SulfaTreat® DO
TDA's Direct Oxidation Technology for the Oil and Gas Industries

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Outline

- Background of sulfur recovery
- Direct oxidation Field Test
- Concept of SulfaTreat DO
- Economics of the process
- Market for technology
- License to SulfaTreat
- Conclusions

Why Sulfur Recovery?

PRIMARY ENERGY CONSUMPTION IN THE U.S. IN 2002

Oil	Gas	Coal	Nuclear	Hydro	TOTAL	Comment
894.3	600.7	553.8	185.8	58.2	2293	Millions of tonnes equivalent oil
35.77	24.03	22.15	7.43	2.33	91.71	BTU (quads)
39.0%	26.2%	24.2%	8.1%	2.5%		Percent of total

- The U.S. consumed 92 x 10^{15} BTU (92 quads) in 2002 (of which 26% was gas)
- The U.S. consumed 65 billion cubic feet per day of natural gas
- About 25% of natural gas is sour (contains H_2S)
- H_2S is toxic and corrosive (pipeline max = 4 ppm)
- Annual cost of sulfur removal from gas and petroleum estimated $5 billion.
- New worldwide sulfur recovery capacity (2002 Hydrocarbon Processing Box scores) was about 30,000 ton/day

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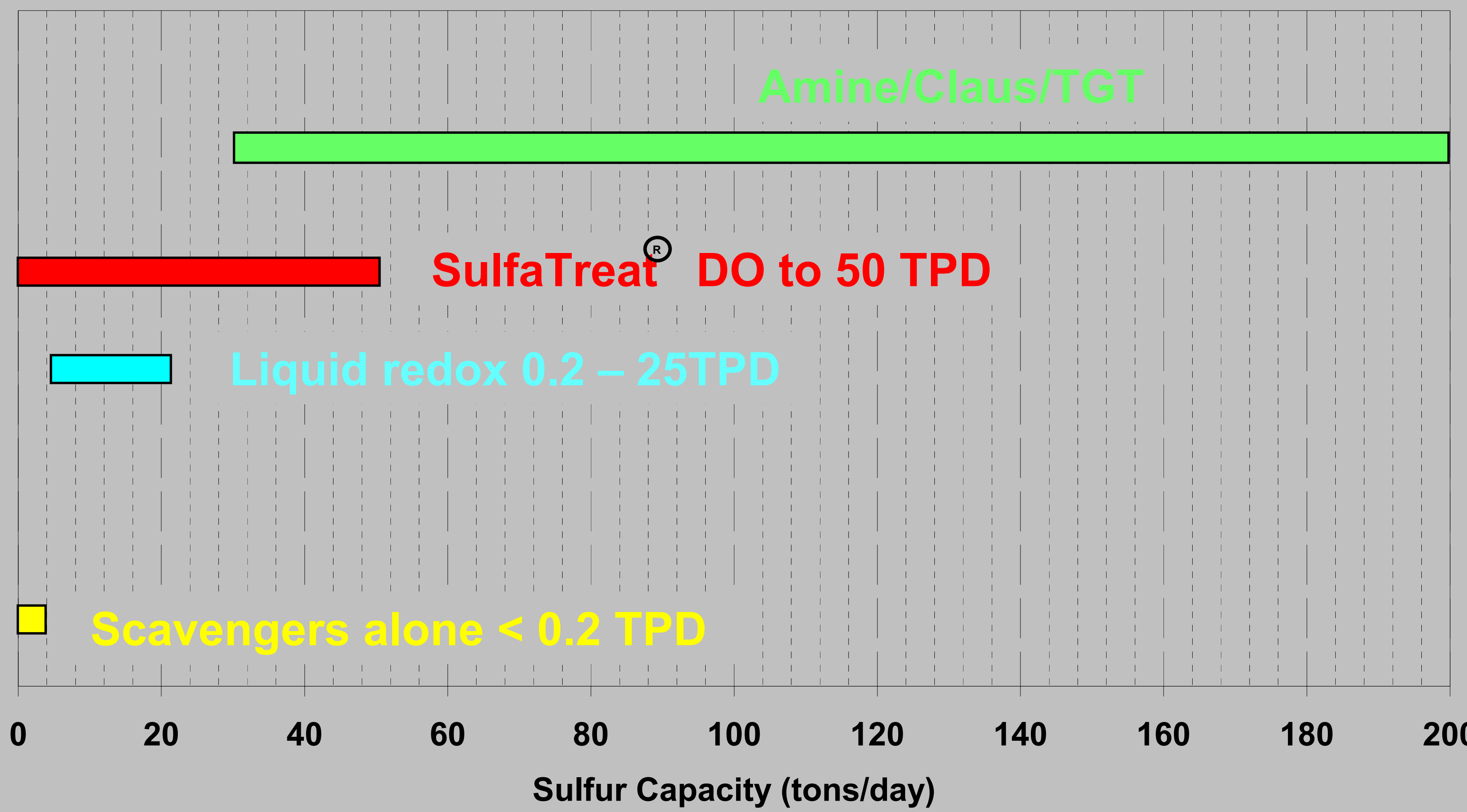
Commercial Sulfur Recovery Processes

- Small (less than ~0.2 LTPD), H_2S scavengers least expensive option, well proven
- Medium (~0.2 to ~25 LTPD), aqueous-iron ‘liquid redox’ (well proven, “high” chemical costs)
  - SulfaTreat® DO is a medium scale process
- Large (greater than ~25 LTPD) amine/Claus/TGT least expensive, well proven but only economical at large scales

Sulfur Recovery Plant Sizes



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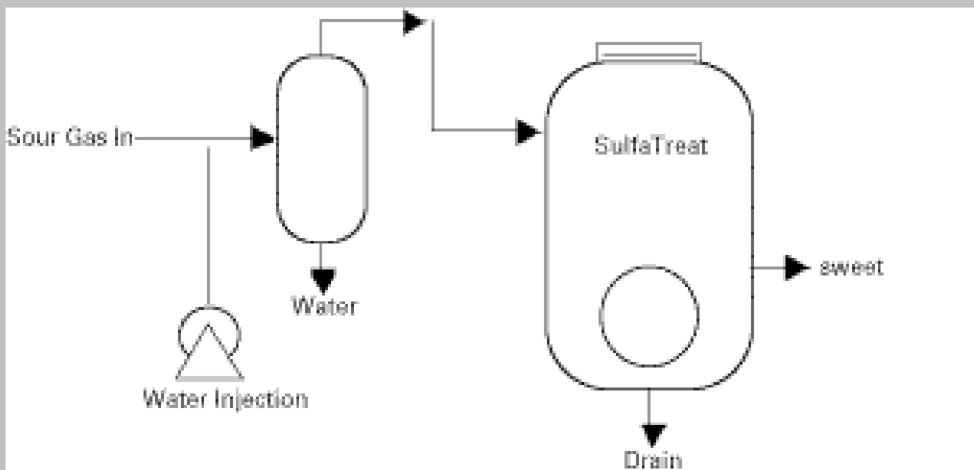
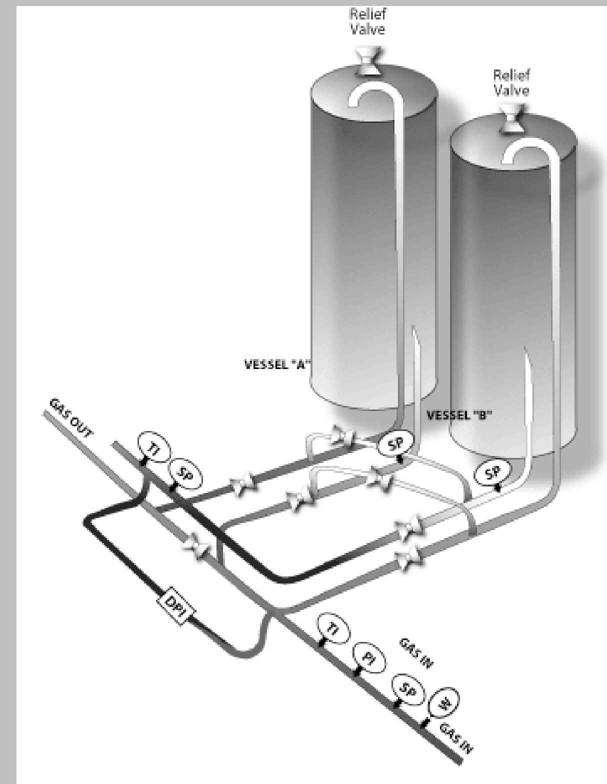
Small (< ~0.2 TPD)





- Scavengers (e.g. SulfaTreat®) are typically iron based
- Scavenger must be very inexpensive
- Only practical for small amounts of H_2S

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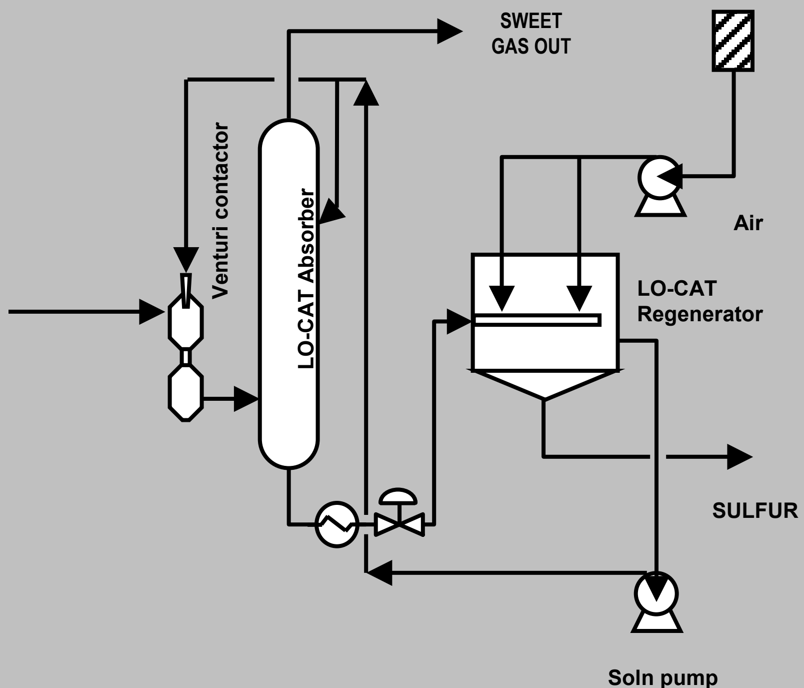
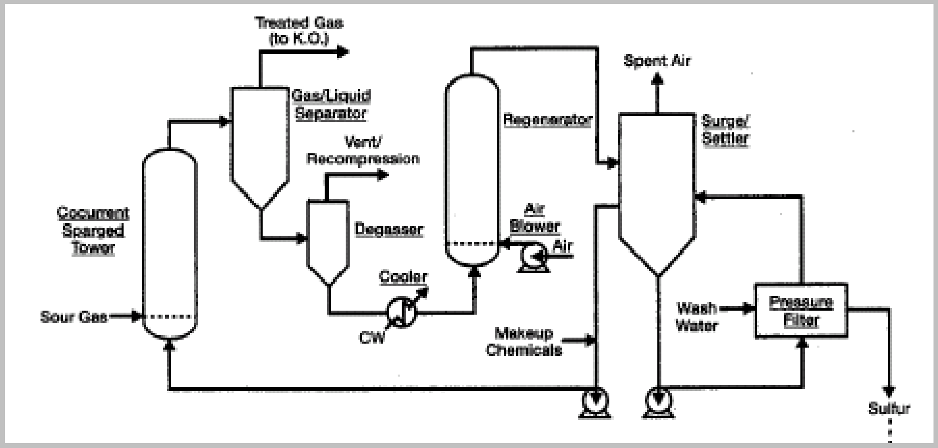
Medium (~0.2 to ~25 TPD)





- LO-CAT® (GTP)
- Aqueous chelated Fe catalyst
- Sulfur form insoluble slurry
- Cannot tolerate much SO_2

- Sulferox® (Shell/Westfield)
- Iron based liquid phase catalyst
- Cannot tolerate much SO_2
- Sulfur removed from a slurry

- **Liquid redox systems recover sulfur as slurry or solution**
- **High chemical costs, somewhat complex to operate**

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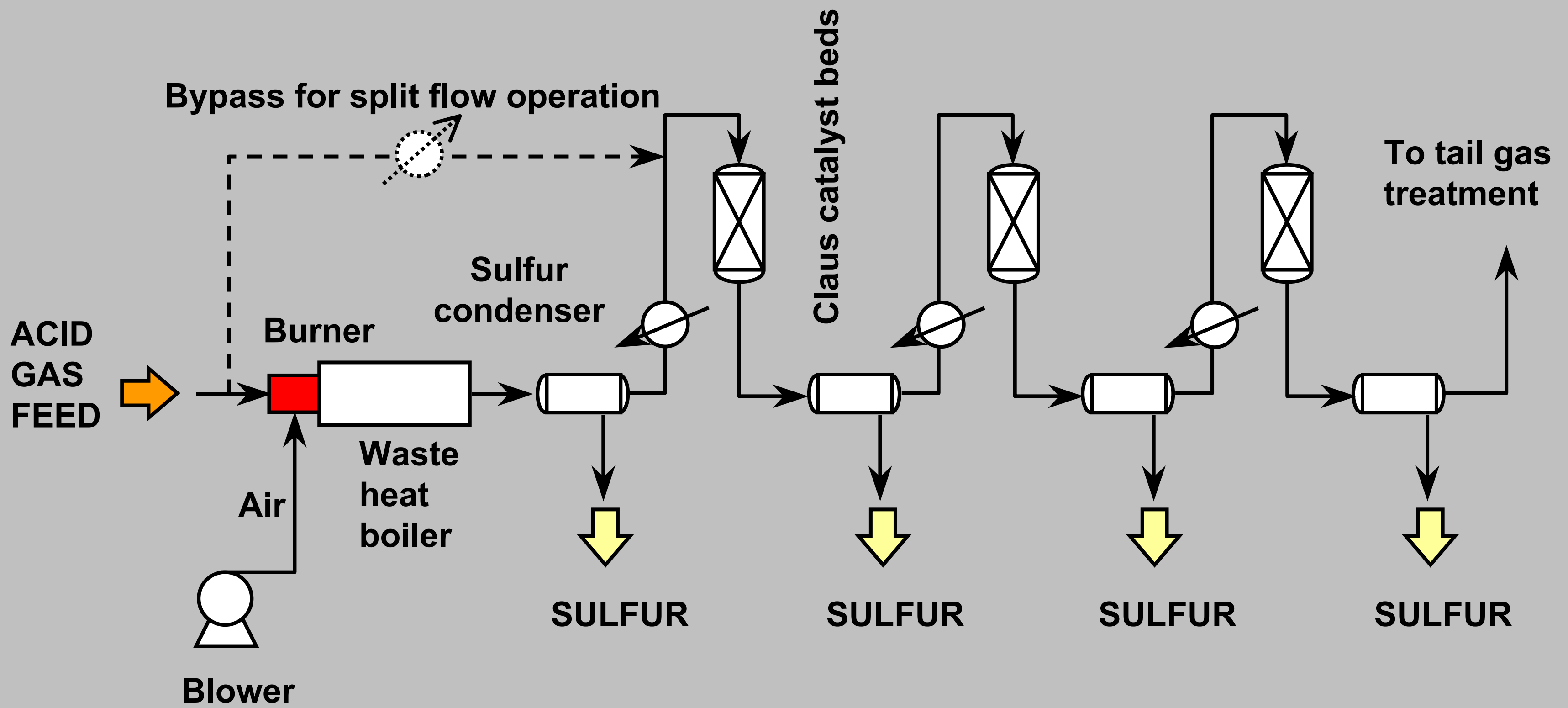
Large (> ~25 TPD)



- Claus process only economical at large scales (many licensors)
- H_2S concentrated in an amine unit
- Most of sulfur recovered during H_2S combustion in the furnace
- Multiple reactors needed because Claus reaction is equilibrium limited

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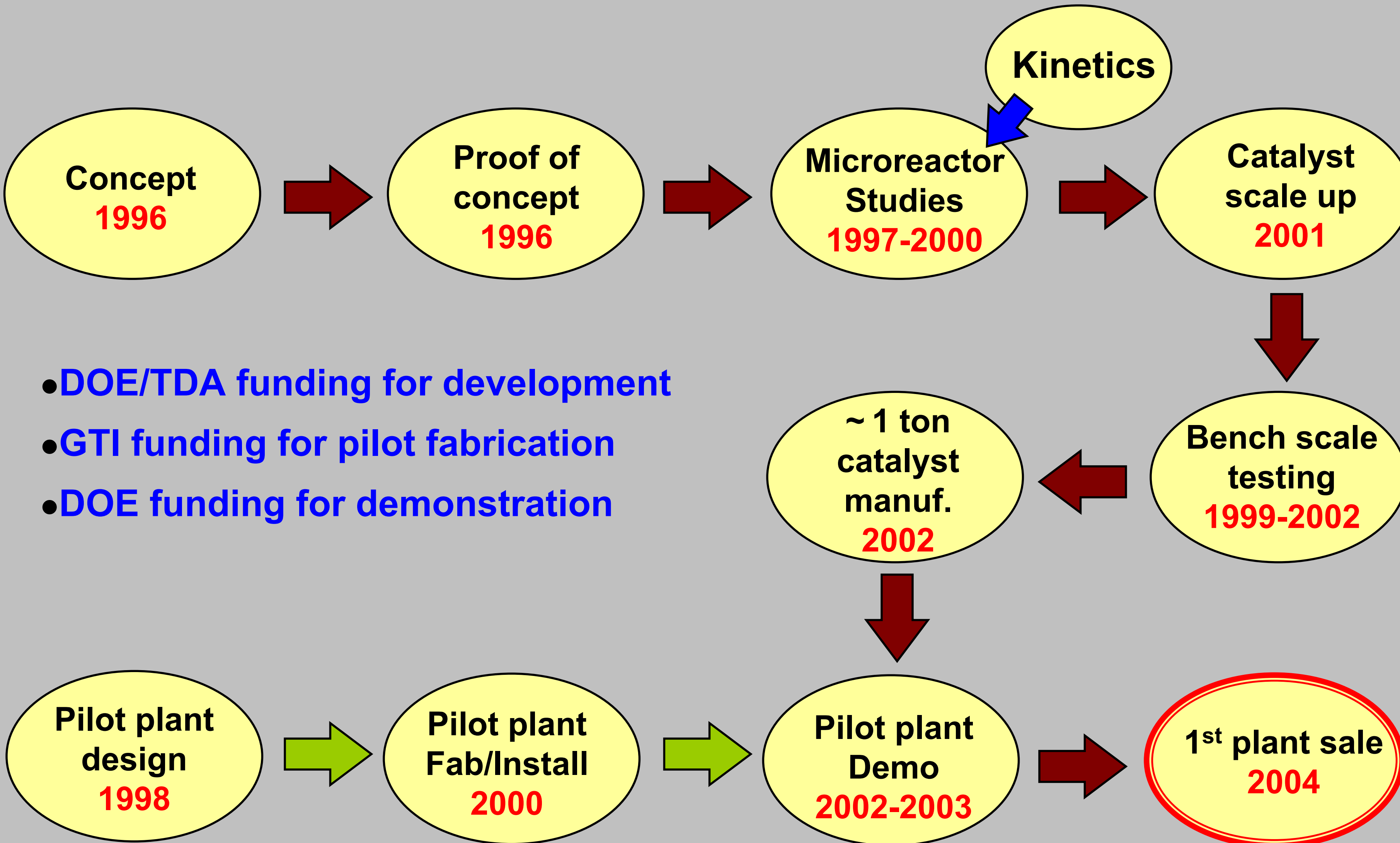
SulfaTreat® DO Process

- **TDA Research has developed a catalytic sulfur recovery process that**
  - Selectively oxidizes H_2S to S and water

$$H_2S + 0.5\ O_2 \longrightarrow S + H_2O$$

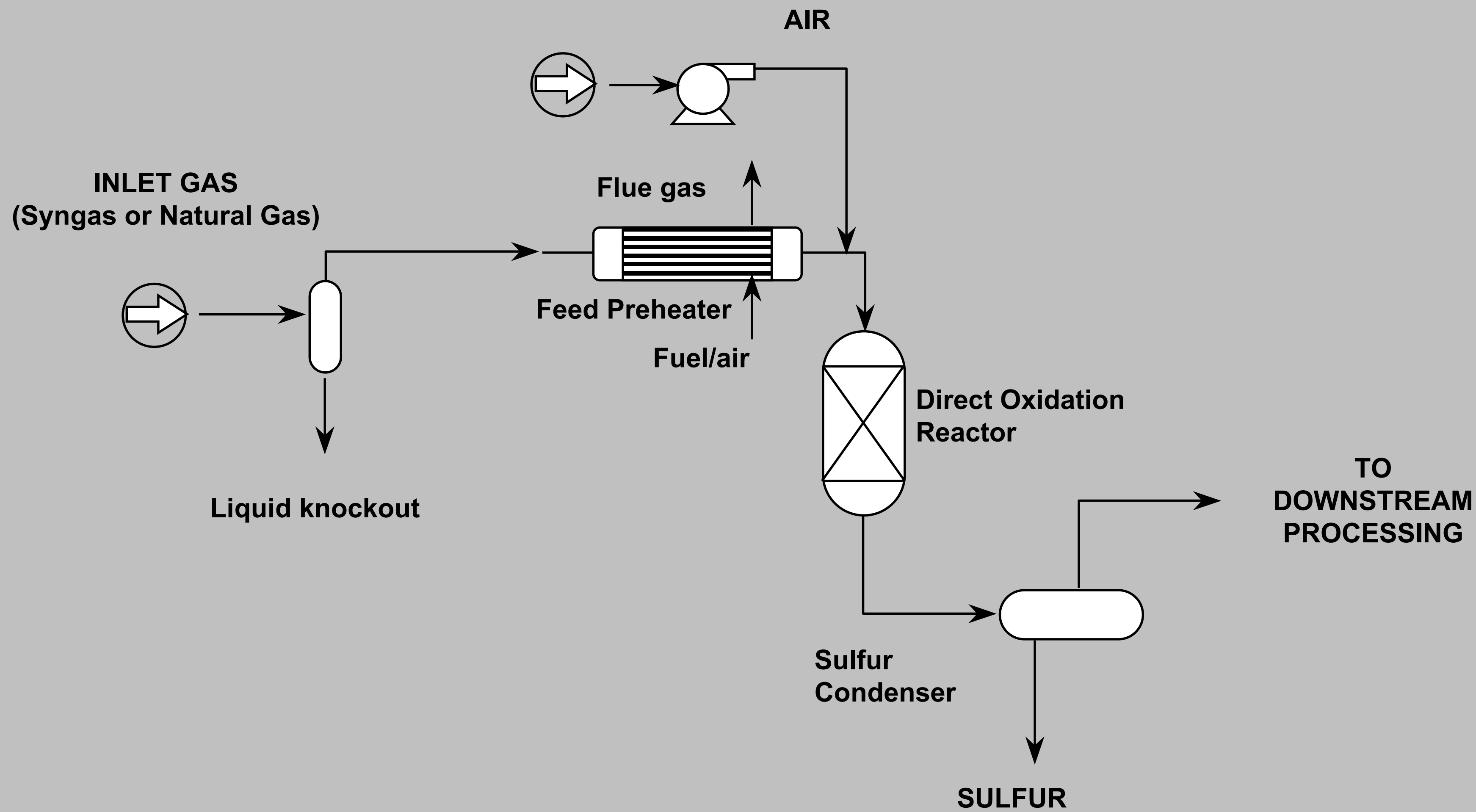
  - No equilibrium limitations because of good catalyst selectivity
  - Recovers >90% of the H_2S as S in a single step
  - Uses a patented catalyst
  - Has very low capital and operating costs
  - Can be directly operated on natural gas, syngas and hydrogen streams
  - Has a smaller footprint than liquid redox or Claus processes

Steps to Commercialization



- DOE/TDA funding for development
- GTI funding for pilot fabrication
- DOE funding for demonstration

SulfaTreat® DO Process



- Single step recovery efficiency ≈ 90%

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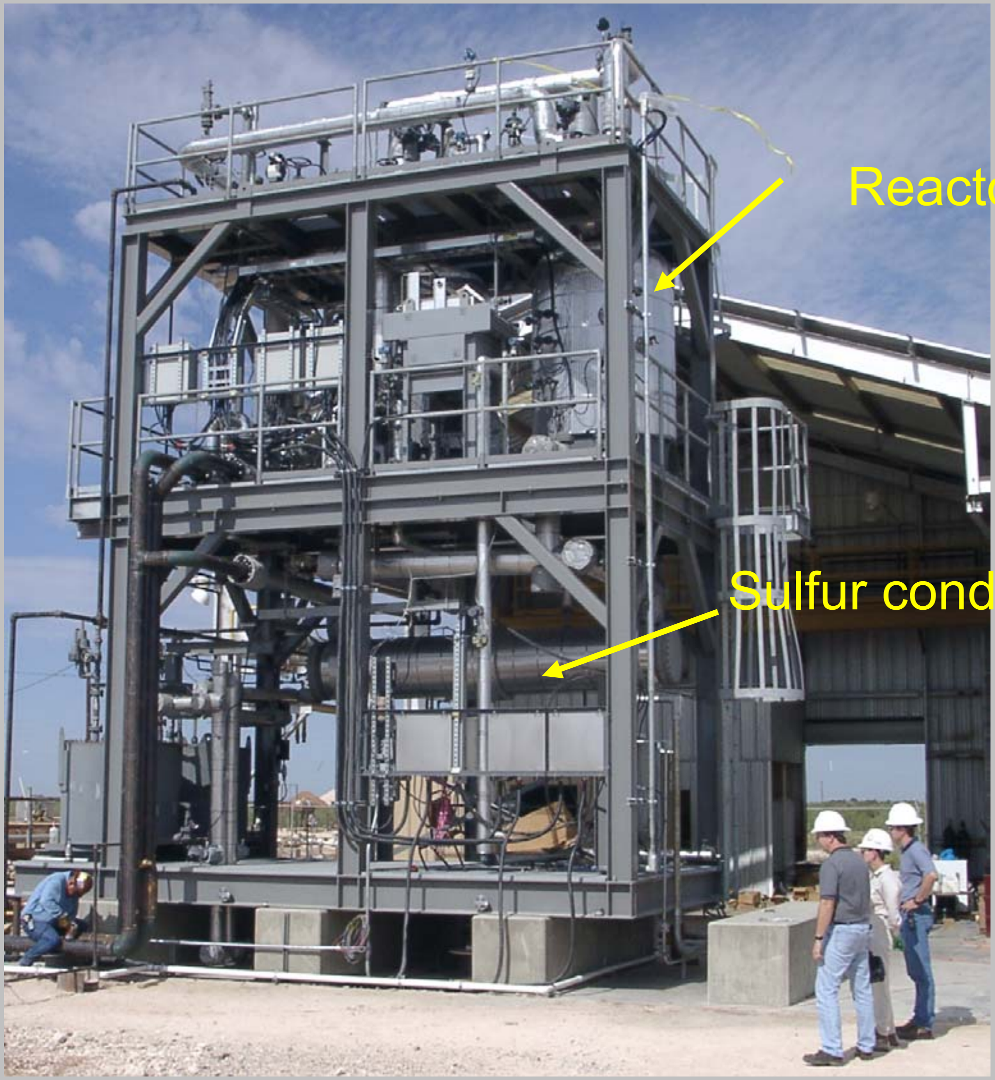
Process Variables

- **Catalyst** – TDA patented mixed metal oxide
- **Temperature** – ca. 350ºF
- **Pressure** – ambient to 1000 psi
- **H_2S concentration** – few ppm to about 3% (in single stage)
- **O_2/H_2S ratio** – 0.5 to 1.5
- **Space velocity** – 1000 – 10,000 h^{-1}

Direct Oxidation of H_2S

Pilot Demonstration

Demonstration Unit



- Catalyst development and pilot test funded by DOE
- Pilot unit design and fabrication funded by GTI
- Pilot unit capable of handling
  - 1 MM scfd
  - 1 tpd sulfur

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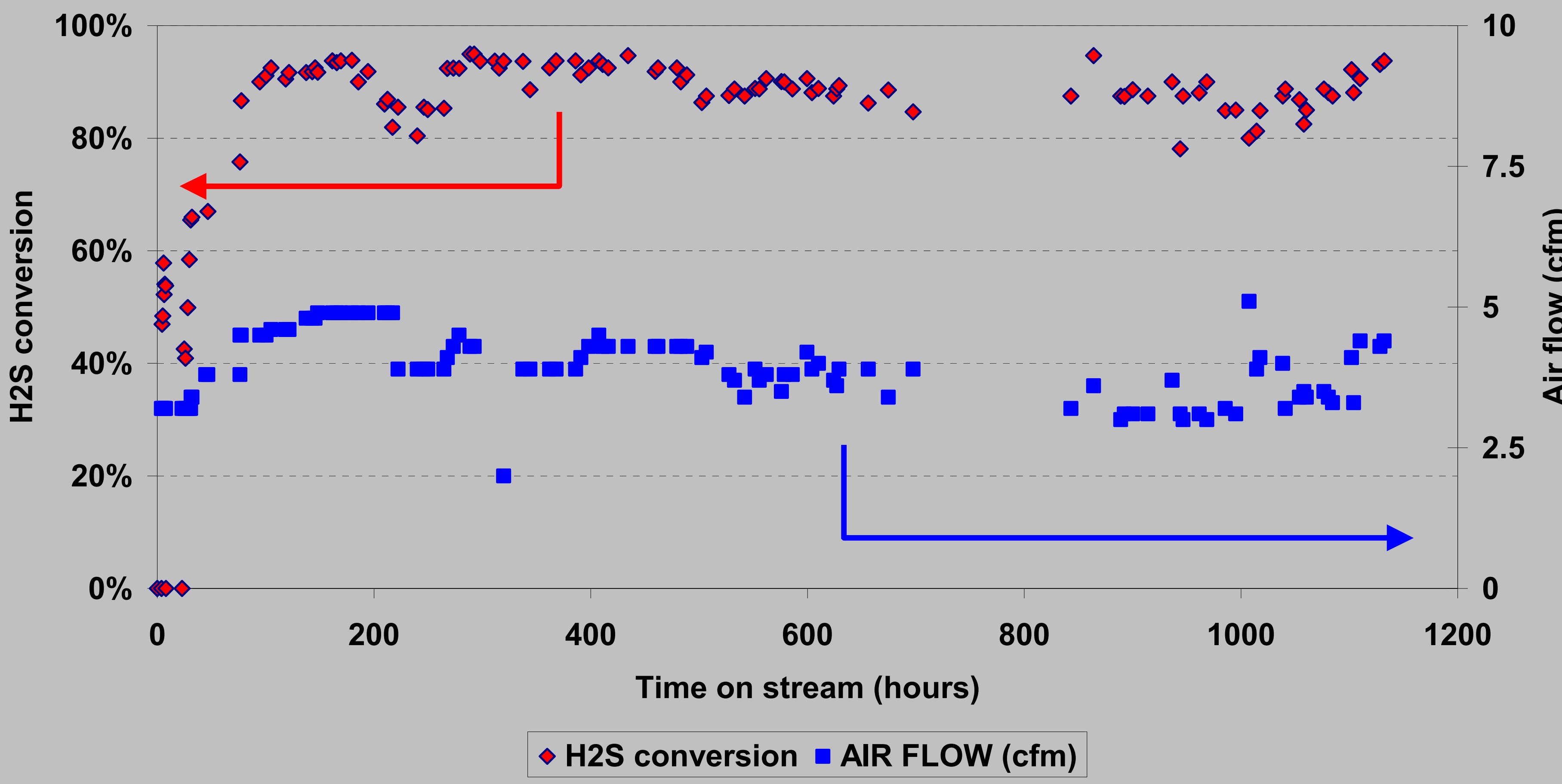
Demonstration Test

- **TDA has completed > 1200 h test in West Texas in 2003**
  - Whiting Petroleum's associated gas (0.6 MMSCFD from an oil field)
    - 0.8% H_2S
    - 20% methane
    - 15% ethane
    - 10% propane
    - Balance CO_2
    - $\geq$ 2300 ppm BTEX
    - $\approx$100 ppm mercaptans

Demonstration Test Data



- Sulfur recovery efficiency tracks air flow rate
- H_2S conversion ~90%
- 80% of the mercaptans removed

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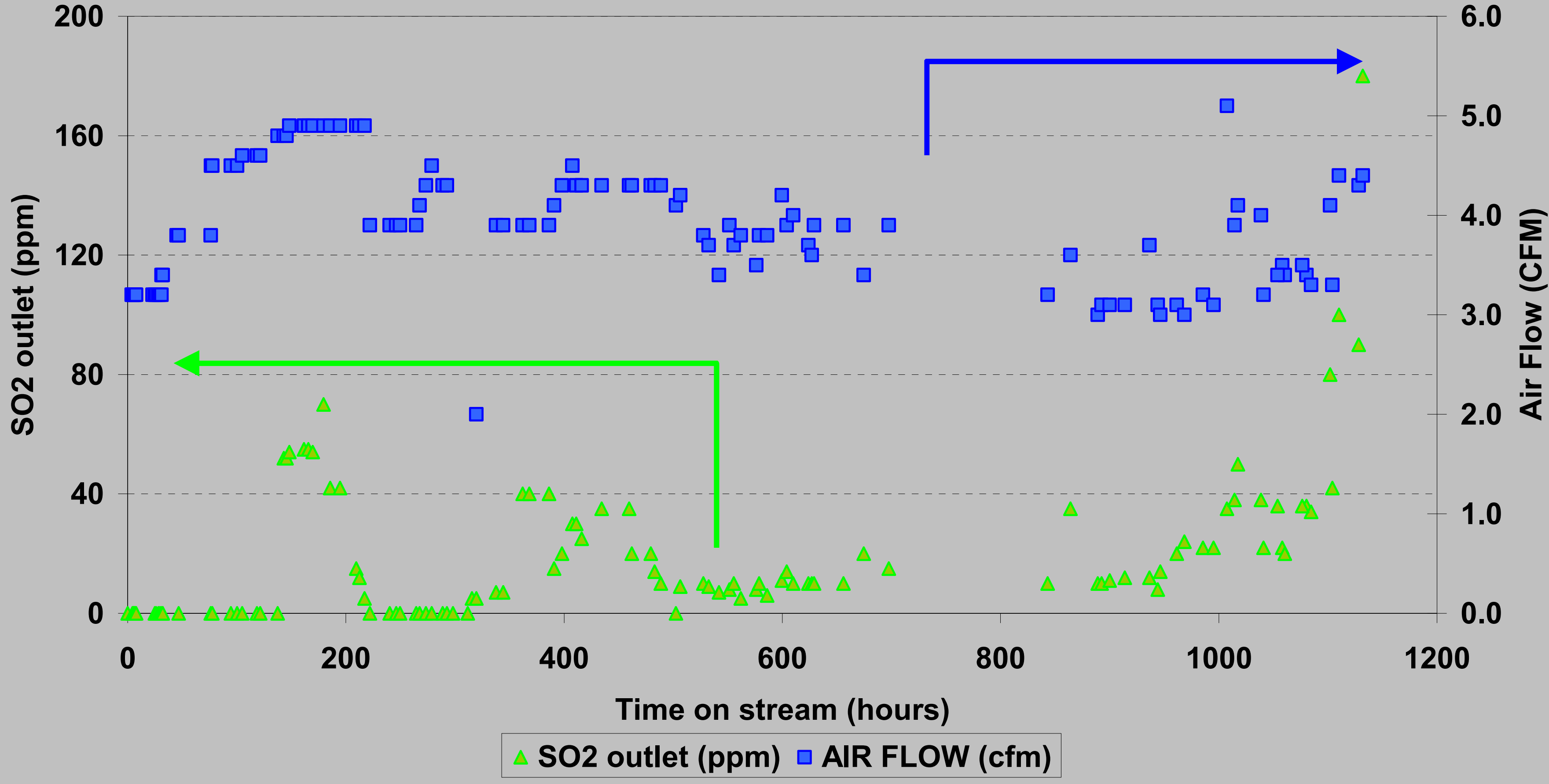
Demonstration Test Data



- SO_2 selectivity tracks air flow rate
- SO_2 selectivity can be controlled by temperature, air flow rate, and catalyst composition

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Inlet and Outlet Gas Analysis

COMPONENT	INLET (MOL%)	OUTLET (MOL%)
H_2S	0.8000	0.095
N_2	1.5972	2.8794
CH_4	17.6750	17.7853
CO_2	58.6264	58.6625
Ethane	8.7006	8.5607
Propane	6.4640	6.2643
isobutane	0.9798	0.9228
n-butane	2.3841	2.3154
isopentane	0.7385	0.7115
n-pentane	0.7715	0.7453
cyclopentane	0.0105	0.012
2-methylpentane	0.1512	0.1354
3-methylpentane	0.1345	0.1203
n-hexane	0.2658	0.2353
methylcyclopentane	0.1375	0.1144
benzene	0.2107	0.1692
cyclohexane	0.1698	0.1387
n-heptane	0.0976	0.0703
methylcyclohexane	0.0517	0.0378
toluene	0.0218	0.0136
n-octane	0.0053	0.0032
ethyl benzene	0.0029	0.0024
p and m xylene	0.0029	0.0027
o-xylene	0.0007	0.0004
Mercaptans	1.01E-04	2.00E-05

- **H_2S reduced by 88-92%**
- **Mercaptans reduced by 80%**
- **Minimal amount of C_5+ hydrocarbons oxidized.**
- **Less than 10 ppm SO_2**

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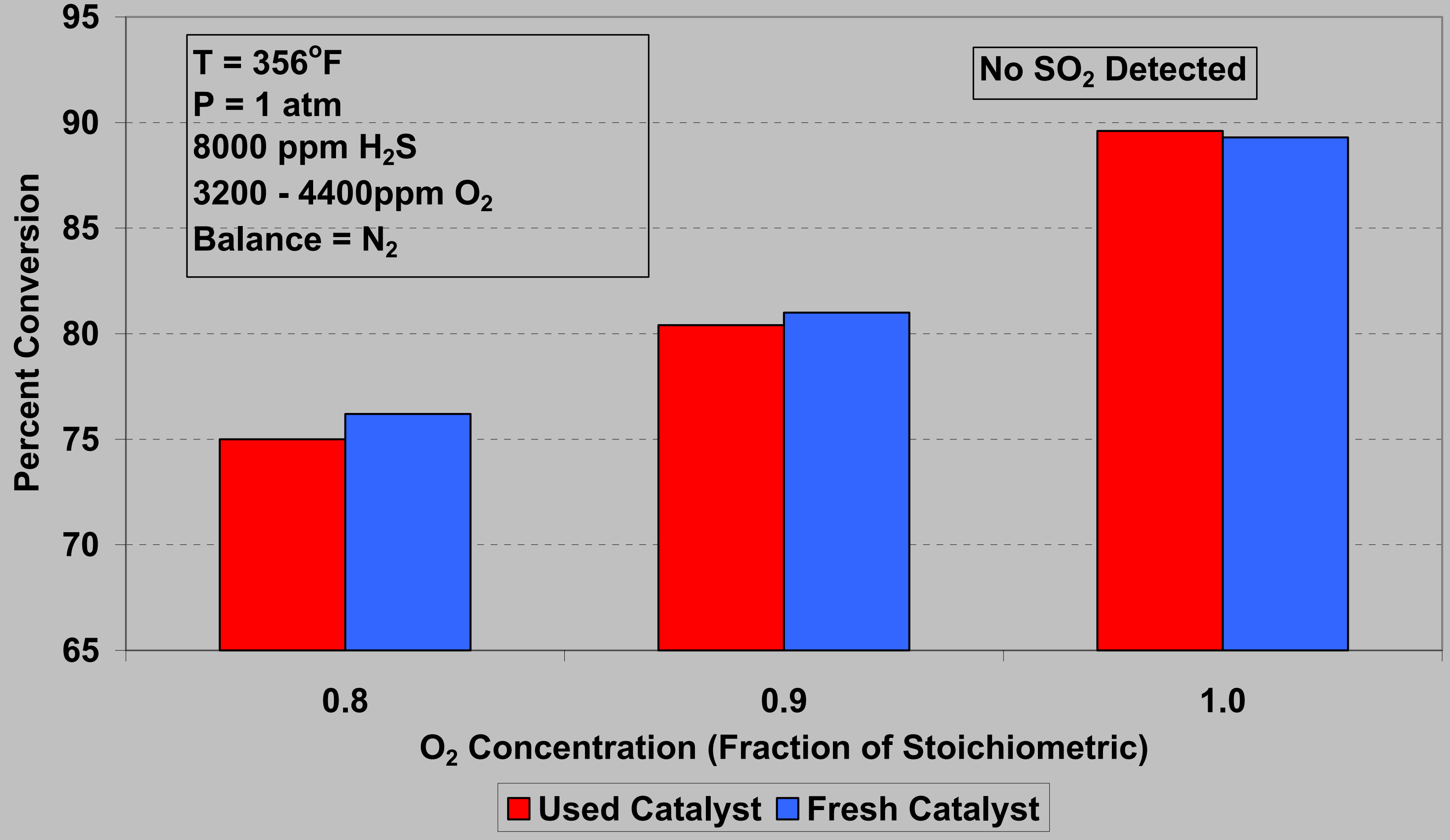
Laboratory Test of Used Catalyst



- Catalyst shows no deactivation after 1200 hours of operation

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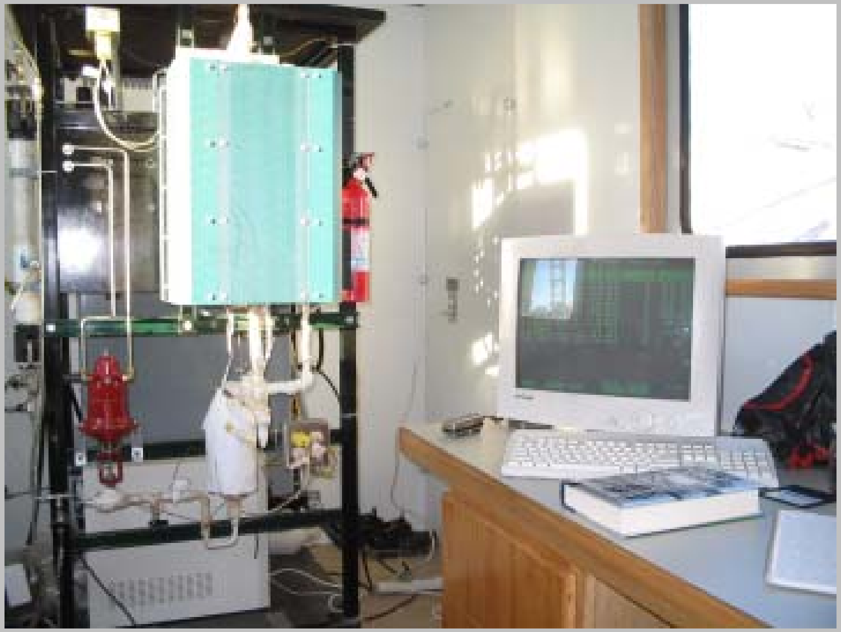
Field Test on Landfill Gas



- Slip stream of landfill gas
- Continuous operation

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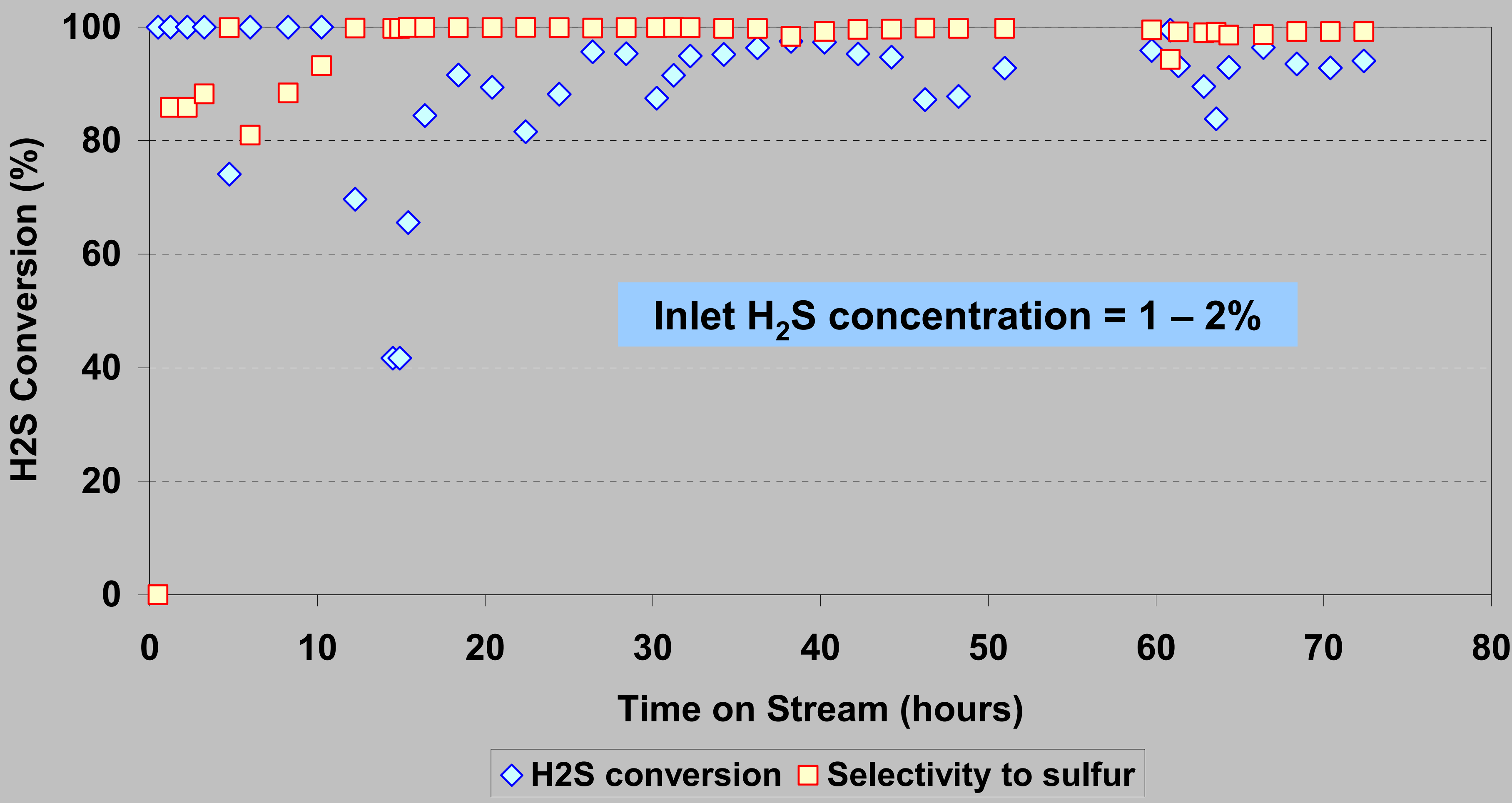
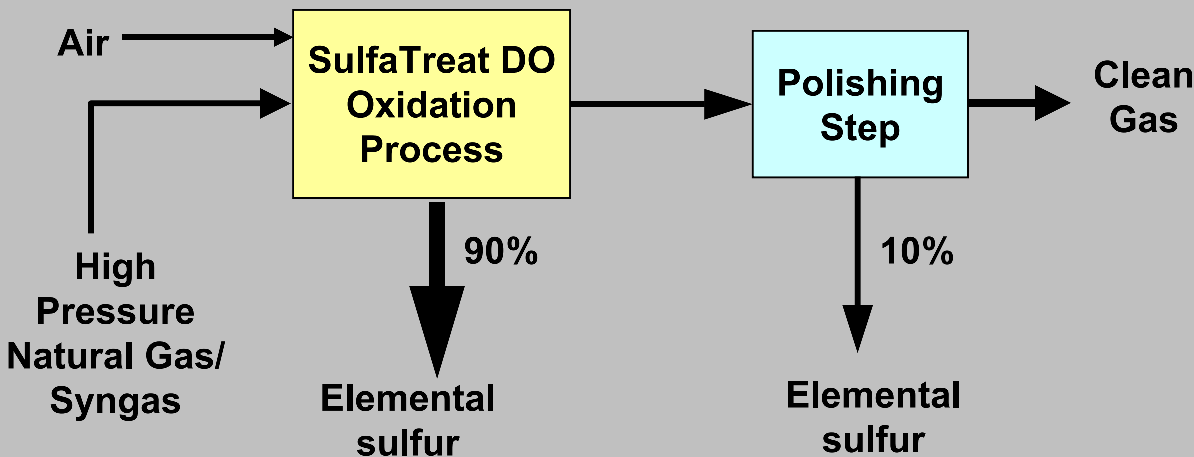
Field Test on Landfill Gas



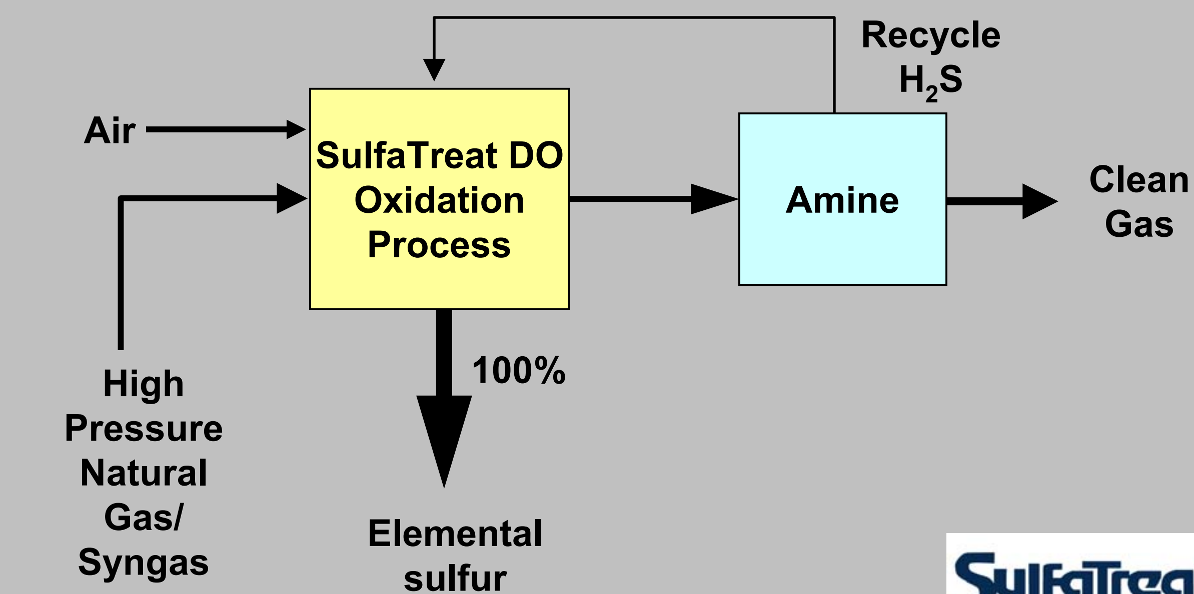
Extending DO Application

- **Combines the low cost bulk removal of DO with the high efficiency of polishing steps**



Polishing Steps

- SulfaTreat® - low SO_2
- Shell-Paques® – low SO_2
- Lo-Cat® - low SO_2
- Sulferox® – low SO_2
- CrystaSulf℠ - high SO_2



Polishing Step

- Amine – low SO_2

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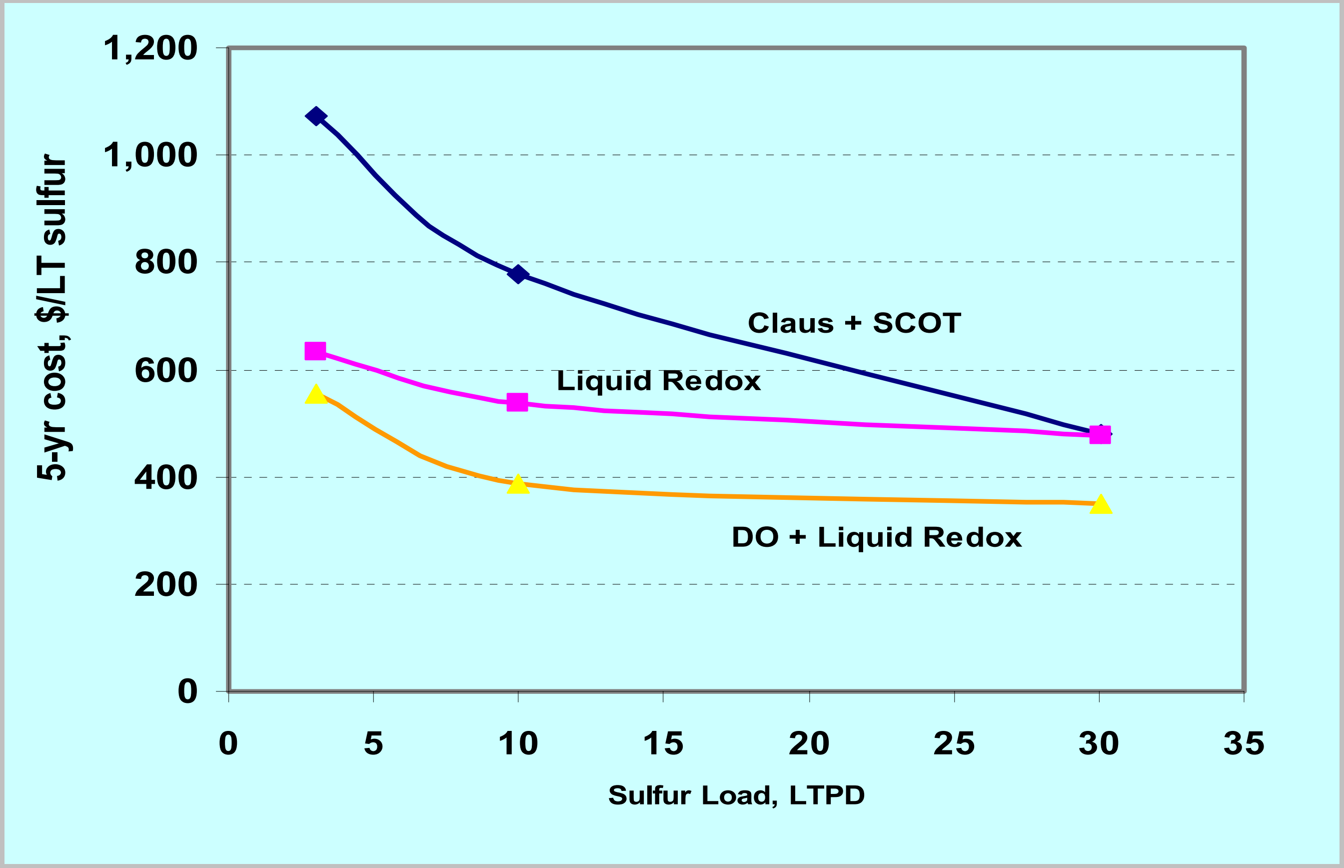
DirectTreat Concept

- **TDA has one patent issued and additional patents pending on catalyst formulations for DirectTreat**
- **Strong attributes of DO**
  - Low cost
  - Single-step bulk S removal
  - No chemical make-up costs
  - Can be operated selectively to remove H_2S from
    - Natural gas
    - Syngas
    - Hydrogen streams in refineries
- **Strong attributes of liquid polishing steps**
  - Excellent for combining with Direct Oxidation
  - Can recover > 99% of the H_2S
- **Combining the two provides high efficiency at low cost**

Costs vs. Other Technologies

Independent analysis



- Total Annual Cost = Annual op cost + 0.2 x Cap cost
- DO + Liquid Redox includes cost for amine plant

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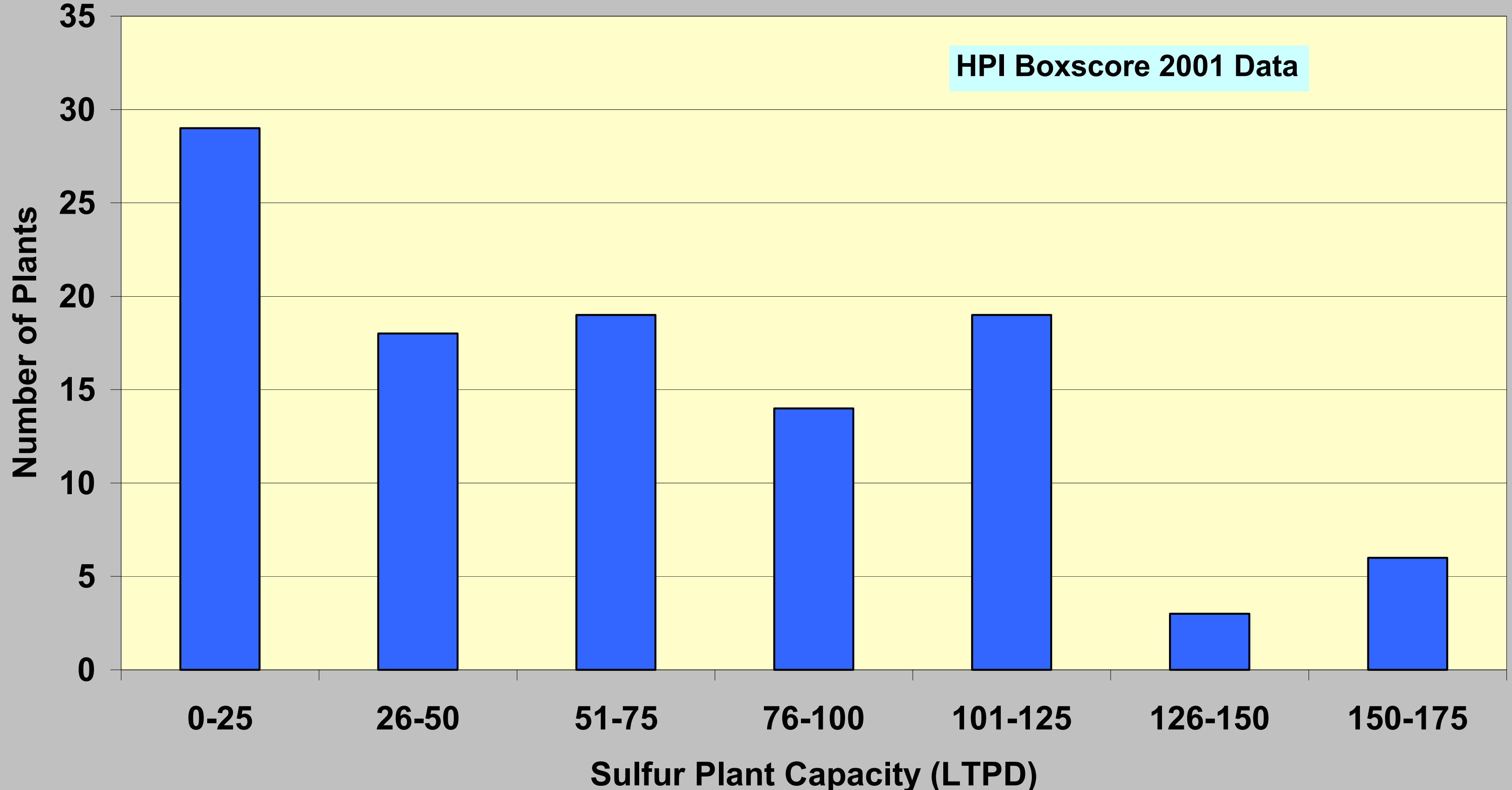
Market Potential for Natural Gas Treatment



- **Total new worldwide capacity in the 10 – 175 tpd range ~ 7100 tpd**
  - Estimate of total capital ~ $2 billion/year
  - Many plants between 0 and 50 LTPD
  - Natural gas @ 25% of total market ~ $500 million/yr
  - 10% of natural gas market ~ $50 million/yr

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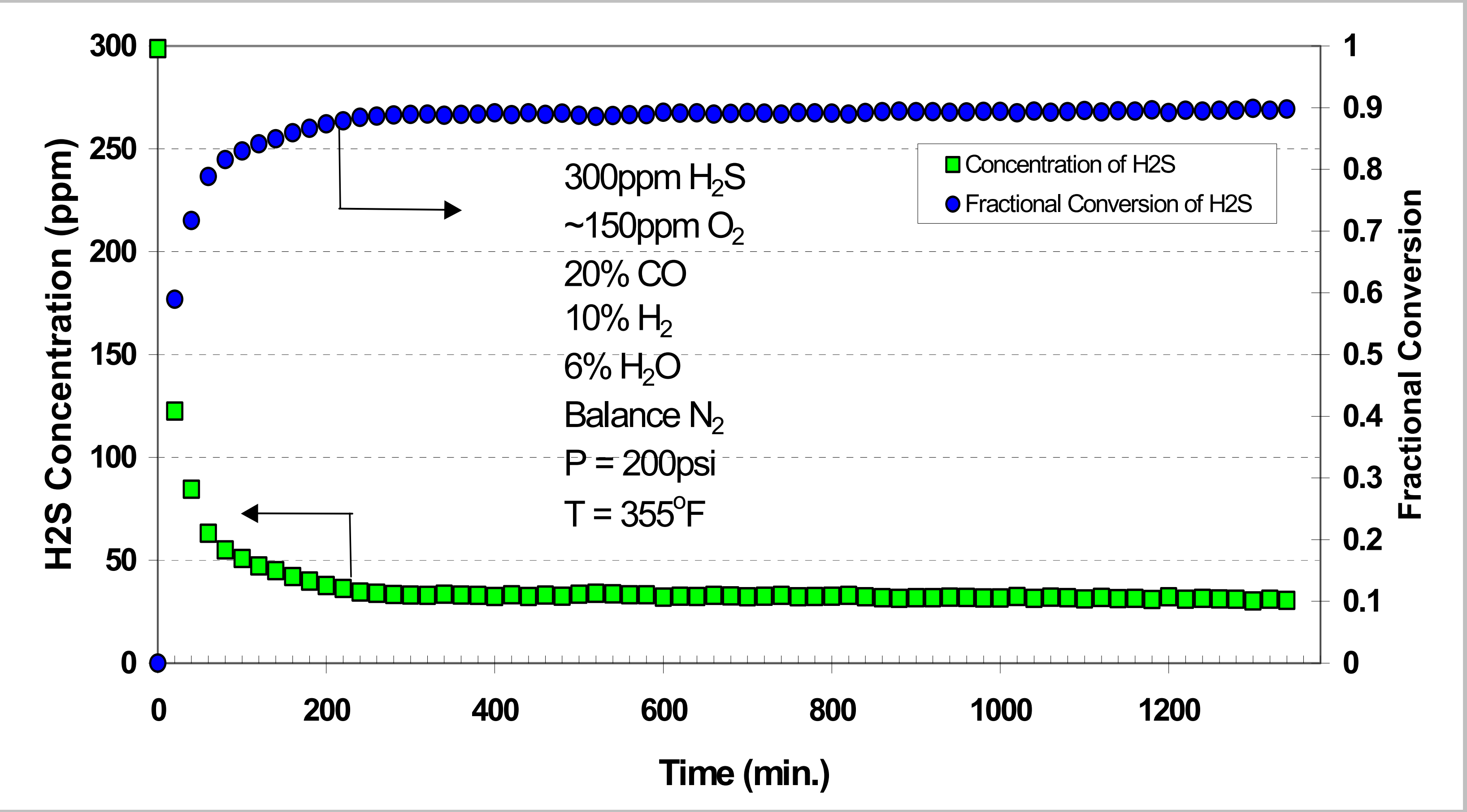
Direct Oxidation for Syngas Treating



- TDA's catalyst selectively oxidizes H_2S in the presence of CO/H_2

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Technology Licensing

- TDA signed a License Agreement with SulfaTreat in January 2004.
- SulfaTreat is actively marketing the technology
- SulfaTreat is seeking potential applications/ sublicenses
- Westfield Engineering will design, engineer, and fabricate units

Acknowledgments

- Saint-Gobain Norpro
- Huzyk Energy Management