Evaluation of H₂ Production at Refineries in China
The New UOP SeparALL™ Process and UOP Polybed™ PSA
# UOP Company Profile

**Serving the Gas Processing, Refining & Petrochemical Industries**

## Profile — Significant Technology Position

**Business Units:**
- Gas Processing and Hydrogen (GP&H)
- Process Technology & Equipment (PT&E)
- Catalysts, Adsorbents & Specialties (CA&S)
- Renewable Energy and Chemicals (RE&C)

**Offering:**
- Technology, catalyst & services to the refining, petrochemical and gas processing industries
- Supplier of molecular sieve adsorbents to process and manufacturing industries

## Sales: Breakdown

<table>
<thead>
<tr>
<th>Category</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equipment</td>
<td>45%</td>
</tr>
<tr>
<td>Products</td>
<td>35%</td>
</tr>
<tr>
<td>Services</td>
<td>13%</td>
</tr>
<tr>
<td>Licensing</td>
<td>7%</td>
</tr>
</tbody>
</table>

## UOP Facilities — Global Footprint

**Worldwide Headquarters**
Des Plaines, Illinois (suburban Chicago)
3,500+ Employees

- 20 Offices
- 17 Countries
- 12 Manufacturing Facilities
- 5 Engineering Centers

## Sales: Geographic

- **North America**: 32%
- **Asia Pacific**: 19%
- **China**: 12%
- **South America**: 9%
- **Middle East**: 9%
- **E&A**: 9%
- **CIS**: 5%
- **India**: 5%

**Global Customers**
Our technologies and products are designed to deliver superior performance, safety and value when combined in an integrated system:

- High availability and reliability of processes and products
- Lower capital expenditure and operating costs resulting in lower cost of production of hydrogen
Hydrogen Dynamics in China

1. Critical feedstock for various industries
   - Refining industry
     - Hydrocracking, hydrotreating and isomerization processes
   - Ammonia Production
     - Approx. 0.18 – 0.20 kg hydrogen per kg of ammonia required

2. Environmental regulation / improved refinery performance
   - State Mandate – upgrade diesel and gasoline
   - Process heavier and more sour crude
   - Long on Heavy Fuel Oil (HFO) and Petroleum Coke
   - Improve margins by maximizing high-value refined product output

3. Demand for transportation fuels
   - Oil demand rising at >8% CAGR
   - Refining capacity to double from 2012 to 2022
   - China’s footprint expanding as a global supplier of refined products and fuels

Growth for hydrogen will mainly come from the oil refining industry.
Growth Potential for Hydrogen

Hydrogen segment assessment in China (Million tons)

Source: Chem1 Market Assessment Study for Hydrogen

Growth for hydrogen will mainly come from the oil refining industry.
### Fuel Standards

<table>
<thead>
<tr>
<th></th>
<th>State II Current</th>
<th>State III 2013</th>
<th>State IV 2015</th>
<th>State V</th>
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<tbody>
<tr>
<td><strong>GASOLINE</strong></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Sulfur, ppm</td>
<td>500</td>
<td>150</td>
<td>50</td>
<td>10</td>
</tr>
<tr>
<td>Olefin, v%</td>
<td>35</td>
<td>30</td>
<td>28</td>
<td>25</td>
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<tr>
<td>Manganese, g/L</td>
<td>0.018</td>
<td>0.016</td>
<td>0.008</td>
<td>0.002</td>
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<tr>
<td>Vapor pressure (Summer), kappa</td>
<td>74</td>
<td>72</td>
<td>40–68</td>
<td>40–65</td>
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<tr>
<td><strong>DIESEL</strong></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Sulfur, ppm</td>
<td>500</td>
<td>350</td>
<td>50</td>
<td>10</td>
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<tr>
<td>Cetane number</td>
<td>49</td>
<td>49</td>
<td>51</td>
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<tr>
<td>Density, 20°C kg/cm³</td>
<td>820-860</td>
<td>810-850</td>
<td>820-845</td>
<td></td>
</tr>
<tr>
<td>Fatty acid ester</td>
<td>0.5%v, 11%m</td>
<td>0.5%v, 11%m</td>
<td>0.5%v, 11%m</td>
<td></td>
</tr>
<tr>
<td>Heavy Aromatics</td>
<td>820-860</td>
<td>810-850</td>
<td>820-845</td>
<td></td>
</tr>
</tbody>
</table>

### Comments

China relies heavily on the ME for most of its oil supplies which is sour.

**ME Crude Oil Specs:**

- **Current**
  - API = 34
  - S (wt%) = 1.75

- **Current**
  - API = 33.9
  - S (wt%) = 1.84

**Improving energy efficiency combined with reducing greenhouse gas emissions are key in the five year plan.**

*Source: Chem1 Market Assessment Study for Hydrogen; Hart Energy Consulting Analysis (2010)*

*Increasing sour crude processing and stricter sulfur controls requires added capacity for hydrogen production*
Breakdown of Feedstock for Hydrogen Production

Hydrogen market assessment in China (Million tons)

<table>
<thead>
<tr>
<th>Year</th>
<th>others</th>
<th>coal</th>
<th>NG</th>
<th>ROG</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>2008</td>
<td>0.1</td>
<td>1.1</td>
<td>0.6</td>
<td>1.8</td>
<td>3.6</td>
</tr>
<tr>
<td>2009</td>
<td>0.7</td>
<td>1.2</td>
<td>0.1</td>
<td>2.0</td>
<td>3.4</td>
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<tr>
<td>2010</td>
<td>0.8</td>
<td>1.3</td>
<td>0.1</td>
<td>2.2</td>
<td>3.4</td>
</tr>
<tr>
<td>2011</td>
<td>0.8</td>
<td>1.4</td>
<td>0.1</td>
<td>2.4</td>
<td>3.8</td>
</tr>
<tr>
<td>2012</td>
<td>0.9</td>
<td>1.5</td>
<td>0.1</td>
<td>2.5</td>
<td>4.6</td>
</tr>
<tr>
<td>2015</td>
<td>1.1</td>
<td>1.7</td>
<td>0.6</td>
<td>3.4</td>
<td>6.8</td>
</tr>
<tr>
<td>2020</td>
<td>1.9</td>
<td>1.9</td>
<td>0.6</td>
<td>4.4</td>
<td>8.8</td>
</tr>
<tr>
<td>2022</td>
<td>2.1</td>
<td>2.1</td>
<td>0.8</td>
<td>5.0</td>
<td>9.0</td>
</tr>
</tbody>
</table>

CAGR 2012-2022

- others: 18%
- coal: 9%
- NG: 4%

Source: Chem1 Market Assessment Study for Hydrogen

Coal gaining prominence as an alternative cheaper feedstock
Case Study Comparing SMR & Gasification

1. Basis

- **Natural Gas Price**: $13/MMBtu (HHV = 22,400 Btu/lb) - based on LNG imports
- **Petcoke Price**: $1/MMBtu (HHV = 15,000 Btu/lb)
- **Coal Price**: $3.50/MMBtu (HHV = 12,000 Btu/lb)
- **Hydrogen required for refinery**: 100,000 Nm3/h

2. Configurations
Hydrogen Production Cost

Hydrogen production cost in China, $/Nm³

- Natural gas: 0.212
- Coal: 0.153
- Petcoke: 0.110

Cheaper feedstock cost directly influences the cost of hydrogen production

SENSITIVITY ANALYSIS FOR PETCOKE FEED

- Capex $ MM: 0.10 to 0.14
- Feedstock $/MMBTU: 1.01 to 1.67

SENSITIVITY ANALYSIS FOR NATURAL GAS FEED

- Feedstock, $/MMBTU: 0.18 to 0.24
- Capex $MM: 11.89 to 14.11

UOP processes drive value in hydrogen production
What is the UOP SeparALL Process?

Absorption / regeneration process for selective removal of H₂S, COS, & CO₂

- Uses a “next generation” physical solvent (SELEXOL™ MAX Solvent)
- Uses a typical solvent-extraction flow-scheme
- Loading directly proportional to partial pressure

Physical vs Chemical
Typical Gasification Application

High Pressure is advantageous
SELEXOL MAX Solvent Characteristics

- SELEXOL MAX Solvent: A physical solvent
  - Chemically similar and completely compatible with SELEXOL Solvent
  - Clear fluid that looks like tinted water

- Regenerated by changing pressure, temperature or applying a stripping gas

- Unique selectivity characteristics desirable for gasification syngas treating

Relative Solubility Data

- $H_2$ ~ 1
- CO ~ 2.2
- $CO_2$ ~ 76
- COS ~ 175
- $H_2S$ ~ 680

SELEXOL MAX Solvent = Selective
Two Basic Flow-schemes

**Sulfur removal only**
- Typically for power applications
- Can reduce treated gas any desired sulfur level
- One solvent absorber with solvent regeneration

**Sulfur removal with separate CO$_2$ removal** (CCS or chemicals production)
- Typically for chemicals, SNG or coal to liquids applications
- Typically involves more stringent product specifications
- Integrated solvent absorbers and solvent regeneration
UOP SeparALL Process Advantages

- Mild chilling
- Simple flow schemes with few pieces of equipment
- Lower solvent losses
- Absorbs NH₃, HCN and other trace contaminants, without the need for additional equipment
- Removes metal carbonyls
  - Metal carbonyls in treated syngas decompose at gas turbine burners and potentially plate-out on the gas turbine blades
  - Metal carbonyl can also act as catalyst poisons for chemical applications

Through its improved efficiency and next generation technology, the SeparALL process can reduce capital expenditures by up to 10 percent and operating expenditures by more than 20 percent.
The UOP SeparALL process provides > 99% availability.

Availability exceeds typical gasifier availability (typically 80 - 90%)

UOP training and services teams work with operators to help optimize and maintain the system at peak efficiency.
## Sarlux IGCC Complex Plant

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td>Start-Up</td>
<td>2000</td>
</tr>
<tr>
<td>Application</td>
<td>Power H₂ Production</td>
</tr>
<tr>
<td>Production</td>
<td>550 MW net / 40000 Nm³/h</td>
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<tr>
<td>AGRU Duty</td>
<td>Sulfur</td>
</tr>
<tr>
<td>Syngas Flow</td>
<td>404 MMSCFD @420 psia</td>
</tr>
<tr>
<td>Feedstock</td>
<td>Visbreaker Residue</td>
</tr>
</tbody>
</table>
Block Flow Diagram | Sarlux IGCC

- **Air Separation Unit**
  - Air
  - O₂

- **Combined Cycle Power Plant**
  - Electric Power
  - Steam for Export
  - Purified Syngas

- **Gasifier w/ Quench & Scrubbing**
  - Feed

- **Gas Cooling & COS Hydrolysis**
  - SELEXOL

- **Polybed™ PSA**
  - High Purity to Hydrocracker
  - Raw H₂

- **Polysep™ Membrane**

- **Claus Plant**
  - Elemental Sulfur

- **Tail Gas**
## API Energia IGCC Complex Plant

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Start-Up</strong></td>
<td>1999</td>
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<tr>
<td><strong>Application</strong></td>
<td>Power</td>
</tr>
<tr>
<td><strong>Production</strong></td>
<td>250 MW net</td>
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<tr>
<td><strong>AGRU Duty</strong></td>
<td>Sulfur</td>
</tr>
<tr>
<td><strong>Syngas Flow</strong></td>
<td>169 MMSCFD @744 psia</td>
</tr>
<tr>
<td><strong>Feedstock</strong></td>
<td>Visbreaker Residue</td>
</tr>
</tbody>
</table>

API Energia IGCC Complex Plant

Falconara, Italy
# Commercial Experience in Gasification

## Coffeyville Resources Plant

<table>
<thead>
<tr>
<th>Feature</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Start-Up</td>
<td>2000</td>
</tr>
<tr>
<td>Application</td>
<td>Ammonia Urea</td>
</tr>
<tr>
<td>Production</td>
<td>21 T/h</td>
</tr>
<tr>
<td>AGRU Duty</td>
<td>Sulfur &amp; CO₂</td>
</tr>
<tr>
<td>Syngas Flow</td>
<td>151 MMSCFD @535 psia</td>
</tr>
<tr>
<td>Feedstock</td>
<td>Petcoke</td>
</tr>
</tbody>
</table>

Coffeyville, Kansas
Block Flow Diagram | Coffeyville Resources

Air Separation Unit → Ammonia Synthesis → UAN Plant → NH₃ Product

Air → Separation Unit → Purification → High Purity H₂ → Polybed PSA → Raw H₂ → CO₂ Purification → Raw CO₂

Polybed PSA → Quench Gasification → Syngas Scrubbing → CO Shift & Gas Cooling → SELEXOL 2-Stage → Acid Gas

Petroleum Coke → Claus Plant → Vent
Commercial Experience in Gasification

Coffeyville Resources
Gasification Ammonia Complex

SELEXOL Unit

POLYBED PSA Unit
H₂ Purification – Polybed PSA Systems

**FEED GAS**

H₂ + Impurities
High Pressure

**TAIL GAS**

Impurities (+H₂)
Low Pressure

**PRODUCT**

H₂ @ High Purity
High Pressure

**Specifications**

- **H₂ Purity**: 99.9 – 99.9999%
- **H₂ Recovery**: 60 – 90%
- **H₂ Feed pressure**: 6 - 40 bar g
- **H₂ Product pressure**: 5 - 39 bar g
Components of a PSA Unit

1. Control System
2. Valve Skid
3. Vessels & Adsorbents
4. UOP Service & Support
For a customer in China that needs a reliable source of high purity hydrogen, UOP Polybed™ PSA provides greater than 99.8% on-stream availability that results in $500,000/day of additional value due to downtime avoided versus local PSA suppliers. We do this by providing proven designs, proprietary adsorbents, and equipment.

Assumptions:

- 100,000 Nm³/hour product PSA unit
- H₂ value = 15000 RMB/MT = $0.21/Nm³
- Calculation: 100,000 x 24 x 0.21 = $504,000/day
- The cost from the loss of production from the downstream hydroprocessing units, if known, would be added to the cost of the loss of H₂