Gas-to-Liquid Technologies: Recent Advances, Economics, Prospects

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Gas-to-Liquid Technologies:
Presentation Outline

- Drivers for use of GTL technology
- Historical, current, and planned GTL applications
- GTL chemistry, processes, products
- Key GTL technologies
- GTL CAPEX and economics
- Synergies and commercial issues

Drivers for Chemical Conversion of Natural Gas using GTL

- Need for economic utilization of associated gas
- Desire to monetize significant reserves of non-associated and, particularly, stranded natural gas
  – 80% of the 5,000 TCF proven NG reserves are stranded
- Reduction in cost of transport of NG from producing to consuming regions (same principle as with LNG)
- Environmental concerns
  – The development of clean fuels regulations throughout the world (gasoline, diesel, fuel oils)
- (Aside: GTL can be combined with gasification—coal, bitumen, petroleum coke)

Brief GTL History

- 1922: Franz Fischer and Hans Tropsch used iron-based catalyst to convert an CO/H_2 mixture to mixture of HCs and oxygenated compounds
- 1925: used both iron and cobalt-based catalysts to synthesize HCs
- WW II: chemistry contributed ton Nazi Germany war effort
- 1950s-1990s: South Africa SASOL developed F-T commercially (in conjunction with coal gasification) to convert coal to HCs—total capacity 4,000,000 MT/year in three plants; two still in operation
- 1980s-present: Shell using F-T to convert NG to fuels and waxes in Bintulu, Malaysia—recently increased wax capacity to approx. 500,000 MT/year along with diesel, gasoline, etc.
- 1980-present: a number of entrants into the fields, a number of projects announced and planned (including demonstration projects), Qatar and Nigeria have started design and construction on world-scale GTL facilities

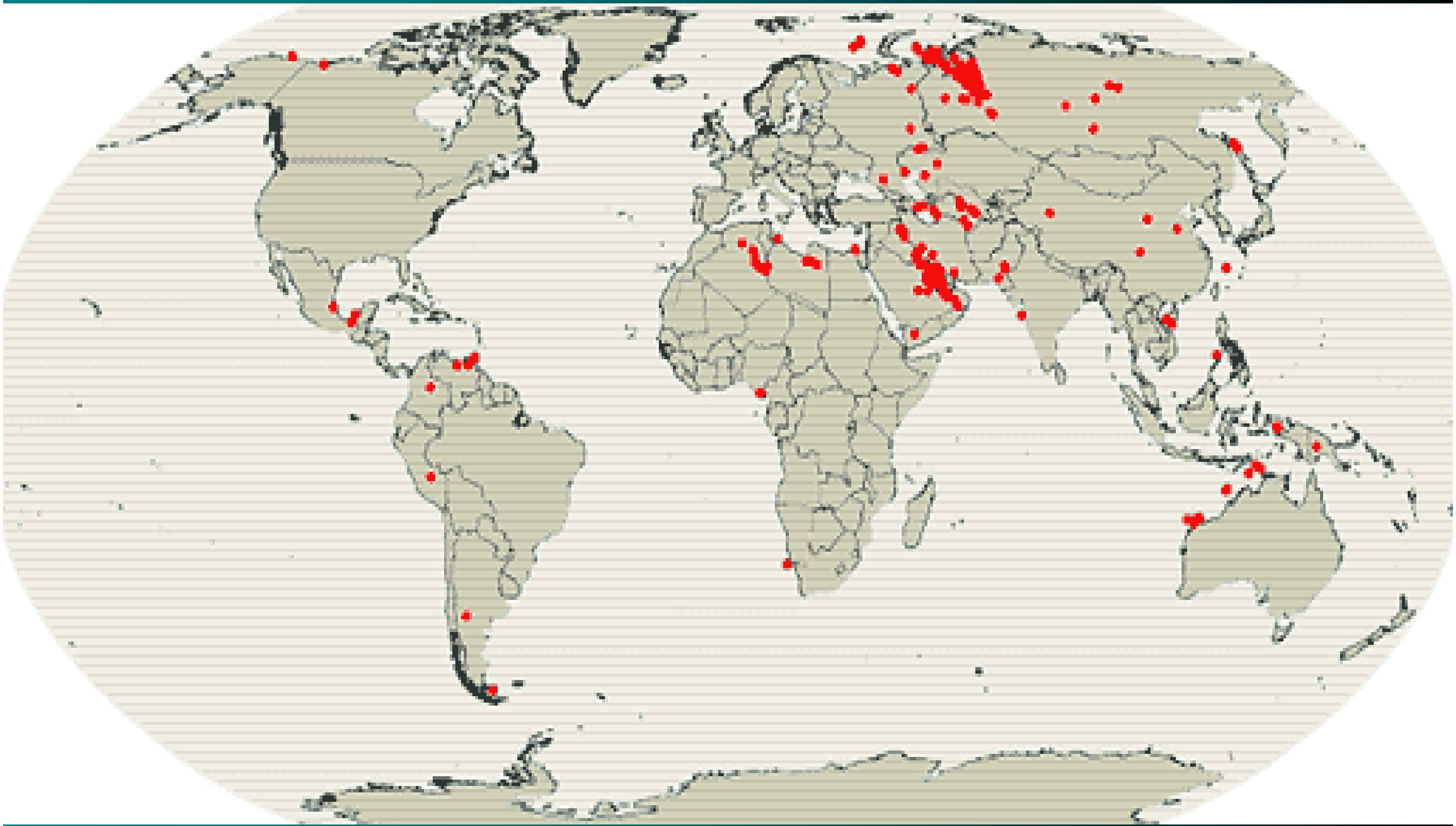
4.1 TCF Natural Gas Flared in 2000

Excluding FSU

Region	BCF Flared
Africa	1,640
Middle East	923
Central and South America	569
North America	524
Far East	296
Europe	148

After A. D. Little, Inc. Study (2000)

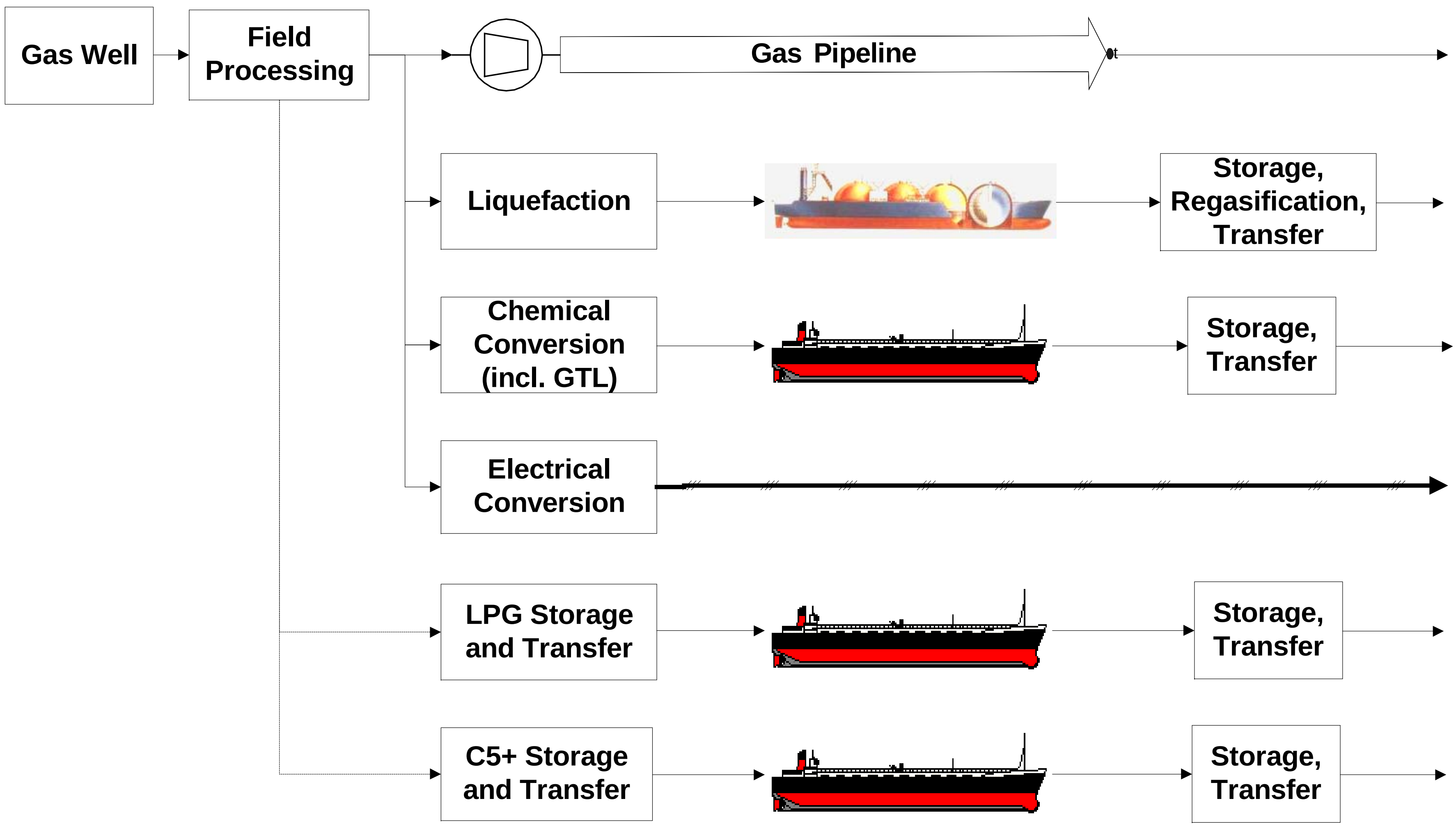
Stranded NG Fields in the World



From ConocoPhillips web-site

Natural Gas Transport Mechanisms

PRODUCTION/PROCESSING **TRANSPORTATION** **DISTRIBUTION**



After "Natural Gas Production, Processing, Transport" by Rojey et al.

Key US and EU Sulfur Specifications

DIESEL	US EPA		EU		World Wide Fuel Charter
Implementation Date	Current	2006	Current	2005	Category 4
Sulfur, wppm	500	15	350	50[(1)] [(2)]	10
Cetane Index	40	40	51 (#)	57 (#)	52/55 (#)

GASOLINE/PETROL	US EPA [(3)]		EU	
Implementation Date	2004	2006	Current	2005
Corporate Annual Average	120	30		
Per Batch Cap	300	80	150	50

(1) Down to 10 wppm ("sulfur-free") in 2004

(2) Many members have tax incentives to reduce sulfur to 10 wppm

(3) Sulfur specs are phased in over time with full implementation by 2008

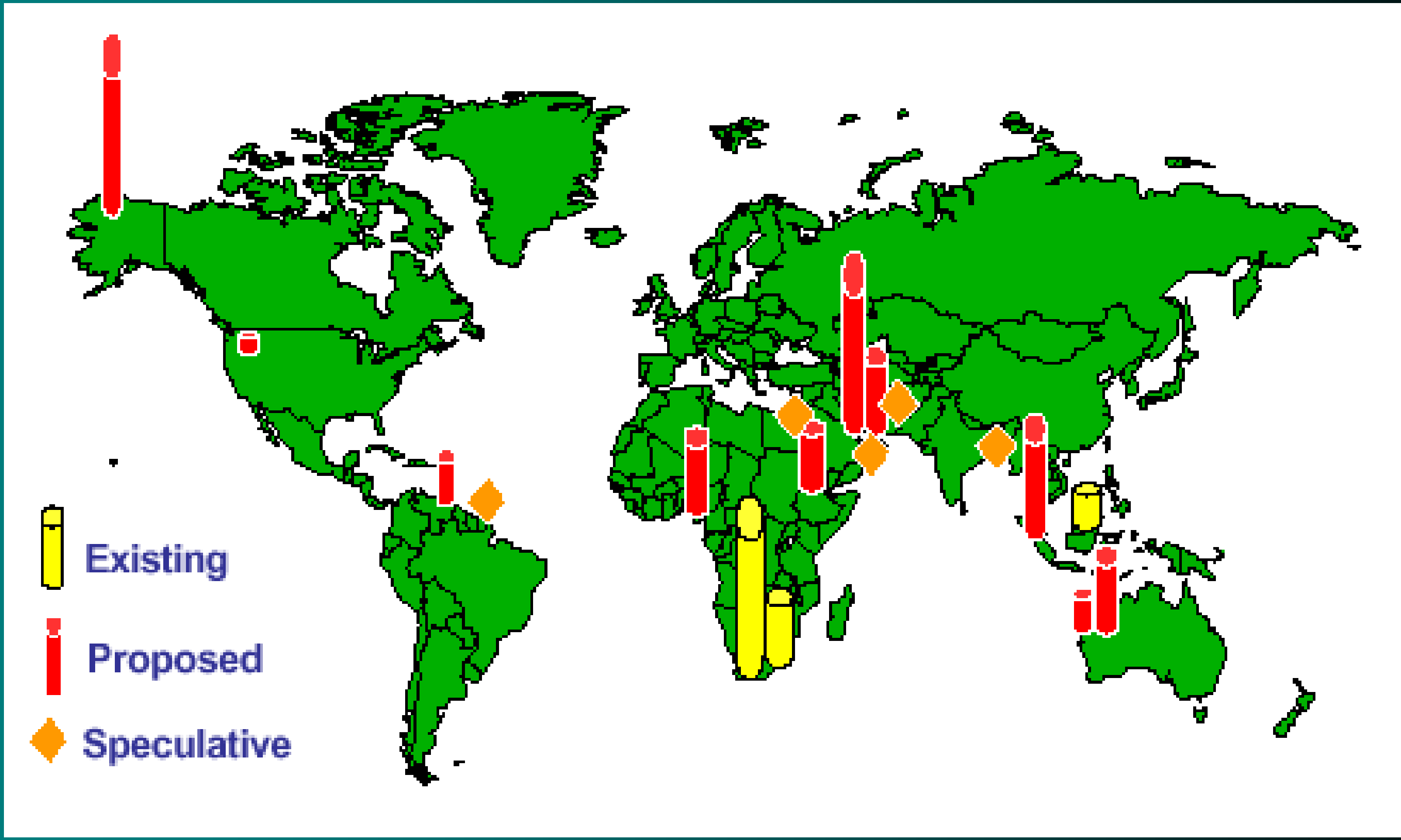
Diesel Sulfur Specifications in Select Countries

	Year	Sulfur, wppm
Australia	2006	50
Hong Kong	Under Consideration	50
India (Delhi)	Current	500
Japan	Current/2005	500/50
Mexico	Current	500
Republic of Korea	200 Max	130 Max (2002)

Gasoline Sulfur Content in Select APEC Countries

	2000 Sulfur, wppm	2005 Sulfur, wppm
Australia	150 Ave	
China	1000 Max	
Hong Kong	500 Max	150 Max
Indonesia	2000 Max	
Japan	100 Max	30-50 Max (?)
Malaysia	1500 Max	
Republic of Korea	200 Max	130 Max (2002)
Philippines	1000 Max (Unleaded)	
Singapore	130	
Taiwan	275 Max	
Thailand	900 Max	

GTL Projects—2001



From Gaffney, Cline & Associates study (May 2001)

Key Commercial GTL Plants

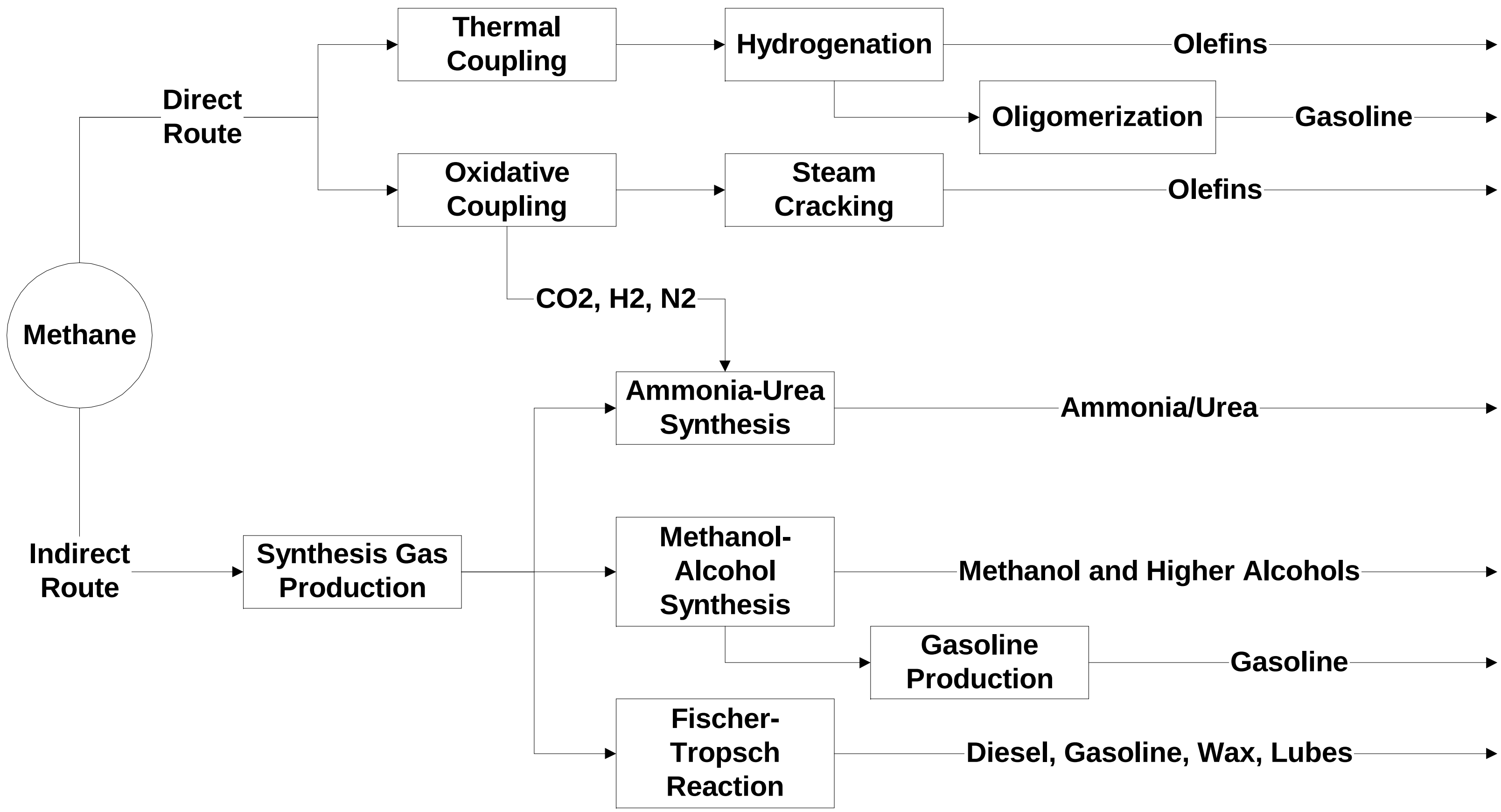
Company	Location	Size (BPD)	Comments
Sasol	South Africa	124,000	1955; Light olefins and gasoline
Mossgas	South Africa	22,500	1991; Gasoline and diesel
Shell	Malaysia	20,000 (12,500 pre-1997)	1993; Waxes, chemicals, diesel; recently revamped
Demonstration Plants			
BP	Alaska	300	Start-up 1Q2003
ConocoPhillips	Oklahoma	400	Start-up 1Q2003
In Engineering and Construction			
Sasol Chevron	Nigeria	34,000	2006 completion; FW; $1,200 MM
Sasol ConocoPhillips	Qatar ("Oryx GTL")	33,700	2006 completion; Technip-Coflexip; $850 MM

…A Number of Other GTL Plants are at Study or Planning Stage…

Location	Technology	Size (BPD)	Comments
Argentina	Shell		
Australia	Shell		
Australia	Syntroleum	11,500	Est. budget~$600 mil.
Bolivia		10,000	
Chile		10,000	
Egypt	Shell	75,000	Est. budget~$1,700 mil.
Iran		70,000+ 40,000	
Peru	Syntroleum	5,000	
Qatar	ExxonMobil	100,000	
South Africa	Statoil (?)	1,000	

Total of 45-55 with projected 1.3-2 MBD of liquid product

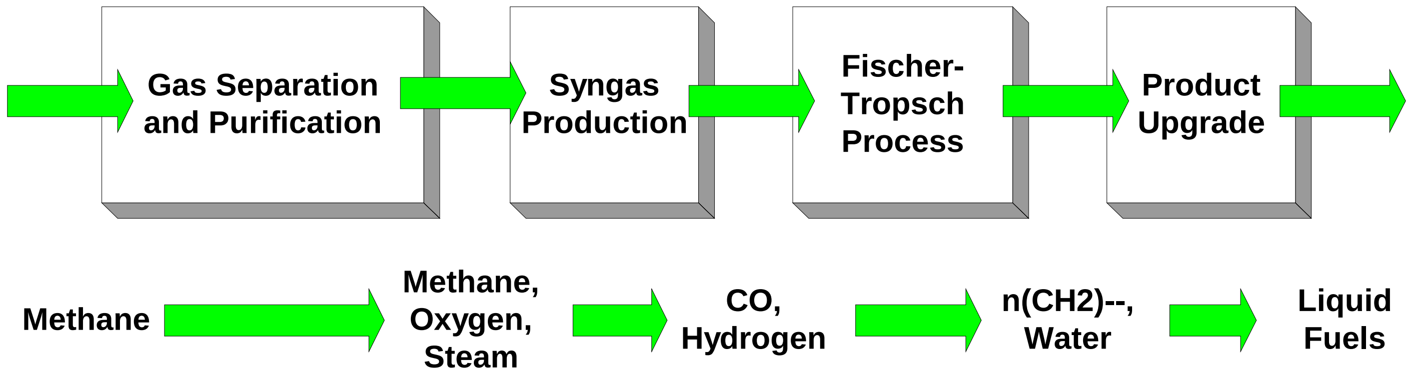
Conceptual Routes for the Chemical Conversion of Methane



After "Natural Gas Production, Processing, Transport" by Rojey et al.

- Problem: methane is stable
- Commercial routes: methanol, Fischer-Tropsch products

Key Steps in GTL Process



Includes air separation

GTL Chemistry

- Production of synthesis gas ("syngas") occurs using either partial oxidation or steam reforming
  - Partial oxidation: $CH_4 + 1/2\ O_2 \rightarrow CO + 2\ H_2$ (exothermic)
  - Steam reforming: $CH_4 + H_2O \leftrightarrows CO + 3\ H_2$ (endothermic)
  - Other possible reactions:
    - $CO + H_2O \leftrightarrows CO_2 + H_2$
    - $CH_4 + CO_2 \leftrightarrows 2\ CO + 2\ H_2$
- Fischer-Tropsch synthesis
  - $CO + 2H_2 \rightarrow$ —CH_2— $+ H_2O$ (very exothermic)

More on Partial Oxidation Synthesis Gas Production

- $CH_4 + 1/2\ O_2 \rightarrow CO + 2\ H_2$
- Combustion chamber at high temperature (1200-1500°C); no catalyst
- Some key vendors: Texaco, Shell
- Main competing reaction: decomposition of methane to carbon black (due to high temperature, non-catalytic nature of the chemistry)
- Three process sections:
  - Burner section where combustion occurs (with oxygen to avoid presence of nitrogen—nitrogen is desirable only when making ammonia)
  - Heat recovery section
  - Carbon black removal section: first by water scrubbing, then extraction by naphtha from the sludge

More on Steam Reforming Synthesis Gas Production

- $CH_4 + H_2O \leftrightarrows CO + 3\ H_2$
- Carried out in the presence of catalyst—usually nickel dispersed on alumina support
- Operating conditions: 850-940°C, 3 MPa
- Tubular, packed reactors with heat recovery from flue gases using feed preheating or steam production in waste heat boilers
- New process combines steam reforming with partial oxidation—uses the heat produced from partial oxidation to provide heat for steam reforming; resulting combination is autothermic
  - Developed by Société Belge de l'Azote and Haldor Topsøe (ATR process)
  - Gases from partial oxidation burner are mixed with steam and sent to the steam reformer

More on Fischer-Tropsch

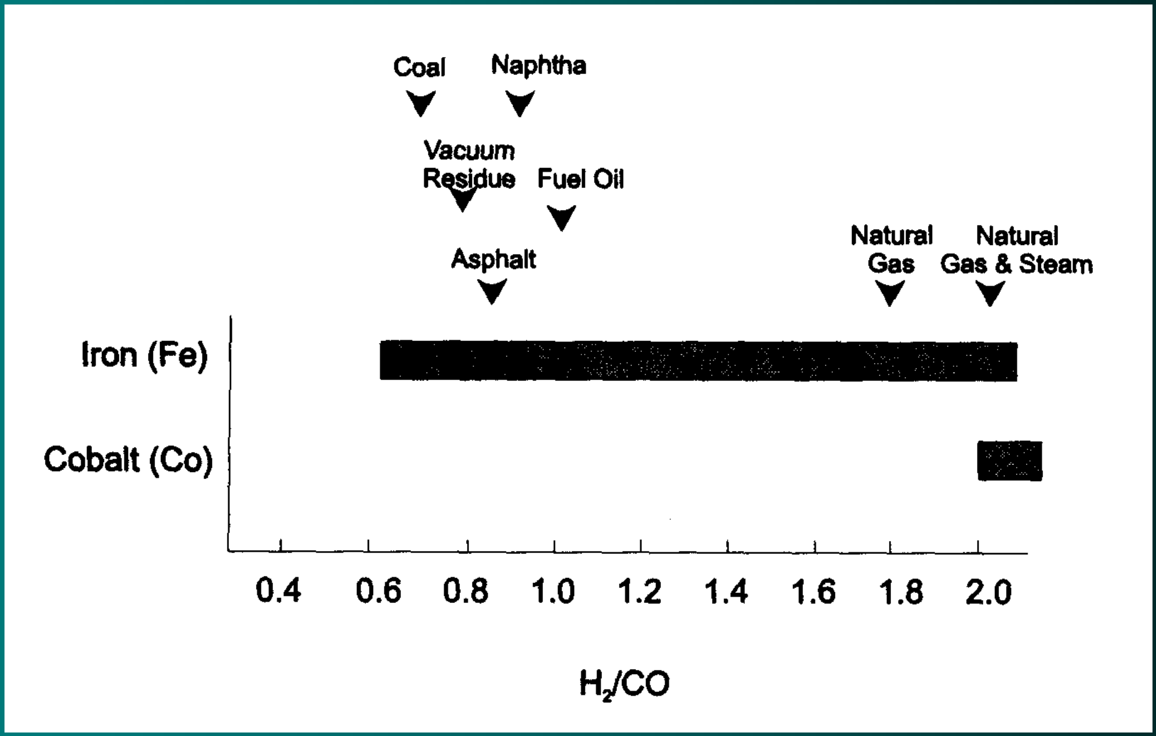
- $CO + 2H_2 \rightarrow$ —CH_2— $+ H_2O$ (very exothermic)
- Competes with methanation (reverse of steam reforming) which is even more exothermic:

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

- To promote F-T over methanation, reaction is run at low temperatures: 220-350°C; pressure: 2-3 MPa
- Catalysts
- Operating conditions and chain growth
- Reactor types

Iron v. Cobalt-Based F-T Catalysts

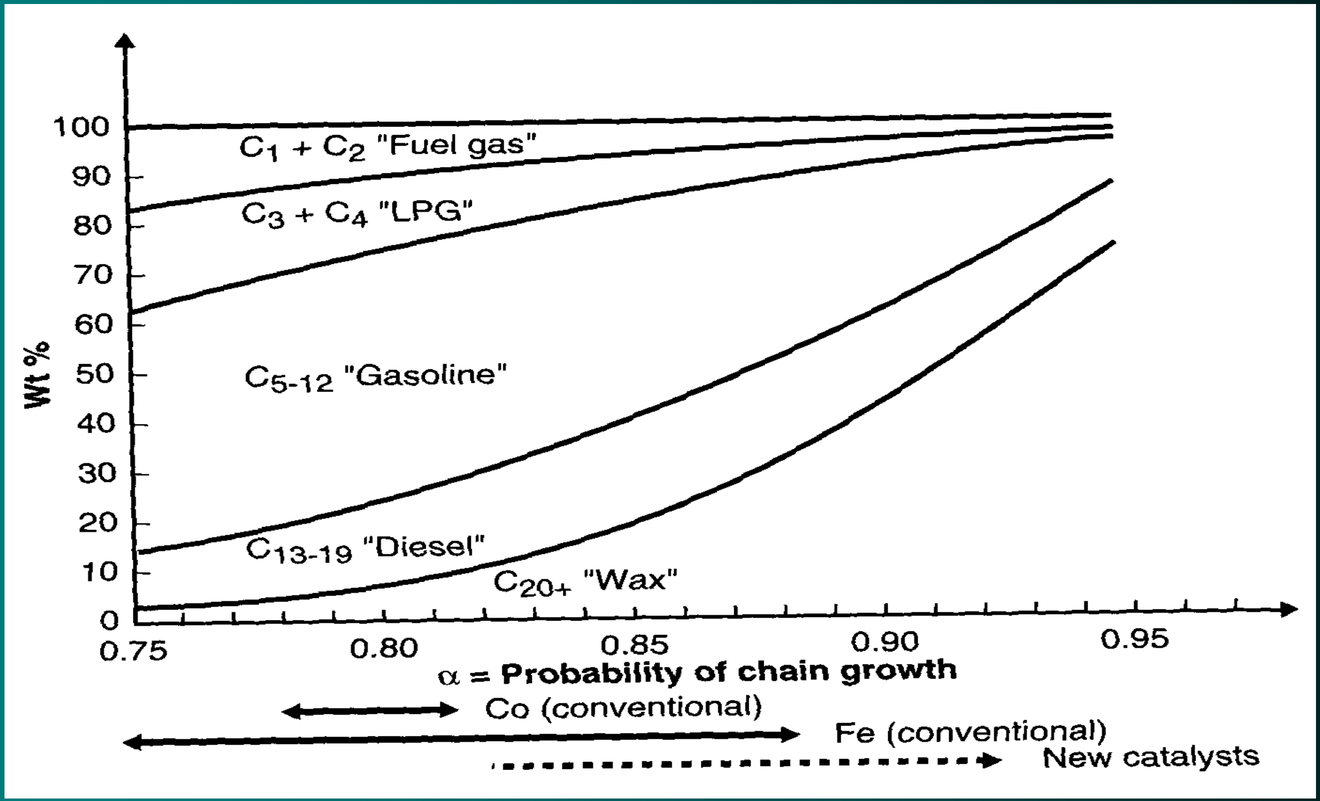
- Key catalyst types: iron or cobalt-based (though cobalt-based is becoming more common in new applications)
- Cobalt is poisoned by sulfur—syngas is desulfurized to about 0.1 ppmv S
- Issue of stoichiometric ratios of H_2 and CO



From Van der Laan (1999)

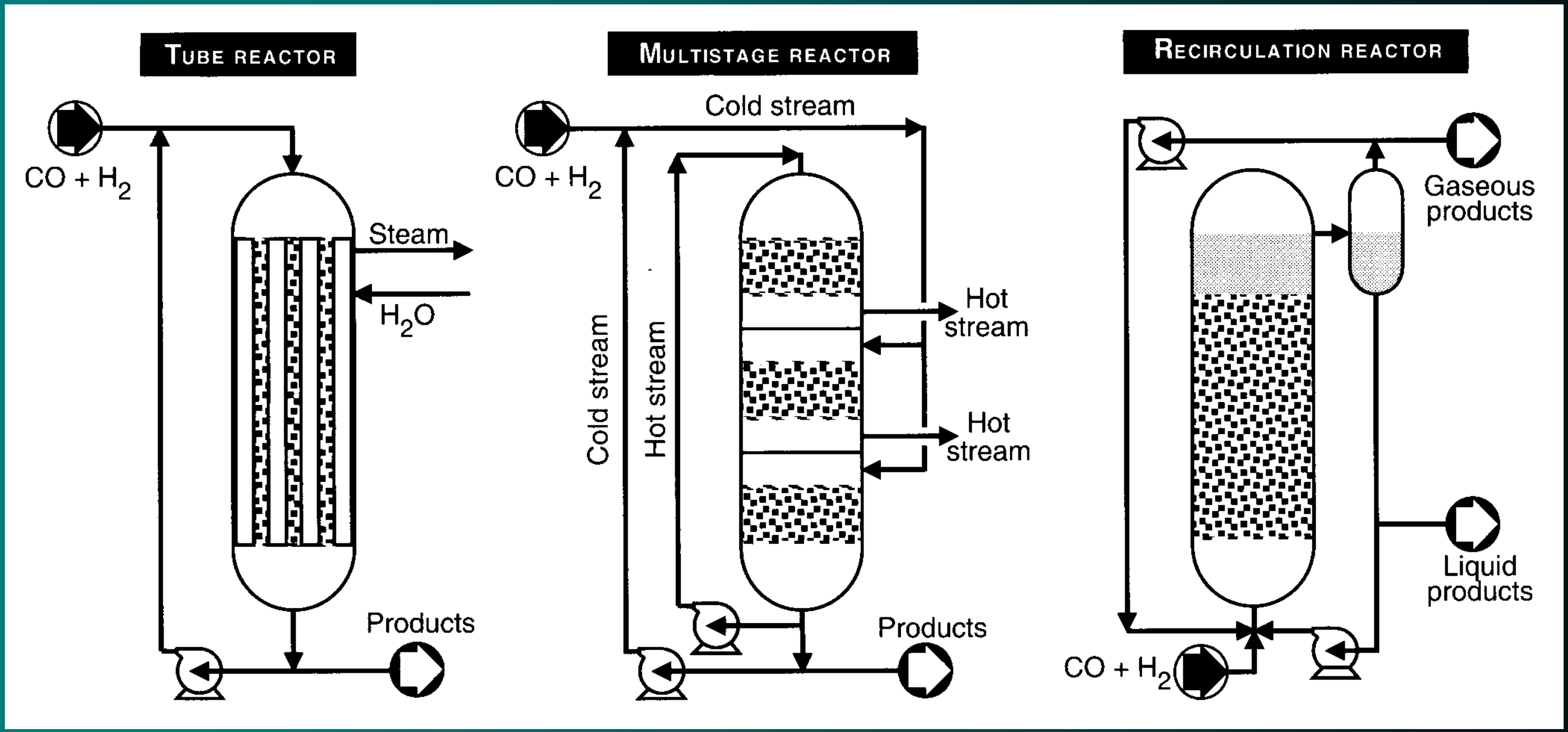
MW Distribution in Raw FT products

Degree of chain growth (MW distribution of products) is affected by operating condition, reactor design, catalyst selectivity, and contaminants such as sulfur and oxygenated compounds



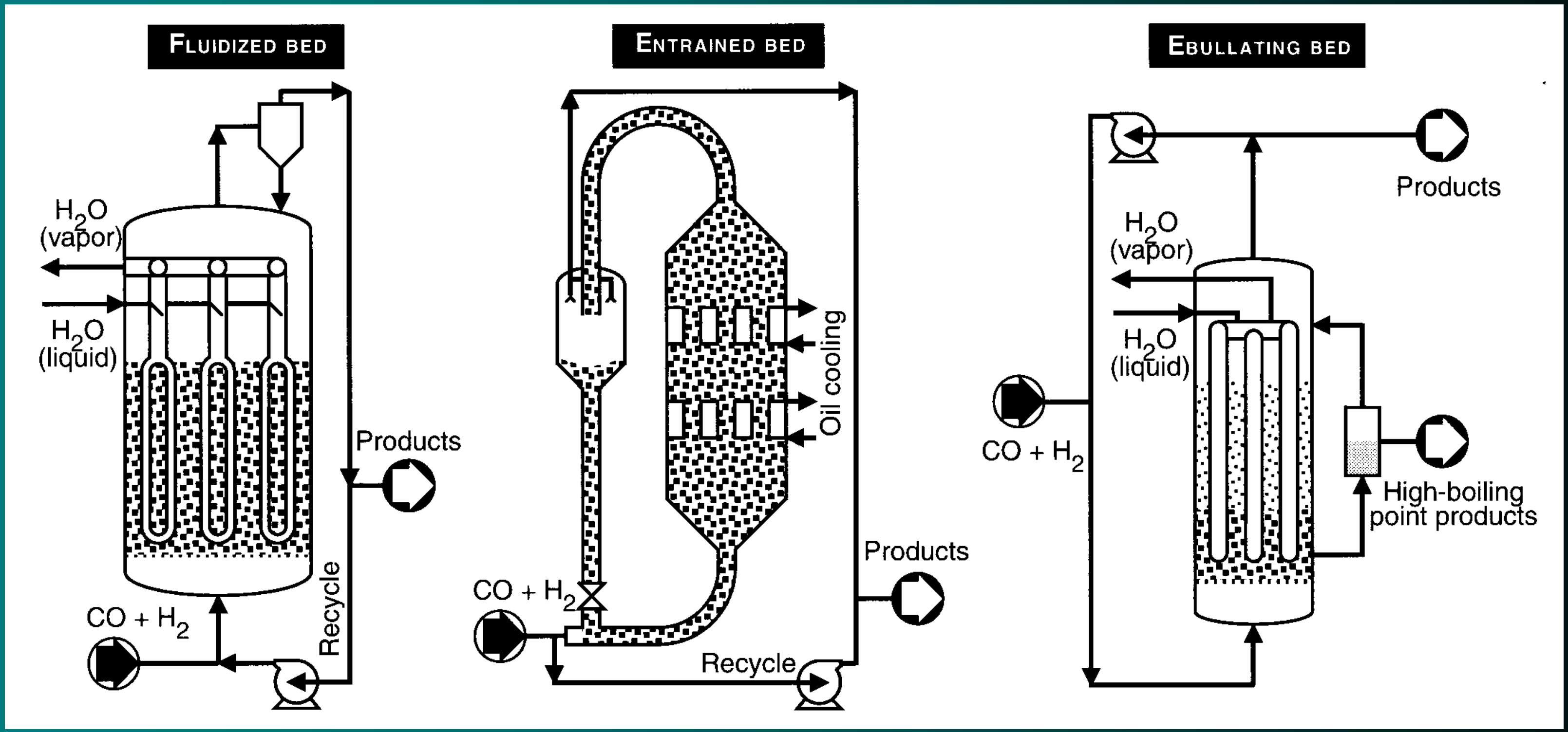
From “Natural Gas Production, Processing, Transport” by Rojey et al.

Fixed-Bed FT Reactors



From "Natural Gas Production, Processing, Transport" by Rojey et al.

Moving-Bed FT Reactors



From “Natural Gas Production, Processing, Transport” by Rojey et al.

Comments on GTL Products

- All white oil or high value lube/wax products
- No bottom of barrel
- GTL Diesel likely to be used as blendstock and not separate fuel
  - EP590 spec. issues
  - Separate distribution chain cost prohibitive
- Small markets for lube and oil (e.g., total global wax market ~ 70 MBD)
- Overall emissions per barrel upon consumption similar to crude oil
- Example: 1021 lb/CO_2 v. 1041
- GTL-FT emissions shifted to plant site (v. city)

(Typical Products)	**Refined Brent (vol%)**	**GTL-FT (vol%)**
LPG	3	
Naphtha + Gasoline	37	15-25
Distillates	40	50-80
Fuel Oils	40	
Lubes + Wax		0-30

After BP study (Euroforum, Feb. 2003)

Some Key GTL Technologies

- Nearly all have three key steps: syngas production, F-T hydrocarbon synthesis, waxy intermediate upgrading to lighter (D, G) products
- Differences relate to reactor design and catalyst technology
- <u>Sasol Chevron:</u>
  - South Africa plants have used Lurgi coal gasifiers to produce syngas and multitubular fixed-bed (3 MBD) and fluidized-bed reactors (110 MBD circulating, 11 MBD non-circulating) for the F-T step
  - Jointly have access to the Texaco gasifier
  - Developed slurry-phase distillate process (SSPD) with cobalt catalyst in 1990s
  - Combined with Chevron product upgrading technology and partial oxidation syngas
  - F-T designs tested and commercially available include circulating fluid bed (Synthol), multitubular fixed-bed with internal cooling (Arge), non-circulating fluid bed reactores (SAS), as well as SSPD
  - Have contracts for Nigeria and Qatar (Sasol ConocoPhillips)

Some Key GTL Technologies (2)

- Shell:
  - Partial oxidation based syngas manufacture
  - Multi-tubular fixed trickle bed reactors (SMDS)
  - Recently expanded Bintulu after S/D due to air separation explosion (1997)
  - Possibilities: Argentina, Australia, Egypt
- ExxonMobil:
  - AGC 21 includes fluidized syngas production (catalytic partial oxidation) coupled with slurry-phase bubble-column F-T and hydro-isomerization of waxy product
  - Primarily cobalt and ruthenium-based catalysts
  - 200 BPD GTL pilot plant operated in Baton Rouge since 1996
  - Possibility: 100,000 MBD in Qatar

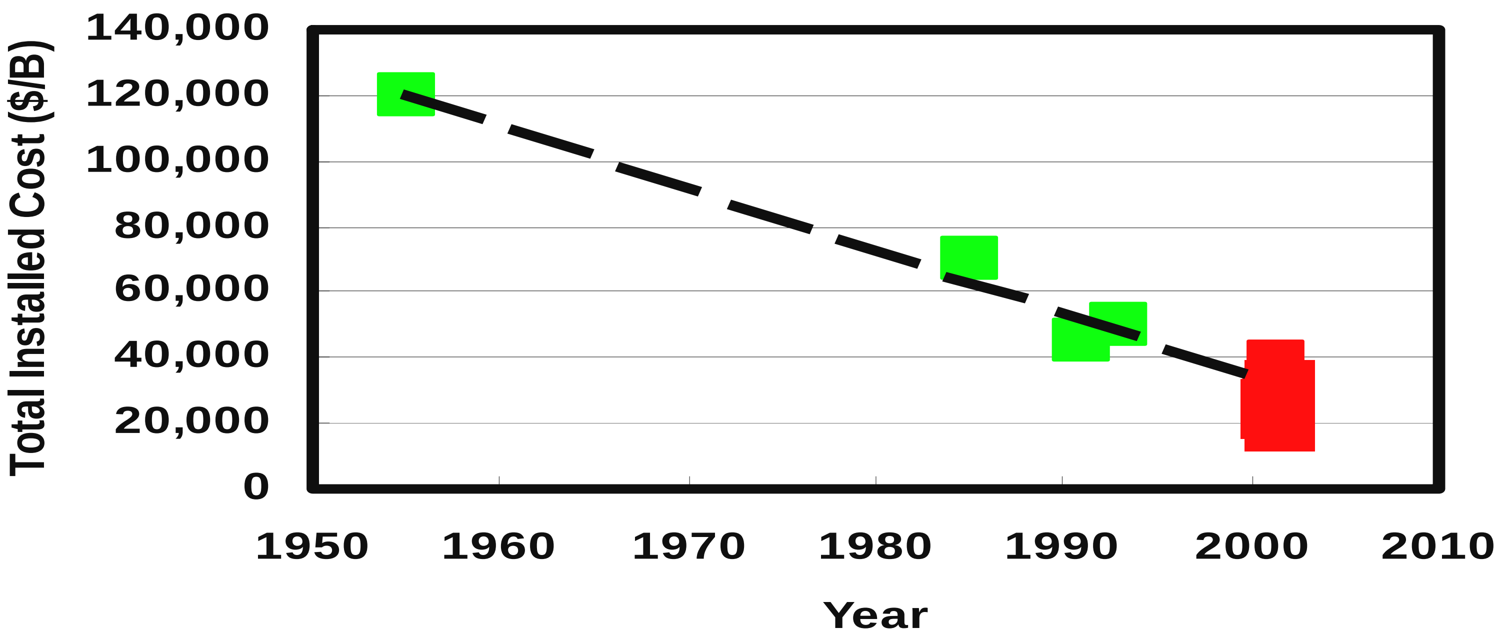
Some Key GTL Technologies (3)

- ConocoPhillips:
  - Catalytic partial oxidation syngas production process
  - Proprietary F-T catalyst and “high efficiency” reactor design
  - Ponco City, OK demonstration plant in start up (1Q2003)
  - Have Qatar joint contract with Sasol
- BP:
  - Compact steam reformer (1/40th conventional in size)
  - Fixed bed F-T with more efficient catalyst
  - Wax hydrocracking
  - Alaska demonstration plant in start up (1Q2003)
  - Eye towards ANS natural gas conversion and transportation through TAPS

Some Key GTL Technologies (4)

- Syntroleum:
  - Small OK-based technology firm; offers for licensing
  - Uses nitrogen in air to remove heat from syngas production (called ATR: autothermal reformer) → does not need air separation unit
  - Reduced capital cost
  - Fixed-bed or fluid-bed F-T (using cobalt-based catalyst) followed by hydrocracking
- Rentech:
  - Small Colorado company; offers for licensing
  - Formerly had strong working agreement with Texaco (with access to the Texaco gasifier)
  - Combined partial oxidation and SMR for internal heat balance
  - Iron-based catalyst and slurry phase process
  - Iron-based catalyst is less active than cobalt-based, but is more versatile and can process syngas from SMR, solid gasifiers (coal), or liquid gasifiers (refinery resids)
  - Sasol also offers iron-based F-T

GTL-FT CAPEX Reduction Due to Improved Technology



- Capacity differences
- Lube and wax manufacture v. no lube/wax
- Financing structure
- Short-term v long-term (increased capacity) case
- Technology differences

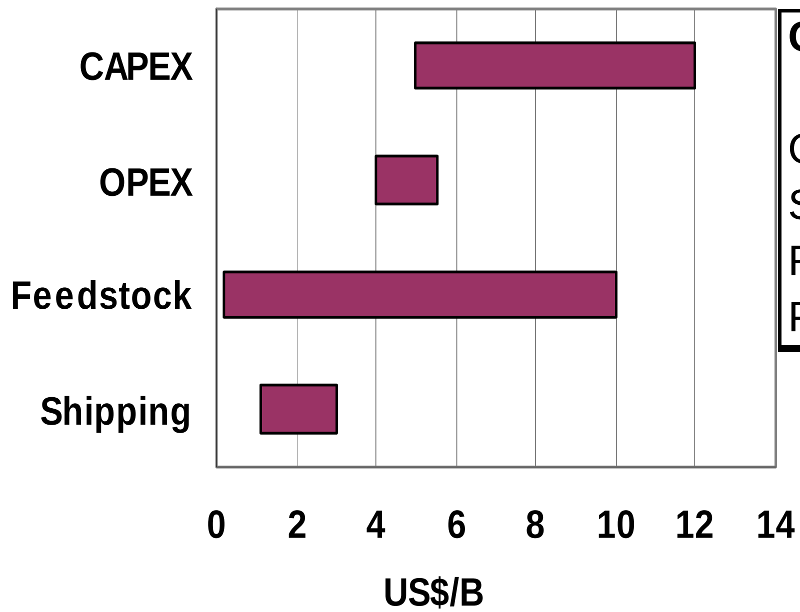
Economic Analysis of Some Key Proposed GTL Cases

	Exxon Mobil	Shell	Sasol	Syntroleum	Rentech
Short-Term Case					
Liq. Yld (BPD)			15,300	12,000	16,450
TIC ($MM)			395	455	468
TIC ($/B)	29,000	30,000	25,800	37,920	28,450
IRR (%)	12.9	12.5	14.5	11.2	13.9

Long-Term Case	No Lube	Lube	No Lube	Lube	No Lube	Lube	No Lube	Lube	No Lube	Lube
Liq. Yld. (BPD)					50,900		40,000		54,900	
TIC ($MM)					1,039	1,095	1,258	1,302	1,268	1,324
TIC ($/B)	24,000	25,000	26,000	27,000	20,410	21,510	31,450	32,550	23,100	24,120
IRR (%)	14.3	18.2	13.2	16.9	16.7	21.3	10.7	15	15.4	19.4

After Oil & Gas Journal (March 2001)

Typical GTL Product Cost and CAPEX Breakdowns



CAPEX Breakdown (Typical)	
Oxygen plant and gas purification	35%
Synthesis gas production	25%
Fischer-Tropsch reaction	30%
Product upgrade	10%

After Gafney, Cline & Assoc. (2001/2003)

Note: feedstock price range due to local (stranded or near

GTL v. LNG Economics—1BCFD

	GTL-FT	LNG
Product Capacity	~110,000 BPD	~7 MMTPA
CAPEX (Full Chain)	$2.2 B (mostly in producing location)	$2.4 B ($1.2 Plant) ($0.8 Ships) (0.4 Regasification)
Product Value	$24-27/B $4.40-4.90/MMBtu	$16-19/B $2.75-3.10/MMBtu
Energy Efficiency	60%	85%
Carbon Efficiency	77%	85%

After BP study (Euroforum, Feb. 2003)

Some Commercial Issues

- Market size:
  - GTL feeds directly into transportation fuels with a very large market
  - LNG has certain demand constraints due to relatively small market
- In December 2000, US classified GTL product as “alternative fuels” under the EPACT 1992→tax implications
  - EU is considering
- Manufacture of clean fuels (low sulfur) in refineries is another key competition for GTL
  - Many US, EU, and other refineries are in the process of installing, enlarging, or otherwise improving hydrotreating and hydrocracking capabilities
  - Significant new technological improvements are making refinery clean fuel conversion quite cost effective

A Word on Synergies

- Much analysis and R&D/developmental effort in improving GTL economics by taking advantage of synergies
  - Petroleum coke, coal, oremulsion (bitumen in water, similar to #6) gasification
  - Hydrogen recovery
  - Power generation (combined cycle)
  - Integration with methanol and olefin production
- All suggest that, under some circumstances (geography, feedstock availability and pricing, markets, *etc*.) returns improve
- Nearly all cases require higher capital
- Coke, coal, bitumen, refinery bottoms require the more flexible iron-based F-T catalyst (Sasol, Rentech)

About the Speaker

Iraj Isaac Rahmim is a specialist in petroleum technology and economics. He holds B.Sc. and M.Sc. degrees from the University of California and a Ph.D. from Columbia University, all in chemical engineering.

Currently the president of E-MetaVenture, Inc., he was previously employed with Mobil and Coastal corporations. His early career in Mobil Corporation involved responsibilities for the development and commercialization of a variety of process technologies ranging from clean fuels and light gas upgrading to FCC and resid processing. Later with Coastal Corporation, he was responsible for identifying, assessing, and championing novel business and technology opportunities and solutions for integration into the company's petroleum and petrochemical assets. Recent key activities include bitumen recovery and processing technologies, gas-to-liquids technology and markets, Tier II refinery modifications, and training and litigation support. A recent study on medium to long-term gasoline storage contributed to the California Attorney General's report on gasoline pricing.

Dr. Rahmim is the president of the Houston, Texas, Chapter of International Association for Energy Economics, a long-standing member of the American Institute of Chemical Engineers, an associate member of the State Bar of Texas (Oil, Gas, and Energy Resources Law Section). He holds a number of patents in refining technologies, has authored papers in a variety of technical areas, and has presented in and chaired sessions at national and international conferences.

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