Understanding the Potential of CCS in Hydrogen Production
(Review of Current State-of-the-Art)

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Acknowledgement

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  • Guido Collodi
  • Giuliana Azzaro
  • Noemi Ferrari
Presentation Outline

• Overview to the production of hydrogen
• $H_2 / \text{HyCO from Fossil Fuel – Technology Option}$
• Capture Options for SMR
• Review of On-going Pilot & Demo Projects
• Summary and Concluding Remarks
World’s Hydrogen / HyCO Production (Key Facts)

- Hydrogen is a key raw materials for various industries.
  - Hydrogen used could be in the form of high purity hydrogen (i.e. with greater than 99+% purity), or a mixture of hydrogen and carbon monoxide also known as HyCO gas.

- Nearly 90% of global H₂ or HyCO consumption
  - Ammonia/Urea, Methanol and Oil Refining

- Other large users of H₂ or HyCO
  - metal (i.e. DRI production), glass, food, electronics, space/aeronautic, fuel production (i.e. GTL), and other chemical & petrochemical industries (i.e. H₂O₂ production, paint)
World’s Hydrogen / HyCO Production (Key Facts)

- Around 95% of the H₂ or HyCO produced is obtained from fossil fuels (natural gas, refinery off-gases, heavy refinery residues, petcoke, coal, and others).
- Other sources could include water (via electrolysis), renewables, as well as by-product from other chemical processes.
- Conversion of fossil fuels to hydrogen also produces significant amount of CO₂ as by-product.
- Most of the modern hydrogen production facilities have already achieved efficiency that could reduce CO₂ emissions down to nearly 10% above its theoretical minimum.
H₂ Production from Fossil Fuel

**STEAM METHANE REFORMER (SMR)**
(Natural Gas or Other Light Hydrocarbons)

- Air
- Fuel
- Feedstock & Steam
- Synthetic Gas (Syngas)
  - ~70%v H₂, 15-45 Bar & ~850°C
- Flue Gas

**AUTOTHERMAL REFORMER (ATR)**
(Natural Gas or Other Gaseous Hydrocarbons)

- Oxygen
- Feedstock & Steam
- Synthetic Gas (Syngas)
  - ~65%v H₂, 40-100 Bar & ~1000°C

**PARTIAL OXIDATION (POX)**
(All Feedstock – NG to Coal)

- Oxygen
- Feedstock
- Synthetic Gas (Syngas)
  - ~50%v H₂, 40-100 Bar & ~1400°C
## H₂ Production from Fossil Fuel

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>SMR</th>
<th>ATR</th>
<th>POX</th>
</tr>
</thead>
<tbody>
<tr>
<td>NG to light HC</td>
<td><strong>Bar(g)</strong> 15-40</td>
<td><strong>30-50</strong></td>
<td><strong>40-80</strong></td>
</tr>
<tr>
<td>NG to Gaseous HC</td>
<td><strong>950-1050</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NG to Coal</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pressure</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td><strong>750-950</strong></td>
<td><strong>950-1050</strong></td>
<td><strong>1200-1400</strong></td>
</tr>
<tr>
<td>Steam/Carbon Ratio</td>
<td>mol/mol 1.8-3.0</td>
<td>1.0-2.0</td>
<td>0.1-0.5</td>
</tr>
<tr>
<td>Syngas Composition (from reactor before shift)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂/CO Ratio</td>
<td>mol/mol 3.5-5.5</td>
<td>2.5-3.5</td>
<td>1.5-2.0</td>
</tr>
<tr>
<td>H₂ mol% (dry)</td>
<td>68-73</td>
<td>63-65</td>
<td>35-45</td>
</tr>
<tr>
<td>CO₂ mol% (dry)</td>
<td>7-10</td>
<td>30-35</td>
<td>6-20</td>
</tr>
<tr>
<td>CH₄ mol% (dry)</td>
<td>2-6</td>
<td>1-3</td>
<td>0.2-1</td>
</tr>
</tbody>
</table>
H₂ Production from Fossil Fuel

- SMR is the most dominant H₂ production from fossil fuel (NG, light HC, Naptha).
  - Tuapse Refinery (Russia) - largest single train SMR @ ~240k Nm³/h H₂ supplied by Technip

- ATR is considered economical for large Syngas Production
  - Oryx GTL (Qatar) - largest single train ATR @ ~ 577k Nm³/h syngas for FT Process supplied by Haldor Topsoe

- POX are predominantly solid HC (coal, petcoke and other refinery residues) base H₂ / Power / Syngas production. Gas based POX are limited in numbers worldwide.
  - Linde’s La Porte POX Facility (USA) – largest single train gas based POX @ ~200k Nm³/h HyCO for chemical (methanol & others) production based on Shell Gasifier
SMR without CO₂ Capture
(Data from Amec FW)

Flue Gas (atm.)
CO₂ 19-20%

Raw Syngas (~23 Bar)
CO₂ 7-10%
CO 12-19%
CH₄ 2-6%

Shifted Syngas (~22 Bar)
CO₂ 15-16%
CO 4-5%
CH₄ 3-4%

Feedstock
Steam

Steam Reforming

Shift

PSA (H₂ Purification)

H₂ (99.9+%)
By firing H₂ fuel instead of NG/light HC, CO₂ Capture of ~90% could be achievable for options #1 and #2.
CO$_2$ Capture Technologies

- Chemical Absorption
  - MEA, MDEA, Benfield Process, etc…
- Physical Absorption
  - Selexol, Rectisol
- Adsorption
  - PSA, VPSA
- Low Temperature ("Cryogenic") Process
- Membrane
- Others…
Review of Large Scale / Demo CCS Projects for Gas Based H₂ Production

• Large scale demo project
  • AP Port Arthur Project (USA)
  • Shell Quest Project (Canada)

• Large scale pilot project
  • Japan CCS Tohokamai Project (Japan)
  • AL Port Jerome Project (France)
Review: Port Arthur Project

- **H₂ Plant – SMR**
  - Merchant plant owned and operated by Air Products
  - Consists of 2 Trains of SMR

- **OTF supplier**
  - Providing H₂, steam & electricity to Valero Refinery
Air Products’ Gulf Coast Hydrogen Pipeline Network - 2012

<table>
<thead>
<tr>
<th>APCI H₂ Plants</th>
<th>USGC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity</td>
<td>1.2+ BSCFD</td>
</tr>
<tr>
<td>Pipeline Length</td>
<td>~ 600 miles</td>
</tr>
</tbody>
</table>
Process Flow Diagram of Port Arthur II SMR Plant
(Figure from Air Products)

Notes:
PSA = pressure swing absorber
SCR = selective catalytic reduction
SMR = steam methane reformer
Port Arthur CO₂ EOR Project

• US DOE funding:
  • Granted $284 MM (66% of Total Cost - ~$430MM) under the Industrial CCS Demo Programme

• Other Key Information
  • Construction started in Aug. 2011 (site prep. et. al.)
  • CO₂ Capture from Port Arthur II online in Dec. 2012 and Port Arthur I online in Mar. 2013. (Full capacity achieved in Apr. 2013)
  • ~1.0 million tpy CO₂ is captured (50 MMscfd)
  • CO₂ recovery is >90% and CO₂ purity is >97%
Simplified Block Flow Diagram

Port Arthur 2 Facility

- Natural Gas
- Utilities
- HP Steam Export
- Power Export

Existing SMR (note 1)

- Purge Gas
  - Export Hydrogen

- Syngas
  - CO₂ Removed
  - Export CO₂

New VSA

- Wet CO₂
  - New Compressor/Drier

New COGEN

- Steam/Power

Note 1: Burner and Other Retrofits Required

Port Arthur 1 Facility

- Natural Gas
- Utilities
- HP Steam Export
- Power Export

Existing SMR (note 1)

- Purge Gas
  - Export Hydrogen

- Syngas
  - CO₂ Removed
  - Export CO₂

New VSA

- Wet CO₂

Note 1: Burner and Other Retrofits Required

Stream Color Legend

- Existing Stream - Black
- New Stream - Blue
- Revised Stream - Red

Picture from Air Products and Chemicals, Inc: Port Arthur 2

- Existing SMR
- Co-Gen Unit
- CO₂ Compressor & TES Unit
- CO₂ Surge Tanks
- Blowers

- CO₂ VSA Vessels

Eight-stage, integrally geared centrifugal CO₂ compressor
Major Equipment List & Plant Modification

- Modification to the existing burners (i.e. NOx)
- VPSA vessels (2 trains)
- CO$_2$ export compressor (1 train)
  - Export pressure ~140 Bar
  - 8 stages (with 5 intercoolers)
  - Tri-ethylene glycol (TEG) dehydration system
- 13 miles CO$_2$ Pipeline – connecting to existing Denbury CO$_2$ Pipeline
  - via excavation & horizontal drilling
- GT Cogen (~28 MWe of steam and power to cover additional requirements for VPSA, compressors and others)
Denbury’s 323-Mile “Green” Pipeline

Data source is Denbury, December 2011, CO₂ Flooding Conference

Picture from Air Products, Denbury and NETL
MVA Project Area: West Hastings Field

Picture from Air Products, Denbury and NETL

Source: UT BEG
Port Arthur EOR Project
(Concluding Remarks)

• New technology for CO\textsubscript{2} capture from H\textsubscript{2} plant demonstrated at scale.
  • Integrated to the Denbury pipeline and CO\textsubscript{2} storage at Hasting Field is monitored.

• Important Challenge:
  • \textbf{Does not affect the H\textsubscript{2} business of Air Products}
  • Covered by US DOE funding and EOR revenues
Review: Tomakomai Project
Capture of CO₂ from SMR

- Japan CCS Co. Ltd.
- H₂ production from SMR provided to Idemitsu Kosan’s Hokkaido Refinery
- EPC awarded to JGC
- Capture of 200,000 t/y
- Off-shore storage in two separate reservoirs – at Hokkaido Subsea Sandstone Bed
- Operation to start 2016/2017
- Duration: 3 yrs operation
Key Information

- **CO₂ capture from the PSA Off-Gas**
  - ~200k t/y CO₂ captured with 99+% (dry) purity
  - Capture based on activated amine (BASF solvent)

- **Additional Utilities**
  - Power (imported) 0.49 MWe
  - Steam 10.4 t/h LP steam to reboiler
  - Cooling Water 465 t/h (delta =10°C)
  - Process Water: 0.92 t/h
Tomakomai Storage Site
(Picture courtesy of Japan CCS Ltd.)
Tomakomai Project
(Concluding Remarks)

Japan CCS Co., Ltd. (JCCS)

Date of Incorporation:
May 26, 2008

Business Description:
A comprehensive investigation for CCS Projects in Japan

Capital: 243 mm yen (ca. US$3.0mm)
Shareholders: 36 companies
11 electric power, 4 petroleum, 5 engineering, 4 petroleum resource developing, 4 general trading, 2 iron and steel, 2 city gas, 1 chemical, 1 non-ferrous metal and cement, 1 steel pipe, 1 special trading
List of Shareholders

Hokkaido Electric Power Co., Inc.
Tohoku Electric Power Co., Inc.
The Tokyo Electric Power Co., Inc.
Chubu Electric Power Co., Inc.
Hokuriku Electric Power Co., Inc.
The Kansai Electric Power Co., Inc.
The Chugoku Electric Power Co., Inc.
Shikoku Electric Power Co., Inc.
Kyushu Electric Power Co., Inc.
The Okinawa Electric Power Co., Ltd.
Electric Power Development Co., Ltd.
COSMO OIL CO., LTD.
Idemitsu Kosan Co., Ltd.
Japan Energy Corporation
JX Nippon Oil and Energy Corporation
Showa Shell Sekiyu K. K.
Chiyoda Corporation
JGC Corporation
JFE Engineering Corporation

Nippon Steel Engineering Co., Ltd.
Toyo Engineering Corporation
Arabian Oil Company Ltd.
INPEX CORPORATION
Japan Petroleum Exploration Co., Ltd.
Mitsui Oil Exploration Co., LTD.
JFE Steel Corporation
Sumitomo Metal Industries, Ltd.
Tenaris NKK Tubes
ITOCHU Corporation
Marubeni Corporation
Mitsubishi Corporation
Sumitomo Corporation
Marubeni-Itochu Steel Inc.
Tokyo Gas Co., Ltd.
Osaka Gas Co., Ltd.
MITSUBISHI GAS CHEMICAL CO., INC.
Mitsubishi Materials Corporation
Review: Port Jerome Project
Capture of CO₂ from SMR

Cryocap™ H₂ project at Port Jérôme, France

- First Worldwide reference of Cryocap™ H₂ Technology for SMR
- Designed and under construction by Air Liquide on an industrial unit:
  - 100 ktpy CO₂ capture, purification (food-grade) and liquefaction
  - Upscalable technologies
  - Start-up end 2014
Key Facts

- SMR owned by Air Liquide – delivering H₂ to ExxonMobil’s Port Jerome Refinery
- Project supported by French government
- Expected to be online Q2 – 2015
- CO₂ capture from PSA off-gas (2/3 slips stream)
  - Capturing 100k t/y as “Food Grade CO₂”
- Capture technology is a derivative of CPU technology for oxyfuel combustion.
  - Based on low temperature “cryogenic” separation
  - Use of Autothermal Refrigeration
  - Additional recovery of H₂ (~10-20%) from PSA off-gas
Simplified Block Diagram
(Courtesy of Air Liquide)
Key Information

• **CO₂ capture from the PSA Off-Gas**
  • ~100k t/y CO₂ captured with 99+% (dry) purity due to additional purification process (i.e. CATOX et al)

• **Additional Utilities**
  • Power (imported) Not Available
  • Steam 0.60 t/h
  • Cooling Water 400 t/h (delta =10°C)
  • Process Water: 0 t/h
  • Waste Water: 0.10 t/h
Port Jerome Project
(Concluding Remarks)

• New novel technology developed from CO$_2$ Capture Technology from oxyfuel combustion
  • Demonstrated the Technology Transfer from one sector to another.
  • Alternate demo option.
  • Expected that this technology is applicable to:
    o Iron and Steel Industry
    o Oil Refining Industry (i.e. oxy-FCC)
Concluding Remarks

• Capture of CO₂ from SMR is not new.
  • Low hanging fruit but not cheap
• Large scale demonstration of the integration of CO₂ capture, transport and storage is important; and this has been achieved.
• Development of new novel technologies are on-going to reduce cost

Figure 4. Repsol, Spain, H₂ plant with partial CO₂ capture.

• Repsol SMR Plant (67,000 Nm³/h H₂)
• Operational since 2002
• ~60,000 TPD of CO₂ captured via aMDEA from syngas for food market
Concluding Remarks

• Addressing the market competitiveness issue
  • CAPTIVE MARKET – with straightforward relation between customer & supplier. (based on long term OTF contract)
  • Early deployment was made possible due to government support and additional revenues.
IEAGHG H₂ Techno-Economic Study

• Project Contractor – Amec FW

• Scope:
  • Review – Current State-of-the-Art
    - H₂ Production (including efficiency improvement)
    - CO₂ Capture Options
    - Large Scale Pilot and Demo Project
  • Techno-Economic Study
    - 5 Main Options (Technologies still to be determined)
    - Cover both merchant and captive plants (integrated)

• Project Completion: Q3 / Q4 of 2015.
Thank you

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