12-5 Hydrogen production and energy storage

- Technical processes and cost
Hydrogen Production By Steam Reforming

Management of the gas is critical for petroleum refiners

Ray Elshout
Energy Systems Engineering

Steam reforming of natural gas at petroleum refining facilities is the predominant means of producing hydrogen in the chemical process industries (CPI). Areas where hydrogen is heavily consumed include ammonia production, the cryogenics industry and methanol production (Table 1)[1]. Because hydrogen needs within various sectors of the CPI are at their highest during peak periods for diesel fuel. Management of hydrogen is critical for the users requiring
Figure 1. Hydrogen costs via electrolysis with electricity costs only

- Commercial System Efficiencies (54-67 kWh/kg)
- Ideal System (HHV of Hydrogen 39 kWh/kg)
Hydrogen cost

- Today the cheaper hydrogen is produced by **steam-methane reforming**
- \[ CH_4 + H_2O \rightarrow 3H_2 + CO \text{ (755-1080K)} \Delta = 206 \text{MJ} \]
- **from CH4 Cost 400$\/T**
- **Hydrogen from electrolysis**: \[1800-2000$\/T\] for an electrical power at 50$\/\text{MWh}
efficiency of the electrolyser for hydrogen production

- CEA/ENSMP thesis R. Rivera-Tinoco 30 March 2009
- Conversion rate:
- 75% at high temperature electrolysis (EPR temperature)
- NREL (innovation for our energy future)-DOE
- **Water to hydrogen conversion efficiency**: 80 to 95%
  - 56% for Proton’s proton exchange membrane (PEM)
  - 73% for Stuart’s and Norsk Hydro’s bipolar alkaline systems
  - 64% for Avalence and Teledyne units
  - *75% to 85% second generation of solid oxide electrolyser cells (SOECs)*
estimation cost for Hydrogen

- from DOE

100kg/day 8.09$/kg - 1000kg/day 4.15$/kg

to reach 3.00$/kg the electricity cost must be below than 4¢ to 5.5¢ per kWh

from Riso National Lab (Denmark)

4.8 $/Gj for H2 production assuming an electricity price of 3.6$/Gj (equivalent to 29$/barrel oil) to 7.8 $/Gj

for CH4 production (48$/barrel oil) or 71 cents /kg H2 using HHV at 950°C for SOECs

if we take into account the degradation property of HHV it gives 108 cents/kg or 46$/barrel

from ENSMP/CEA (2009) thesis R.Rivera-Tinoco

for a 1.5 kg/s hydrogen production and a cost of electricity between 40 to 50 euros /MWh

the cost is between 1.9 to 2.2 euros /kg H2

( electrolyser 900°C with high temperature water 523K from EPR)

notice the price of crude oil barrel is between 72 to 112$/barrel in 2010
FIGURE 3. A typical reformer furnace could have over 300 burners

FIGURE 4. Hydrogen plants with single heaters and capacities up to 100,000 ft³/d have used a down-firing approach
### TABLE 1. HYDROGEN USAGE BY INDUSTRY

<table>
<thead>
<tr>
<th>Hydrogen final usage category</th>
<th>Usage by industry (%)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>37</td>
<td>An ammonia plant is typically a hydrogen plant with a second converter that reacts hydrogen with nitrogen</td>
</tr>
<tr>
<td>Merchant</td>
<td>3</td>
<td>This includes all bottled users, liquid hydrogen supplied in tank trucks, and gaseous hydrogen in short pipe lines (not including the over-the-fence hydrogen suppliers)</td>
</tr>
<tr>
<td>Methanol</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Refinery hydrogenation</td>
<td>19</td>
<td>Hydrocracking and hydrotreating</td>
</tr>
<tr>
<td>Cryogenics</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>Refinery fuel gas</td>
<td>14</td>
<td>Last resort</td>
</tr>
</tbody>
</table>

as well as from direct hydrogen manu- | excess steam. The calculated effluent |
FIGURE 2. Maintaining a tube-wall temperature that is hot enough for the reforming reaction is a critical factor in reformer heater design.
FIGURE 7
A pre-reformer breaks down heavier hydrocarbons into methane ahead of the reforming reactions
FIGURE 5. Most older units remove carbon dioxide from the hydrogen-rich gas with a solvent.

FIGURE 6. A PSA unit separates carbon monoxide, carbon dioxide and unconverted hydrocarbons from hydrogen. Adsorbers operate in a high-pressure to low-pressure cycle to adsorb and then release contaminants.
New cements for CO$_2$ storage

- new cements are able to Storage 0.6 ton of CO$_2$ per ton of cement
- It gives a positive material balance for CO$_2$
The Remix for a Planet Growing Warm

**BOX GIRDER**
- 4% silica
- 25% fly ash
- 71% Portland cement

- 29 percent reduction in CO₂
- Silica fume reduces permeability to salt from road surface, protecting the rebar.

**PIERS**
- 69% slag
- 16% fly ash
- 15% Portland cement

- 85 percent reduction in CO₂
- Fly ash adds strength.

**FOOTINGS**
- 42% slag
- 18% fly ash
- 40% Portland cement

- 60 percent reduction in CO₂
- Slag improves resistance to corrosive sulfates in the soil.

Sources: Kevin A. MacDonald, Ceramstone Products Company; Richard D. Stehly, American Engineering Testing
Flow sheet of a typical, state-of-the-art process for the manufacture of lime and cement. After a preparation and raw milling step, lime is produced through calcination within a kiln. Cement is produced in a further clinkering step and much more elevated temperatures. Most CO$_2$ is produced from the decomposition of carbonates and burning of kiln fuel. Final products are obtained following fine milling steps.
**Nucleation of calcium carbonate clusters**

Denis Gebauer, Antje Völkel, Helmut Cölfen

SCIENCE 322, 1819-1822 (2008), www.sciencemag.org/cgi/content/full/322/5909/1819/DC1

### Process of CaCO₃ precipitation

<table>
<thead>
<tr>
<th>Pre-nucleation</th>
<th>Nucleation</th>
<th>Post-nucleation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Classical</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ionic solution, metastable clusters</td>
<td>Cluster of critical size</td>
<td>Particles and crystals</td>
</tr>
<tr>
<td>Stable-cluster equilibrium</td>
<td>Single ion attachment</td>
<td>Calcite, aragonite, amorphous</td>
</tr>
</tbody>
</table>

**Novel**

<table>
<thead>
<tr>
<th>Pre-nucleation</th>
<th>Nucleation</th>
<th>Post-nucleation</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH-dependent</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Fig. 4.** Schema of the classical and novel view on precipitation (not to scale). Prenucleation-stage calcium carbonate clusters provide an early precursor species of different ACC phases giving rise to an alternative crystallization-reaction channel.
Fig. 3. Time development of the free ion product. Shown are averaged values obtained from a sample of three measurements. Because averaging is not appropriate during nucleation, the particular developments are indicated by dashed lines. We find two different ACC phases with solubility products of $\sim 3.1 \times 10^{-8} \text{ M}^2$ (ACC I) and $\sim 3.8 \times 10^{-8} \text{ M}^2$ (ACC II), corresponding to the pH dependency of the prenucleation cluster equilibrium. Also given are the solubilities of vaterite, aragonite, and calcite (27) (SOM section 2.5.)

**SCIENCE 322, 1819-1822 (2008), www.science mag.org /cgi/content/full/322/5909/1819/DC1**
Fig. 2. Schematic illustration of the free reaction enthalpy $\Delta_R G$ versus the reaction coordinate. In the classical view (bold line), metastable clusters form and nucleation occurs when the critical nucleation enthalpy $\Delta G^*$ is overcome. In fact, stable clusters (dashed line) are formed with an activation barrier negligible compared to thermal energy. The structure and depth of the indicated minimum remain unknown, as well as the height of the activation barrier for nucleation.
Polymer synthesis from CO$_2$

- One of the main fields for CO$_2$ polymerisation is to produce polycarbonate material which are biodegradable molecules and are able to storage 50% of CO$_2$ in the weight.

- It decreases the consumption of hydrocarbons of 50%.
Polymer synthesis with CO$_2$ give polycarbonates which can storage 50% of CO$_2$ in weight.

Greener carbonates

Eghbali and Li fashioned a direct route to cyclic carbonates from an olefin and CO$_2$ that bypasses the extra step of making an epoxide starting material.
Figure  Modulus data for PPC, PPC composite, and general-purpose plastics

Significant Property Improvement of plastic made from carbone dioxide
AIST  Nov 18,2008
Hiroshi Shimizu,Li Yongjin,Nanotechnology Research Institute .Dir Nobutsugu Minani
Of National institute of Advanced Industrial Science and Technology (AIST)
President Hiroyuki Yoshikawa
Figure 1: Stress – strain curves of PPC and PPC composites

[Curve 1: pure PPC, Curves 2 to 5: PPC composites, (2: PPC/X=70/30, 3: PPC/X/Y=70/30/2.5, 4: PPC/X/Y=70/30/10, 5: PPC/X/Y=70/30/5)]
## Table 1: Mechanical properties at room temperature (25°C)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Modulus (MPa)</th>
<th>Strength (MPa)</th>
<th>Elongation at break (%)</th>
<th>Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPC</td>
<td>101</td>
<td>4.8</td>
<td>578</td>
<td>30.4</td>
</tr>
<tr>
<td>PPC/X=70/30</td>
<td>1564</td>
<td>8.4</td>
<td>390.6</td>
<td>36.7</td>
</tr>
<tr>
<td>PPC/X/Y=70/30/5</td>
<td>2431</td>
<td>17.9</td>
<td>322</td>
<td>39.8</td>
</tr>
<tr>
<td>Low-density polyethylene</td>
<td>142</td>
<td>16.6</td>
<td>616</td>
<td>-128</td>
</tr>
<tr>
<td>iso-polypropylene</td>
<td>979</td>
<td>26.1</td>
<td>1077</td>
<td>-0.1</td>
</tr>
</tbody>
</table>

**Significant Property Improvement of plastic made from carbon dioxide**

AIST Nov 18, 2008

Hiroshi Shimizu, Li Yongjin, Nanotechnology Research Institute. Dir Nobutsugu Minani Of National institute of Advanced Industrial Science and Technology (AIST)

President Hiroyuki Yoshikawa
CO2 for ENERGY STORAGE

• **energy storage** from decarbonated sources

  • *** technical and financial data
  • *** capture unit from exhaust gas
  • *** thermodynamic data
  • *** Redox processes and catalysist material
CO$_2$ a good candidat for
ELECTRICAL ENERGY STORAGE

Great advantages of chemical plant with REDOX reactions for carbon recovery: large chemical facilities

- OXY + ne \(\rightarrow\) RED
- CO$_2$ + H$_2$ \(\rightarrow\) CH$_4$ + 2 H$_2$O
- \(\rightarrow\) CH$_3$OH + H$_2$O
- \(\rightarrow\) F.T. process

• The key step is hydrogen production
energy management and electrical storage

- evolution of the fossil carbon fields (including coal, petroleum, gas)
  - electrical energy storage
  - carbon recovery
  - energy cost and energy storage cost
  - geopolitical problems of the energy resources
a reversible storage of CO2 capture
gives carbon resources for the futur of our civilization
Financial aspects

one of the main working parameters is how much it was the deal of Kyoto program for carbon dioxide regulation it is the challenger of Cancun conference this week (30 nov-7 dec 2010)
Total emissions USA 2002 in MMt (10^6t)

<table>
<thead>
<tr>
<th>Sector</th>
<th>Emissions (MMt)</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Total US</td>
<td>5752</td>
<td>%</td>
</tr>
<tr>
<td>2. Electric Power</td>
<td>2250</td>
<td>39</td>
</tr>
<tr>
<td>3. Transportation</td>
<td>1868</td>
<td>32</td>
</tr>
<tr>
<td>4. Industrial Processes</td>
<td>1042</td>
<td>18</td>
</tr>
<tr>
<td>5. Residential Homes</td>
<td>365</td>
<td>6</td>
</tr>
<tr>
<td>6. Commercial Buildings</td>
<td>227</td>
<td>4</td>
</tr>
</tbody>
</table>

Total emissions USA 2002 in MMt (10^6 t) (non-energy related processes)
energy efficiency of coal energy processes

• coal burning system for electrical power station
  • in the main countries 30%
  • new plants 37%
  • supercritic news plants 45 to 58%
energy from industrial processes

Energy sources
- Sun power
- Agricultural activities
- Water

Key steps for human activities
- Climat change

Constraints
- Sustainable industrial activities

Non carbonated energy sources
- Electrical source

Fossil carbon resources
- Liquide/hydrocarbon gas

CO2 Raw material
- Carbon storage CCS

Energy storage Carbon recovery

control of carbon dioxide level

European Parliament STOA 22 / 3/2011
EMRS/UPMC
Fourth Part

• main ways for **energy storage from electron to carbon recovery** by using CO2 molecule

• **Electron to chemical synthesis**: Hydrogen + CO2
to Methanol
to Methane
to synfuel by FT processes

• **electron to plasma processes**
• thermal or non equilibrium plasmas

• **Photon to thermolysis** of water or CO2 dissociation