Recent Selexol™, PolySep™ and PolyBed™ Operating Experience with Gasification for Power and Hydrogen

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**Presentation Overview**

- **Technologies for Synthesis Gas Treatment**
  - SELEXOL Process - Acid Gas Removal
  - POLYSEP Membrane System - H₂ Recovery and H₂/CO Adjustment
  - POLYBED PSA System - H₂ Purification

- **Recent Operating Experience**
  - SARLUX IGCC Project
    - at Sarroch, Sardinia, Italy
  - FARMLAND Ammonia Fertilizer Project
    - at Coffeyville, Kansas, USA
Case Study:

Refinery Hydrogen & Power Production

- Gasification of Refinery Residues for Hydrogen and Power
- Benefits of High Purity Hydrogen for Hydrotreaters & Hydrocrackers
  - Existing units
  - Grass root units

Conclusions
Selexol Process

- Cyclic absorption/regeneration process for selective removal of $\text{H}_2\text{S}$, COS, & CO$_2$
- Uses a physical solvent
  
  \[
  \text{Chemical formula: } \text{CH}_3\text{O}(\text{C}_2\text{H}_4\text{O})_n\text{CH}_3 \text{ where } n \text{ is between 3 & 9}
  \]
- Selectivity
  
  - $\text{H}_2\text{S} / \text{CO}_2 \sim 9$
  - $\text{CO}_2 / \text{H}_2 \sim 76$
- 55 operating units in syngas and natural gas service
PolySep Membrane System

- Gas-permeable hollow fiber polymer membranes
- Concentration (or Recovery) of H₂ and adjustment of syngas H₂/CO ratio
- Separation based on difference in permeation rates between H₂ and impurities (H₂ is fast)
- Partial pressure difference across membrane provides driving force
- Supplied as a skid-mounted system
- ~ 40 operating units
PolyBed PSA System
Pressure Swing Adsorption

- Multiple vessels containing adsorbent
- Impurities adsorbed at high partial pressure
- Impurities desorbed at low partial pressure to regenerate bed
- $\textbf{H}_2$ recovered at high purity (typically 99 to 99.9999 vol%)
- Supplied as a skid-mounted system
- $\sim 700$ operating units
Sarlux S.r.L.
Sarroch, Sardinia, Italy
IGCC Complex
## Sarlux IGCC Complex

**Feedstock:** 173 T/H visbreaker residue to gasifier

**Products:** 35.8 MM SCFD H₂ for SARAS hydrocracker, 550 MW electricity, & sulfur

**Commissioning:** August 2000

**Process Licensors**

- **Gasification:** ChevronTexaco
- **Acid Gas Removal:** UOP Selexol
- **H₂ Purification:** UOP PolySep Membrane & PolyBed PSA
- **Sulfur:** Lurgi
Sarlux Block Flow Diagram

- Air Separation Unit
  - Air
  - O₂

- Combined Cycle Power Plant
  - Electric Power
  - Steam for Export

- PolyBed PSA
  - Raw Hydrogen

- PolySep Membrane
  - High Purity Hydrogen for SARAS Hydrocracker

- Gasifier with Quench & Scrubbing
  - Feed

- Gas Cooling & COS Hydrolysis
  - Purified Syngas

- SELEXOL
  - Tail Gas

- Claus Plant
  - Elemental Sulfur
Sarlux Selexol Units

Two parallel UOP Selexol Units
Sarlux $H_2$ Purification Unit

UOP PolyBed PSA Unit & UOP PolySep Membrane Skids
<table>
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Farmland Industries
Coffeyville, Kansas, USA
Gasification Ammonia Complex
Farmland Ammonia Fertilizer Complex

Feedstock: 45 T/H petroleum coke
Products: 90 MM SCFD High Purity H₂
          10.6 MM SCFD CO₂
Commissioning: July 2000

Process Licensors

Gasification: ChevronTexaco
Gas Purification Block:  
  - Acid Gas Removal: UOP Selexol (2-stage unit)
  - H₂ Purification: UOP PolyBed PSA
Sulfur: Black & Veatch Pritchard
Ammonia / UAN: Ammonia Casale / Weatherly
Farmland Ammonia Fertilizer Complex
Operating Results

- **Raw H₂ from Selexol unit to PSA unit**
  - > 93 mole % H₂
  - < 5 mole % CO₂
  - < 1 ppm H₂S & < 1 ppm COS

- **High Purity H₂ product from PSA to ammonia syngas loop**
  - 90 MM SCFD High Purity H2 (> 99.9%)
  - 90 % hydrogen recovery

- **Raw CO₂ from Selexol unit to CO₂ purification reactor**
  - 10.6 MM SCFD Raw CO₂ (> 95 mole %)
  - < 1 ppm H₂S & < 10 ppm COS
Case Study
Refinery Gasification Complex for Hydrogen & Power Production
**Case Study: Refinery Gasification Complex for Hydrogen & Power Production**

**Scope**

- Gasification complex converts Petroleum Coke to Syngas
- Uses low value (or negative value) feed
- Power, steam, and hydrogen produced for export back to the refinery
  - Production of ultra high purity hydrogen (> 99.9 mole % \( \text{H}_2 \)) for hydroprocessing units
  - Removal of CO\(_2\) stream for sequestration and dilution of gas turbine feed (> 98 mole % CO\(_2\))
  - Removal of concentrated H\(_2\)S stream to Claus (35 to 65 mole % H\(_2\)S)
Case Study: Refinery Gasification Complex for Hydrogen & Power Production

Feed & Product Summary

- Feedstock
  - 100 T/H petroleum coke
- Products
  - 500 MW electricity
  - 80 MM SCFD Ultra High Purity H₂
  - Steam
  - CO₂
Case Study: Refinery Gasification Complex for Hydrogen & Power Production

Process Technologies

- Gasification
- COS Hydrolysis * on unshifted Syngas to Gas Turbine
- CO Shift on Syngas to H₂ Purification
- Gas Purification Block
  - Acid Gas Removal UOP Selexol (2-stage)
  - H₂ Purification: 99.9 % H₂ with PSA or 95.0 % H₂ with Methanator
- Claus Unit

* requirement depends on split between power & H₂ production
Case Study: Refinery Gasification Complex for Hydrogen & Power Production

Study of H₂ Purity - Options Considered

■ Option 1:
  – Single stage of CO shift with “partial” CO₂ removal
  – PSA with 99.9 mol% H₂ purity

■ Option 2:
  – Two stages of CO shift with “complete” CO₂ removal
  – Methanation with 95 mol% H₂ purity
Case Study: Option 1 - PSA System

Air Separation Unit

Air

N₂

O₂

Gasifier with Quench & Scrubbing

Feed

COS Hydrolysis & Gas Cooling

1-Stage CO Shift & Gas Cooling

SELEXOL 2-stage

PolyBed PSA

Combined Cycle Power Plant

Electric Power

Steam for Export

N₂

Treated Unshifted Syngas

N₂ / CO₂ Diluent

High Purity H₂

PSA Tail Gas

Elemental Sulfur

Claus Plant

Treated Syngas

Tail Gas

Acid Gas

Raw H₂

Electric Power
Case Study: Option 2 - Methanator

- Air
  - Air Separation Unit
    - N₂
    - O₂
    - Gasifier with Quench & Scrubbing
      - Feed
    - COS Hydrolysis & Gas Cooling
    - 2-Stage CO Shift & Gas Cooling
  - SELEXOL 2-stage
    - Raw H₂
    - Treated Unshifted Syngas
    - Acid Gas
    - Tail Gas

- Electric Power
- Steam for Export
  - Combined Cycle Power Plant
  - Methanator
    - Low Purity H₂
    - Claus Plant
      - Elemental Sulfur
      - Steam for Export
      - Electric Power

- SELEXOL 2-stage
  - Raw H₂
  - Acid Gas
  - Tail Gas

- Gasifier with Quench & Scrubbing
  - Feed
  - O₂
  - N₂

- Air Separation Unit
  - N₂
  - O₂
Advantages of High Purity $H_2$ in Refinery Hydrotreating

Advantages of 99.9 % $H_2$ over 95 % $H_2$

- Minimize capital cost of new hydroprocessing units
- Minimize operating costs by extending catalyst life - by as much as 100%
- Increase throughput of existing units
Advantages of High Purity $H_2$ in Refinery Hydrotreating

Advantages of PSA over Methanation

- PSA removes CO and CO$_2$ to ppm levels
- CO Shift
  - 1-stage required for PSA
  - 2 to 3 stages required for Methanation
- CO$_2$ Slip in Selexol Unit
  - PSA allows higher slip (%) since it is not sensitive to CO + CO$_2$ levels in feed
  - Methanation requires low slip (ppm level) since CO + CO$_2$ levels > 1.5 % cause excessive temperature exotherm
- PSA can remove N$_2$ and Ar - thus O$_2$ purity is not critical
Benefits of 99.9% PSA H₂ vs. 95% Methanator H₂ for Existing Units

**Existing Hydrotreater #1**

- **Basis:** 40,000 BPD operating with 95% makeup H₂
- **Benefit:** 30 vs. 17 month cycle resulting in $500,000/yr lower annualized turnaround cost

**Existing Hydrotreater #2**

- **Basis:** 16,500 BPD operating with 95% makeup H₂
- **Benefit:** 5 vs. 3.5 year cycle resulting in $100,000/yr lower annualized turnaround cost
Benefits of 99.9% PSA $H_2$ vs. 95% Methanator $H_2$ for Existing Units

Existing Hydrocracker

- **Basis:** 44,500 BPD operating with 90% makeup $H_2$ from Methanator and Platforming net gas

- **Benefit:** 4 vs. 3 year cycle resulting in $1.2$ million/yr lower annualized turnaround cost

  or

  Equivalent cycle length and 8% more feed resulting in $3$ million/yr higher profit
Benefits of 99.9% PSA $H_2$ vs. 95% Methanator $H_2$ for Grass Roots Units

**Grass Roots Hydrotreater**

- **Basis:** Hydrotreater for Ultra-Low Sulfur Diesel Production - 5 ppm Sulfur Product, 50,000 BPD capacity designed for 95% makeup $H_2$

- **Benefit:** Equivalent cycle length with 160 psi lower design pressure resulting in 13% lower capital cost - an $8 million savings
UOP Gas Purification Block Conclusions

Sarlux & Farmland Units Demonstrate

- UOP Gas Purification Block optimizes acid gas removal and hydrogen purification
- Selexol, PolySep Membrane, & PolyBed PSA are well suited for gasification service
- High overall sulfur recovery (> 99.75%)
- High H₂S concentration in acid gas to Claus unit
- Bulk CO₂ removal if necessary
- Very stable operation
- Minimal operator attention required

UOP GTC-30
Co-production of Power & High Purity H₂ using PolySep Membrane and PolyBed PSA in a Refinery Gasification Complex

- High Purity H₂ for Existing Hydroprocessing Units
  - Extension of cycle time to reduce OPEX for Hydrotreater
  - Extension of cycle time or increase in capacity for Hydrocracker

- High Purity H₂ for Grass Roots Hydroprocessing Units
  - Reduction in CAPEX & OPEX for Hydrotreaters
  - Similar benefit for Hydrocrackers
Questions?