Hydrodesulfurization Technologies and Costs

By

Nancy Yamaguchi

Trans-Energy Research Associates, Inc.

For

The William and Flora Hewlett Foundation Sulfur Workshop

Mexico City, May 29-30, 2003

Objective

- Overview of hydrotreating technology
- World HDT capacity
- Sampling of technology vendors and costs

Purposes of Hydrotreating

- *Note: some fluidity in use of terms hydrotreating, hydrorefining, hydroprocessing, hydrodesulfurization*
- Heavy naphtha treated prior to cat reforming
- Jet fuel treated to reduce sulfur and convert aromatics to naphthenes, raising smoke point
- Diesel sulfur reduced, cetane number enhanced, some aromatics may be saturated
- Heavy fuels may be desulfurized, though pressures must be kept high to minimize coking
- Gasoils may be treated prior to cat cracking

Hydrodesulfurization Process

- C_6+ streams likely to have sulfur compounds attached anywhere in the molecule, with heavier fractions more difficult to desulfurize
- Hydrogen used with catalyst, 500-800 ^{o}F (260-425 ^{o}C), H_2 combines with S to form H_2S, 95%-99%+ of sulfur is removed
- Some nitrogen compounds converted to ammonia
- Metals deposited onto catalyst (CO-MO for S, NI-MO or NI-W for N and HDA)
- Some aromatics, olefins, naphthenes are saturated, creating methane, ethane, propane, butanes

Typical Hydrodesulfurizer Flow

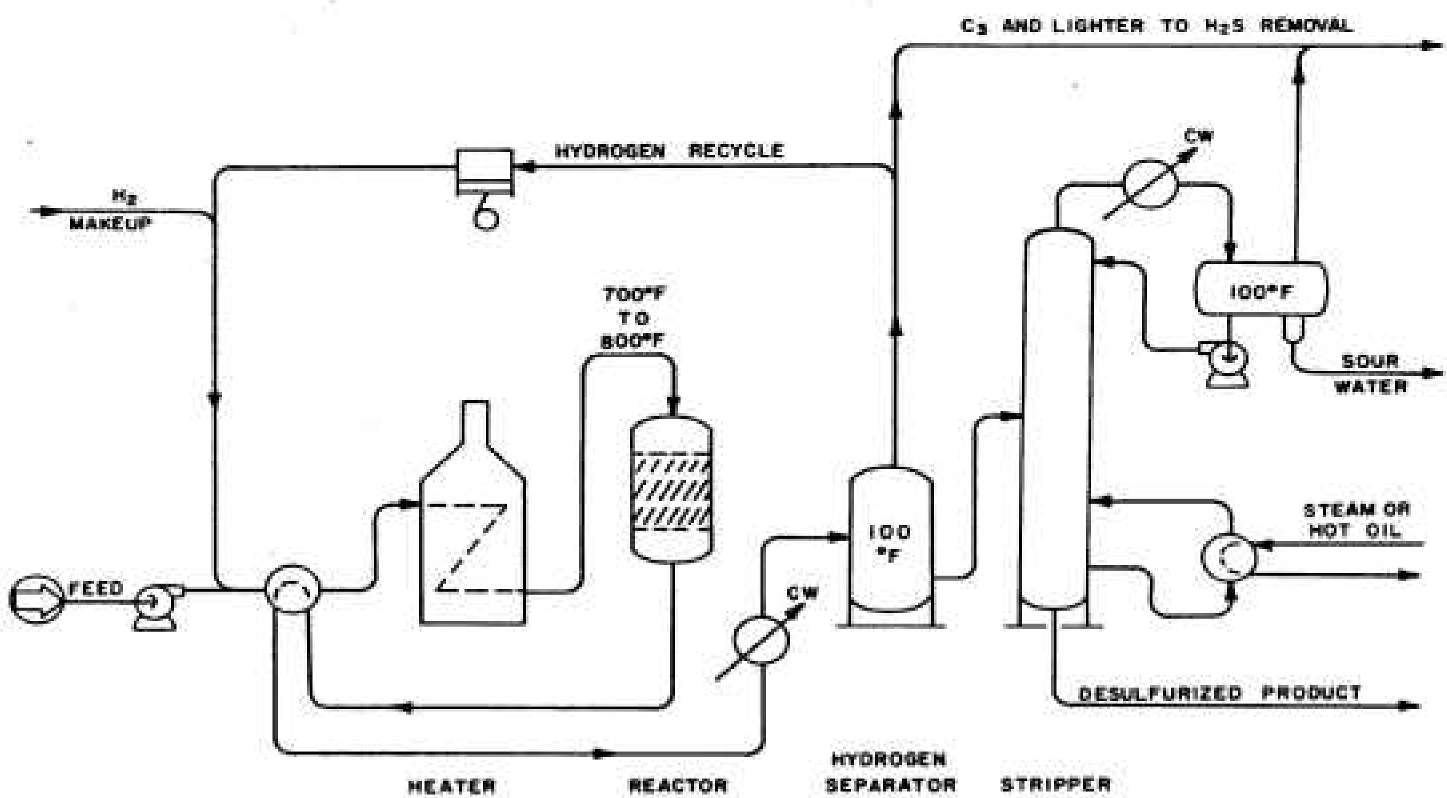
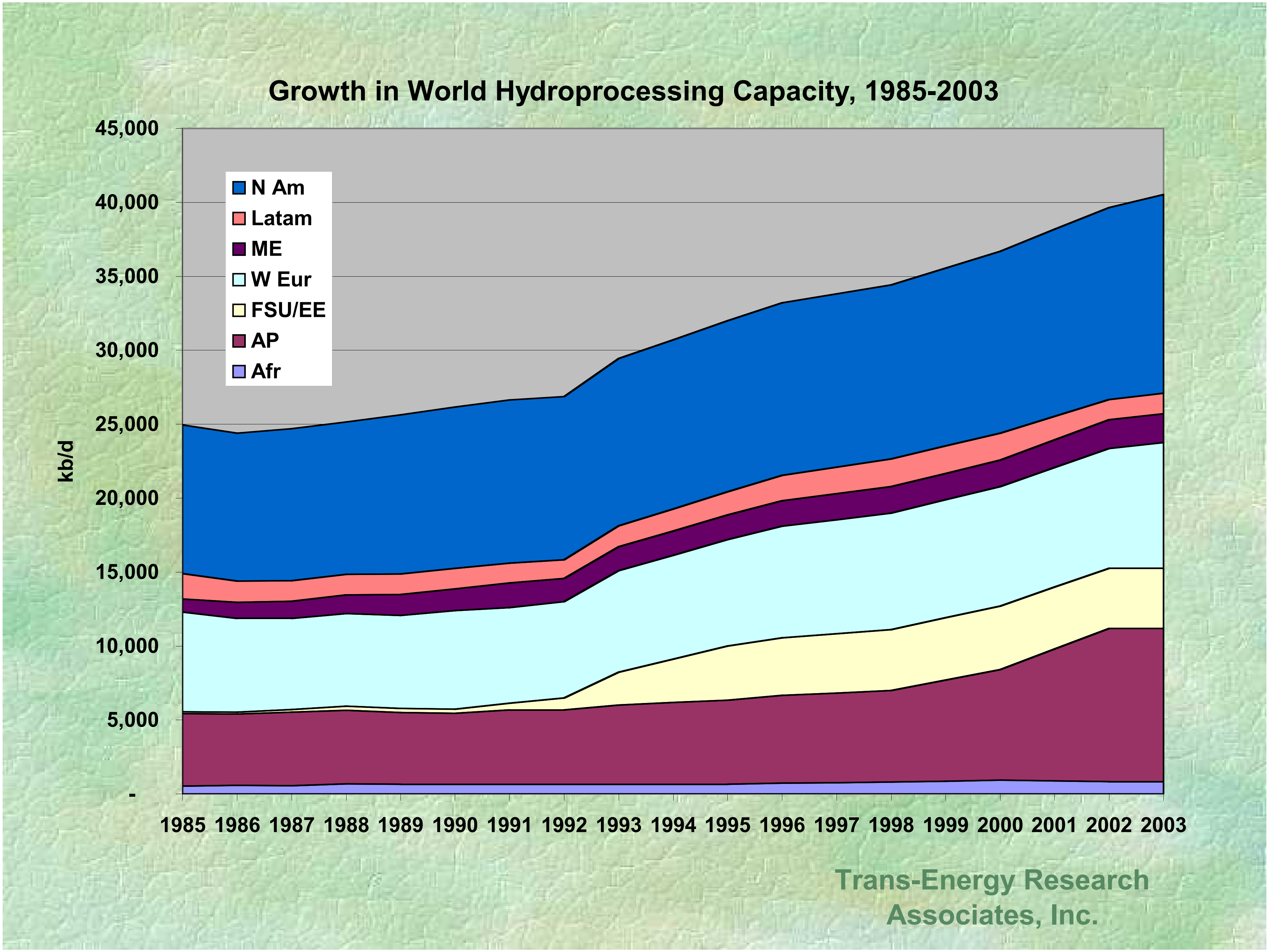


FIG. 9.1. Catalytic hydrodesulfurizer.

Source: Gary and Handwerk

Growth in World HDT Capacity

- World HDT capacity grew from 24.9 mmb/d in 1985 to 40.5 mmb/d in 2003--a 2.7% increase per year.
- CDU capacity grew at only 0.7%/year
- Further expansions expected with many markets working to improve fuel quality
- Automakers ask for "as close to zero-sulfur as soon as possible."


Growth in World Hydroprocessing Capacity, 1985-2003
N Am
Latam
ME
W Eur
FSU/EE
AP
Afr
45,000
40,000
35,000
30,000
25,000
20,000
15,000
10,000
5,000
-
kb/d
1985
1986
1987
1988
1989
1990
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
Trans-Energy Research Associates, Inc.

Regional Variations in HDT

- N. Am. and W. Eur accounted for two-thirds of HDT capacity until the 1990s, when share fell to 54%
- Despite growth in HDT capacity in FSU/EE, Mideast, Asia & Africa, N. Am. and W. Eur still have more HDT capacity as % of crude capacity (64% and 58%)
- Lat. Am lags with HDT:CDU of just 23%, (though Pemex has large HDT cap)

Gasoline-Oriented HDT Techs

- HDT heavy naphtha pre- cat reforming is very common
- HDT of FCC naphthas becoming more common and more sophisticated
- 95-99%+ of sulfur may be removed
- Saturation of olefins and aromatics possible but typically avoided because of octane loss
- Costs range $10-70 mn.

Hydrotreating Technologies and Vendors, Gasoline-Oriented

Licensor	***Technology Name***	***Purpose***	***Notes***	***Costs***
CDTech	CDHydro and CDHDS	Selectively treat FCC nap, flexible of olefins and aromatics saturation	Cat dist selectively treat gasoline fractions	35 kb/d approx $26 mn capcost ISBL, opcost $0.04/gal FCC nap treated
ConocoPhillips Co	S Zorb	FCC nap treatment using proprietary solvent	97% sulfur removal, 25 ppm product to 100% sulfur removal	25 kb/d unit with 25-ppm S output =$900 per bbl capcost 0.9 c/gal opcost
UOP, w/ PDVSA-INTEVEP	ISAL	Gasoline blendstock desulf, flexible modes	5-25 ppm output dep. on mode (1-3 octane loss)	Above conventional HDT. Example 44 kb/d unit $87 mn
Howe-Baker Engineers Inc.		Naphtha desulf	98.5-99% product recovery	
Exxon/Mobil	Octgain	Gasoline blendstock desulf, olefins reduced as needed	Up to 99.8% sulfur removal, 5-10 ppm; followed by isom	
GTC Technology	GT-DeSulf	FCC nap desulf and aromatics extraction w/ no octane loss	H2 use reduced via solvent use, no octane loss, <20 ppm sulf	
Axens NA (IFP and Procatalyse)	Prime G+	Selectively treat FCC gasoline to retain olefins and octane	97.5% HDS, 30-50 ppm product (10 ppm achieved in Germany)	Grassroots ISBL capcost=$600-800 per bpsd. Example 18 kb/d=$18 mn Uruguay

Diesel Hydrotreating Technologies

- Tightening sulfur specs have stimulated massive investment in new HDT techs
- 95-99% of sulfur typically removed
- HDT improves cetane # and saturates some olefins and aromatics
- HDA techs have evolved to saturate aromatics and eliminate sulfur
- GTL technologies also evolving to produce zero-sulfur synthetic diesels
- Costs range $50-200 mn, HDA

Hydrotreating Technologies and Vendors, Middle Distillate-Oriented

Licensor	*Technology Name*	*Purpose*	*Notes*	*Cost Notes*
Badger Tech on behalf of SK Corp	SK HDS	Pretreatment process to improve performance of existing HDS units	Strips NPCs (nitrogen- bearing polar compounds) pre-HDS. Sulf as low as 10 ppm	
Howe-Baker Engineers, sub. of Chicago Bridge & Iron Co.		Removal of organic sulfur and nitrogen	Sulf removal 98.5% to 99%+	
Linde BOC Process Plants and Process Dynamics	IsoTherming	Pretreatment before conventional HDS	Sulf down to 10 ppm	Basis 15-20 kb/d unit $500 per bpsd diesel
UOP LLC	Unionfining and MQD Unionfining (various)	Removal of organic sulfur and nitrogen, cetane improvement, aromatics saturation	HDS many streams incl diesel; hundreds of units installed	Typical investment $1,200-2,000 per bpsd. Example 48 kb/d=$66 mn Barauni
ABB Lummus Global "SynAlliance" (Criterion & Shell)	SynSat/SynShift	Sulfur removal, cetane enhancement, aromatics saturation	Can take sulfur and nitrogen to zero. 11 units operating, 7 planned as of Nov 2002	30-35 kb/d ISBL capcosts per bpsd: Revamp existing unit=$450-950; New unit for deep HDS=$1,100-1,200
ABB Lummus Global for "SynAlliance"	SynTechnology (SynSat/SynShift, SynHDS, SynFlow	Ultra-deep desulfurization, aromatics saturation, cold-flow improvement	Can convert very difficult feeds (LCOs) into ULSD	30-35 kb/d unit ISBL capcosts per bpsd: Deep HDS=1,100-1,200; Cetane improvement and HDA=1,500-1,600
Akzo Nobel, Fina, ExxonMobil, Kellogg Brown Root	MAKfining, UDHDS and CFI, also HDAr and HDHDC	Ultra-deep desulf, dewaxing for cold flow improvement, arosat, heavy diesel hydrocracking	CFI can crack some paraffins also. Sulf <10 ppm, PAH 2-6% and under. 15 units in operation	15-20 kb/d unit grassroots unit $1,000-2,000 per bpsd
Haldor Topsøe	Topsøe ULSD	Ultra-low sulfur diesel from cracked and SR dists, aromatics sat possible	Sulf <5 ppm, density, cetane, aromatics improved w/ higher pressures	Est $90 mn for 70 kb/d unit in Kuwait

Resid/VGO Hydrotreating Techs

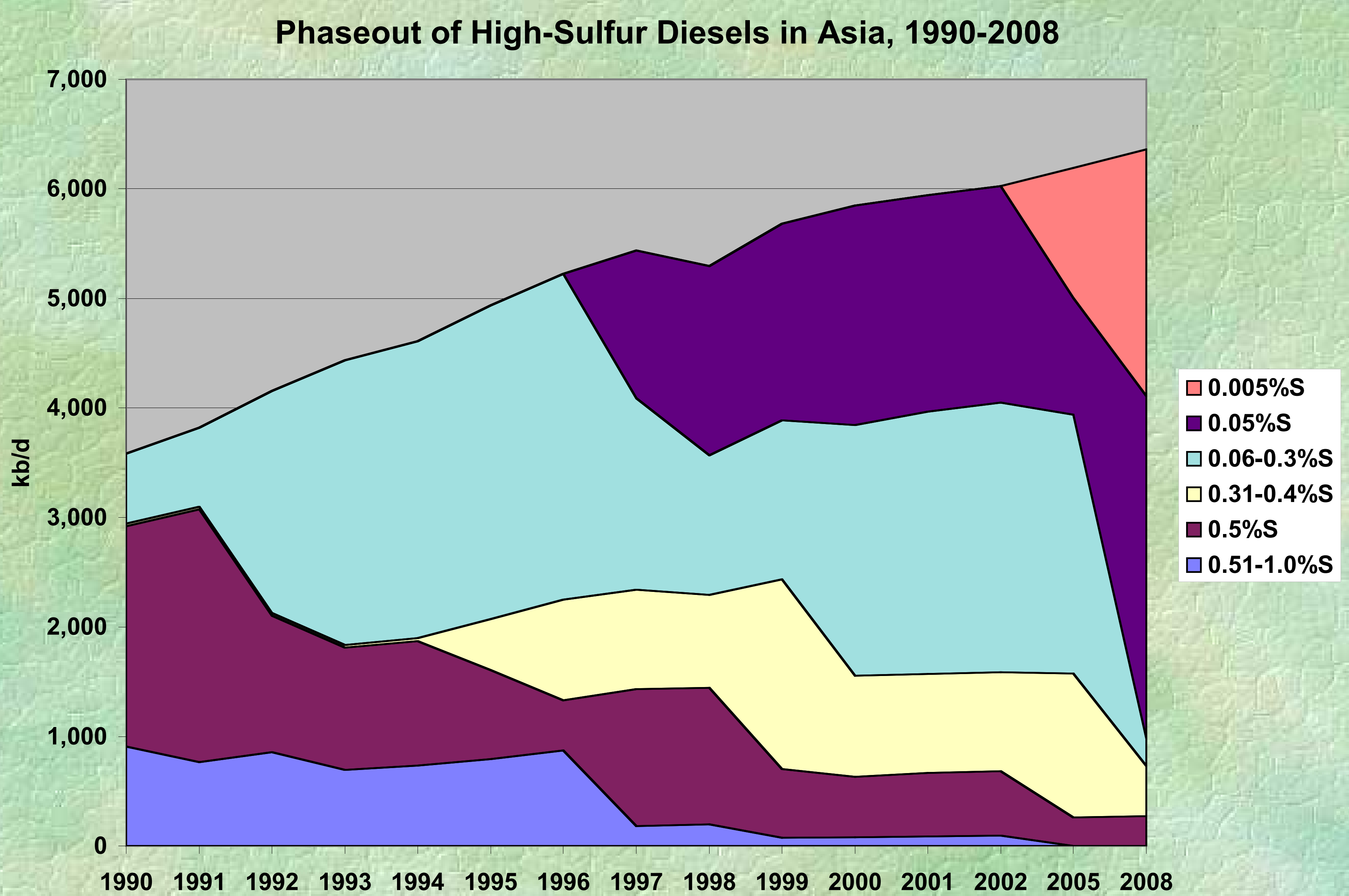
- RDS was rare outside of Japan (Belgium, Kuwait, S. Korea, UK, US also have)
- FCC feed (VGO) pretreatment more common, resulting in lower-sulfur light and middle distillate output
- May also be considered mild hydrocracking depending on level of conversion
- Costs approx $70-300 mn

Hydrotreating Technologies and Vendors, Resid and Cracker Feed Oriented, Other

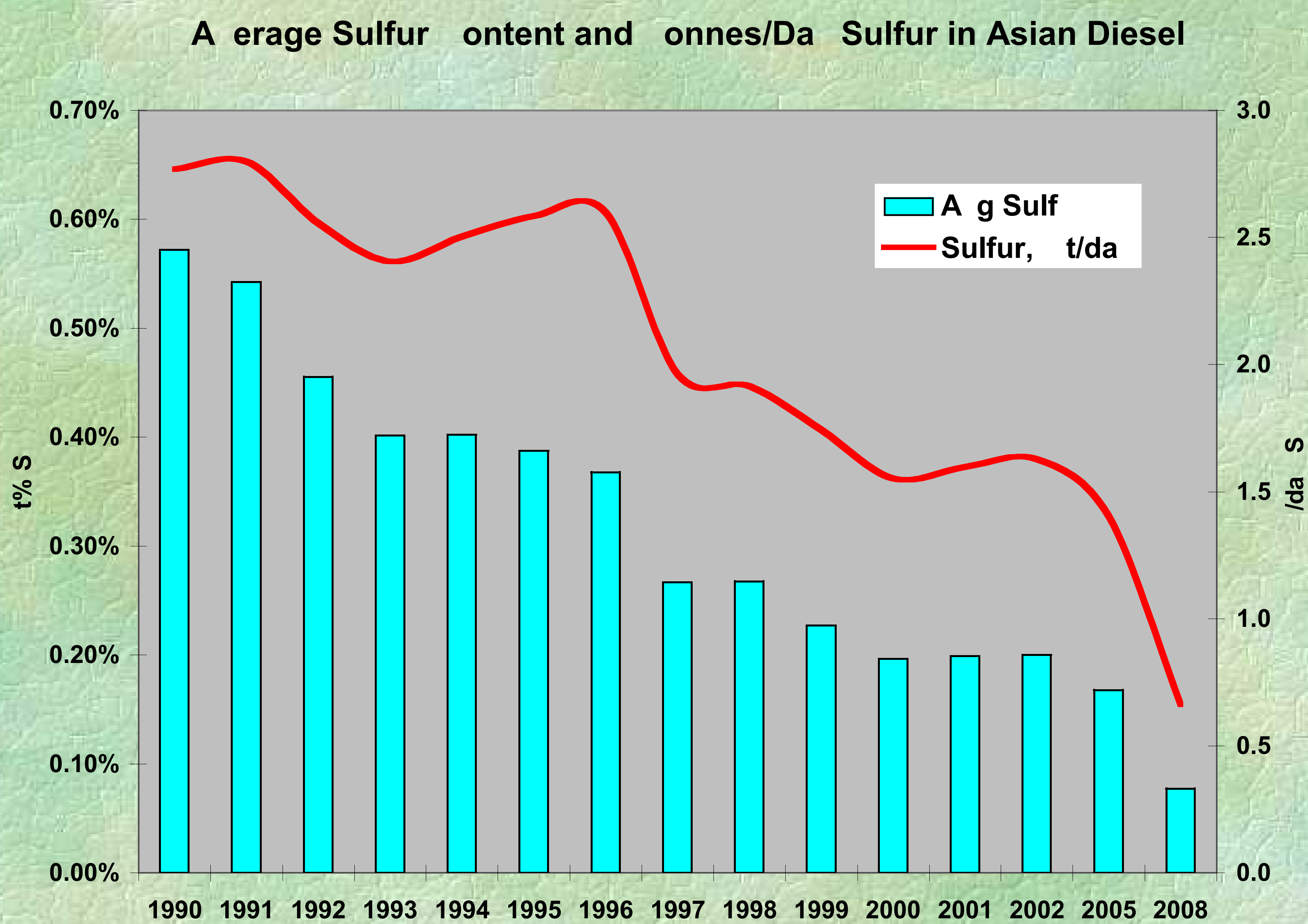
Licensor	*Technology Name*	*Purpose*	*Notes*	*Cost Notes*
Chevron (w/ Lummus Global)	RDS/VRDS HDT	HDT atmospheric or vac resid to reduce, sulfur, nitrogen, metals, asphaltenese, CCR	Can be run in mild HDC mode	
Haldor Topsøe	Mild HDC/VGO HDT	Upgrades/converts VGOs incl thermal VGO, LCO, DAO	Can pretreat cracker feed or work as mild hydrocracker	
UOP LLC	RCD Unionfining	Reduce sulfur, nitrogen, asphaltenese, organometallic compounds, Conradson carbon no.	Can use atmospheric and vacuum resids and solvent-derived feedstocks	Basis 15-20 kb/d unit= $2,000-3,500 per bpsd
Shell Global Solutions	SR HYCON Residue hydroprocessing	Reduce sulfur, vanadium, CCR pre-RCC and for fuels	Can use atmospheric and vacuum resids and solvent-derived feedstocks	New 5 tpsd unit $200-300 million, higher figure includes integrated HDC
Axens (incl IFP)	T-Star	Pre-treatment of vacuum gasoils	Best for difficult feeds incl coker VGO and DAO	Capcost $1,200-2,500 per bpsd
Axens (incl IFP)	Hyvahl fixed bed process	Upgrade and/or convert atmospheric and vacuum resids	Can achieve 30-50% conversion of 565 C fraction to distillates. 3 units operating.	40 bpsd AR to VR feeds unit costs=$3,500-5,500 per bpsd
JGC (early history 1928 was Japan Gasoline Co.)	JUST refinery concept	Treats mixed stream light and mid distillates	Simplified crude fractionator splits 2 cuts and sends all distillate to a single HDT	30% reduction in CAPEX possible

Conclusion: Major Growth in HDT

- Significant regional variations in specs and HDT capacities
- Growth in HDT worldwide; development of better technologies
- Expect continued interest in lower sulfur fuels and technologies
- Zero-sulfur fuels are possible
- Other Trans-Energy analyses have indicated costs of approx 1.5-3.5 c/g for reformulating gasoline, 3.7-8.7 c/g for reformulating diesel
- Asia example of reducing diesel sulfur, 1990-2008: Major shift in average sulfur needed just to keep pace with demand.



Trans-Energy Research Associates, Inc.



Trans-Energy Research
Associates, Inc.