Overview on 1\textsuperscript{st} and 2\textsuperscript{nd} generation coal-fired membrane power plants (with and without turbo machinery in the membrane environment)

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Contents

• A membrane application of today: CO₂ separation from natural gas

• Coal-fired membrane power plants (MPPs) – Classification

• Several concepts in development - 1st generation MPPs:
  Compressors required for membrane operation

• “IG-SWEEP-JÜL” - Opening the road to 2nd generation MPPs
  → w/o additional turbo machinery in the membrane environment
  → Driving force by dilution of H₂ into a sweep gas (in modified IGCC)
CO$_2$ Removal from Natural Gas by Polymer Membranes

Arian Nijmeijer / SHELL
One of the industrial partners of FZJ in the HGF Alliance MEM-BRAIN

Institute of Energy Research – Fuel Cells (IEF-3)
CO₂ Removal from Natural Gas (CH₄)

Example:
NG 100 bar
CO₂ 10 mol%

CO₂ Membrane environment

p_CO₂ = 10 bar

Retentate

no vacuum pump

Permeate 1 bar

"Pure" CO₂

p ~ p_CO₂ = 1 bar

Natural “driving force“ for permeation

No el. energy is needed

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Natural Driving Force in Membrane Power Plants?
Post-combustion: Membrane + Vacuum Pump

**Transport law for polymer and porous ceramic membranes:**
Local CO₂ permeation flux density
= CO₂ permeability * Δp₂CO₂ (Feed side - Permeate side)

"Driving force" for permeation

**El. Power:**
106 kWh/t CO₂ separated for
CO₂ purity: 80 mol%
Vacuum: 30 mbar
(PRO/II simulation)

CO₂ liquefaction: ~100-130 kWh/t CO₂

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The Idea of a Sweep Gas: Driving Force by Dilution!? 

In a CO₂ Membrane environment:

- Flue gas enters with CO₂ at 140 mbar.
- No compressor is needed.
- No vacuum pump.
- Retentate has CO₂ at 0 mbar.

Sweep gas + CO₂ comes in at 50 mbar CO₂, but CO₂ dilution into a sweep gas produces impure CO₂ again!!!
besides post-combustion:

Driving Force by Dilution into a Sweep Gas in Membrane Power Plants?
Coal-Fired Membrane Power Plants
Classification
3 Capture Principles – 4 Membrane Gas Separation Classes

**Post-combustion**
- Combustion with air → CO₂ capture from FG

**Flue gas**
- N₂ → CO₂

+ Impurities
  - N₂ (O₂)
  - from membrane

**Oxyfuel**
- Coal + O₂ → O₂ separation from air
  - Combustion with O₂
  - Cooling by CO₂ recycling

**H₂O + CO₂ + Impurities**

**Pre-combustion/H₂ or /CO₂**
- Partial oxidation (gasific.)
  - CO shift to CO₂
  - → H₂ or → CO₂ separation
  - H₂ combustion

**Shifted coal gas** (pressurized)

Special polymer membranes:
The larger molecule permeates!
Separated Gas Components: Pure or Diluted

<table>
<thead>
<tr>
<th>Post-combustion</th>
<th>Flue gas</th>
<th>Oxyfuel</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ pure</td>
<td>N₂</td>
<td>O₂ pure</td>
</tr>
<tr>
<td>CO₂ diluted</td>
<td>CO₂</td>
<td>O₂ diluted</td>
</tr>
</tbody>
</table>

Air

Dilution of O₂ or H₂ → 2 Chances for successful sweep !!!

Dilution of CO₂ → impure CO₂ again → no chance for successful sweep !!!

Pre-combustion / H₂-sep

H₂ pure

Pre-combustion / CO₂-sep

CO₂ pure

CO₂ multiplied

H₂ dilution

H₂ diluted
### 3 Capture Principles – 3 Technology Platforms

6 Capture classes are of interest for MPPs

<table>
<thead>
<tr>
<th>Pre-comb/H₂ or /CO₂</th>
<th>Oxyfuel</th>
<th>Post-combustion</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Coal</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SPP (Steam Power Plant)</td>
<td>not possible</td>
<td></td>
</tr>
<tr>
<td>IGCC</td>
<td>not possible</td>
<td></td>
</tr>
<tr>
<td>IGCC+Shift/H₂GT</td>
<td>not the best solution</td>
<td></td>
</tr>
</tbody>
</table>

**IGCC:** Integrated Gasification Combined Cycle

**Pre-combustion**

- **Coal**
  - **SPP (Steam Power Plant)**
  - **IGCC**
  - **IGCC+Shift/H₂GT**

**Oxyfuel**

- **SPP / Oxyfuel**
  - **2**
- **IGCC / Total-oxyfuel**
  - **4**
- **IGCC+… / Pre-c.**
  - **5 and 6**

**Post-combustion**

- **SPP / Post-comb.**
  - **1**
- **IGCC / Post-comb.**
  - **3**
- **not the best solution**
  - **not the best solution**
Class 2

SPP / Oxyfuel
3 Measures for Driving Force in the Membrane

Feed side (air): Compressor / Expander

Permeate side (O₂): Vacuum pump

Permeate side: Sweep gas = Hot recycled flue gas

1. Pure O₂
   - “OTM-Clean”/Pressurized

2. Pure O₂
   - “OXYVAC-JÜL”

3. Diluted O₂
   - “OXYCOAL-AC”
"OXYVAC-JÜL": Permeate Compression (Vacuum Pump)

Basic variant: Some NG is burned for final air preheating

**PRO/II simulation:**

Δη = about -10 %p incl. liquefaction

**Source:**
Meulenberg, Baumann, Blum, Riensche: Deutsche Patentanmeldung 10 2007 056 841.1 (PT 1.2366) 23.11.2007
Institute of Energy Research – Fuel Cells (IEF-3)
“OXYCOAL-AC“: Sweep Gas & Compression

Advantage: High driving forces

Theoretical case: Sweep w/o compression
\( \frac{p_{O_2}^{\text{Feed}}}{p_{O_2}^{\text{Perm}}} = 20:1 \) 70:1

\( p_{O_2}^{\text{Feed}} = 4000 \) 2000 mbar
\( p_{O_2}^{\text{Perm}} = 200 \) ~30 mbar

\( O_2: \sim 200 \text{ mbar in air} \)
\( \sim 200 \text{ mbar in sweep gas} \rightarrow \text{Driving force missing} \)

Reason: Air ratio low (\( \lambda \sim 1 \)) in SPPs
\( \rightarrow \) small flow rates of cooling media
\( \rightarrow \) small flow rates for sweep gases

\( \Delta \eta = \text{about } -9 \% \text{ p incl. liquefaction} \)
[Beggel (RWTH) 2008]
Class 4

IGCC / Total-oxyfuel

For O$_2$ membranes
IGCCs have a potential for large sweep gas streams.
Concepts may be developed in future.
Class 5
IGCC+Shift/H2GT / Pre-comb./H2-sep
Pre-combustion: Pure H₂ is Separated - Combined with Recompression

Standard membrane concept

Pressure level of all process gases: 25 bar except H₂ permeate

Energetic losses:
- Excess steam for shift
- H₂ recompression !!!

Δη ~ -10 %-points
[Göttlicher, VDI-Ber. 421, 1999]

for sweep too much O₂
2nd GENERATION MEMBRANE PP CONCEPT:

WITHOUT ADDITIONAL TURBO MACHINERY IN THE MEMBRANE ENVIRONMENT
Membrane Operation w/o Energy Supply

H₂ dilution by sweep gas w/o O₂

Sources:
Menzer, Riensche, Peters, Blum, Scherer: Deutsche Patentanmeldung DE 10 2008 01 17 71.4, 26.02.2008

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IGCC Modified to “IG-SWEEP-JÜL“
Stoichiometric combustion & Recycling of the flue gas: N₂ (O₂-free)

Pressure level of all process gases: 25 bar
Membrane in “IGSWEEP-JÜL“ - H₂ Partial Pressure Profiles

High ratio: Sweep gas / permeated H₂ ~ 4:1 mol/mol !!!

Highest H₂ separation degrees possible !!!

Sweep gas = 4N₂ (no H₂ !!!)
Conclusions

• “Natural driving forces” for permeation do not exist in MPPs, if pure gas components are separated (CO₂, O₂, H₂): Compressors consume much energy (comparable to CO₂ liquefaction).

• “IG-SWEEP-JÜL” opens a new PP route of 2nd generation MPPs with “energy-free” dilution of permeating H₂ (or O₂) into a sweep gas.

• Large sweep gas streams are required and could be found in IGCC modifications w/o significant additional energy demand.

• The total efficiency penalty may approach 5 %-points (after optimization):
  - capture ~1 %p (parasitic losses)
  - liquefaction 4 %p
Coal power plants: ~40% of anthropogenic CO₂ emissions !!!

We need: worldwide acceptable CCS
“energy-free” capture
optimal membrane integration

THANK YOU FOR YOUR ATTENTION
Appendix
What is an Acceptable Capture Technology?

1. High CO₂ purity!
   - In discussion:
     - CO₂ > 80 mol% ???
     - CO₂ > 90 mol% (work hypothesis here)
     - CO₂ > 95 mol% (MEA as benchmark)

2. Low efficiency losses!
   - Hypothesis for successful CCS:
     - All nations of the world may accept year by year
     - 10% more coal input or
     - 10% loss in power production, but not more.
     - η ~ 50% for modern PPs
   - Acceptable Δη: -5 % points (CCS)
   - Compression: Δη = -3 to -4 % points [literature]
   - For capture:
     - Acceptable Δη: -1 to -2 % points
Fossil-Fired Power Plants w/o Capture

- **NG Boiler**
  - Only a few exist
  - Natural gas combustion
  - ST: Steam Turbine

- **NGCC**
  - NG Combined Cycle
  - Natural gas combustion
  - GT: Gas Turbine, η high ~58%

- **Oil Fired PPs**
  - Only a few exist
  - Atmospheric combustion
  - ST: Steam Turbine, η ~45%
  - Mean η world ~30%

- **SPP**
  - Steam Power Plant
  - Pressurized combustion
  - ST: Steam Turbine, not realized in large scale

- **SPP pressurized**
  - Not realized

- **IGCC**
  - Integrated Gasif. CC
  - Only a few exist
  - Pressurized gasification
  - CO, H₂ and O₂
  - Pressurized combustion
  - GT: Gas Turbine, η high ~50%
  - ST: Steam Turbine

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The Idea of a Sweep Gas for CO₂ Dilution

A tricky solution, if
• sweep gas available (p=1 bar or <1 bar)
• flowrate sufficient large
• sweep gas suitable for the membrane and
• [sweep gas + permeate] are “welcome“ downstream
but
• for Post combustion no sweep gas is found up to now
But How to Remove CO₂ from Atmospheric Flue Gas ???

General question in membrane plant development: Are there other ways besides energy consuming compression to realize a positive “driving force“ ???

CO₂ dilution in air ???

Basic steam power plant

Flue gas

CO₂ Membrane environment

p = 1 bar
pCO₂ = 140 mbar
Retentate

no compressor

Air

pCO₂ = 0.3 mbar

Air (O₂, N₂)

Coal

Air

λ~1

CO₂
Low Driving Force for Permeation even at Membrane Inlet

Feed pressure 1 bar
Permeate pressure 30 mbar

Driving force for CO₂ decreases, but not for N₂

Driving force
membrane inlet
110 mbar

Driving force
membrane outlet
40 mbar

CO₂ partial pressure
140 mbar
30 mbar
0

CO₂ separation degree
0 50% 100%

Driving force for CO₂ decreases, but not for N₂
CO₂ Impurities – Strongly Important in a Large Oxyfuel Plant

Flue gas: CO₂, H₂O, O₂, N₂

Coal → ASU → Flue gas

1 bar

Compression

Pipeline

CO₂ to compr.

Steam generator

Coal

O₂ content: 4-8 mol%

Air leakage

N₂ < 1 mol%

Remark

is target for an excellent O₂ membrane

[MEMBRAIN proposal 2007]

Expected CO₂ purity: about 80-85 mol%

Compression → Pipeline

Source: Oxyfuel Conference, Cottbus, April 2007
“OTM-clean/Pressurized“ with Cold Flue Gas Recycling

Air Preheating in Steam Generator

**Disadvantage:** Low driving forces

<table>
<thead>
<tr>
<th>( p_{O_2}^{Feed} )</th>
<th>( p_{O_2}^{Perm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 bar</td>
<td>1 bar</td>
</tr>
<tr>
<td>2 bar</td>
<td>1 bar</td>
</tr>
</tbody>
</table>

OTM-clean

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IGCC/Total-Oxyfuel: O₂ Gasification & O₂ Combustion
Advantage: 1-stage capture w/o CO shift

Vision for Membrane PPs
For O₂ membranes large CO₂ sweep gas streams would be available (pressurized):
→ $p_{O_2}(Feed) / p_{O_2}(Permeate) = 21/12 \approx 2:1$ !!!

[ Göttlicher, VDI-Ber. 421, 1999]

Source: after SIEMENS, Pictures of the Future, Spring 2008
Institute of Energy Research – Fuel Cells (IEF-3)
Transport Mechanisms of Inorganic Membranes

“Dense“ membranes can perfectly select O₂ and H₂ electrochemically

- Multi-layer and/or specific adsorption: carbons, zeolites, amorphous SiO₂
- Molecular Sieves: zeolite, carbons, amorphous SiO₂
- Ionic transport (solid electrolytes): O²⁻, H⁺ in perovskites
- Atomic transport of H: metals, e.g. Ag/Pd, Nb, V, Ta

MIEC: Mixed Ionic Electronic Conductor, O₂/N₂ selectivity ~100,000:1 !!! (theoretically)

150 – 400°C
800 – 1000°C

MPEC: Mixed Protonic Electronic Conductor
500-800°C

After: Caro (Univ. Hannover) 2007