Catalysis and Alternative Feedstocks in the Biofuels Industry Workshop

Industrial Perspectives on Hydrogen Production: Needs and Opportunities

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Agenda

- Industrial gases in the biofuels production chain
- Hydrogen market
- Hydrogen production
  - Production
  - Off-gas
  - Biosource
- Distribution modes
Air Liquide is the world leader in gases for industry, health and the environment.

**Industry**
- For a wide range of industrial processes for customers:
  - energy, metals, food, chemicals, pharmaceuticals, automotive...

**Health**
- For hospitals
- For homecare patients
- For hygiene and disinfection

**Environment**
- For reducing polluting emissions
- For producing the energies of tomorrow

The world leader in gases for industry, health and the environment.
Air Liquide – by the numbers

- 43,600 employees
- Present in 80 countries
- Revenue €13.5 billion
- >1 million customers

2010 Data
Unique expertise and skills

Separating the components of the *air* to take advantage of their properties

Producing molecules from *natural resources* of the Planet

**Air Liquide Technologies**

- Oxygen
- Nitrogen
- Argon & rare gases

- Hydrogen
- Helium
- Carbon monoxide
- Silane
- Acetylene

...
A technological powerhouse

■ Innovation
- €235m innovation budget in 2010
- 8 R&D centers
- 2,500 active patented inventions
- 300 new inventions in 2010
- 100 industrial partnerships
- 120 partnerships with universities and research institutes

■ Molecules and innovative technologies

H₂ + filling station  LENOXe™ + anesthesia workstation  O₂ + burners
Industrial Gases in the Biofuels Production Chain

- Process gases
  - Hydrogen for hydrotreating
  - Oxygen for gasification
  - Carbon dioxide for algae production
- Analytical gases
  - Carrier gases
  - Calibration standards
- Construction and maintenance gases
  - Argon mixtures for welding
  - Oxygen and FLAMAL for cutting
Hydrogen Requirements for Biofuels

- Major components of lignocellulosic biomass are: lignin, hemicellulose, and cellulose
- Biomass contains significantly more oxygen and moisture than fossil hydrocarbons
- Hydrogen is used to
  - De-oxygenate biomass-derived hydrocarbons
  - Saturate double / triple bonds from high temperature processes
- Hydrogen needs per barrel for biofuels can be significantly greater than for fossil fuels

**Lignin: 15-25%**

**Hemicellulose: 23-32%**

**Cellulose: 38-50%**

Source: Larry Felix, GTI July 2011
Biofuels Processing Options

Several options for biofuels processing

- Fermentation
- Gasification and catalytic synthesis
- Pyrolysis with product upgrading

With many final products

- Ethanol
- Methanol
- Gasoline
- Jet fuel
- NH₃ / Urea
- Mixed alcohols
- Waxes
- MTBE
- Acetic Acid
- Aldehydes
- Fischer-Tropsch hydrocarbons

Source: Richard Boardman, Idaho National Laboratory, July 2011

Heat, steam and electrical power required
Uses for Hydrogen, Volume and Market Size

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Needs of Biofuels Producers

**Hydrogen must be:**

- Sustainable
- Safe
- Scalable
- Cost effective
- Reliable
Factors in H₂ Supply Mode

On Purpose H₂ Production
- Electrolysis
- Off-gas upgrading
- SMR / ATR / POX

Delivered H₂
- Cylinder
- Bulk liquid or tube trailers
- Pipeline Supply

Natural gas cost
Proximity to feed source
Scale
Proximity to H₂ pipelines or existing plants
Fixed / variable cost sensitivity
H₂-rich stream availability
Hydrogen Production Technologies

**PRODUCTION**

- **POX**
- **ATR**
- **SMR**

**PURIFICATION**

- **Cryogenic**
- **Membrane**
- **PSA**

**Production Streams**

- **Hydrocarbon**
- **O₂**
- **Off-gas**
- **Electricity**
- **Water**

**Purification Streams**

- **Steam**
- **Pure CO**
- **H₂/CO**
- **Pure H₂**

**Process Descriptions**

- **SMR**: Steam Methane Reformer
- **POX**: Partial Oxydation
- **ATR**: Auto Thermal Reformer
- **PSA**: Pressure Swing Adsorption

*(Lab scale)*
Standard SMR Plant

- Pretreatment
- Pre-Reformer
- Reformer
- Shift
- PSA

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Large Scale H₂ Production Plant

Reformer

PSA

Shift
Reducing CO$_2$ Emissions from SMR

How we reduce CO$_2$ emissions

✓ Improve efficiency and reduce fugitive emissions
✓ CO$_2$ separation and capture
✓ Burn hydrogen in the SMR

Lurgi CryoCap™ Reformer
Off-gas Recovery and Purification

Biomass, Coal, or Petcoke → Gasifier → Shift/Gas Cleanup → Industrial Source → PSA → H₂
Biosourcing of Hydrogen

- Methane from landfill gas can be feedstock for H₂ production via SMR

- Biosourcing is viewed as an off-gas source; not a primary production source
Distribution Methods

Small Quantity Users (1 - 50 m³/hr)

Large Quantity Users (1,000 to 100,000 m³/hr)
U.S. Hydrogen Smaller Usage Operations

- Increased volume scalability
- Lower commitment levels
- Usage flexibility
- Reduced CAPEX

Small Quantity Users
1 - 500 m³/hr
U.S. Hydrogen Large Usage Options

On-purpose Production

- Dedicated supply
- Improved reliability
- Increased economies of scale

Large Quantity Users
1,000 – 100,000 m³/hr

Pipeline Network
Outlook and Conclusions

- Biofuels represent a growth opportunity for the hydrogen market
- Hydrogen production is well established commercially
- Hydrogen can become a critical factor in the planning process of biorefinery projects
- New hydrogen sources and new applications using hydrogen will play an important part in the development of a renewable fuels portfolio
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