Fischer-Tropsch Synthesis: Today's Status and Its Future.

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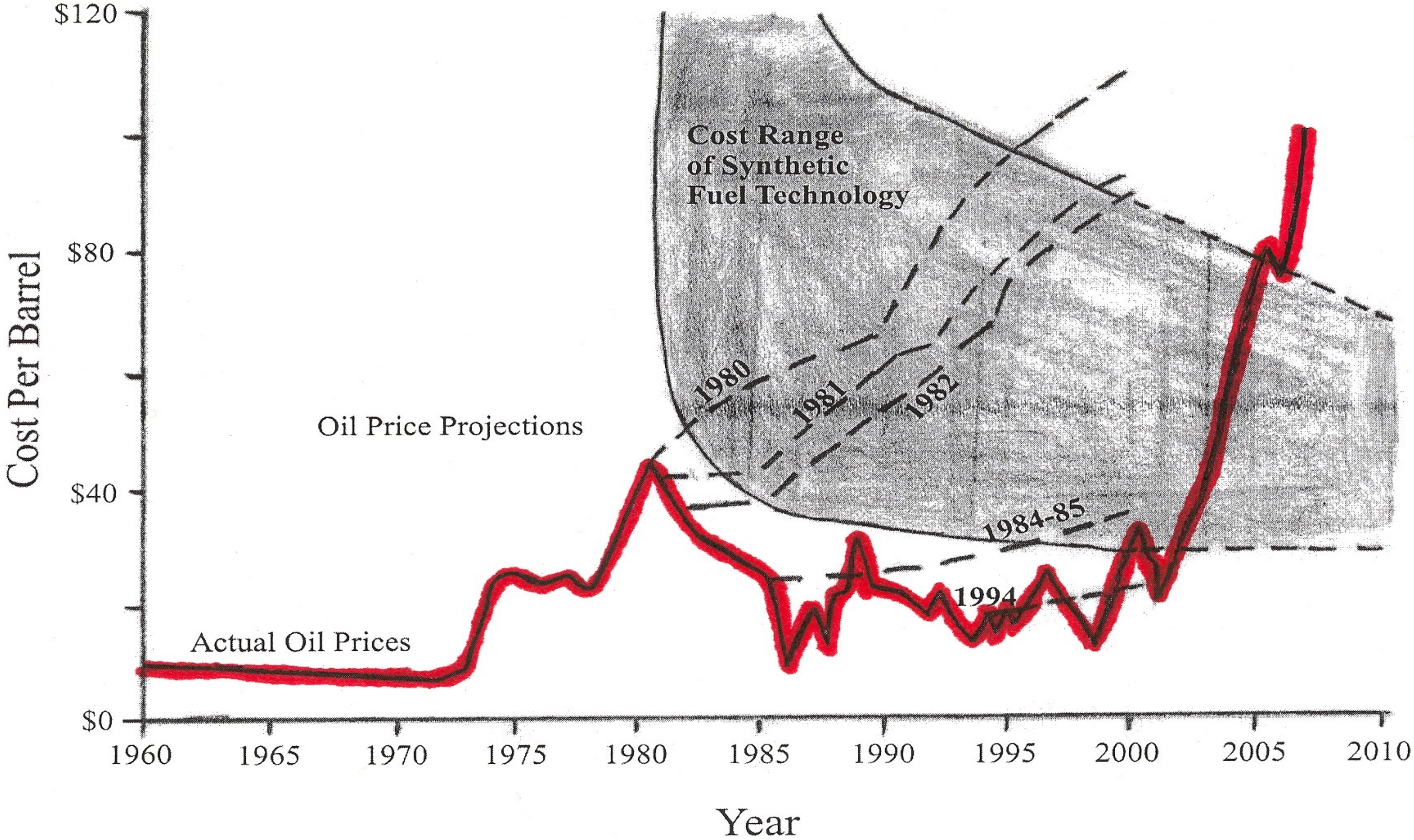
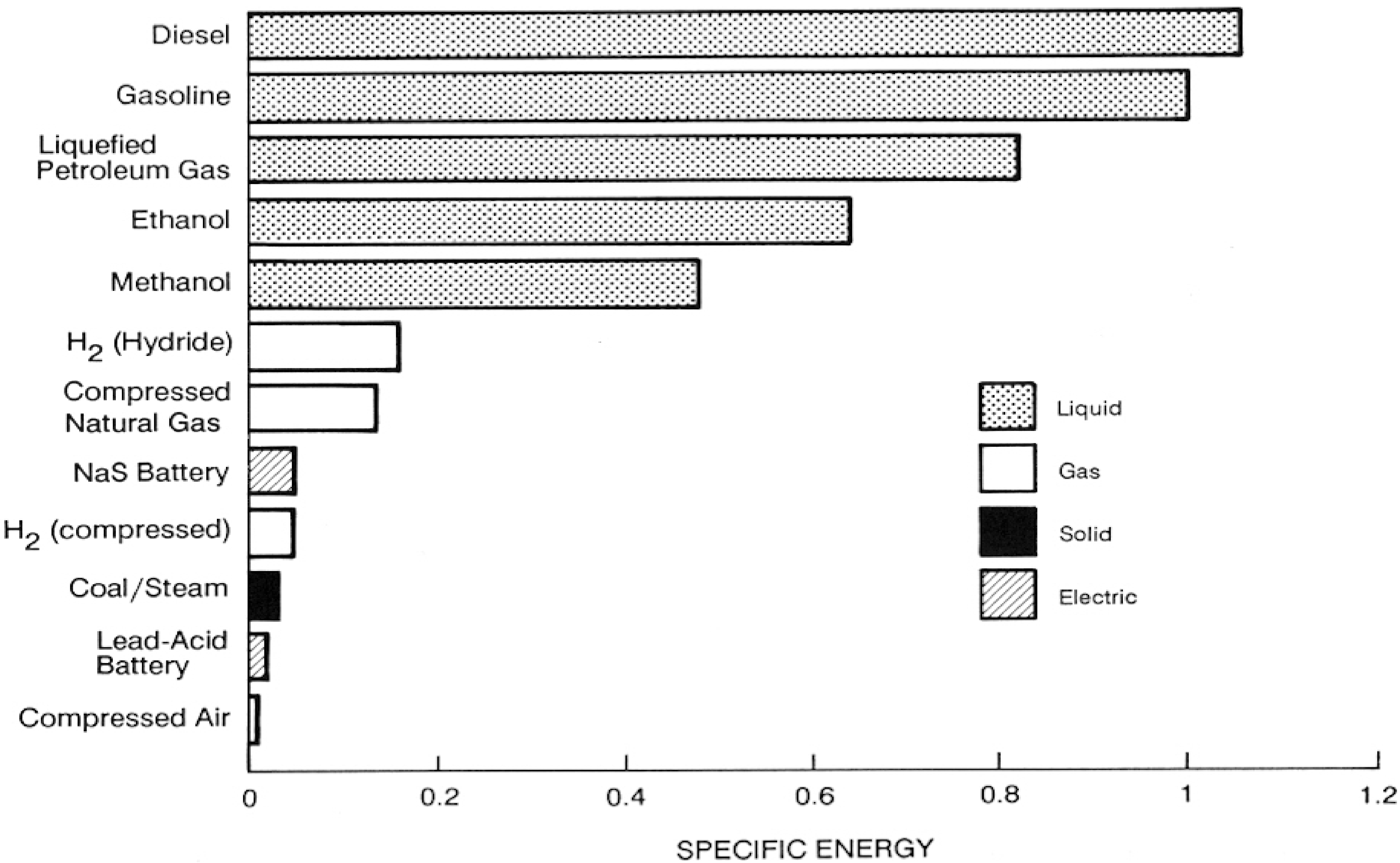
It is difficult to make predictions, especially about the future.

Niels Bohr, Yogi Berra, Sam Goldwyn, Casey Stengel, Will Rogers, Dan Quayle, Mark Twain, Albert Einsteir, Winston Churchill, Enrico Fermi, Groucho Marx, Confucius,



Cost Range
of Synthetic
Fuel Technology
Oil Price Projections
1980
1981
1982
1984-85
1994
Actual Oil Prices
$120
$80
$40
$0
Cost Per Barrel
1960
1965
1970
1975
1980
1985
1990
1995
2000
2005
2010
Year

Why Fossil Fuels?



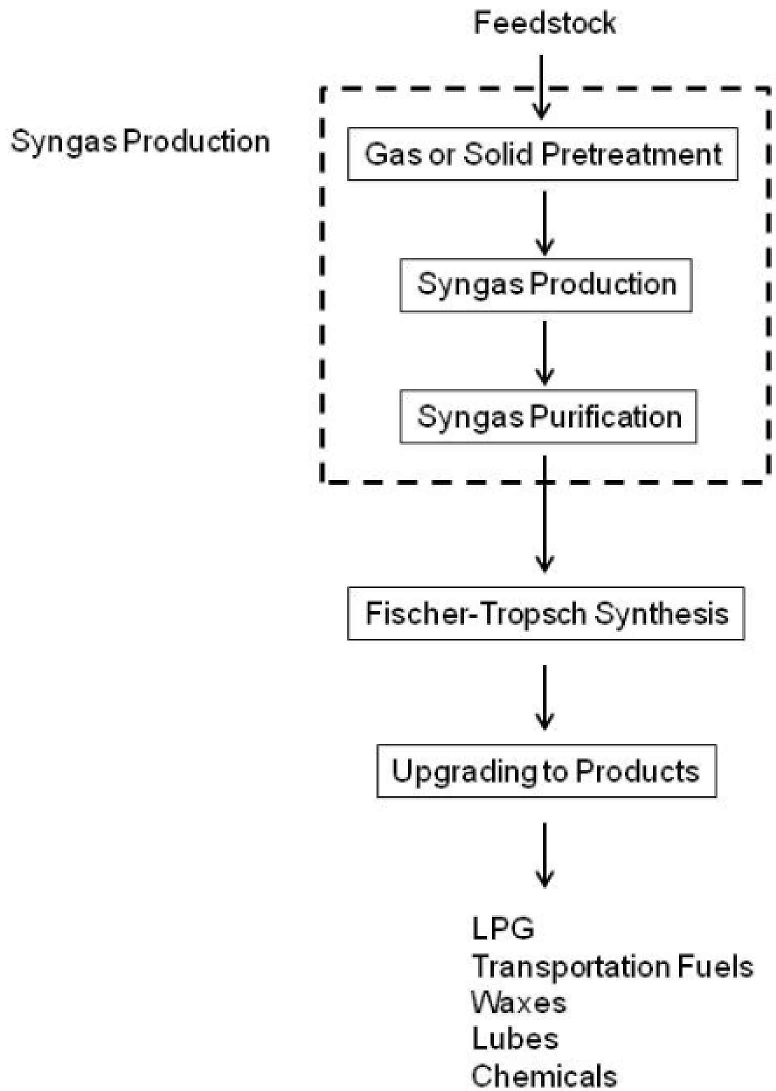
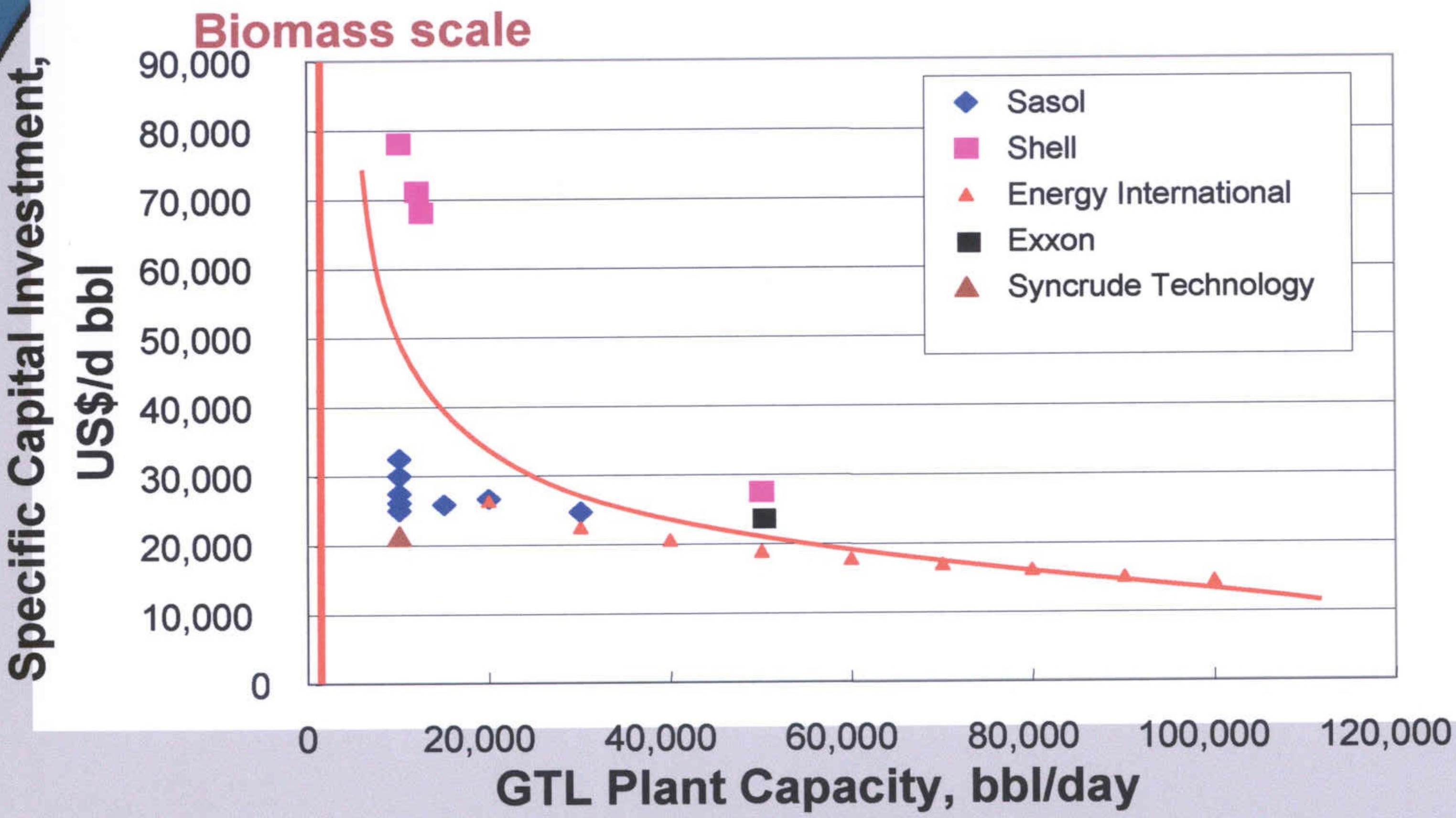


Figure 1. Simplified block-flow diagram for FT conversion of feedstock to products.

COST FOR PLANT

Syngas Generation	65-70%
Fischer-Tropsch Syn.	24-21%
Upgrading to Fuels	19-9%

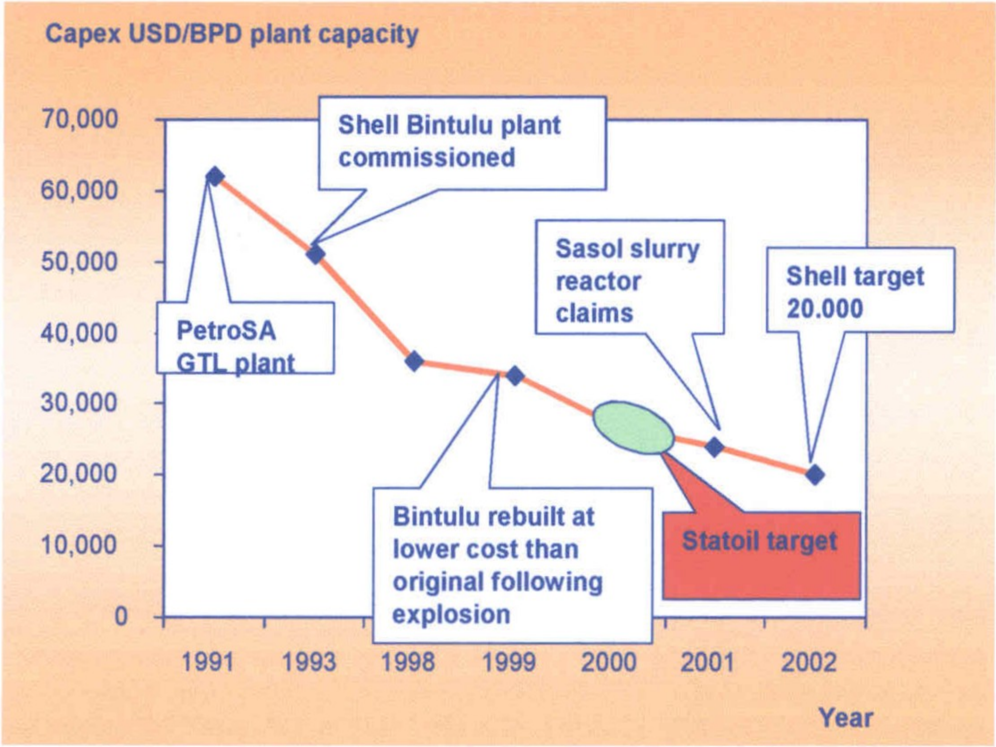
Conventional GTL Plant Capital Investment



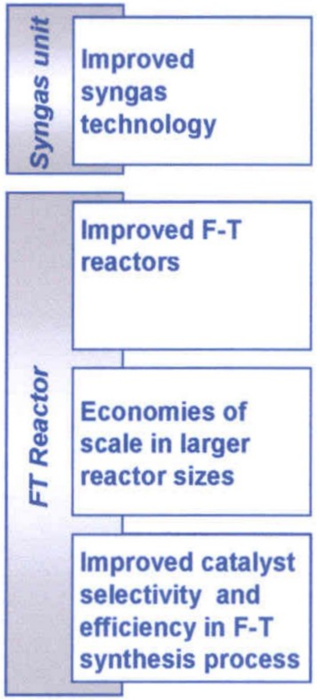
- Conventional GTL plant is not cost competitive at the capacity typical of biomass feedstocks

Significant technology development and capex reduction over time is making GTL attractive

STATOIL



Source: Shell-Hydrocarbon Asia Journal; Sasol



Shell Pearl in 2011 was ca $150,000 bbl/day; Sasol was about $27,000 bbl/day

ECONOMIES OF SCALE

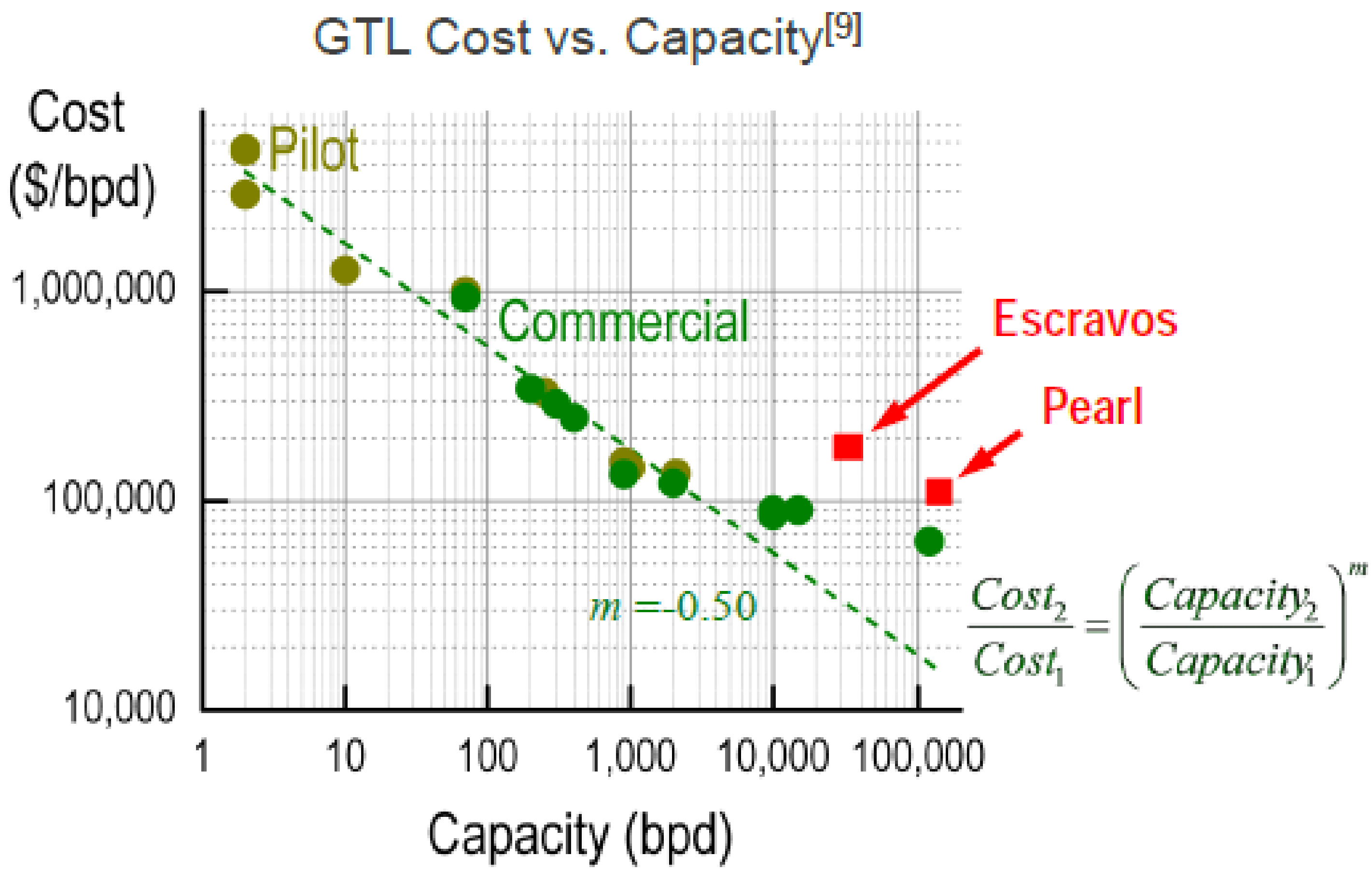
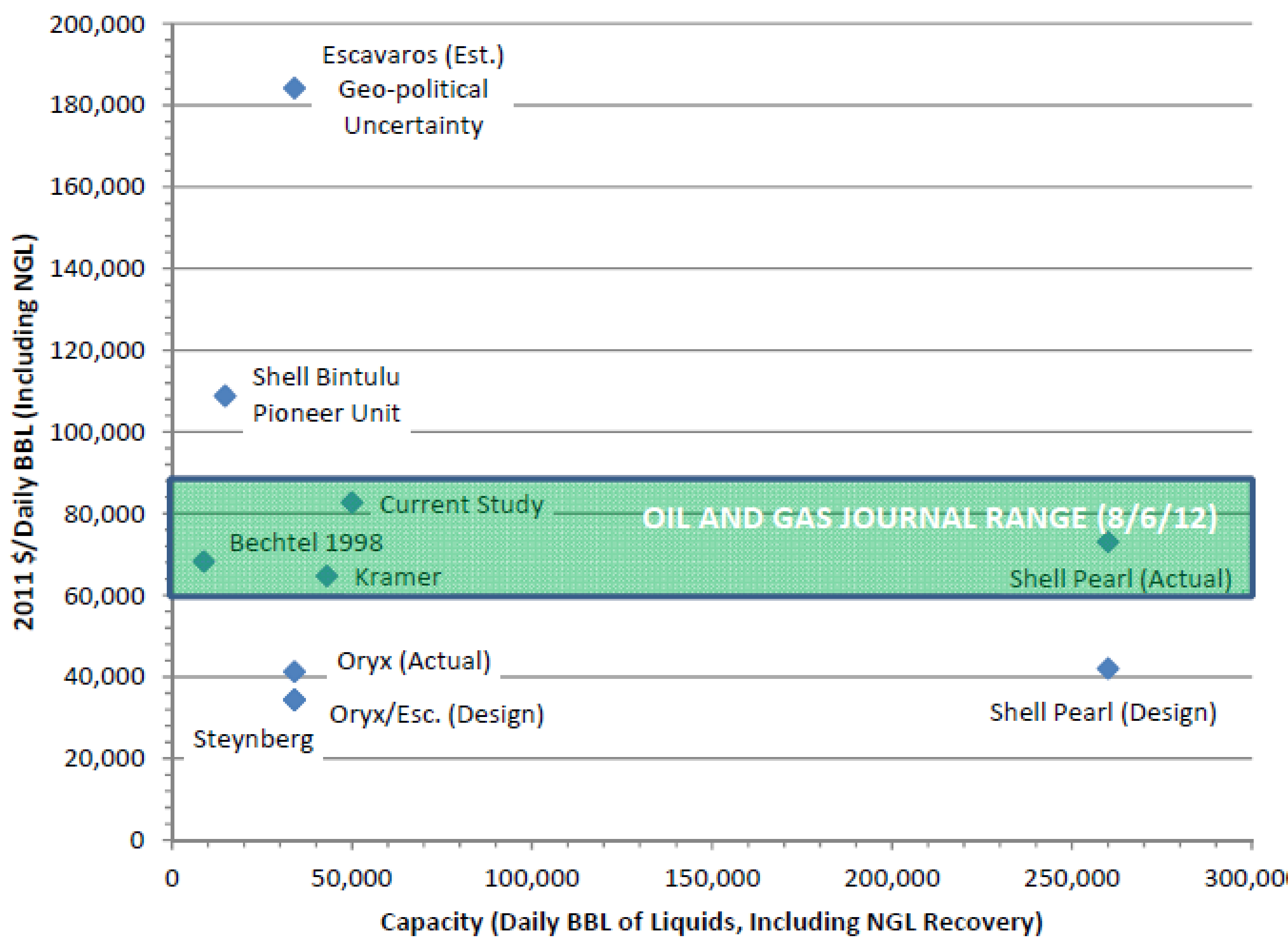


Exhibit 5-3: Capital Costs Per Daily Barrel of Fischer-Tropsch Liquids from GTL Projects and Studies



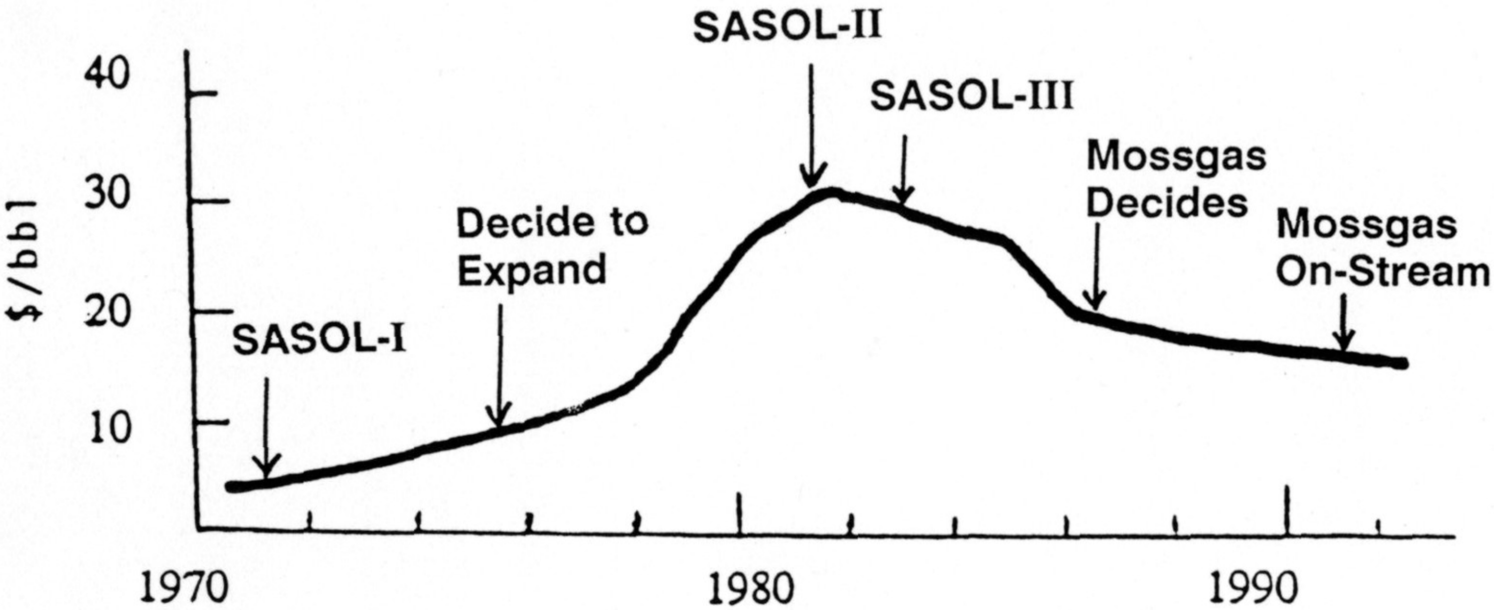


FIGURE 1 Variation of Price of Crude

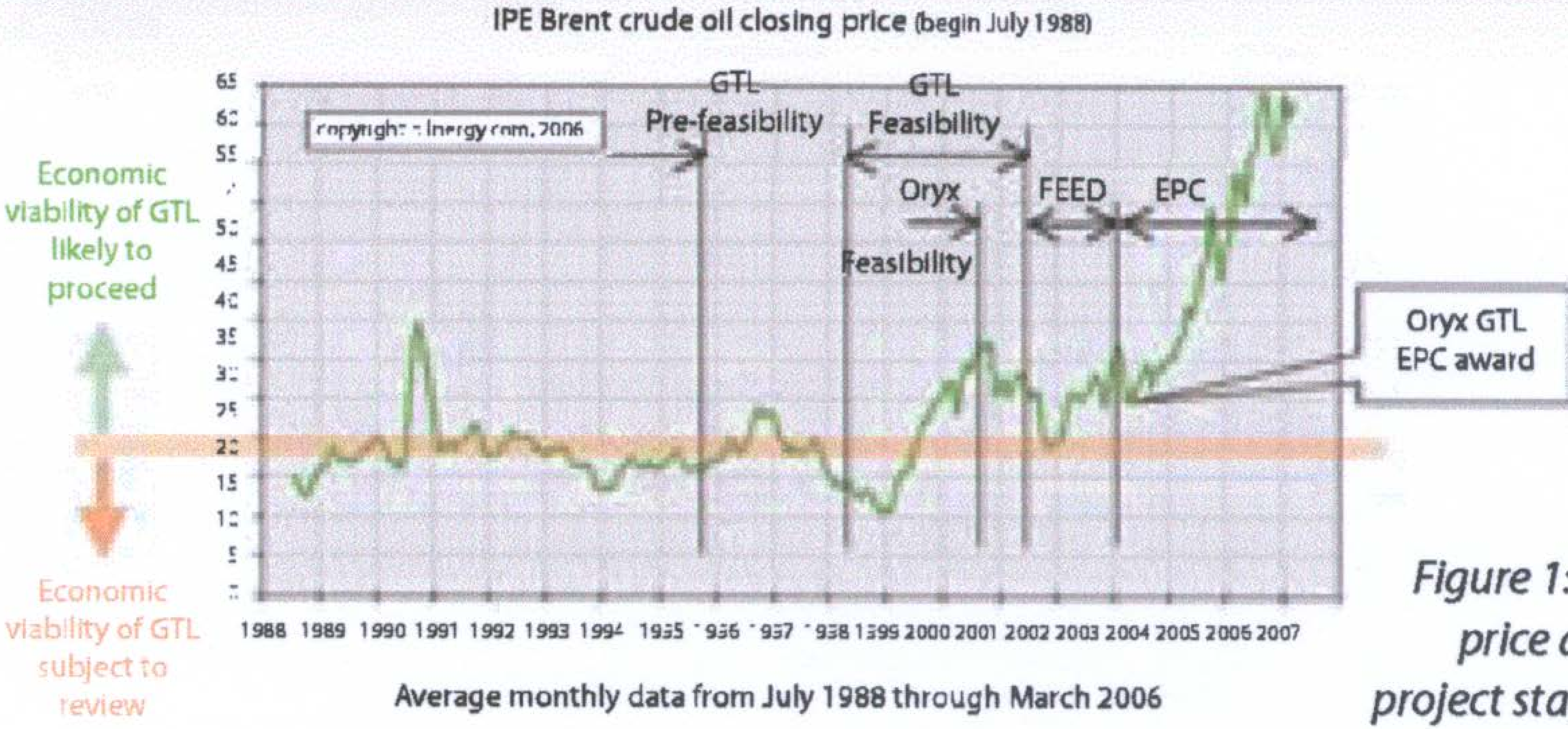
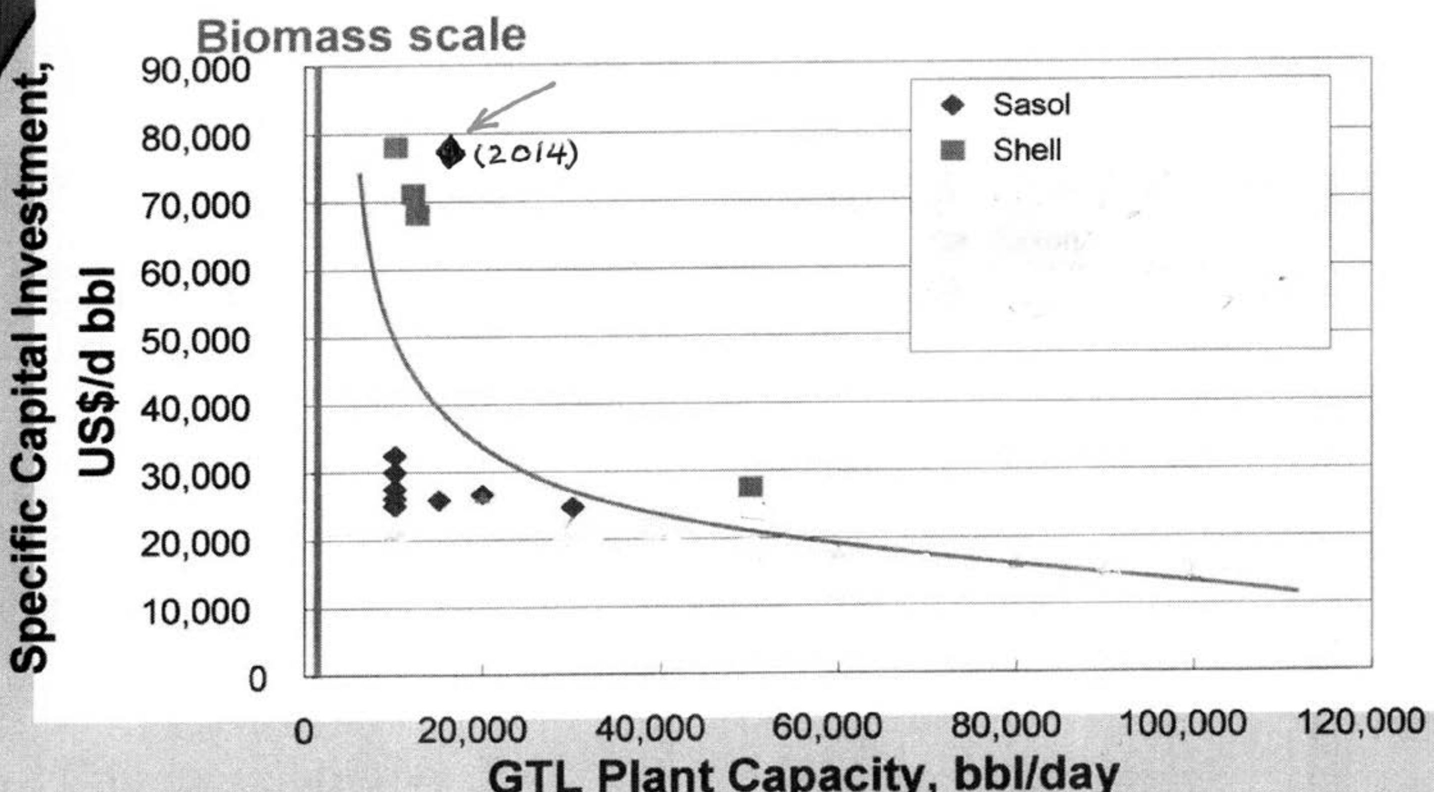


Figure 1: Oil price and project stages

CATALYSIS Research and Testing Center

Conventional GTL Plant Capital Investment



- Conventional GTL plant is not cost competitive at the capacity typical of biomass feedstocks

Feedstock Pretreatment

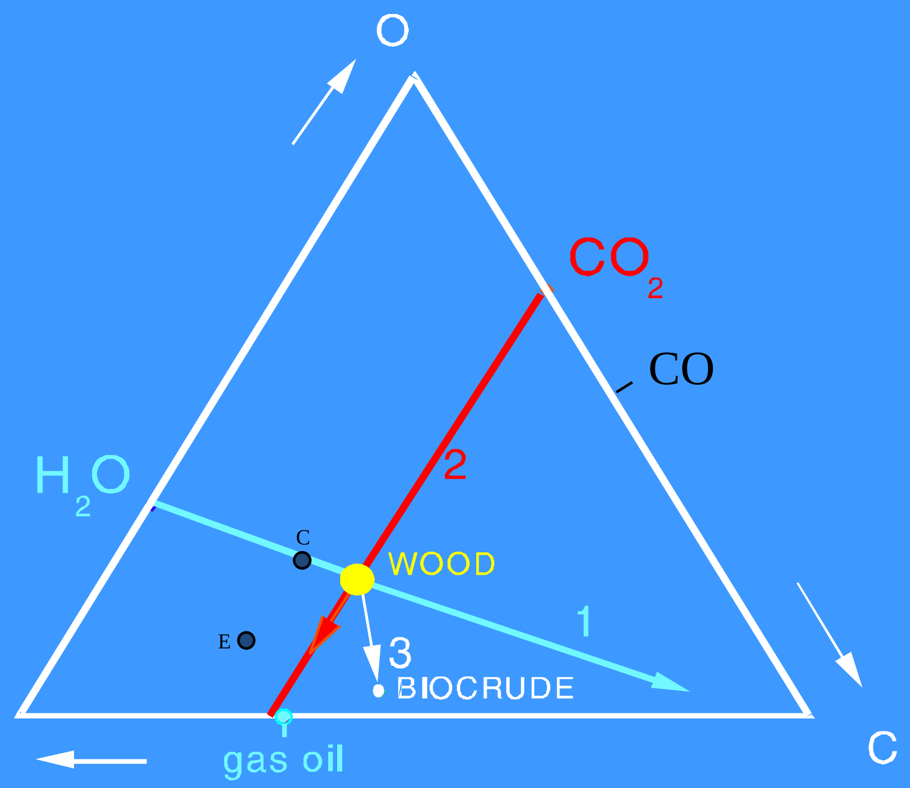
Natural Gas: Easy since a gas

Coal: Remove ash only; heteroatom in carbon fraction.

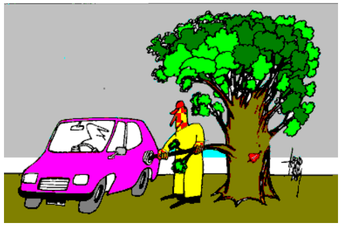
Biomass: Drying is energy intensive; high oxygen content.

The Challenge of Biomass Conversion: Oxygen Removal

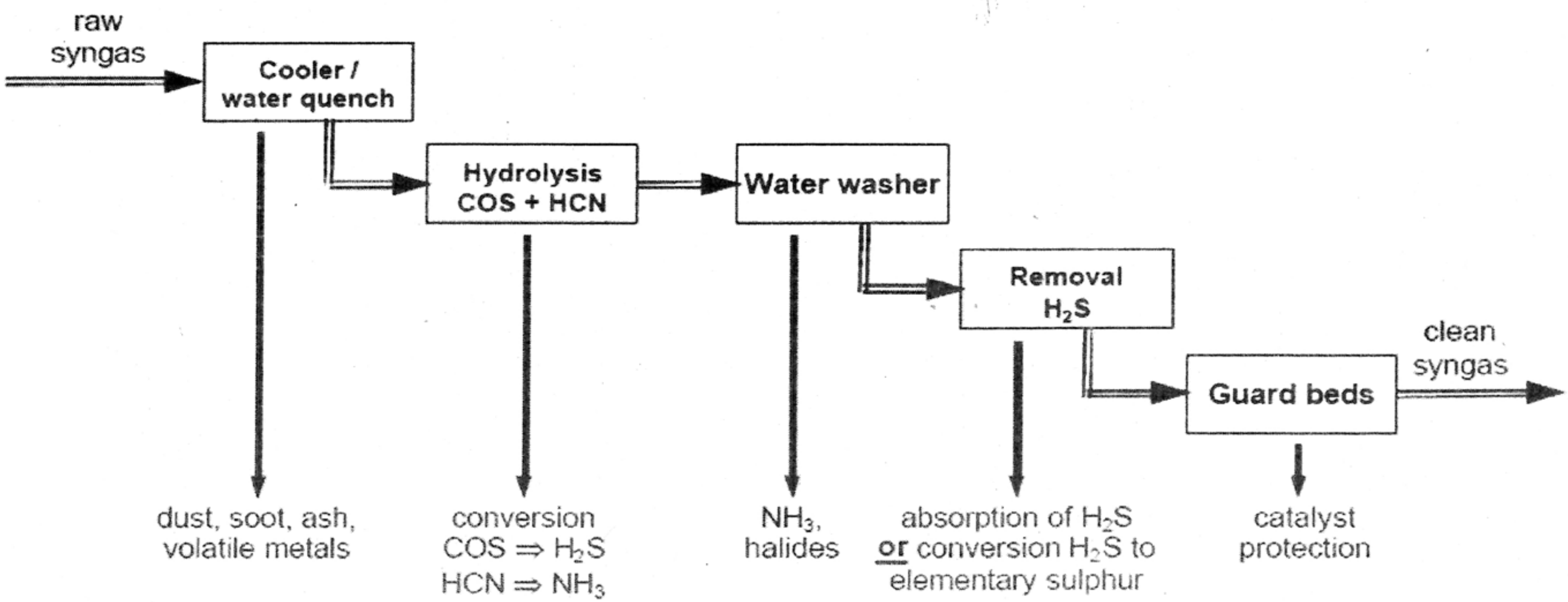
1. Remove H_2O
   (pyrolysis, charcoal)
2. Remove CO_2
3. HTU



BIOFUEL B.V.



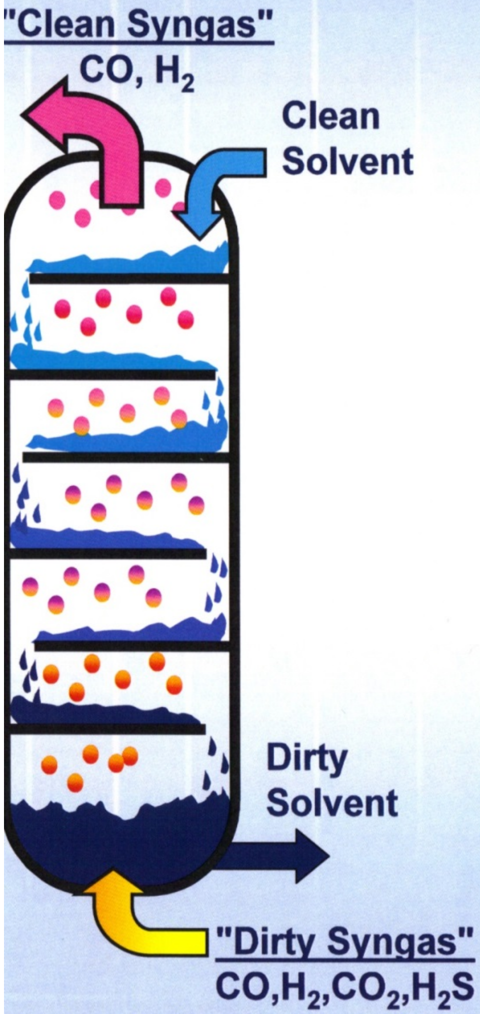
Syngas Purification



raw syngas
Cooler / water quench
Hydrolysis COS + HCN
Water washer
Removal H_2S
Guard beds
clean syngas
dust, soot, ash, volatile metals
conversion
$COS \Rightarrow H_2S$
$HCN \Rightarrow NH_3$
NH_3, halides
absorption of H_2S
or conversion H_2S to elementary sulphur
catalyst protection

AGR Technologies Can Provide Near 100% Sulfur Removal If Required

(AGR = Acid Gas Removal)

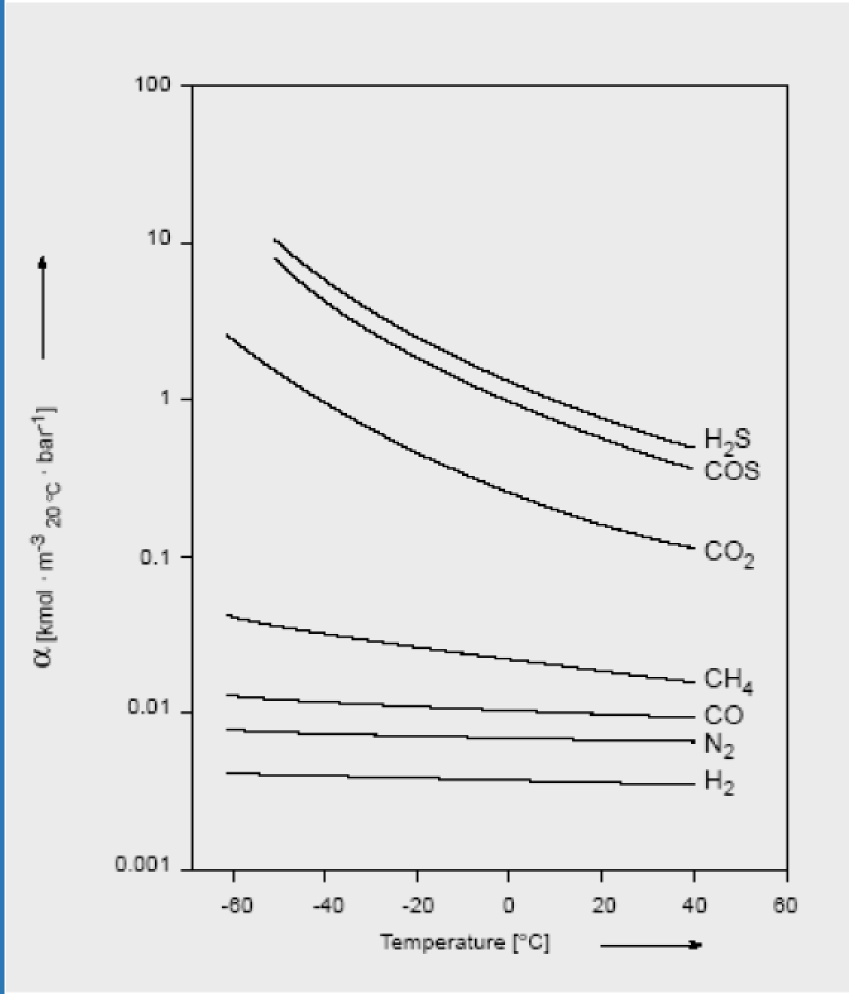


Three Main Technologies:

- **MDEA** (methyldiethanolamine) – Chemical absorption, 98% to 99+% S removal, large CO_2 slip (unless use a second stage for CO_2 recovery), moderate operating temperature, lowest AGR capital cost
- **Selexol** tm (primarily dimethyl ethers of polyethylene glycol, DEPE) – Physical absorption, 99+% S removal, variable CO_2 slip (based on design), higher AGR cost than MDEA but overall AGR/SRU system costs are similar
- **Rectisol** tm (methanol) - Physical absorption, 99.5% to 99.9+% S removal, complete CO_2 removal possible, highest AGR cost, coldest operating temperatures
  [Used by Eastman]

Rectasol Unit

Figure 14: Absorption Coefficients



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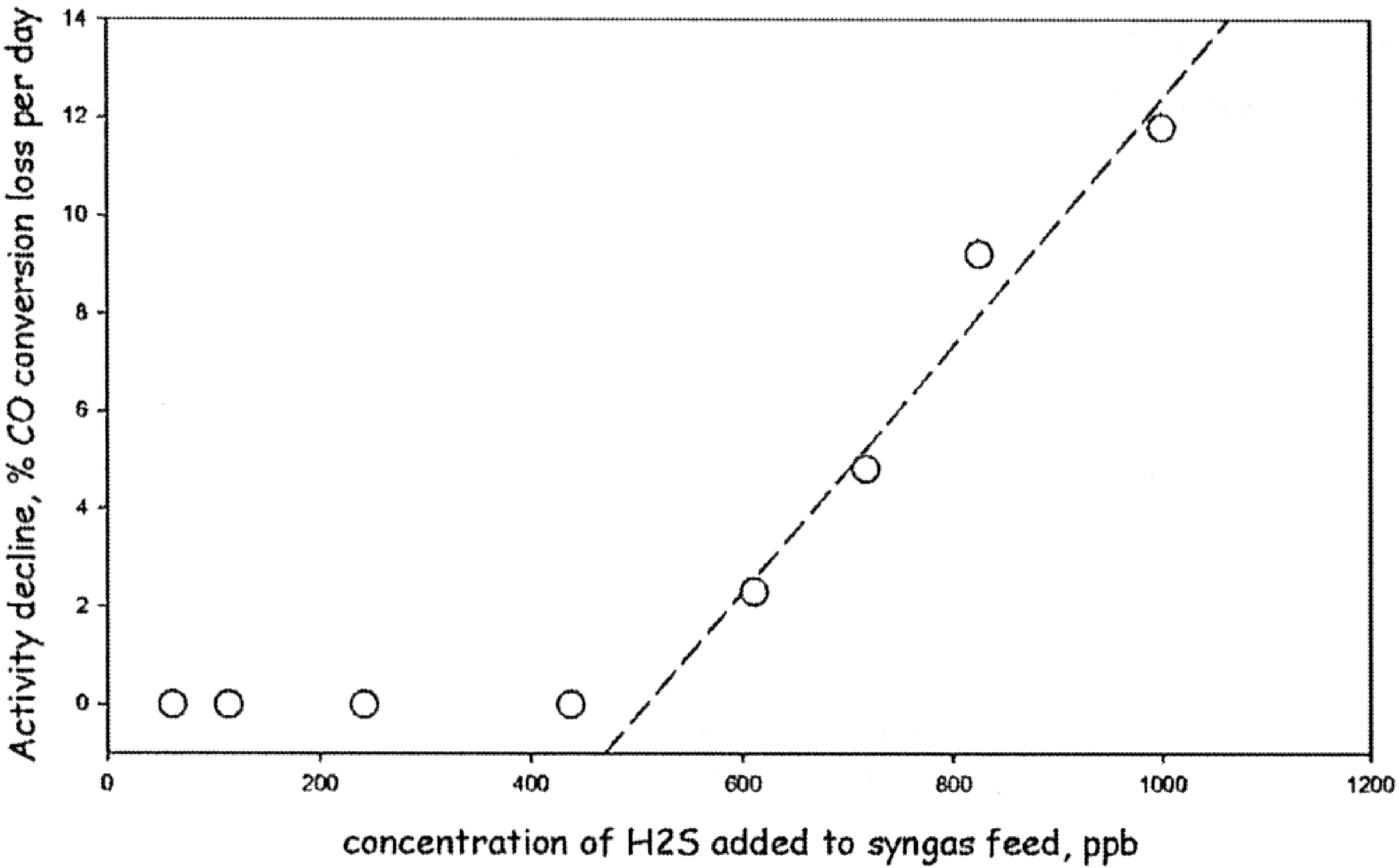
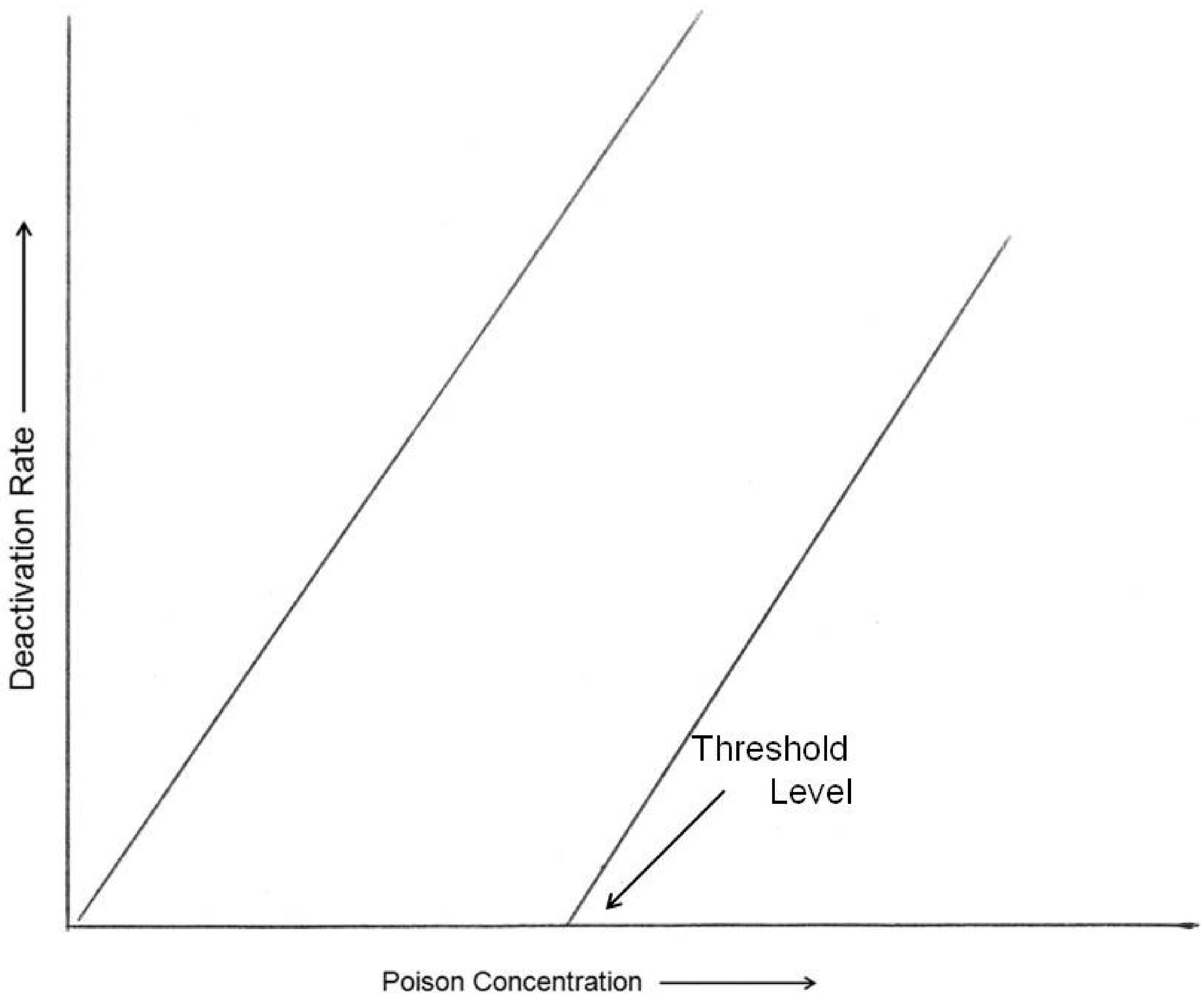
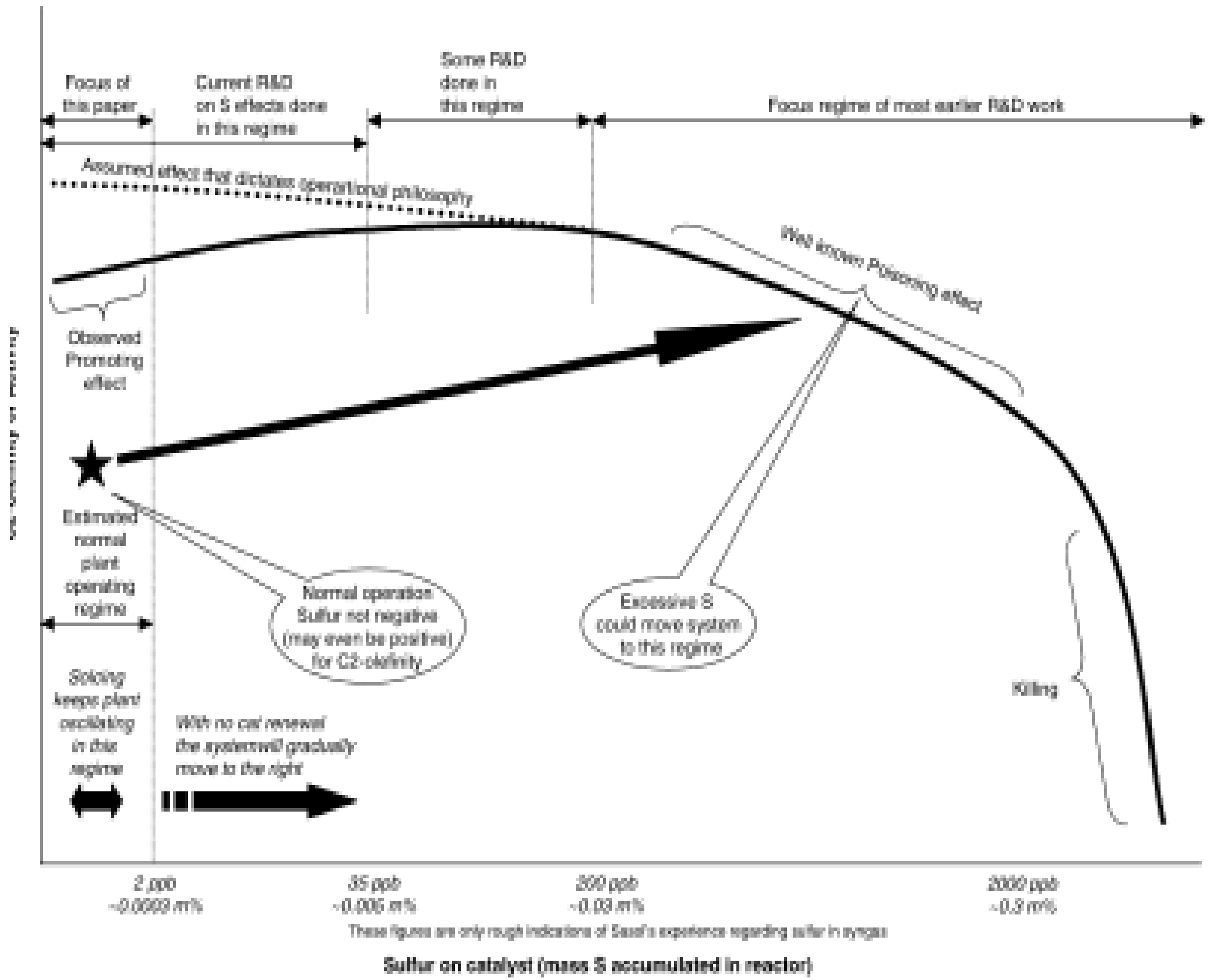
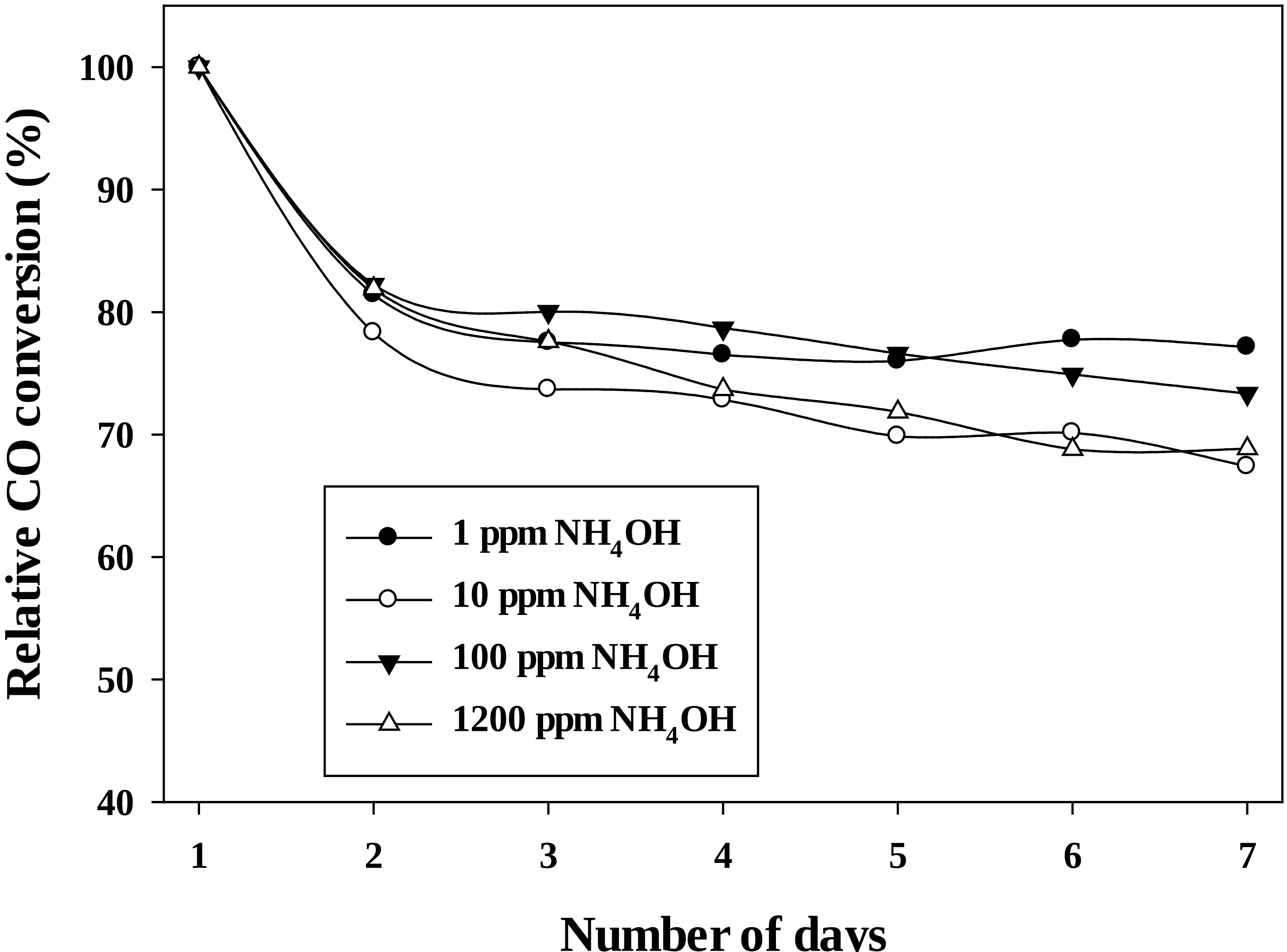



Deactivation Rate
Threshold
Level
Poison Concentration



Focus of this paper
Current R&D on S effects done in this regime
Some R&D done in this regime
Focus regime of most earlier R&D work
Assumed effect that dictates operational philosophy
Observed Promoting effect
Well known Poisoning effect
Estimated normal plant operating regime
Normal operation Sulfur not negative (may even be positive) for C2-olefinity
Excessive S could move system to this regime
Killing
Spiking keeps plant oscillating in this regime
With no cat renewal the systemwill gradually move to the right
2 ppb ~0.0003 m%
35 ppb ~0.005 m%
200 ppb ~0.03 m%
2000 ppb ~0.3 m%
These figures are only rough indications of Sasol's experience regarding sulfur in syngas
Sulfur on catalyst (mass S accumulated in reactor)



Relative CO conversion (%)
100
90
80
70
60
50
40
1
2
3
4
5
6
7
Number of days
1 ppm NH_4OH
10 ppm NH_4OH
100 ppm NH_4OH
1200 ppm NH_4OH

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Syngas Generation 65-70% of Cost

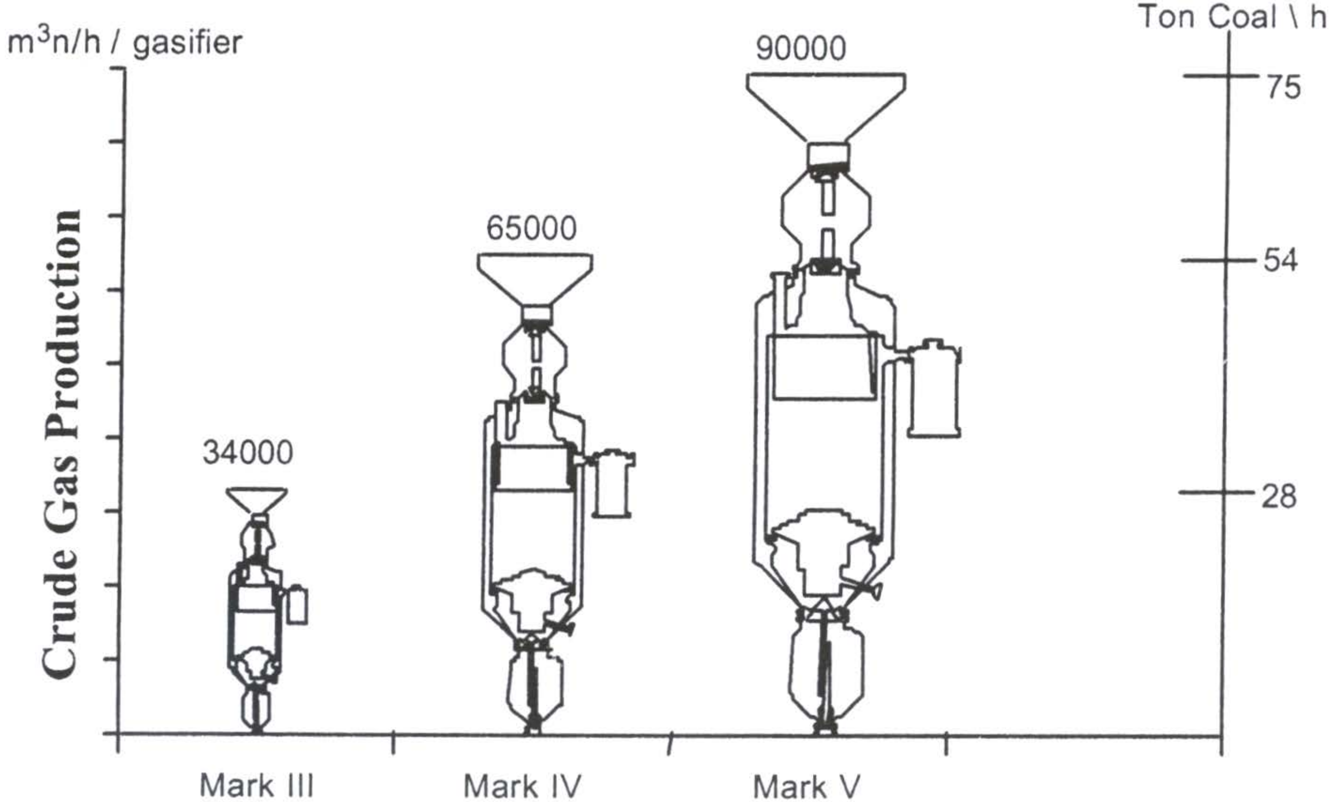
1950: Only proven option was Lurgi and this was used by Sasol.

Today: Many options but most produce low H_2/CO ratio (1.6-2.1).
Commercial versions of most have reached their maximum size.

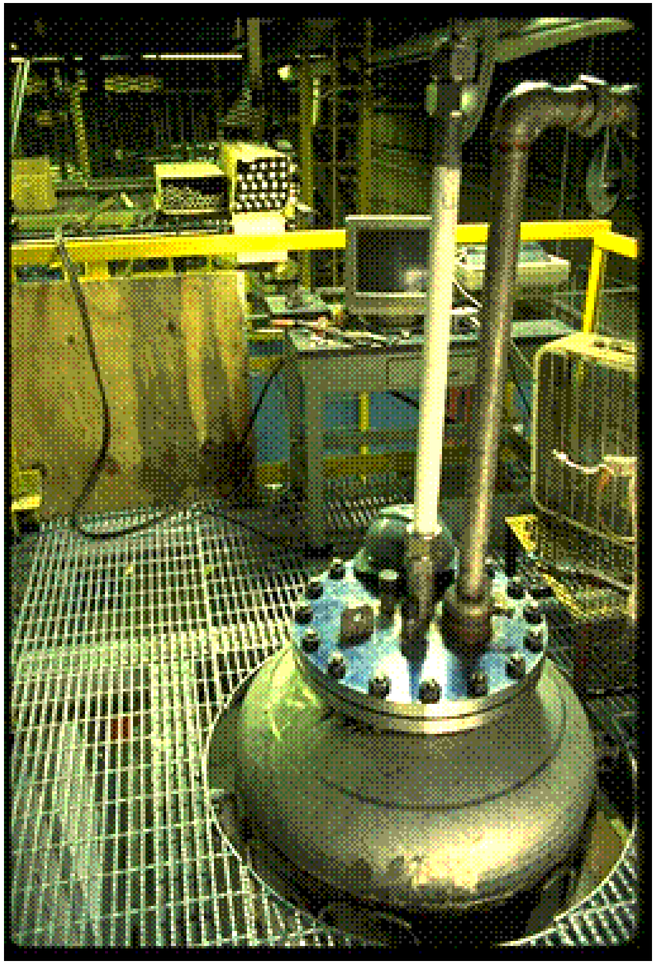
Future: Molten Iron or Molten Salt
Compact Gasifier
Ionic Membrane Separation

MAJOR DIMENSIONS OF GASIFIERS

Scale Up Of Gasifiers At Sasol



Research and Testing Ce
at the UK Center for Applied Energy Rese



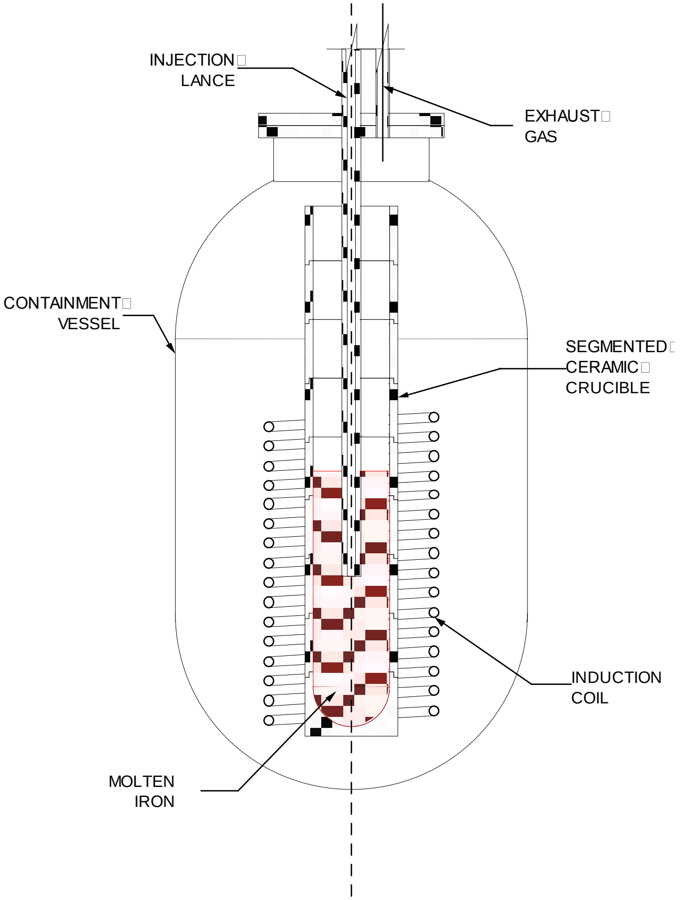


Figure 4. Photograph and schematic of the Catlettsburg, Kentucky bench scale test facility.

(A) (B)

Figure 6. Photographs of key MEFOS facilities: (A) Electric arc furnace, (B) Universal converter

Molten Metal/Salt Gasification (representative, not complete list)

1971	Kellogg Process, molten sodium carbonate (Cover et al., Chem. Eng. Proc., 69, 31, (1973).
1984	Molten Iron Pure Gasification Process, (Henrich et al., Chemie-Technik, 13, 45 (1984).
1996	Hymelt Gasification Process (D. Malone, Commercialization of the Hymelt process for Illinois coal, Final technical report, July 1, 2002 through Sept 30, 2003.
2002	HIsmelt Gasification Process (Burke and Gull, Smelting Reduction for Iron Making, Bhubaneswar, 18-10 December, 2002.
2008	HydroMax Advanced Gasification Technology, Diversified Energy, FeSn alloy.
2012	Molten Salt Gasification, developed by US DOE Idaho National Lab., Western Hydrogen Ltd., licensed rights.

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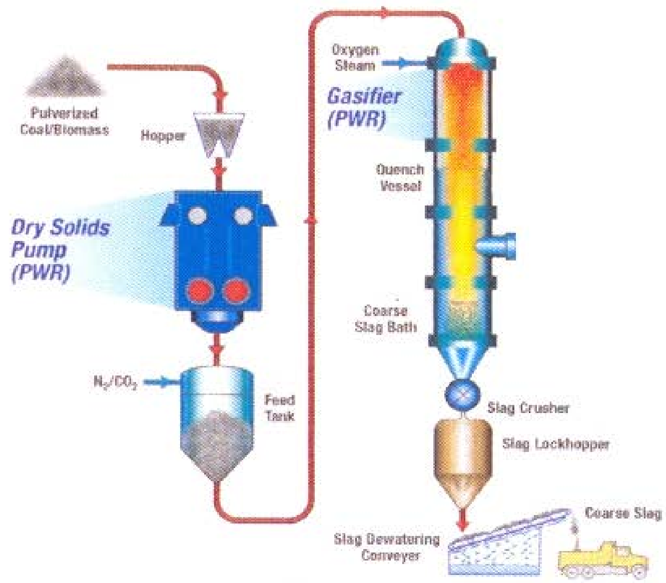
Compact Gasification System

- Next generation Gasification System that is environmentally friendly and lower cost than existing systems

Testing Initiated
March 2012
EERC – North Dakota



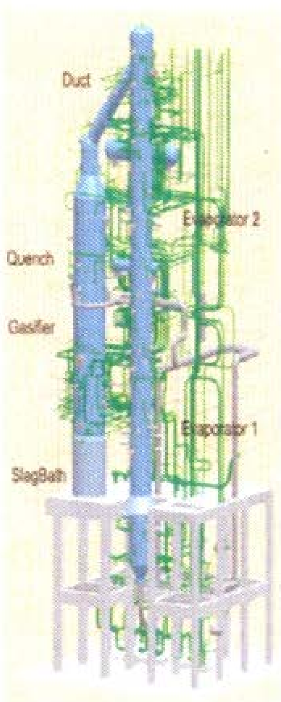
Successful Testing
Completed April 2011
Gas Technology Institute - Illinois

Reduces customer capital and operating cost by 20%

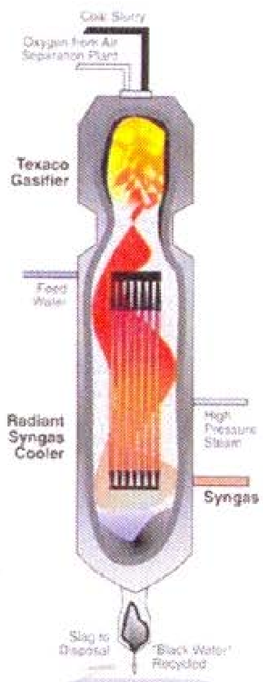
AEROJET ROCKETDYNE

Advantages of the Compact Gasification System

Current Market Leaders

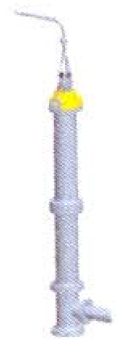


Source: Shell paper (2004)



Source: DOE paper (2006)

Compact Gasification System



- 90% size reduction (gasifier)
- 50% lower cost (gasification system)
- 99% availability (gasification system)
- 99% carbon conversion
- 80% to 85% cold gas efficiency
- Dry feed system
  - Low oxygen consumption
  - Gasify all ranks of coal, petcoke, and biomass blends
- High pressure / water spray quench
  - Ideal for H_2 production
  - Low cost CO_2 sequestration

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AR Rocket Engine Experience Enables Compact Gasifier

AEROJET ROCKETDYNE

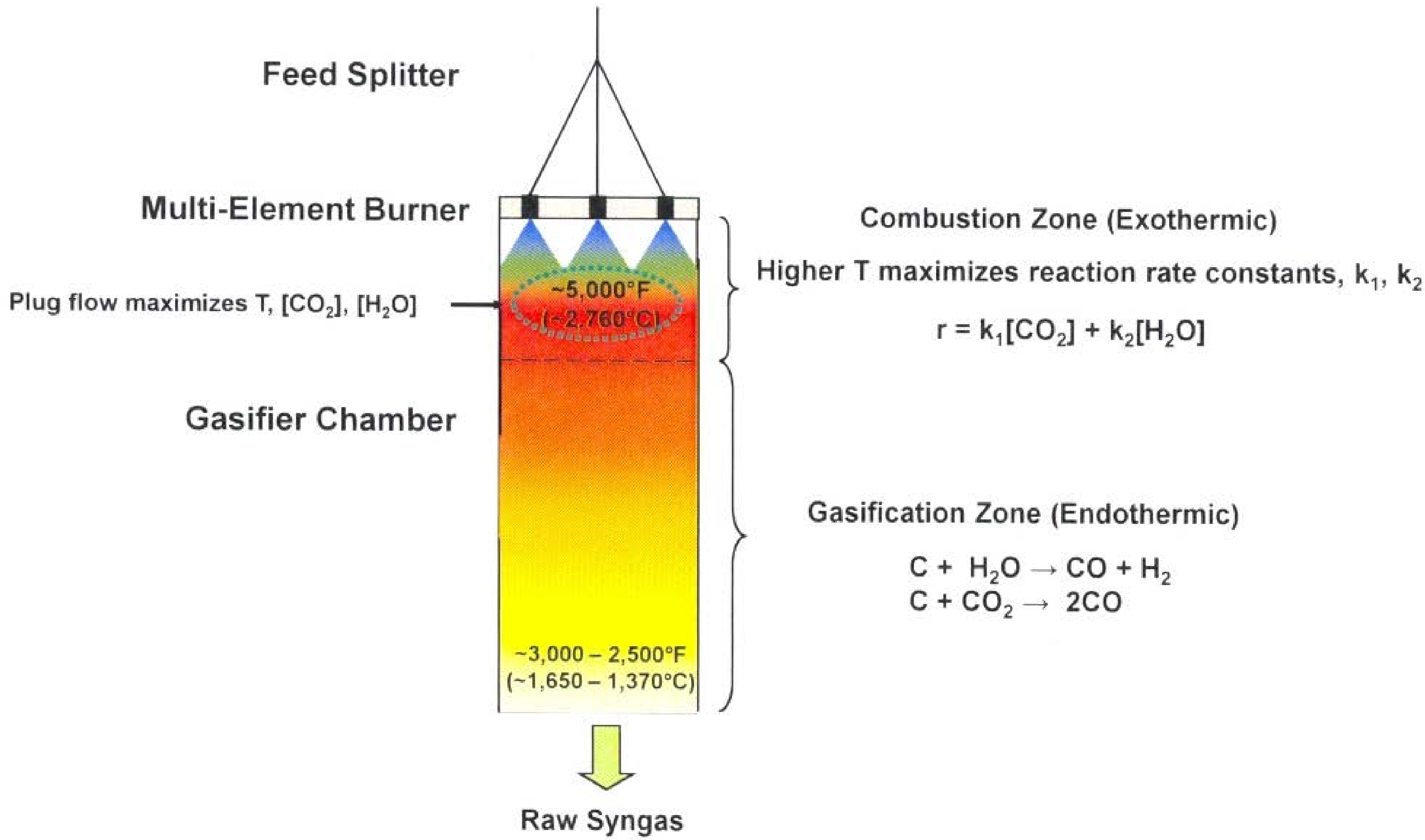
Rocket Engine Experience

- Rapid Mix Injector
- Cooled Nozzle Wall
- Plug Flow

Gasifier Design Features

- Dry feed system enables use of lignite, low rank feedstocks
- Rapid mix injector assures fast and efficient combustion
- 5000° F (2,760° C) flame temperature gasifies most feedstock within three feet of injector
- Active cooling system keeps metal temperatures below 1000° F (538° C)
- Plug flow provides uniform residence time for high carbon conversion
- Rapid spray quench reduces syngas outlet temperature to 700° F (371° C)

Illustration of AR Gasifier Process



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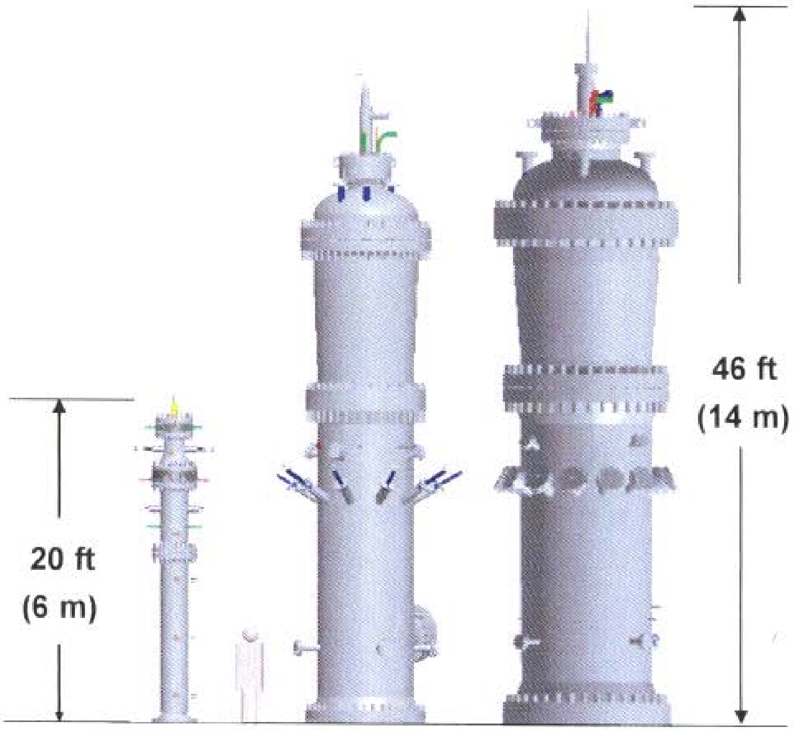
Scale-Up Approach



Pilot Plant 18 TPD

Demo Plant 800 TPD

Commercial Plant 3,000 TPD

Primary Scaling Tools

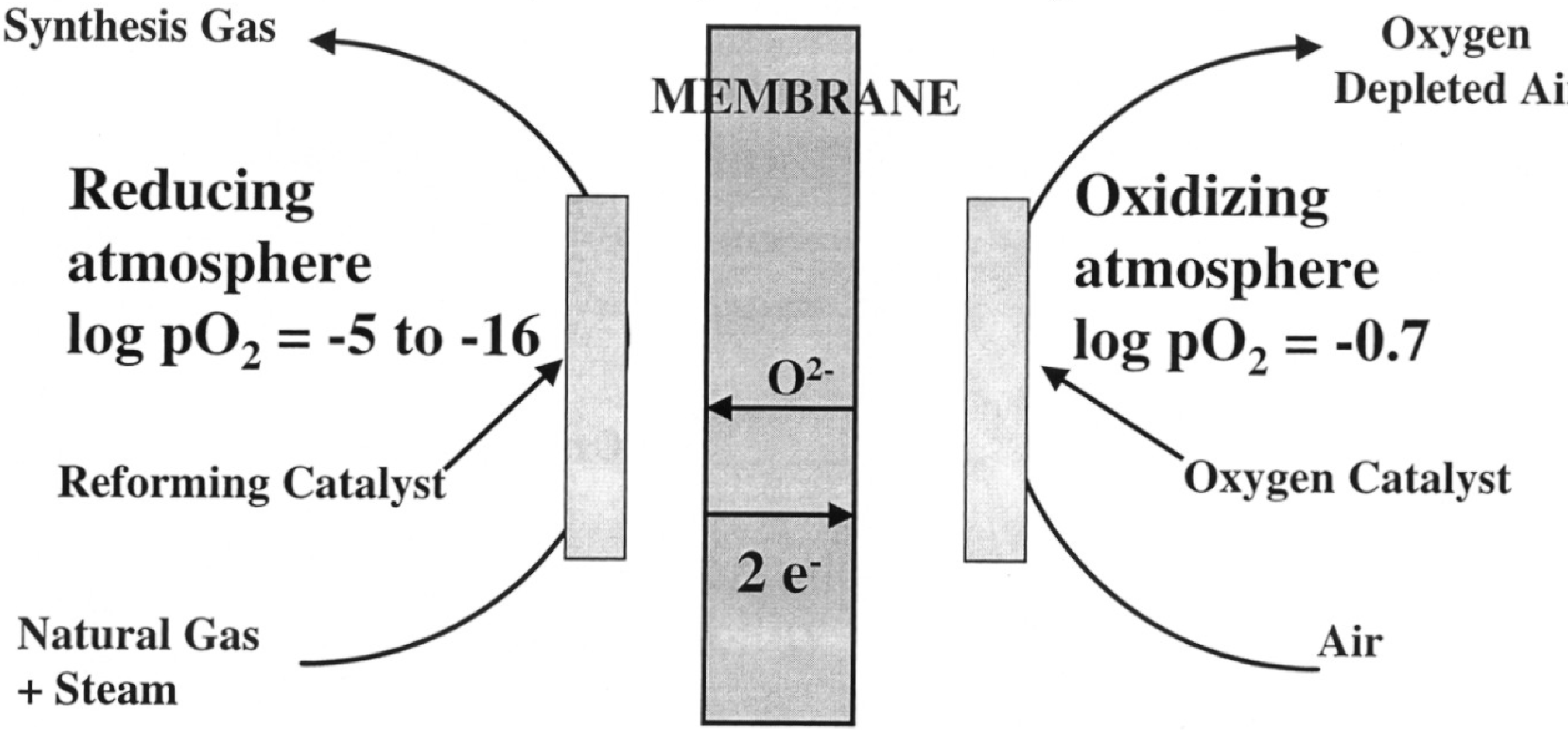
- Gasifier: CFD (Computational Fluid Dynamics) model
- Pump: GSD (Granular Solid Dynamics) model

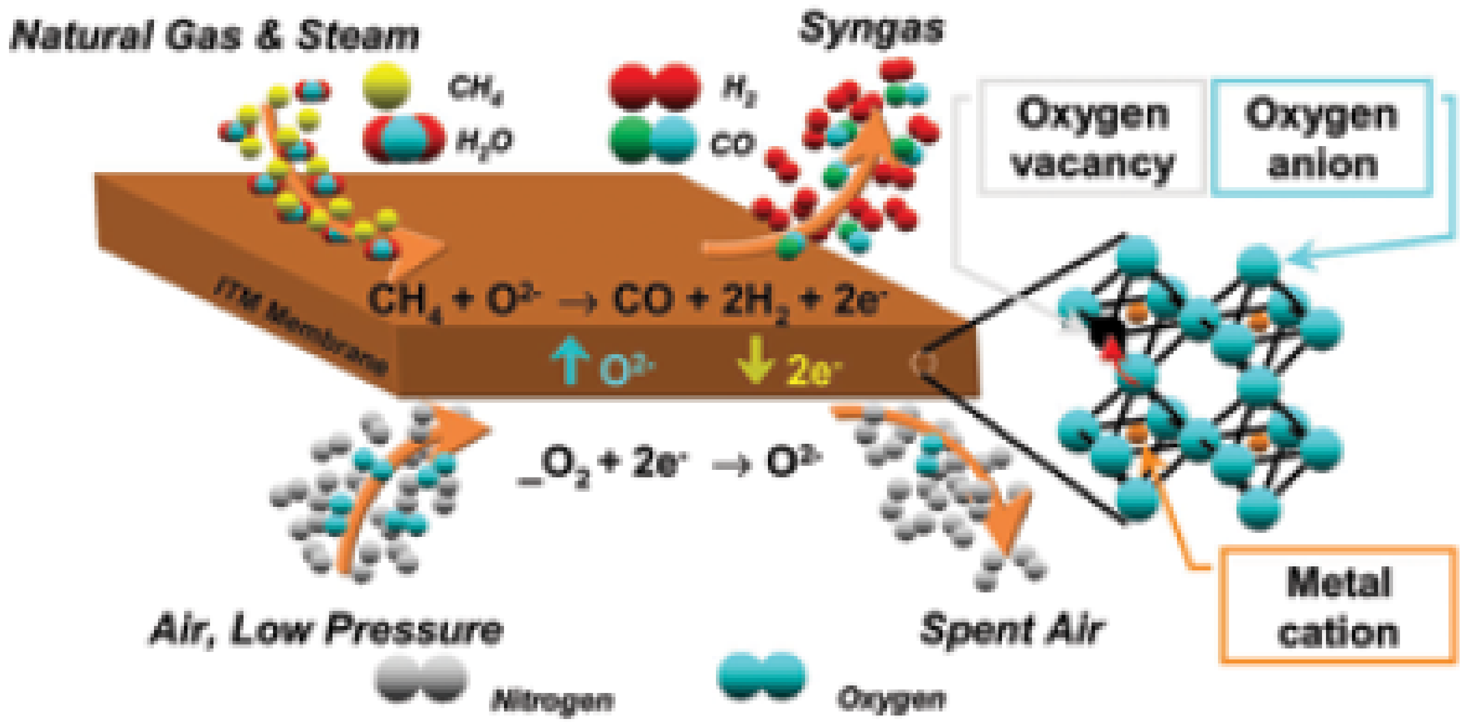
Demo Pump (400+ TPD)
Commercial (~1,000 TPD)

OTM Transport Mechanism

$$CH_4 + H_2O \longrightarrow CO + 3H_2$$

$$CH_4 + 1/2\ O_2 \longrightarrow CO + 2H_2$$

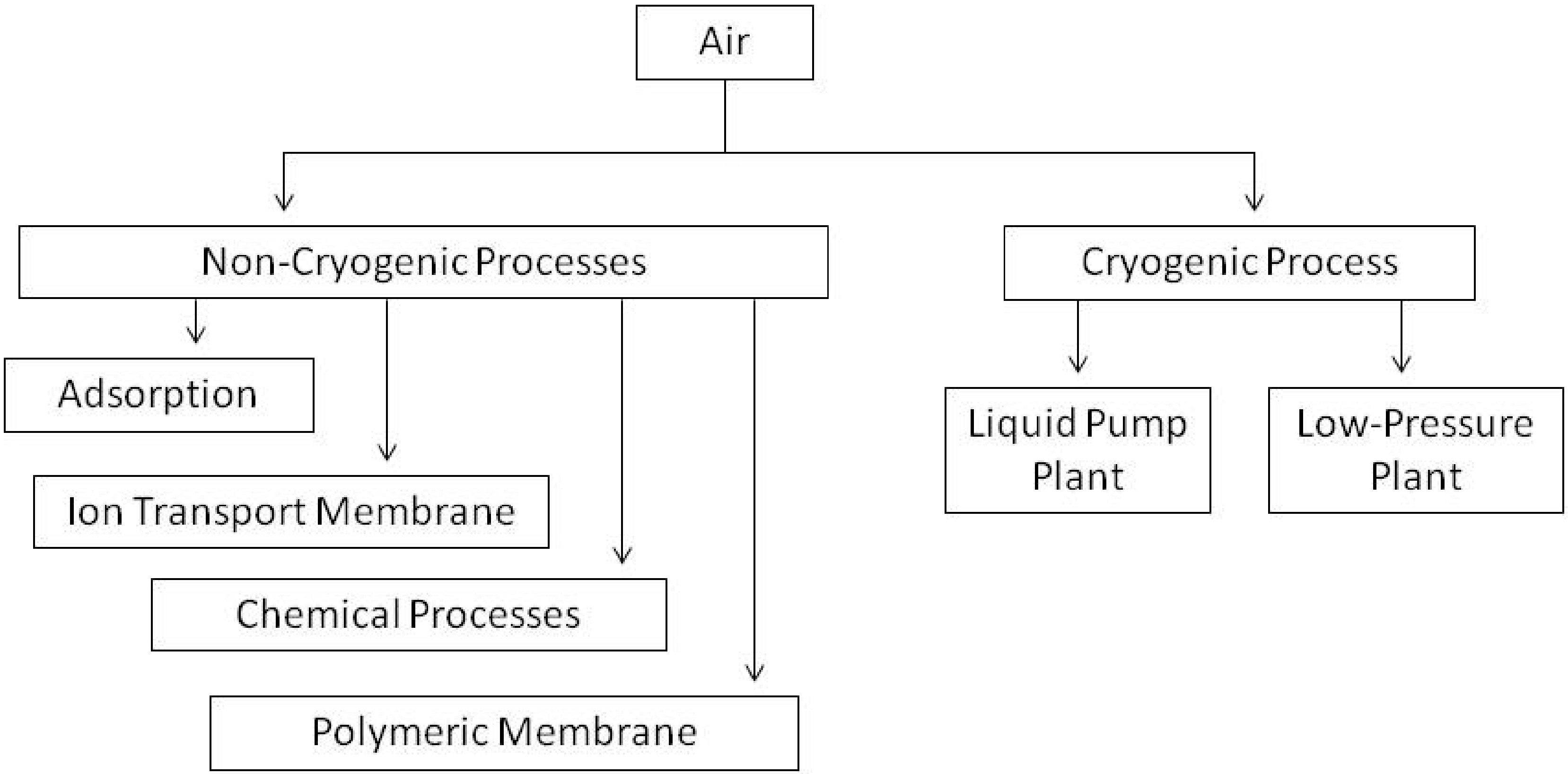


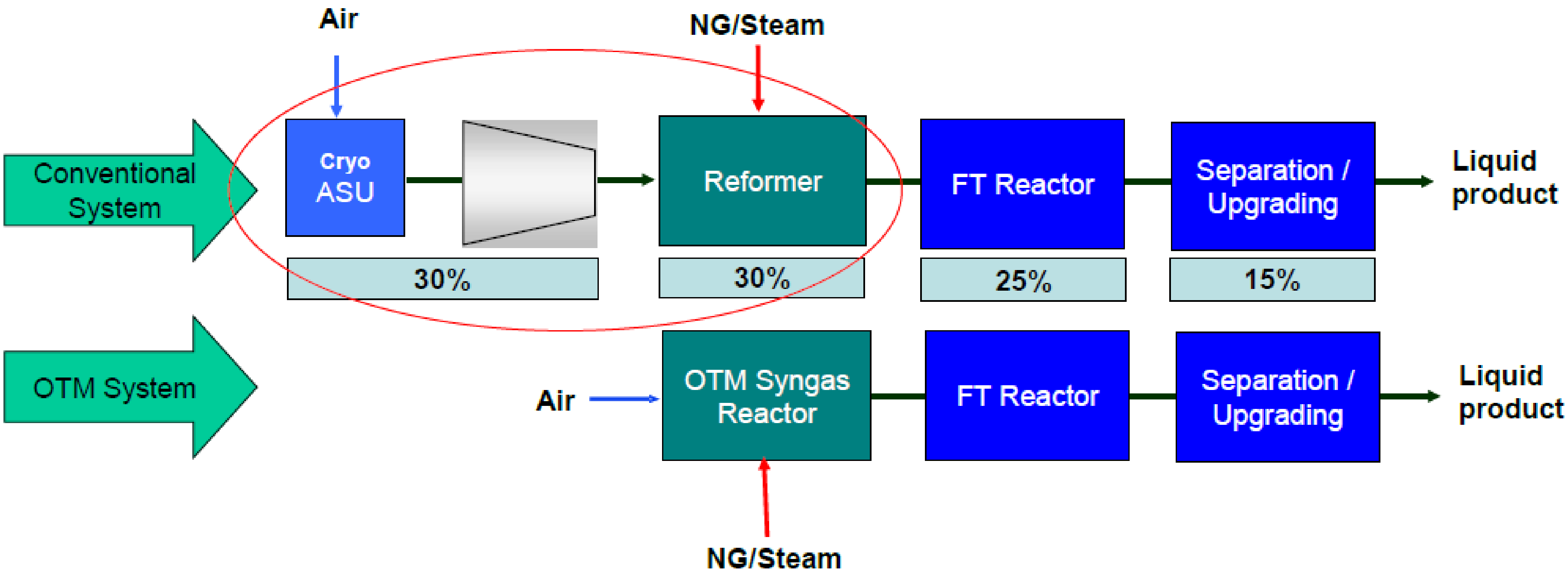


Air Products' ITM ceramic membranes have high oxygen flux and high selectivity for oxygen, making them ideal for tonnage oxygen and syngas production.

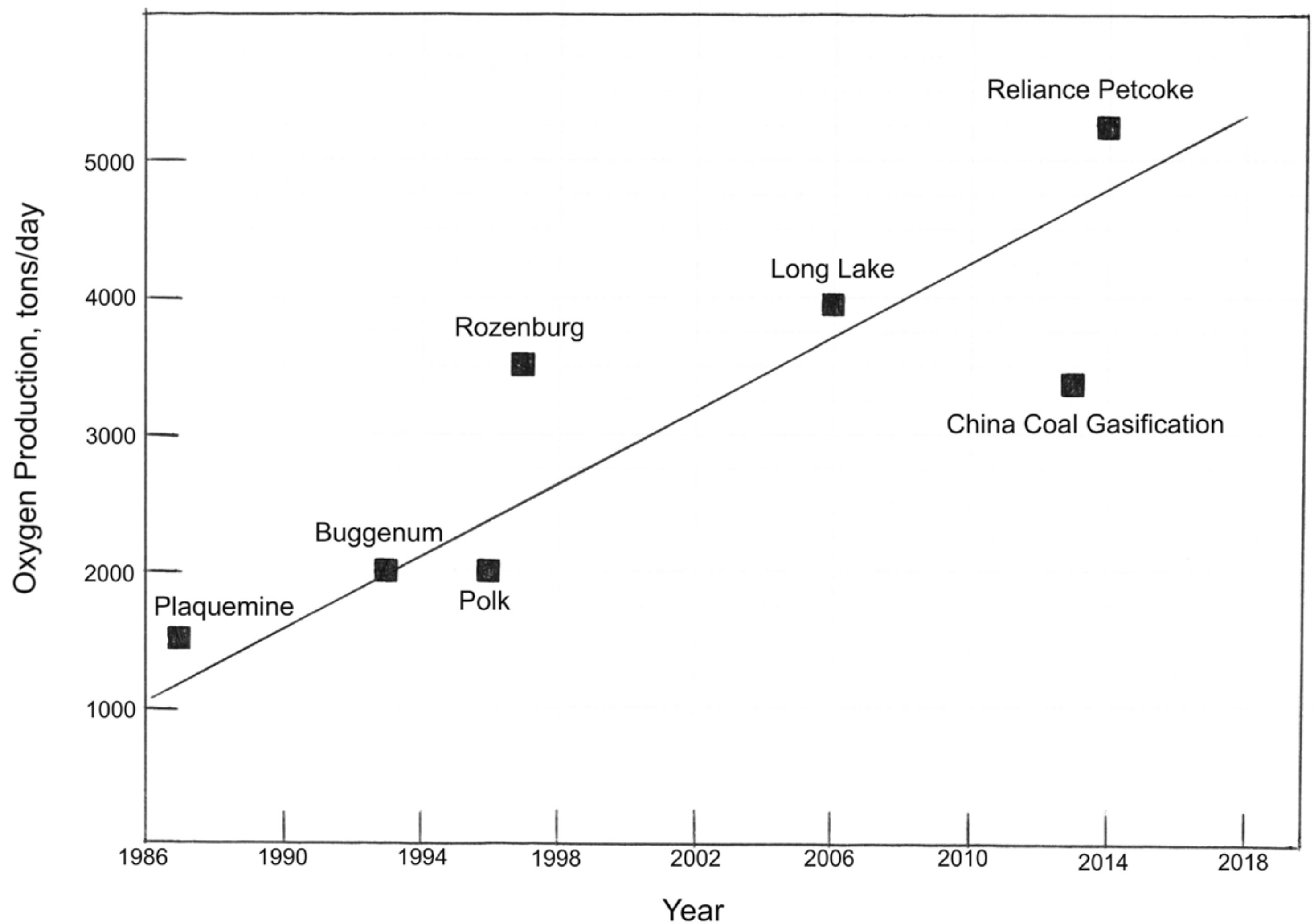
ITM can offer multiple benefits:

- 25%–35% reduction in capital requirements over conventional cryogenic oxygen plants
- 30% reduction in capital requirements for syngas plants
- 30% reduction in operation costs for oxygen
- 35%–60% reduction in power consumption (depending on product pressure) up to 1000 psig
- Consumes no net electricity
- Uses syngas, natural gas or other fuel
- Can be integrated with other high-temperature processes to produce electrical power and/or steam from depleted air
- Substantial reduction in cooling water consumption
- Compact, modular design has significantly smaller footprint than cryogenic ASU plant or the syngas plant

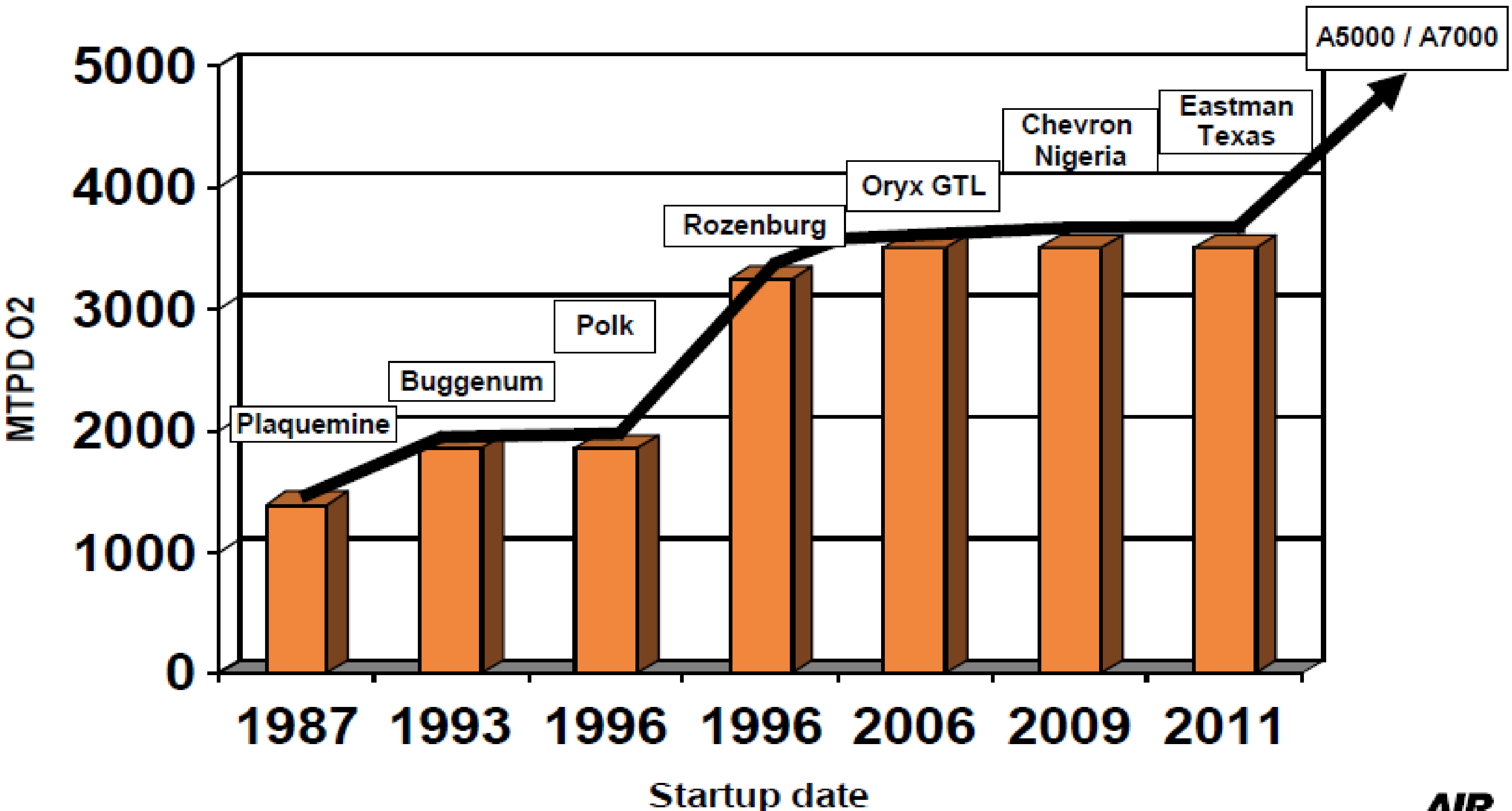

Air
Non-Cryogenic Processes
Cryogenic Process
Adsorption
Ion Transport Membrane
Chemical Processes
Polymeric Membrane
Liquid Pump Plant
Low-Pressure Plant



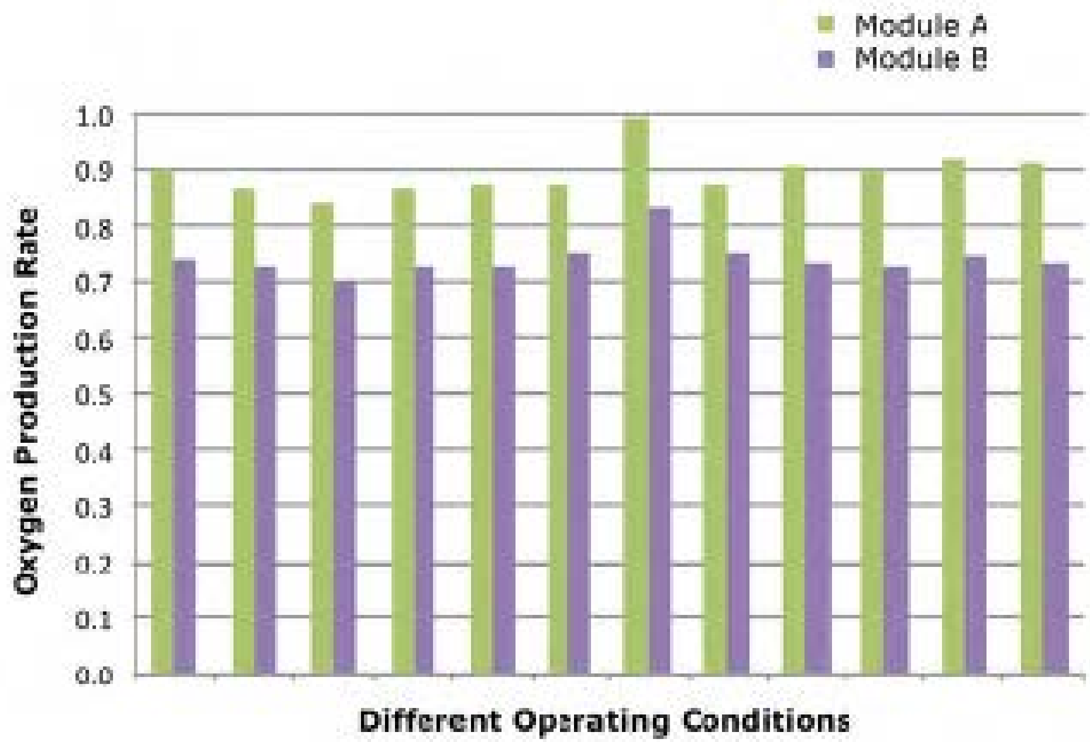
Schematic of units involved in the conventional FTS process (upper) and the one that is possible by eliminating the air separation unit (bottom) .



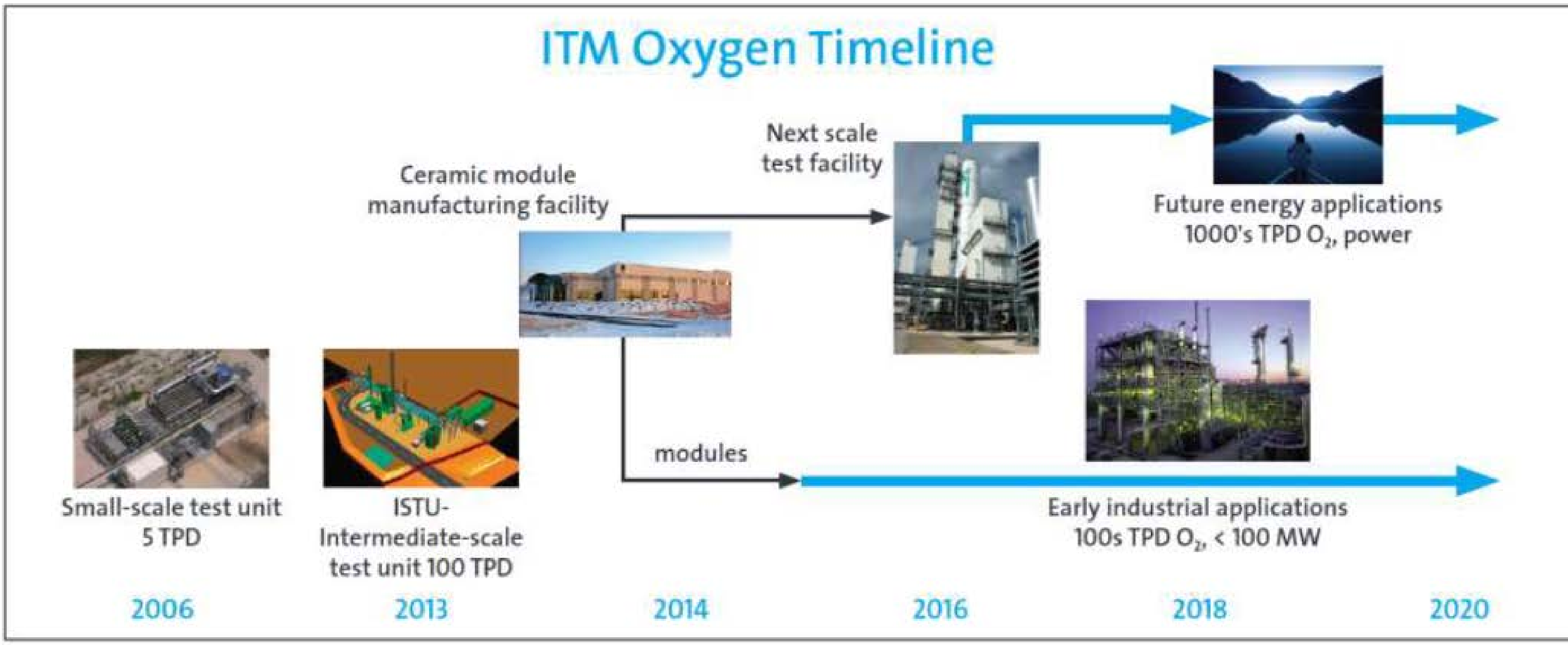
Oxygen Production, tons/day
5000
4000
3000
2000
1000
Reliance Petcoke
Long Lake
Rozenburg
China Coal Gasification
Buggenum
Polk
Plaquemine
1986
1990
1994
1998
2002
2006
2010
2014
2018
Year


A5000 / A7000
Eastman Texas
Chevron Nigeria
Oryx GTL
Rozenburg
Polk
Buggenum
Plaquemine
5000
4000
3000
2000
1000
0
MTPD O2
1987
1993
1996
1996
2006
2009
2011
Startup date

Two 1-TPD modules installed in the flow duct for SEP, February 2010. Oxygen production results for the two modules are shown at various process conditions. For these modules, the membrane active layer thickness was somewhat larger than typical values, reducing flux.



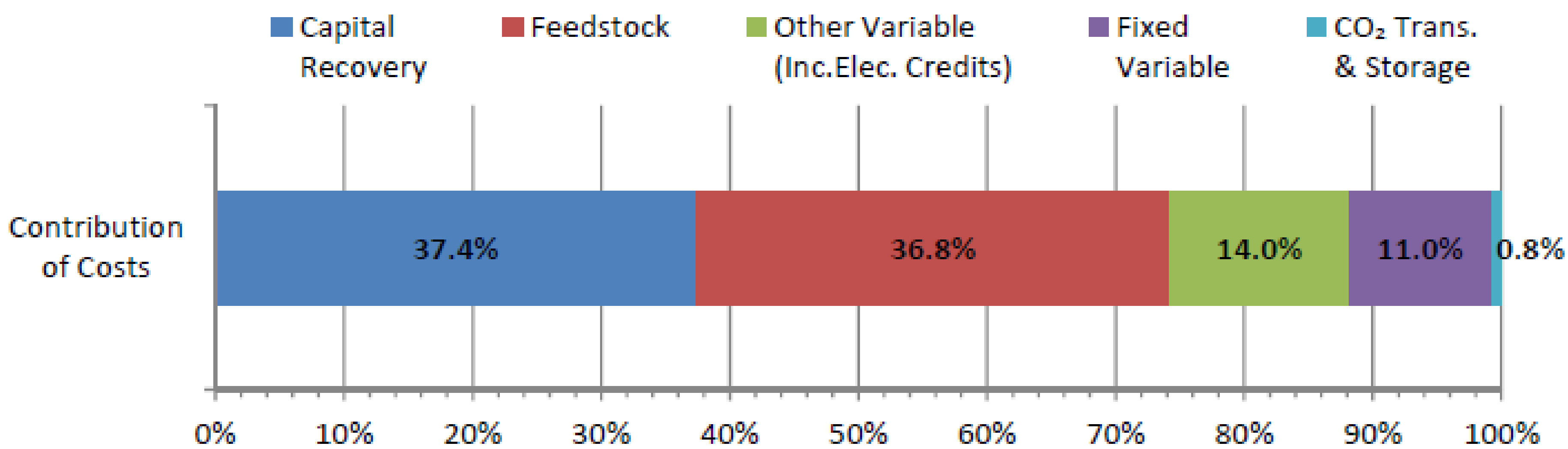
ISTU and CerFab are critical steps to commercialize energy-scale ITM Oxygen



Fischer-Tropsch Synthesis

- Improve Reactor
- Improve Catalyst (ca. 50% of operating cost)
- Improve Process

Exhibit 5-6 Approximate Contribution to Cost of Production of Fischer-Tropsch Liquids



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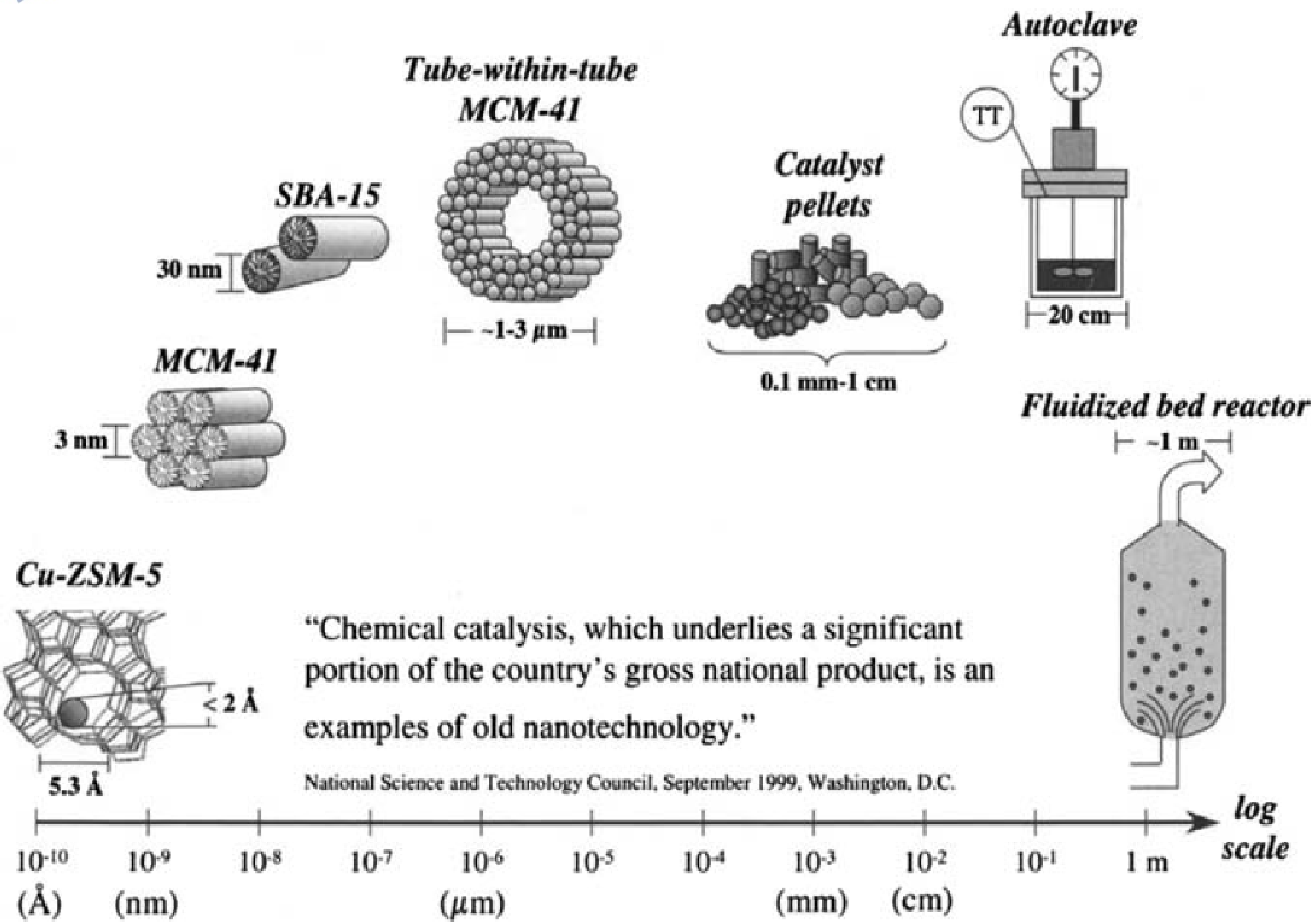


"Chemical catalysis, which underlies a significant portion of the country's gross national product, is an examples of old nanotechnology."

National Science and Technology Council, September 1999, Washington, D.C.

Improve Catalyst

Support Sasol, alumina
Shell, silica, titania
BP, magnesia

Active Component: Increase loading without loss of conversion/metal

Process: Wax/slurry separation

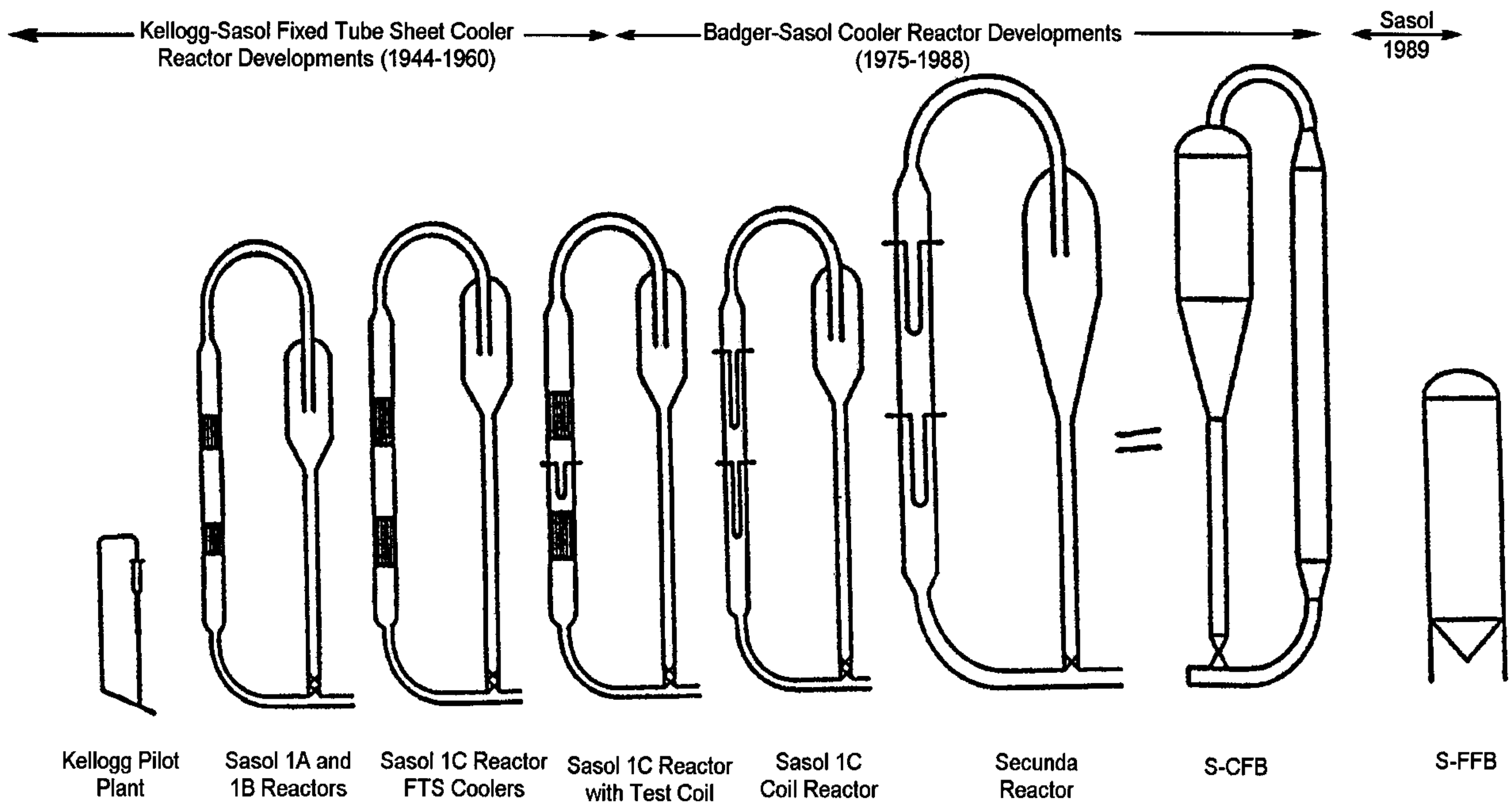
Improve Catalyst

Increase loading of active component.

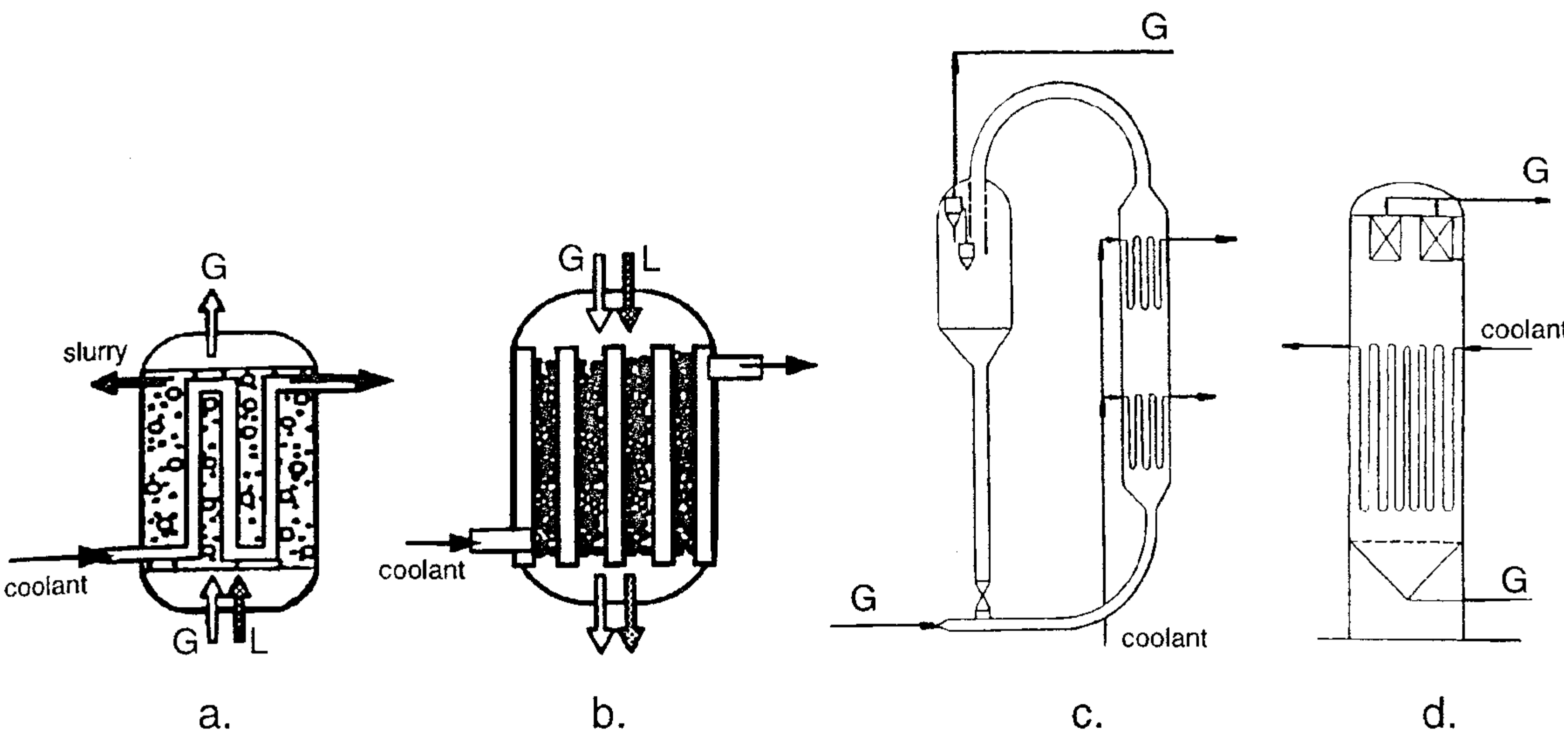
Find a cheaper metal.

Increase catalyst life.

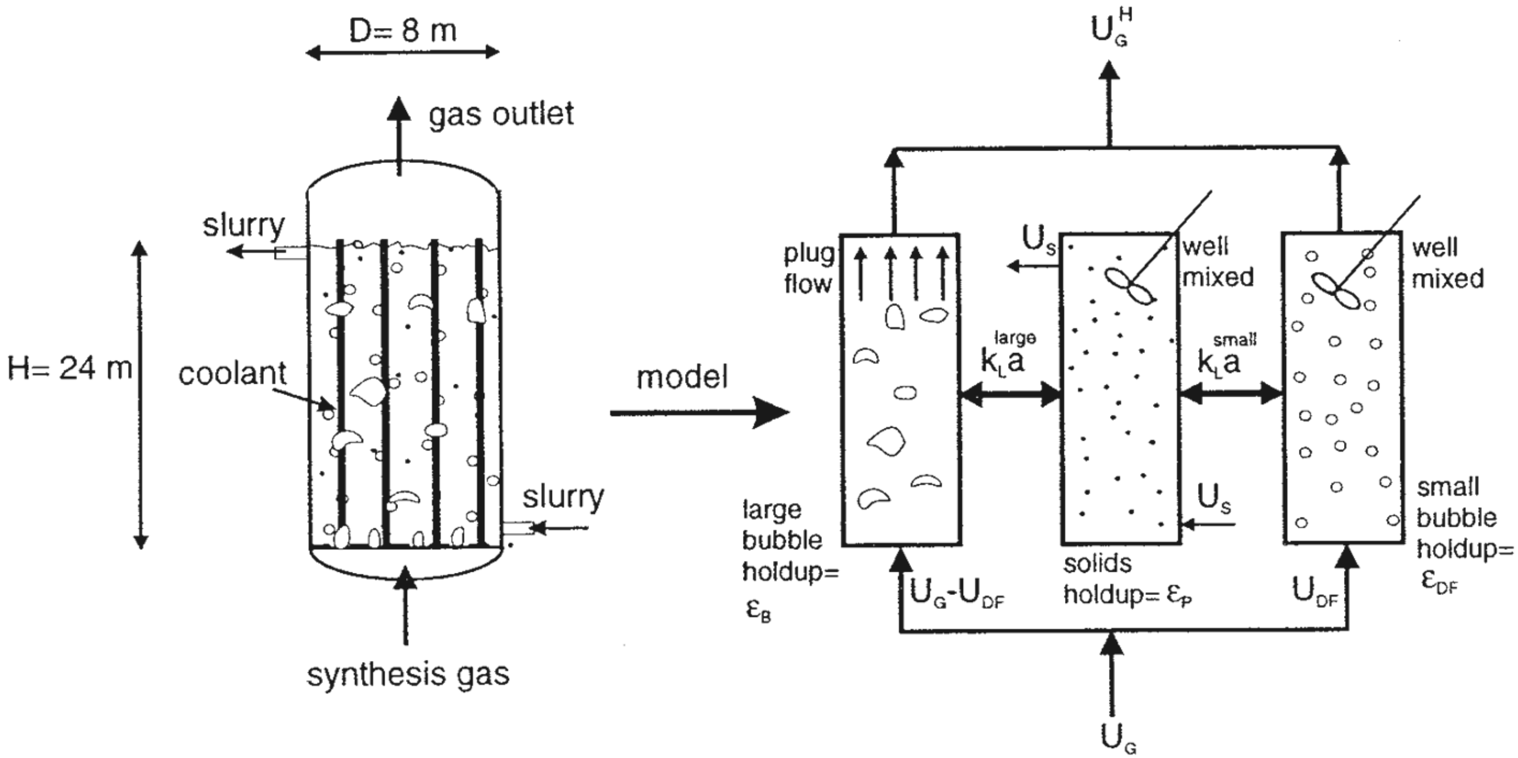
Viable bifunctional catalyst.



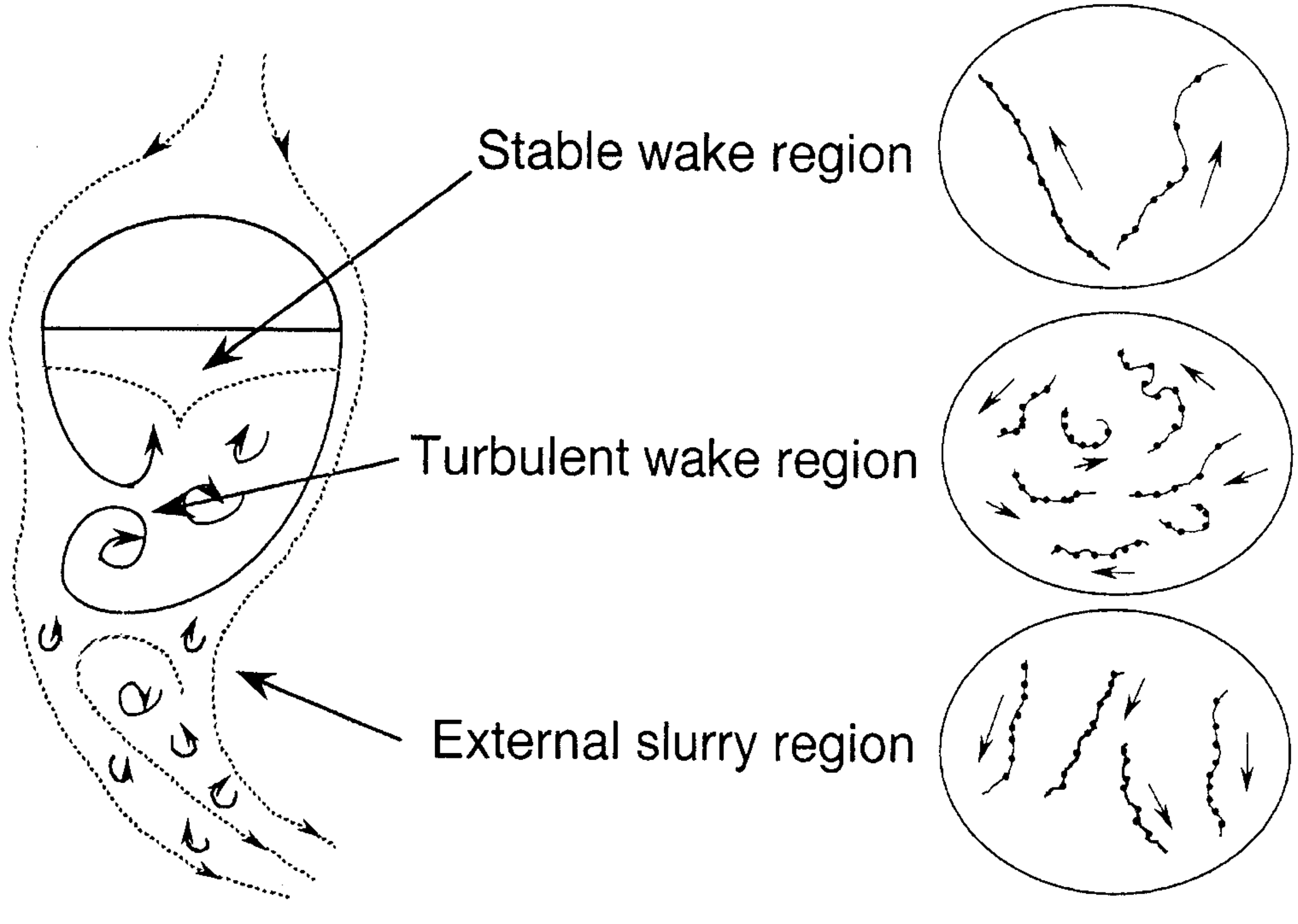
Schematic showing sizes of Sasol fluid-bed reactors [compiled from T. Shingles and D. H Jones, *ChemSA*, August 1986, 179-182 and B. Jager, M. E. Dry, T. Shingles and A. P. Steynberg, *Catal. Lett.*, **7**, 293 (1990)].



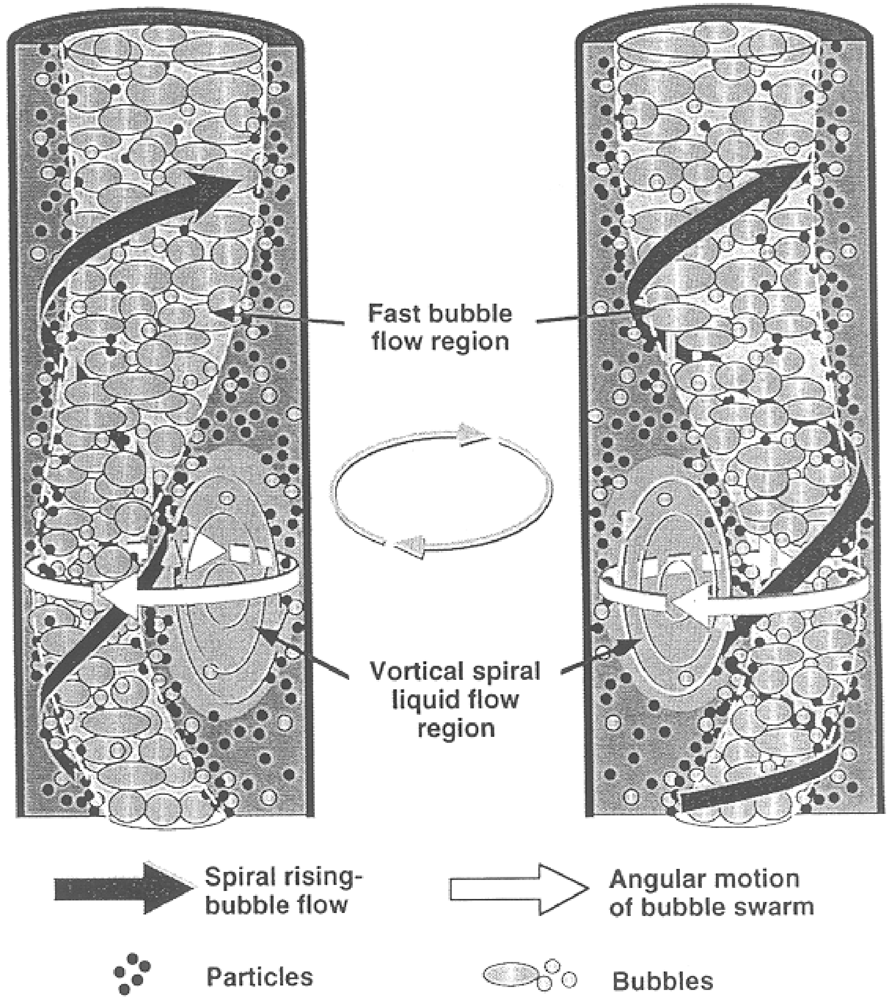
Possible reactors for Fischer-Tropsch synthesis. (a) slurry Bubble column reactor, (b) multitubular trickle bed reactor, (c) circulating- and (d) fluidized-bed reactor.



Hydrodynamic model of slurry bubble column reactor in the heterogeneous flow retime.



Typical particle trajectories within three different flow Regions around a rising bubble.



Model of flow scheme in the slurry bubble column.

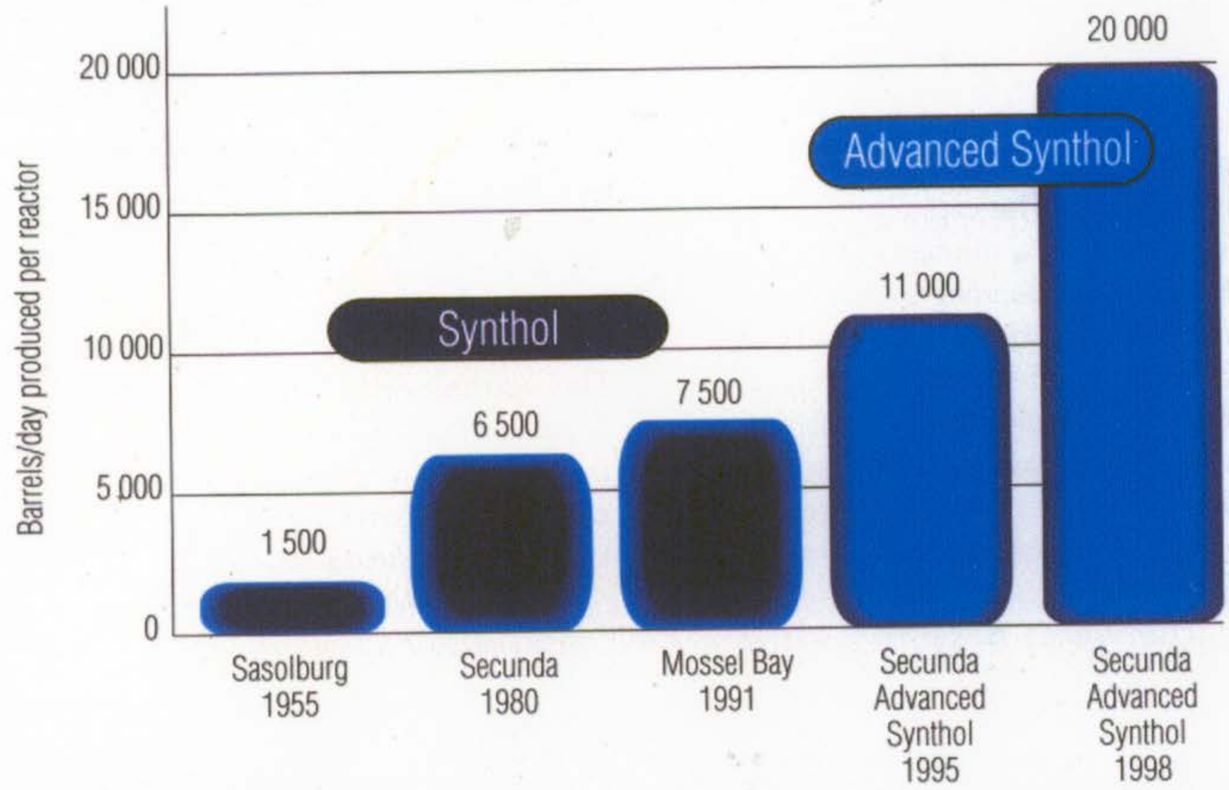


Figure 9: Synthol reactor capacity increase.

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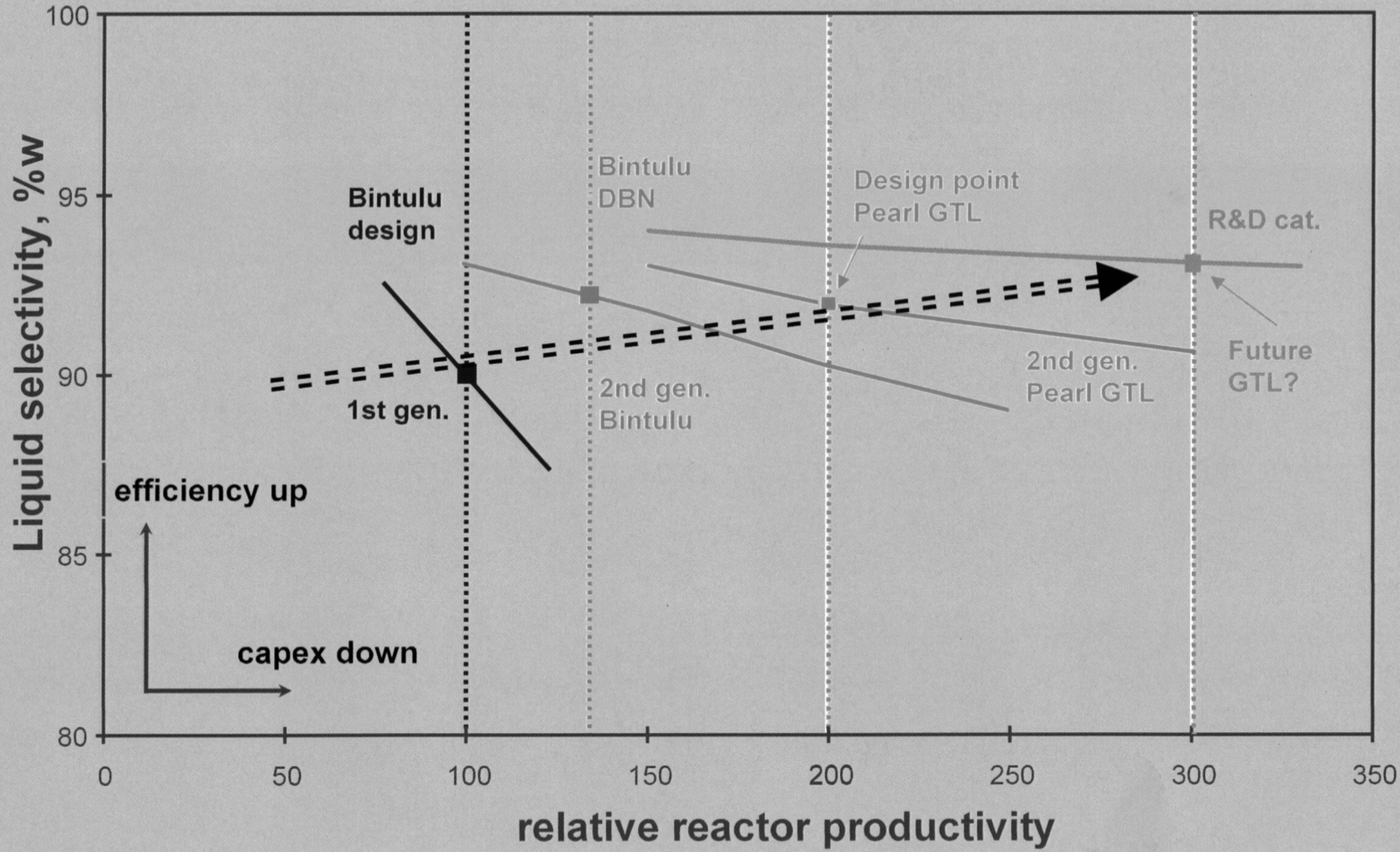
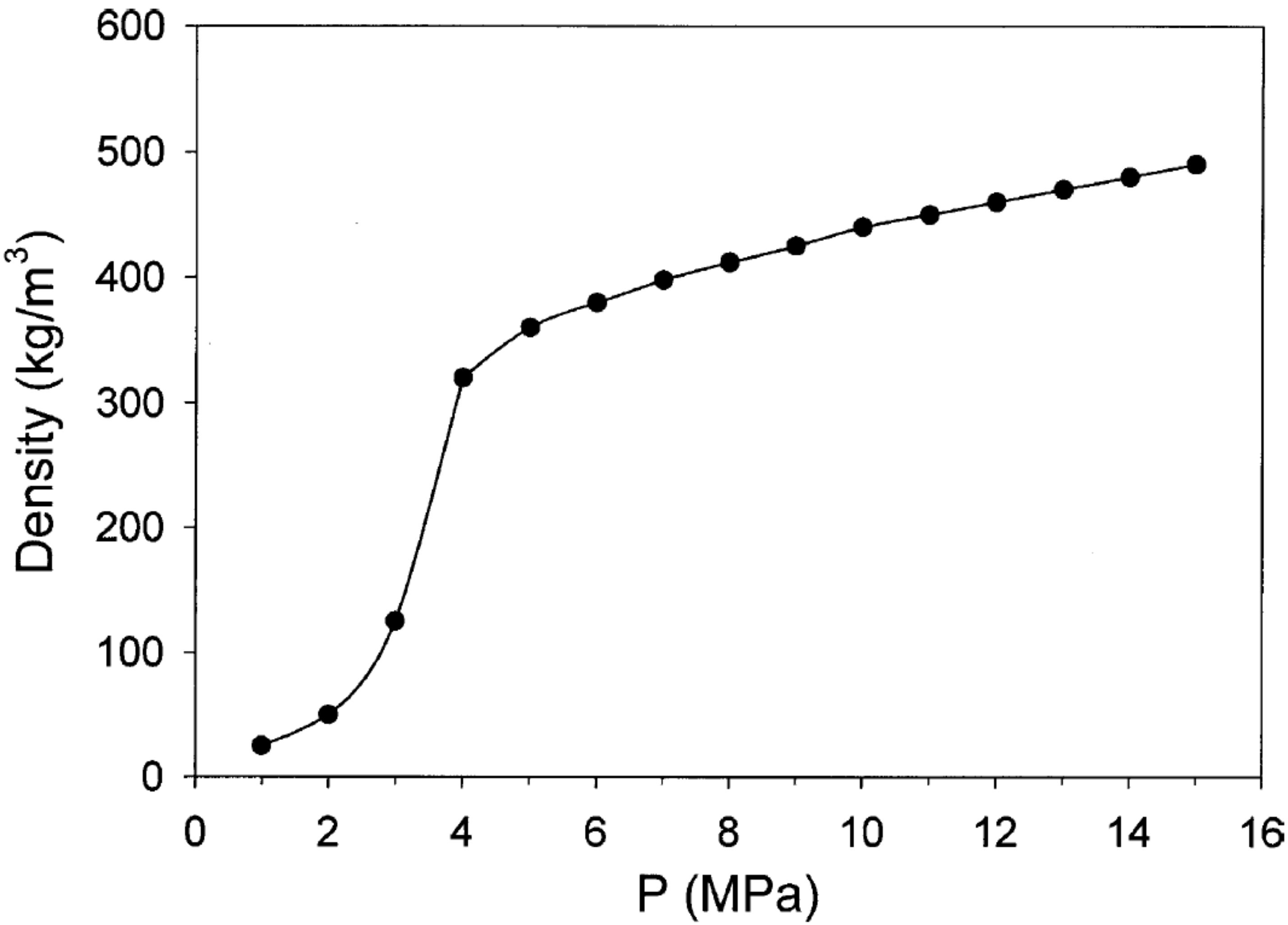
Fischer-Tropsch catalyst R&D



12

Supercritical Reactor



Upgrading

Currently being done by Sasol and Shell.

Little in the open literature until recently.

Amoco (now BP) and UOP did detailed study.

Easier than petroleum so need different catalyst.

io

Future in the US

Biomass:	Transportation of feedstock limits to small plants
Waste:	Transportation of feedstock limits to small plants
Coal:	Large plants possible, carbon dioxide large so incorporating biomass needed
Natural Gas:	Large plants possible

Think Big,
Build Small

What if???

1. Invest 90 billion to build FT plants
2. At 6 billion per plant, have 15 50,000 bbl/day plants (cost of $120,000 per bbl/day)
3. 750,000 bbl/day production from the 15 plants
4. US consumed 19 million bbl/day (1998); imported 10 million bbl/d.
5. 15 FT plants produce 3.95% total consumption; 7.5% of imports.
6. Government provide capital to build 15 plants and operators use and provide upkeep
7. Sasol makes money at $10-25/bbl today operating with coal
8. US operator should make money at $25/bbl.

Impact on US Coal Production

Coal Production 2000 = 1.1 billion tons

At 1 ton coal = 2 bbl FT products need 375,000 ton/day = 12.5% of current production

At 1 ton coal = 3 bbl FT products need 25,000 tons/day = 8.3% of current production

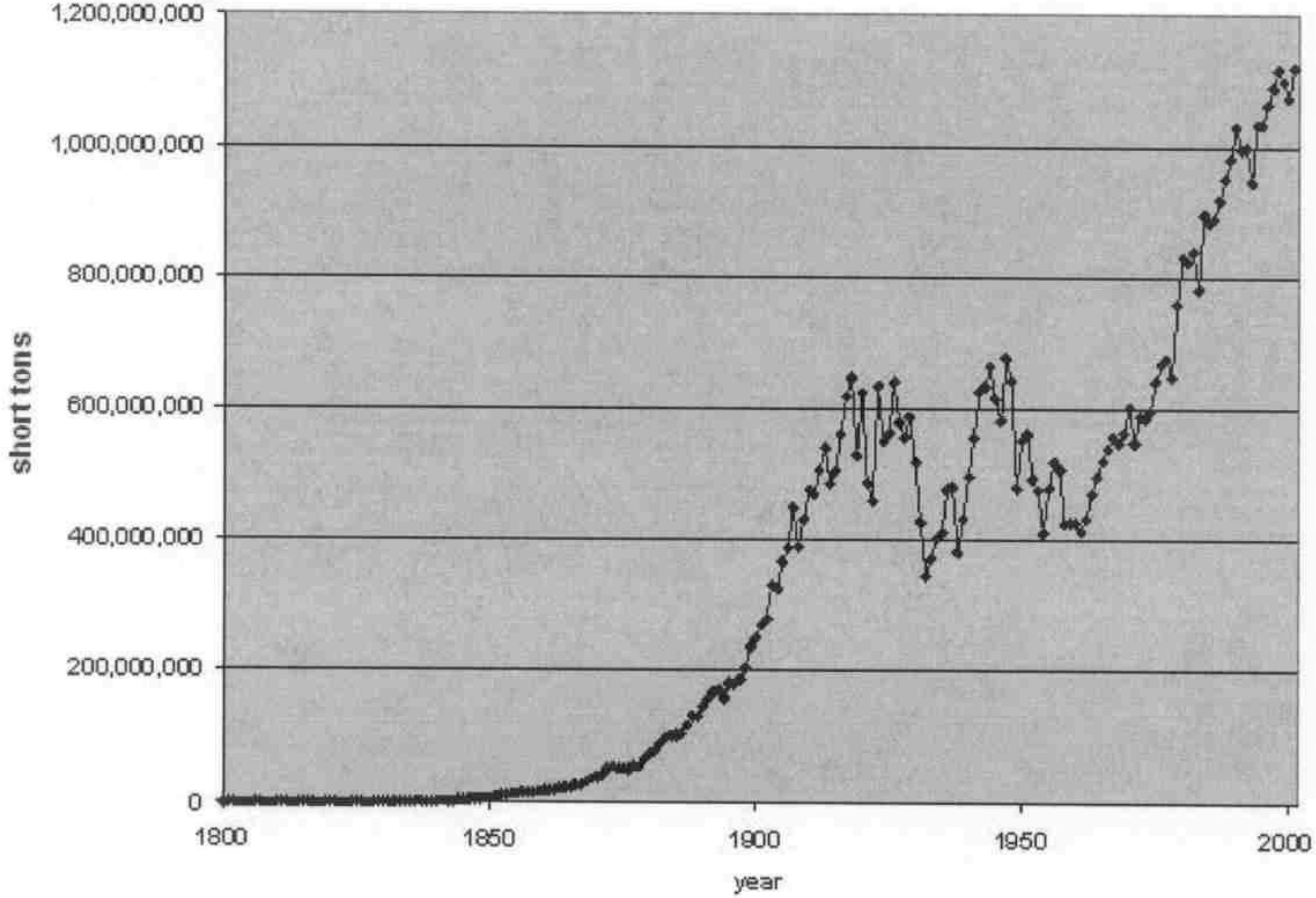
At 1 ton coal = 2 bbl FT products must increase coal production by 12.7%

1960-2000 coal production increased by 51,000 ton/day (1.88%/yr)

At 1 ton = 2bbl need to increase coal production 8 fold for 1 year

Gregson Vaux, The Peak in U.S. Coal Production, www.fromthewilderness.com

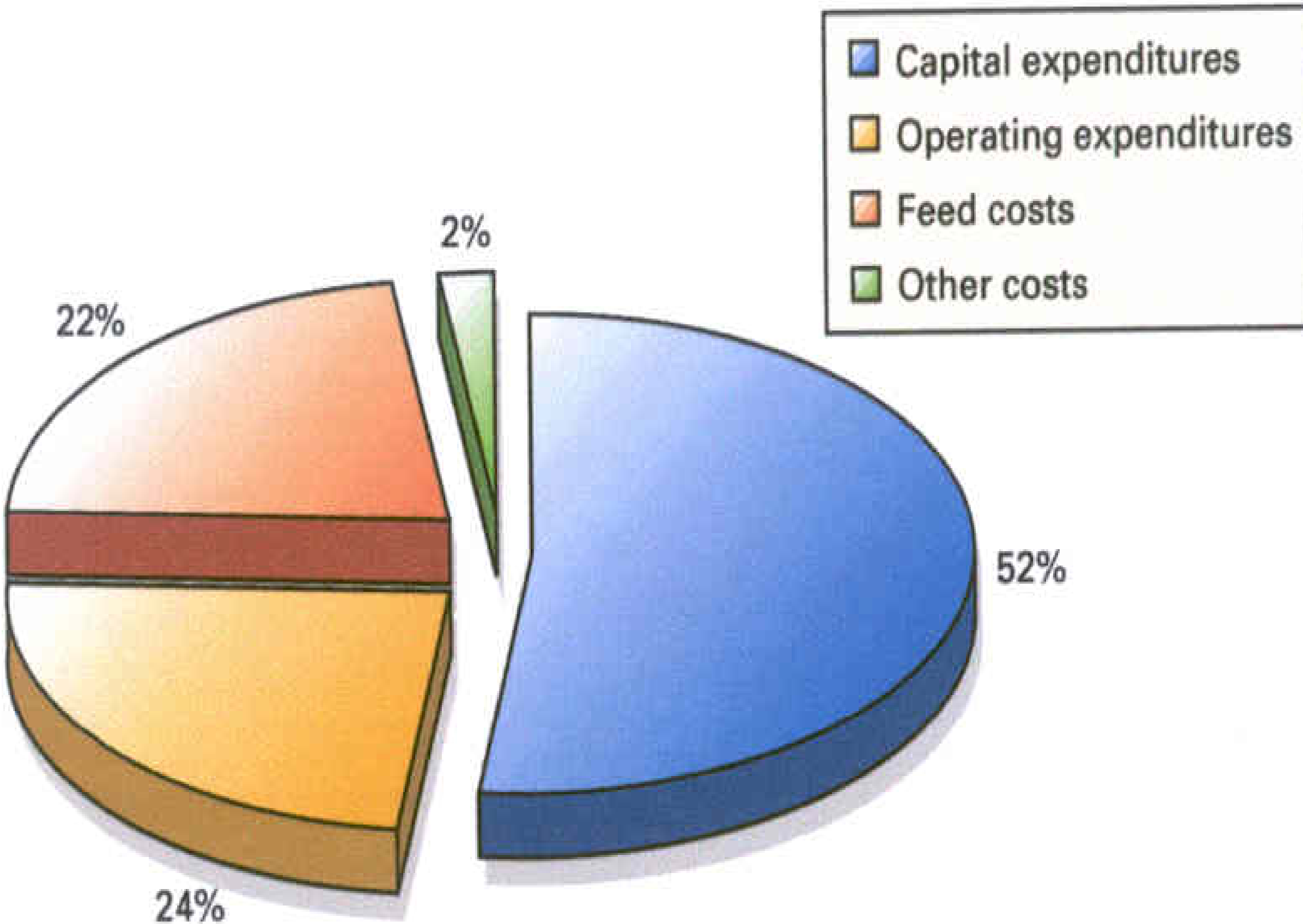
Figure 2: U.S. Coal Production



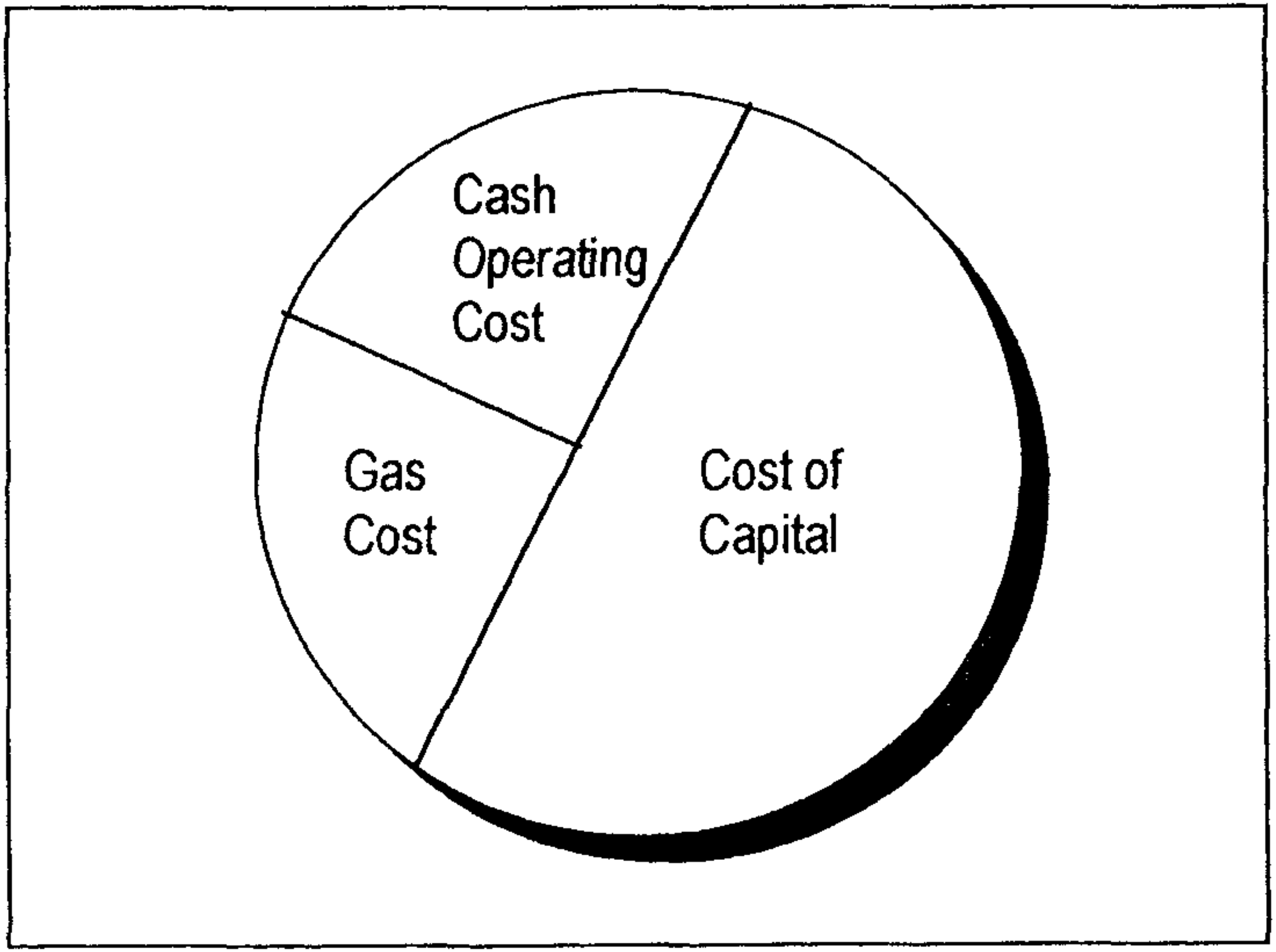
Source of data: EIA, USGS

CASH FLOW BREAKDOWN

Fig. 1



Source: Foster Wheeler Energy Ltd.


Cash
Operating
Cost
Gas
Cost
Cost of
Capital

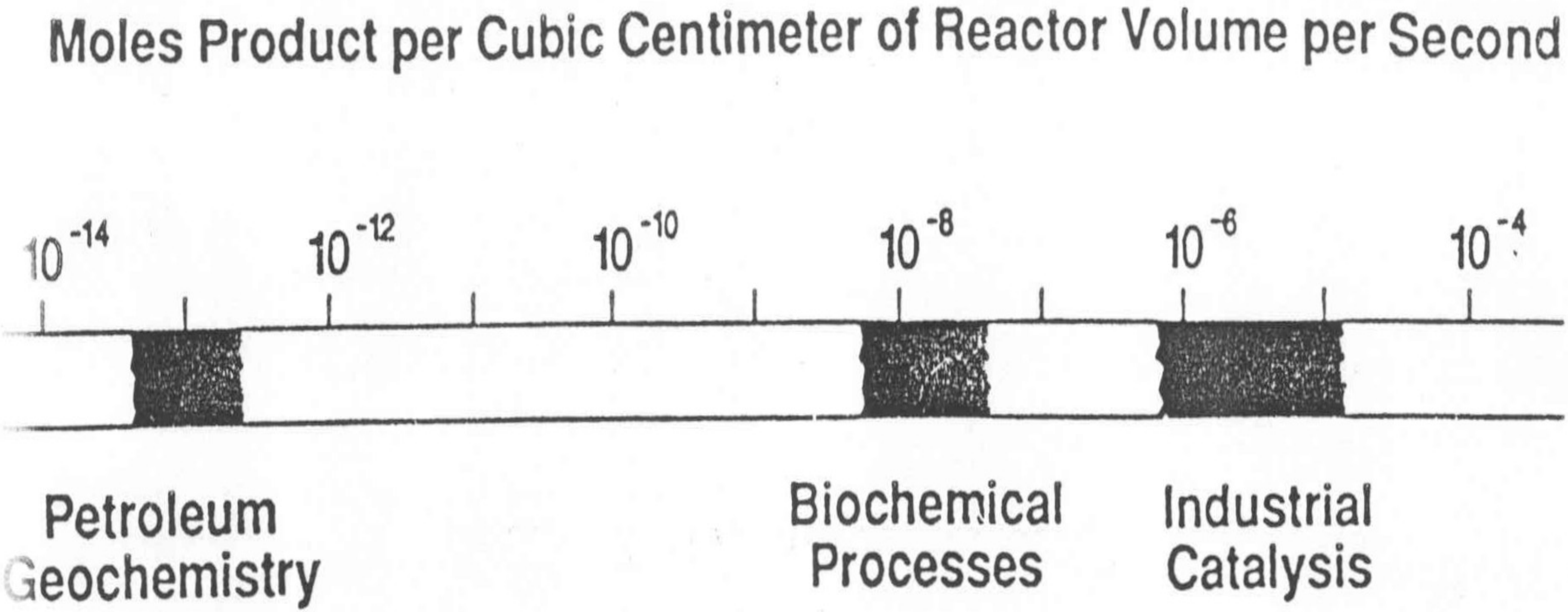


Figure 1. The Weisz window and other windows of activity.

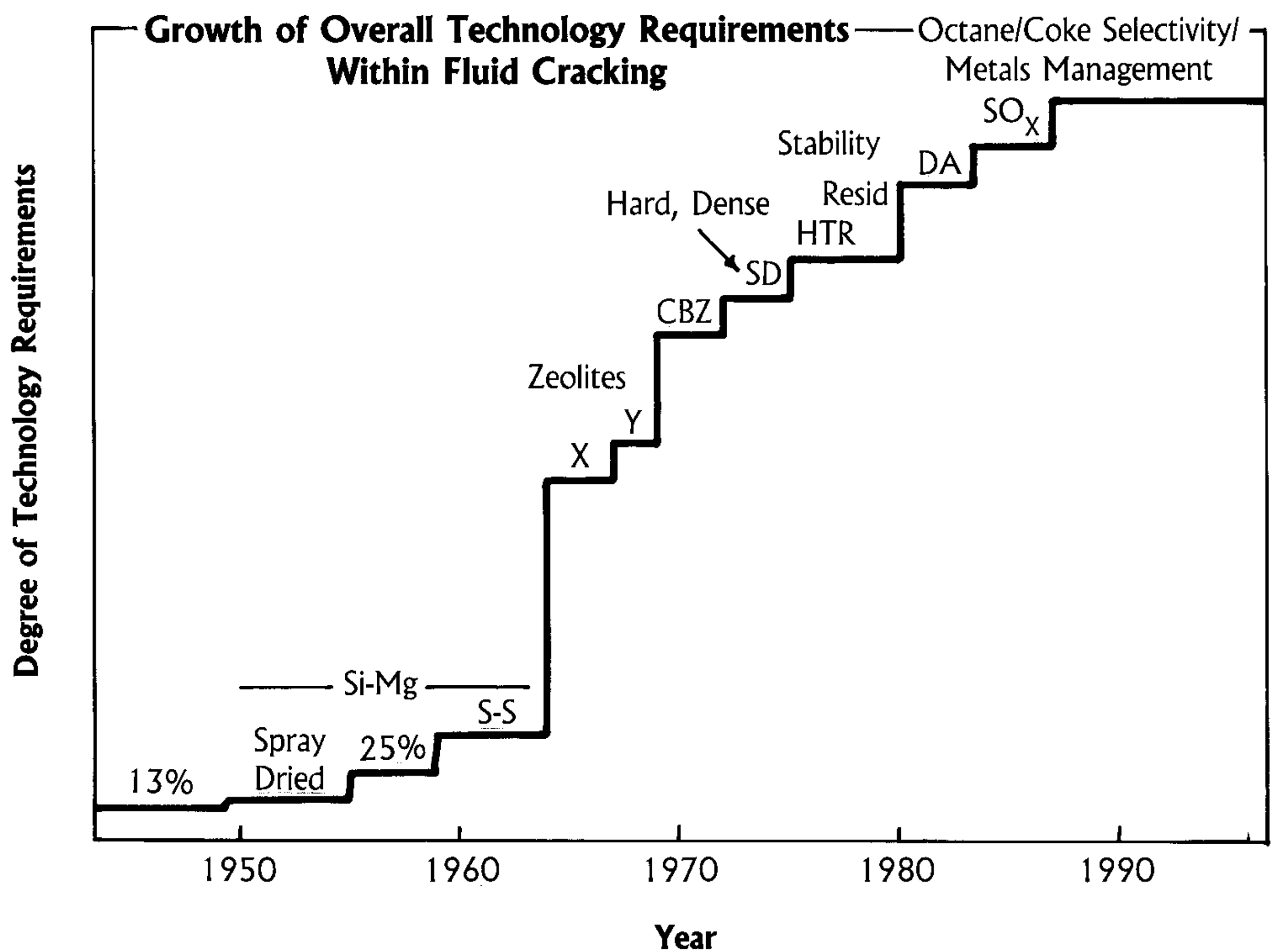
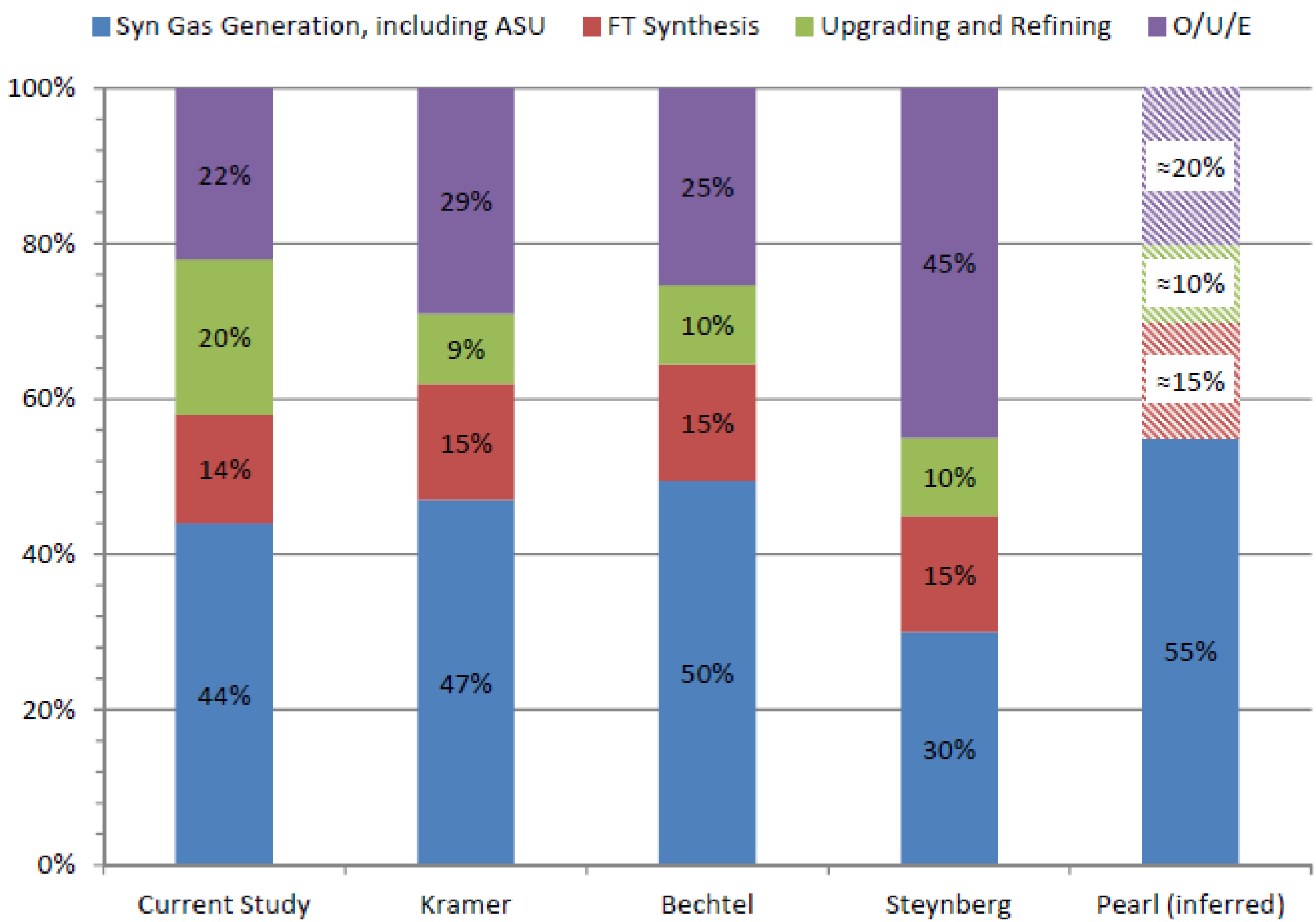

Growth of Overall Technology Requirements
Within Fluid Cracking
Octane/Coke Selectivity/
Metals Management
SO_X
Stability
DA
Resid
Hard, Dense
HTR
SD
CBZ
Zeolites
Y
X
Si-Mg
S-S
Spray
Dried
25%
13%
1950
1960
1970
1980
1990
Year
Degree of Technology Requirements

Exhibit 5-2: Breakdown of Capital Costs by Processing Section



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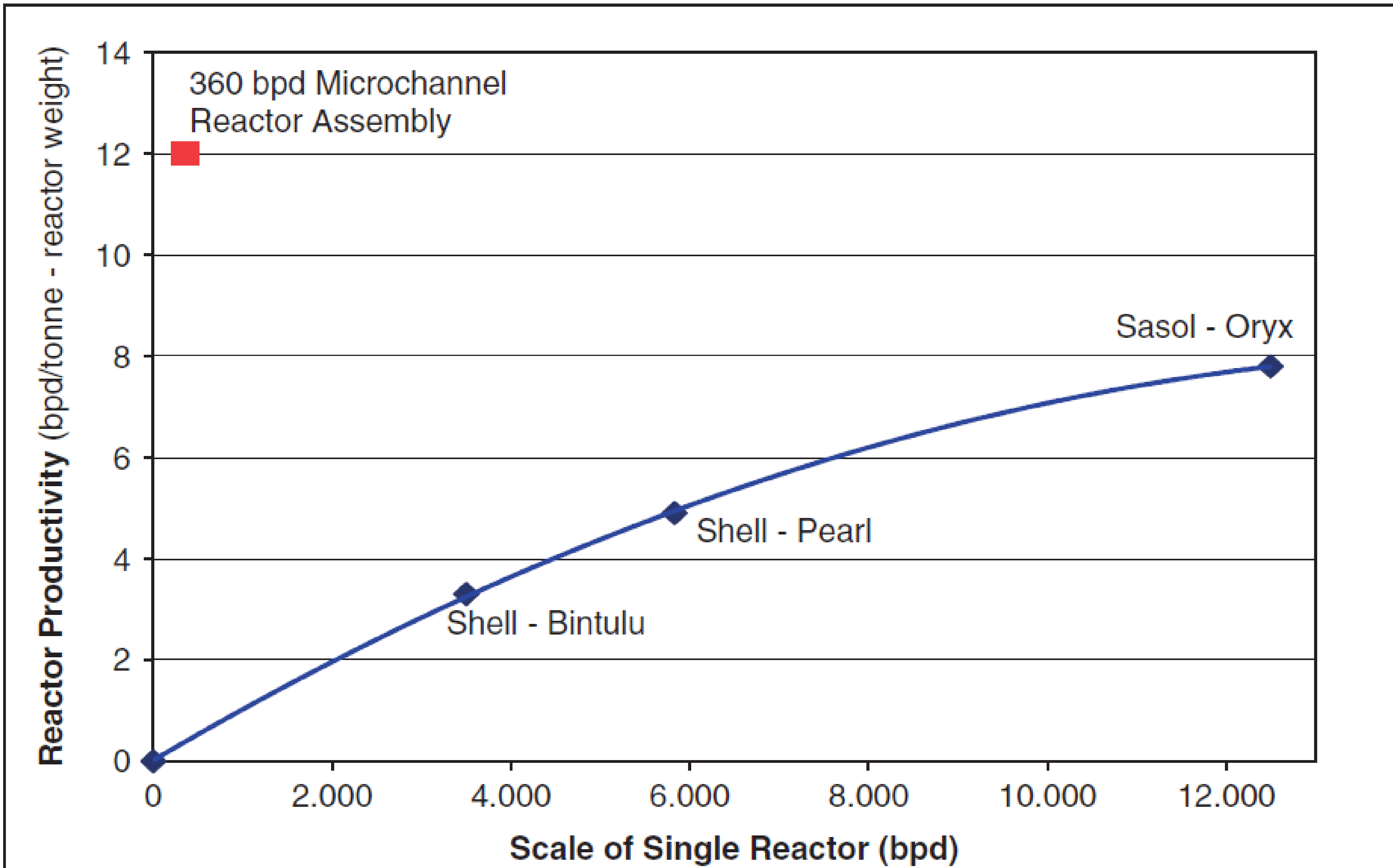
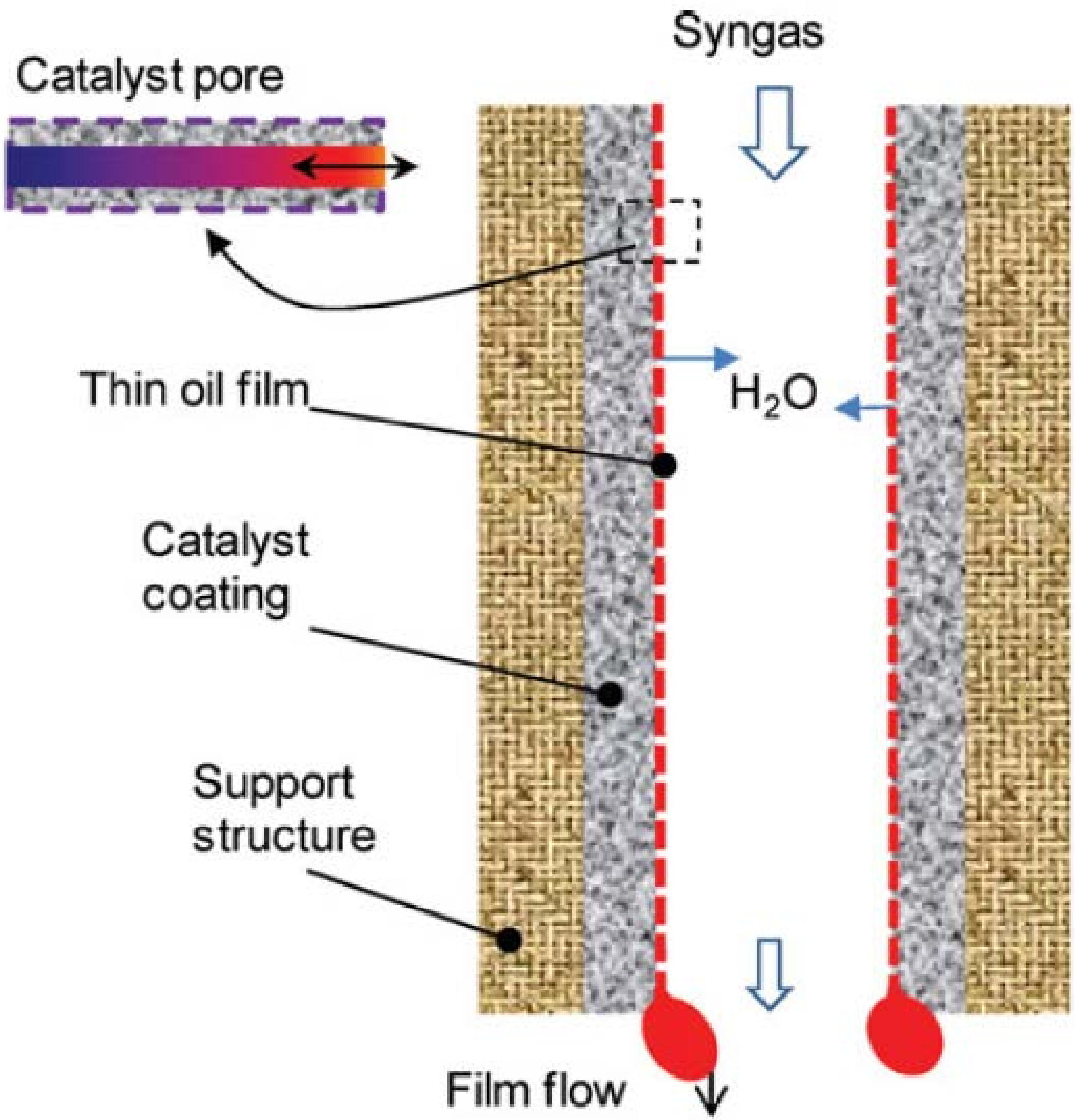
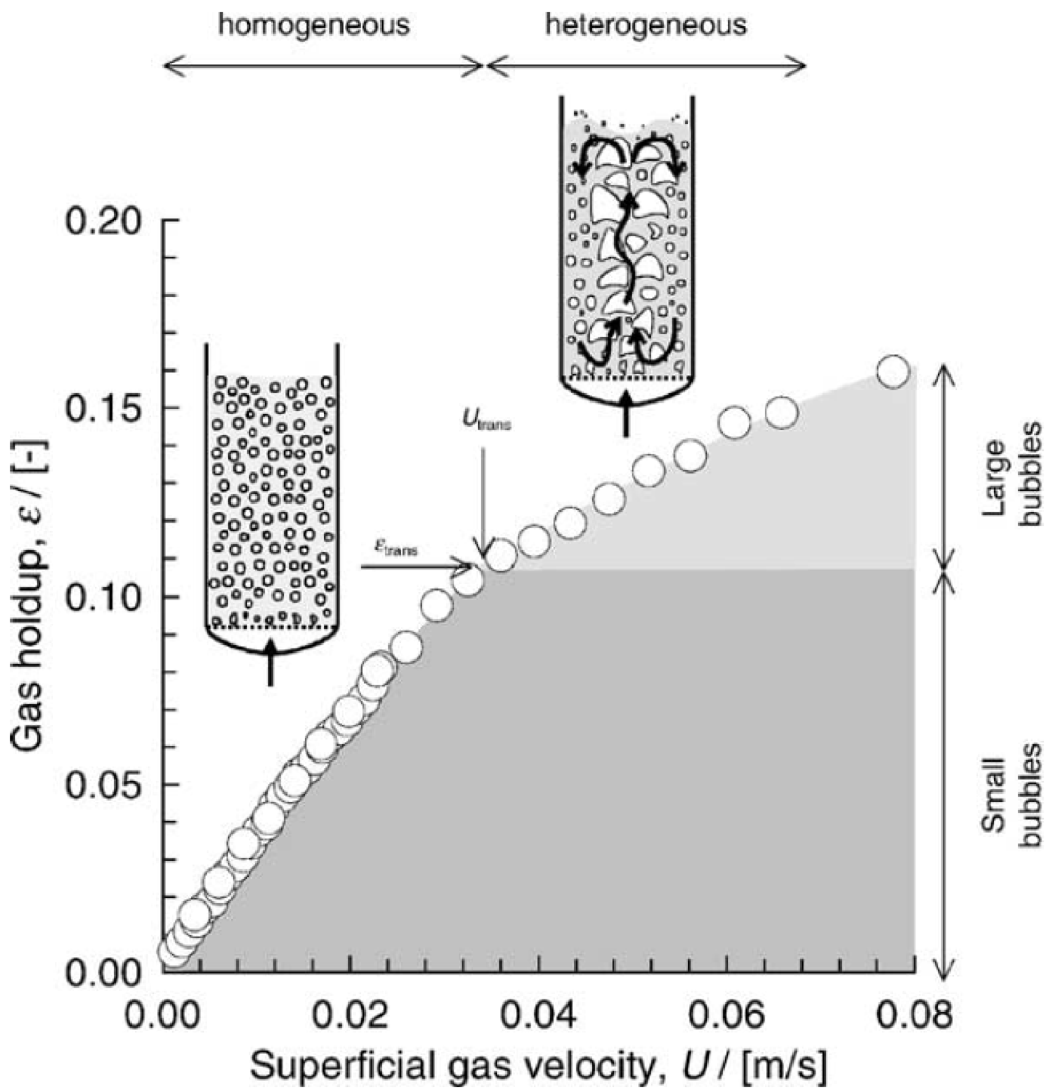
Reactor Productivity Comparison

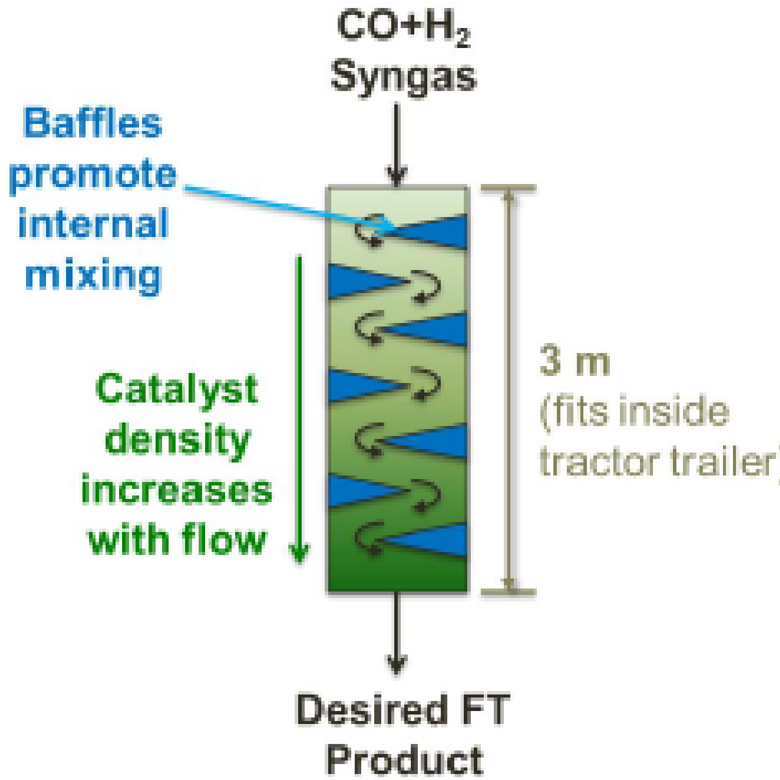




Syngas
Catalyst pore
Thin oil film
H_2O
Catalyst coating
Support structure
Film flow

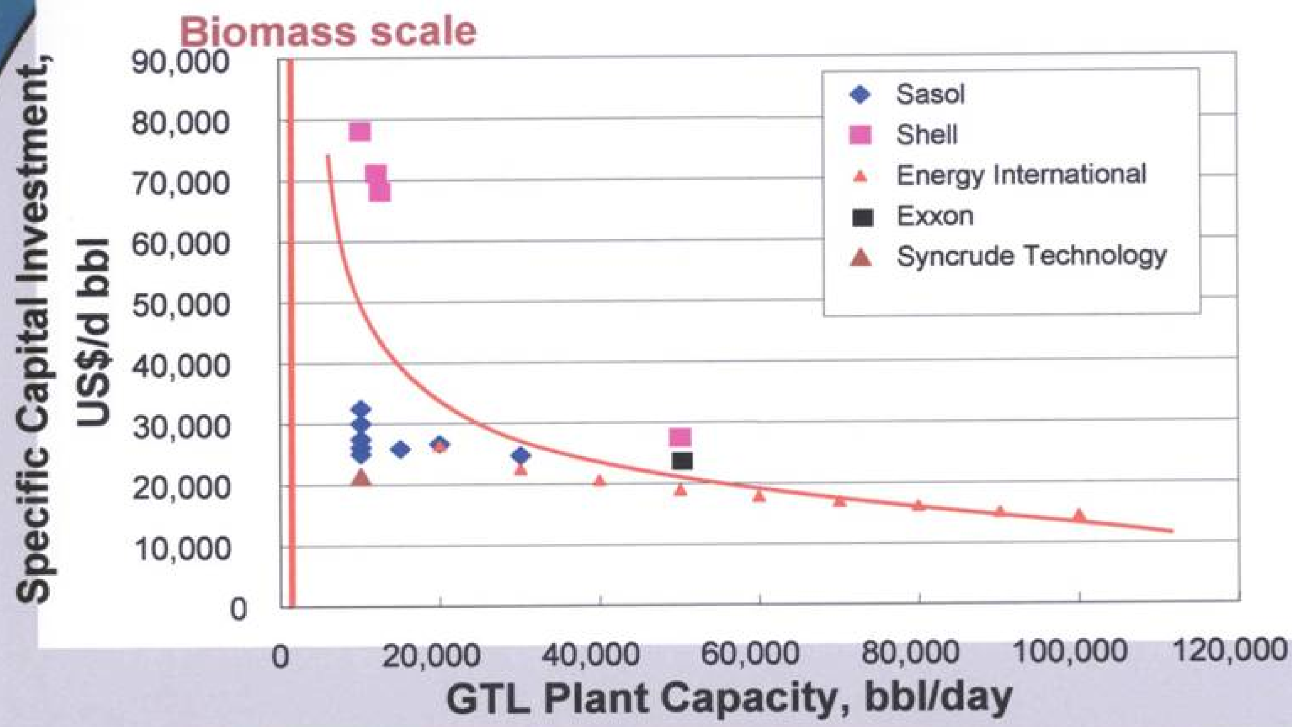


homogeneous
heterogeneous
U_{trans}
ε_{trans}
Gas holdup, ε / [-]
0.20
0.15
0.10
0.05
0.00
0.00
0.02
0.04
0.06
0.08
Superficial gas velocity, U / [m/s]
Large bubbles
Small bubbles



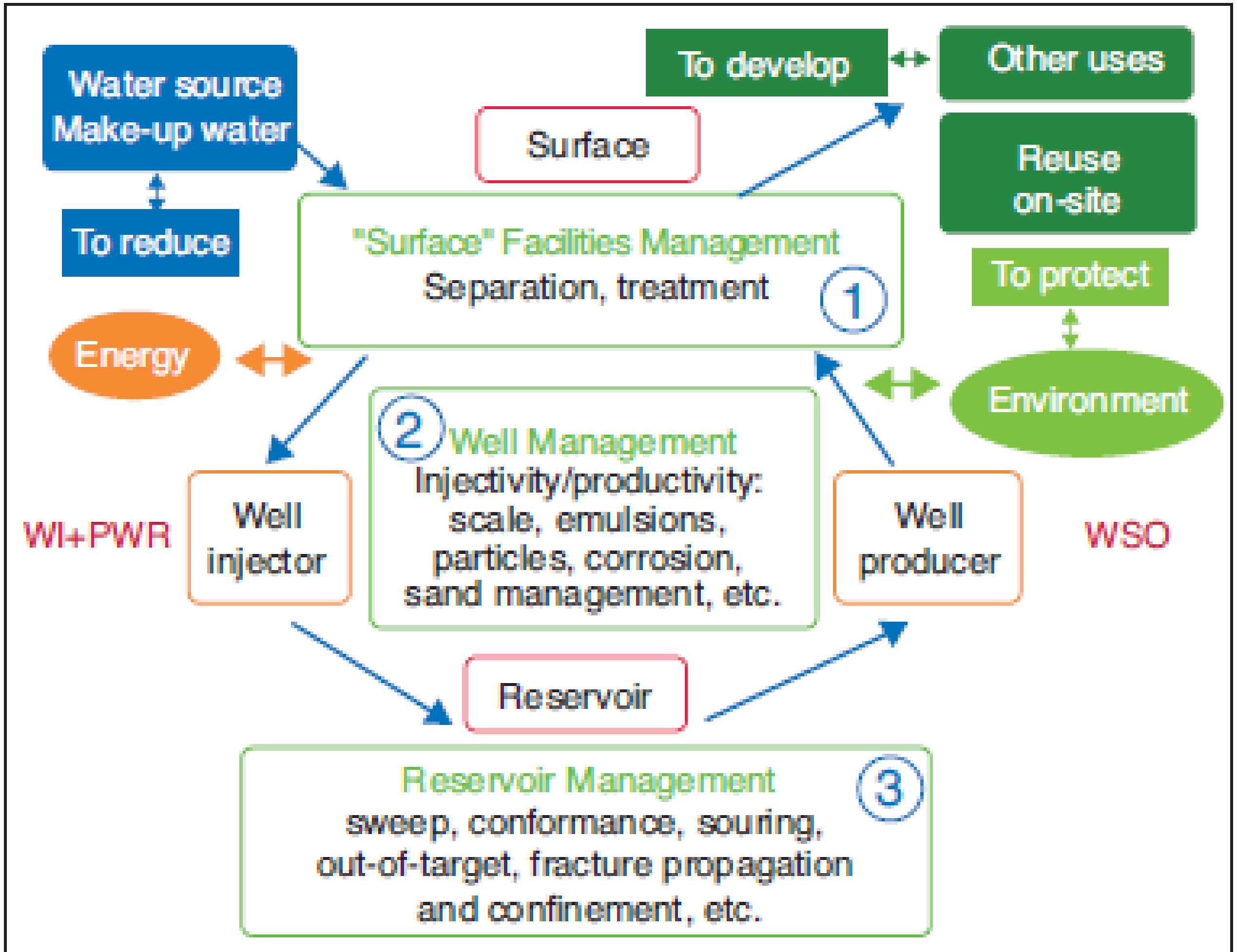
$CO+H_2$
Syngas
Baffles promote internal mixing
Catalyst density increases with flow
3 m
(fits inside tractor trailer)
Desired FT Product

Conventional GTL Plant Capital Investment

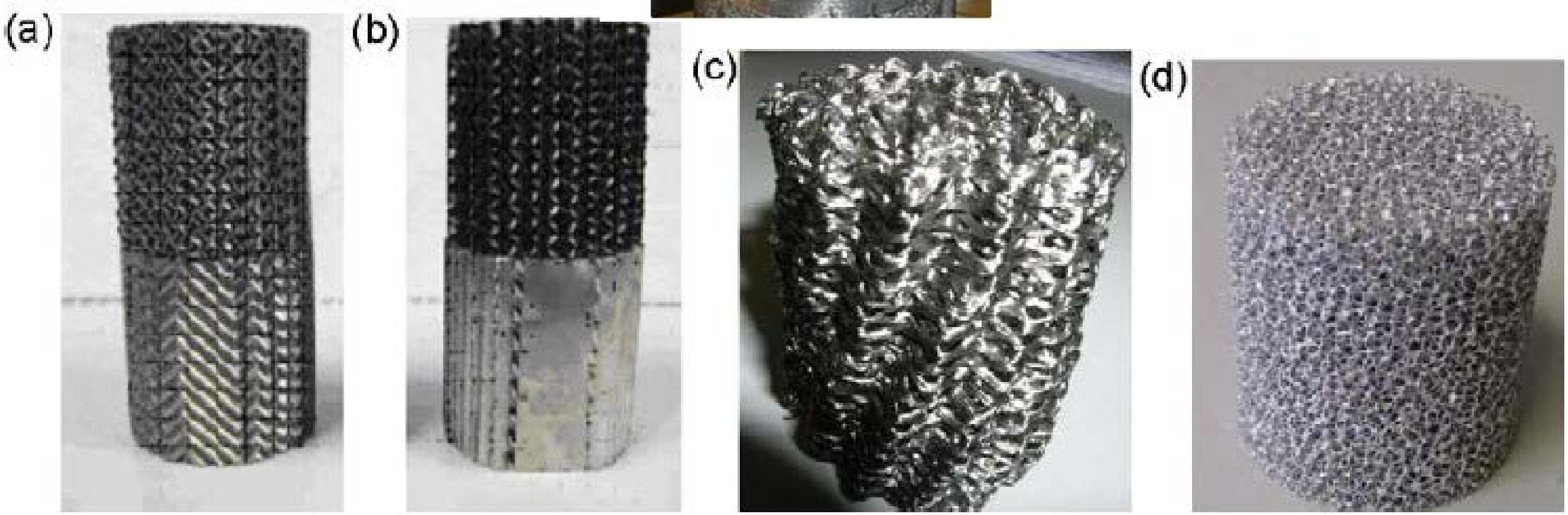


➢ **Conventional GTL plant is not cost competitive at the capacity typical of biomass feedstocks**

Fig. 4 - Water cycle and Integrated Management (IWM)



Source: IFP Energies nouvelles



(a)
(b)
(c)
(d)

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