong>Capital</strong></td>
<td>$1,450</td>
<td>$1,225</td>
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<tr>
<td><strong>Emissions</strong></td>
<td></td>
<td></td>
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<tr>
<td>- NO</td>
<td>0.02</td>
<td>0.02</td>
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<tr>
<td>- SO2</td>
<td>0.01</td>
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<tr>
<td>- PM</td>
<td>0.005</td>
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<td><strong>Efficiency</strong></td>
<td>40%</td>
<td>40%</td>
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<tr>
<td><strong>Fuel Flexibility</strong></td>
<td></td>
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<tr>
<td>Feedstocks</td>
<td>All Coals plus liq. &amp; solid opportunity fuels</td>
<td>Low sulfur (compliance) coals favored</td>
</tr>
<tr>
<td><strong>COE (1st Year)</strong></td>
<td>$4.22</td>
<td>$3.94</td>
</tr>
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</table>
1. Pure Oxigen Combustion

2. $O_2 / CO_2$ Combustion
   ---- Combustor need to be change

3. Shift Syngas to $H_2 + CO_2$, Then Separate $CO_2$ with MEA or Frosting

4. Separation of Flue Gas

5. Similar with Version 21
Compare of IGCC, SCPC + Seperation and O₂ / CO₂ Combustion

1. Retrofit of IGCC
2. O₂ / CO₂ Combustion
3. Separation of Flue Gas
1. Capacity: $2 \times 1000$ MW
2. Capital: 8388.05 Million RMB
3. Capital per KW: 508 $/KW$
4. Coal: Shenfu Dongshen Coal
5. Boiler: 520 Million/Unit
6. Efficiency: 45.16%
7. Coal Consumption: 272 g/kW·h
8. Ratio of Electricity used by Plant: 6.5%
9. COE: 0.392 RMB/kW·h

Compare of IGCC, SCPC + Separation and $O_2/CO_2$ Combustion
With Membrane for CO2 Separation
1. Velocity in the Membrane 0.2m/s,
2. Size of Absorber 90M*90m*90m
3. Price of Membrane: 20yuan/m²,
4. Total area of Membrane: 0.58 Million m²
5. Cost of 2 Separator: 240 Million RMB
6. Cost of the Total System: 600 Millions
7. Separation Efficiency: 90%
8. Capital per KW: 72.7 $/KW
9. COE: increased 0.165 RMB/Kwh
10. Total COE: increased 0.172RMB/Kwh
Compare of IGCC, SCPC + Separation and O₂ /CO₂ Combustion

With CO₂/O₂ Combustion for CO₂ Condensation

1. System for Oxygen 1760 Million RMB
2. Total Cost of Retrofit: 2000 Millions RMB
3. Cost per ton CO₂ RMB/ton CO₂
4. Capital per KW: 242 $/KW
5. COE: increased 0.108 RMB/Kwh
6. Total COE: increased 0.131 RMB/Kwh
Conclusion

- Condensation technology for the CO$_2$ need to be evaluated,
- Utilization of CO$_2$ is a best way for CO$_2$ control, need to be form the cycle—Cycle Economy
Thank You Very Much!