UNIONE EUROPEA
FONDI STRUTTURALI EUROPEI
PON 2014-2020
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Dipartimento per la Programmazione
Direzione Generale per interventi in materia di edilizia scolastica, per la gestione dei fondi strutturali per l'istruzione e per l'innovazione digitale
Ufficio IV
PER LA SCUOLA - COMPETENZE E AMBIENTI PER L'APPRENDIMENTO (FSE-FESR)

POLITECNICO DI MILANO

POLITECNICO
MILANO 1863

How century-old catalytic chemistry can alleviate today's problems: food, energy, pollution, mobility

Laboratory of Catalysis and Catalytic Processes LCCP

Enrico Tronconi

Istituto "Alessandro Greppi"
Monticello Brianza (LC)
April 20th, 2018

Staff @ LCCP

Permanent staff

Pio Forzatti (full professor)

Enrico Tronconi (full professor)

Luca Lietti (full professor)

Gianpiero Groppi (full professor)

Alessandra Beretta (full professor)

Isabella Nova (associate professor)

Lidia Castoldi (associate professor)

Matteo Maestri (associate professor)

Carlo Giorgio Visconti (associate professor)

Alessandro Donazzi (associate professor)

Roberto Matarrese (assistant professor)

PhD Students

Mauro Bracconi

Leonardo Falbo

Morteza Rahmanipour

Alessandro Porta

Matteo Ambrosetti

Federica Gramigni

Umberto Ghelli

Camila Monroy

Andrea Ravanelli

Matteo Molteni

Simone Guffanti

Roberta Villamaina

Post-Doc Researchers

Nicola Usberti

Felice Shaojun

Tommaso Selleri

Laura Fratalocchi

Riccardo Balzarotti

Pedram Aghaei

Senior Scientist

Natale Ferlazzo

Temporary researchers

~50 undergrads-masters/year

Technicians

Roberto Losi

Enrico Aliprandi

Enrica Ceresoli

Visiting scientists from abroad

5-10 people/year

Chemical Engineering and Catalysis

- ✓ **Catalysis** - the process by which the rate and products of chemical reactions are altered by substances unchanged by the reaction – it is at the core of the chemical and petroleum industries.

- ✓ Catalysis-based processes represent more than 90% of current chemical processes and generate 60% of today's chemical products.

- ✓ In addition to traditional roles in the chemical and petroleum industries, catalysts are of growing importance in fields ranging from **environmental protection** and **energy** to pharmaceuticals and the processing of high performance materials.

Catalysis: industrial relevance

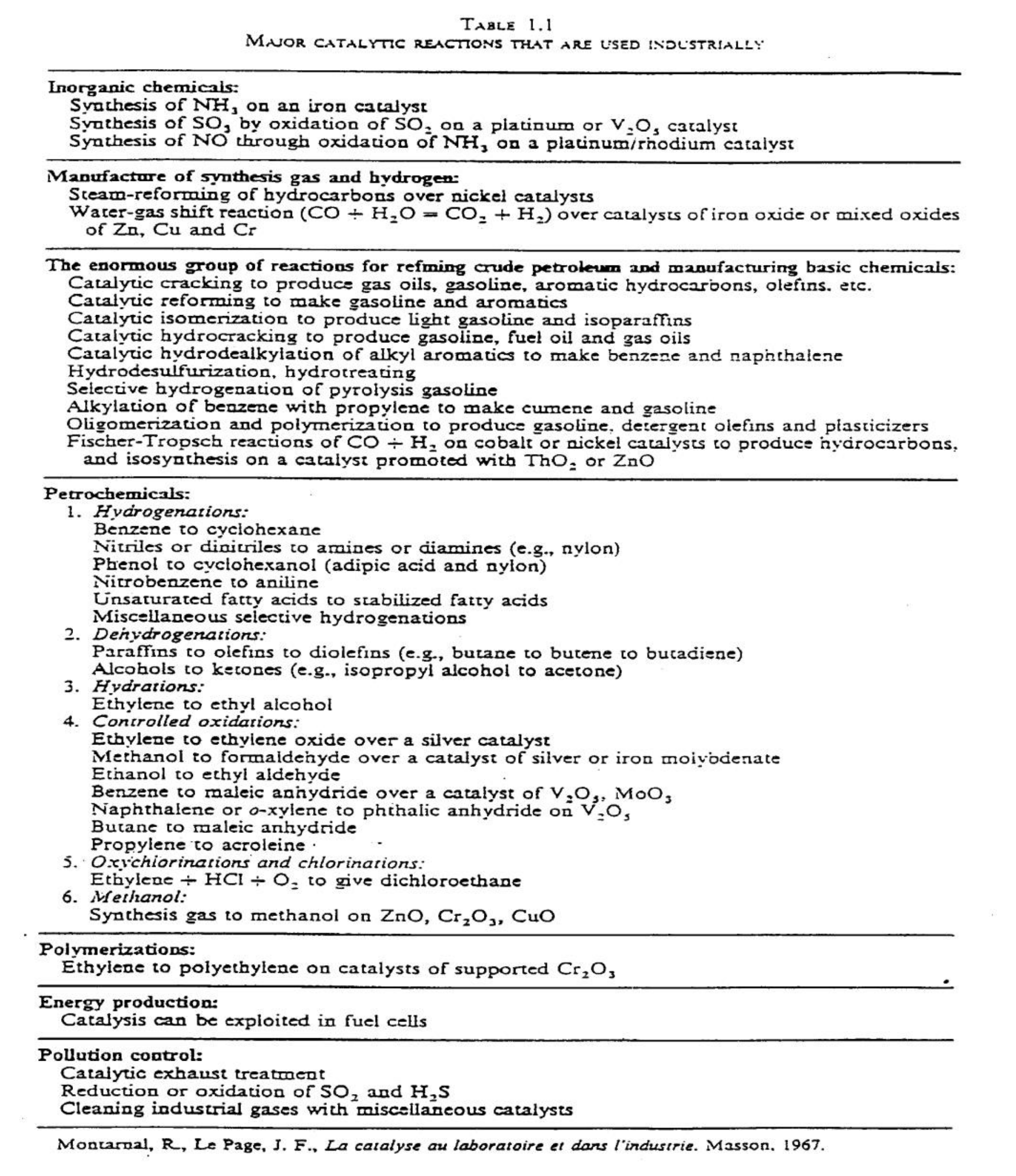


TABLE 1.1

MAJOR CATALYTIC REACTIONS THAT ARE USED INDUSTRIALLY

Inorganic chemicals:
- Synthesis of NH_3 on an iron catalyst
- Synthesis of SO_3 by oxidation of SO_2 on a platinum or V_2O_5 catalyst
- Synthesis of NO through oxidation of NH_3 on a platinum/rhodium catalyst

Manufacture of synthesis gas and hydrogen:
- Steam-reforming of hydrocarbons over nickel catalysts
- Water-gas shift reaction ($CO + H_2O = CO_2 + H_2$) over catalysts of iron oxide or mixed oxides of Zn, Cu and Cr

The enormous group of reactions for refining crude petroleum and manufacturing basic chemicals:
- Catalytic cracking to produce gas oils, gasoline, aromatic hydrocarbons, olefins, etc.
- Catalytic reforming to make gasoline and aromatics
- Catalytic isomerization to produce light gasoline and isoparaffins
- Catalytic hydrocracking to produce gasoline, fuel oil and gas oils
- Catalytic hydrodealkylation of alkyl aromatics to make benzene and naphthalene
- Hydrodesulfurization, hydrotreating
- Selective hydrogenation of pyrolysis gasoline
- Alkylation of benzene with propylene to make cumene and gasoline
- Oligomerization and polymerization to produce gasoline, detergent olefins and plasticizers
- Fischer-Tropsch reactions of $CO + H_2$ on cobalt or nickel catalysts to produce hydrocarbons, and isosynthesis on a catalyst promoted with ThO_2 or ZnO

Petrochemicals:
1. *Hydrogenations:*
   - Benzene to cyclohexane
   - Nitriles or dinitriles to amines or diamines (e.g., nylon)
   - Phenol to cyclohexanol (adipic acid and nylon)
   - Nitrobenzene to aniline
   - Unsaturated fatty acids to stabilized fatty acids
   - Miscellaneous selective hydrogenations
2. *Dehydrogenations:*
   - Paraffins to olefins to diolefins (e.g., butane to butene to butadiene)
   - Alcohols to ketones (e.g., isopropyl alcohol to acetone)
3. *Hydrations:*
   - Ethylene to ethyl alcohol
4. *Controlled oxidations:*
   - Ethylene to ethylene oxide over a silver catalyst
   - Methanol to formaldehyde over a catalyst of silver or iron molybdenate
   - Ethanol to ethyl aldehyde
   - Benzene to maleic anhydride over a catalyst of V_2O_5, MoO_3
   - Naphthalene or *o*-xylene to phthalic anhydride on V_2O_5
   - Butane to maleic anhydride
   - Propylene to acroleine
5. *Oxychlorinations and chlorinations:*
   - Ethylene + HCl + O_2 to give dichloroethane
6. *Methanol:*
   - Synthesis gas to methanol on ZnO, Cr_2O_3, CuO

Polymerizations:
- Ethylene to polyethylene on catalysts of supported Cr_2O_3

Energy production:
- Catalysis can be exploited in fuel cells

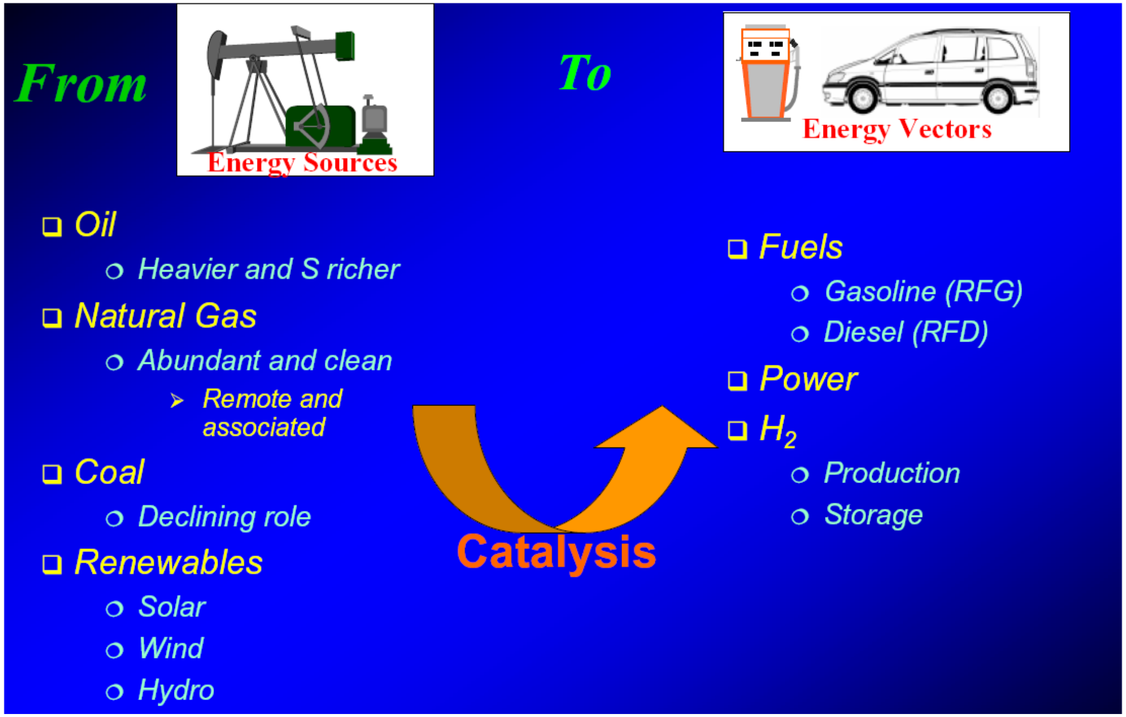
Pollution control:
- Catalytic exhaust treatment
- Reduction or oxidation of SO_2 and H_2S
- Cleaning industrial gases with miscellaneous catalysts

Montarnal, R., Le Page, J. F., *La catalyse au laboratoire et dans l'industrie*. Masson, 1967.

The key role of Catalysis in the energy challenge

“The urgent need for fuels in an era of declining resources and of pressing environmental concerns demands a resurgence in catalysis science (*and engineering*)»

Report from the U.S. DOE Basic Energy Sciences Workshop, Aug. 2007



From

Energy Sources

- Oil
  - Heavier and S richer
- Natural Gas
  - Abundant and clean
    - Remote and associated
- Coal
  - Declining role
- Renewables
  - Solar
  - Wind
  - Hydro

Catalysis

To

Energy Vectors

- Fuels
  - Gasoline (RFG)
  - Diesel (RFD)
- Power
- H_2
  - Production
  - Storage

Catalysis is key to:

- conversion processes
- clean-up processes

Laboratory of Catalysis and Catalytic Processes

- ✓ The Laboratory of Catalysis and Catalytic Processes (LCCP) is a research group at Politecnico di Milano that has pioneered multidisciplinary research in the science and engineering of catalysis.

- ✓ The mission of the LCCP is the education of students via relevant research in the multidisciplinary field of catalysis science, spanning from fundamental research to technical applications, with a strong connection to the industrial world

Laboratory
of Catalysis and
Catalytic Processes
LCCP

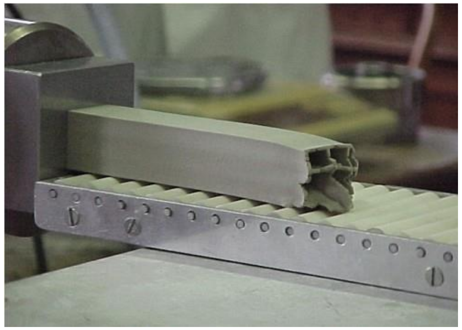
LCCP Laboratories

New LCCP laboratories at Campus Bovisa (B18): July 2014

- ✓ 2000 m^2
- ✓ Laboratories for catalyst preparation and characterization, for catalytic testing under atmosphere and high-pressure

Facilities @ LCCP

Equipment for catalyst preparation

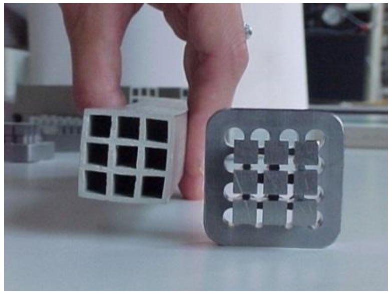


Powdered catalysts:

Dry impregnation, Wet impregnation, Co-precipitation

Coated items:

Ball-milling, Ultracentrifugation Unit, deep coating, spraying, Rheometer



Bulk monoliths:

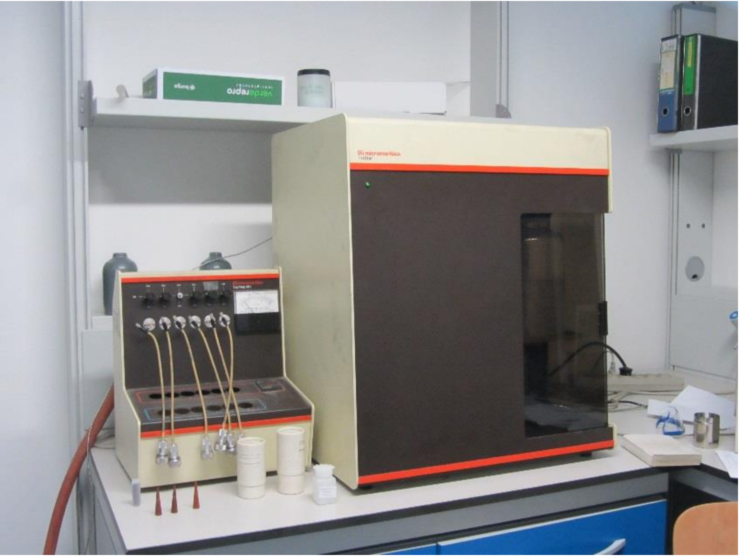
Mixer, Kneader, Screw-Extruder,

Standard techniques:

Climatic Chamber, Filtering Equipments, pH-meters, Drying and Calcination Ovens

Facilities @ LCCP

Equipment for catalyst characterisation (morphological, structural, bulk and surface physico-chemical)
GC-MS, TPD/R/O, FTIR, UV-Vis, XRD, DTA-TG, SEM available inside the group/ Department

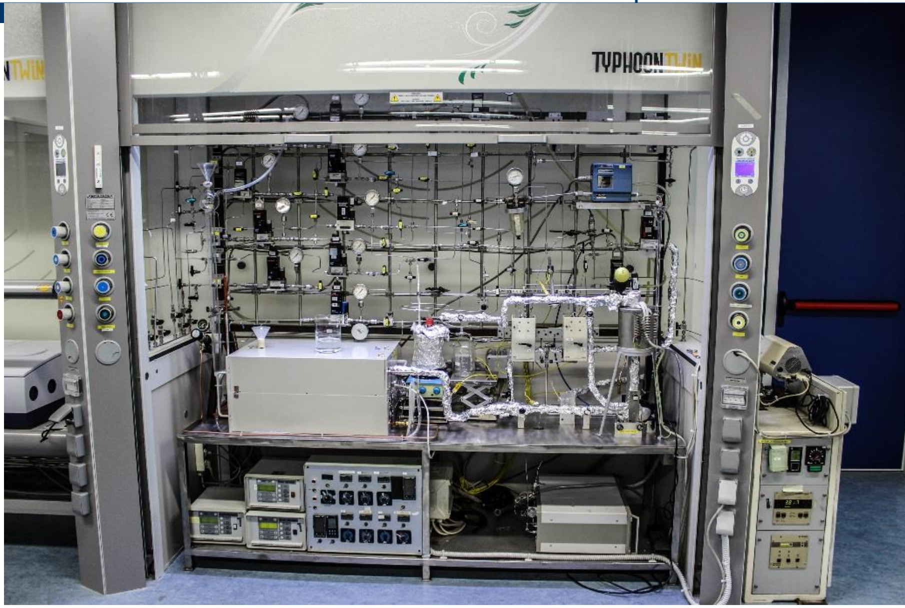


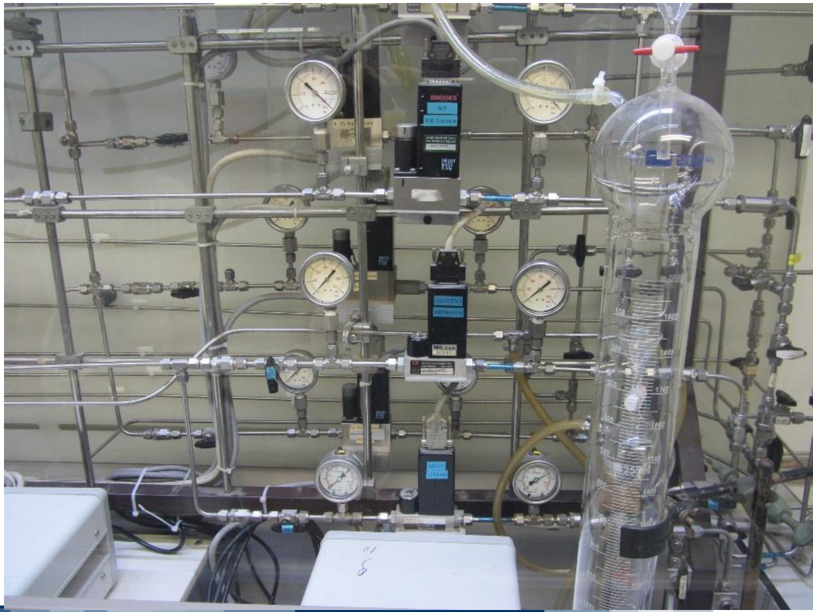
In situ FTIR, probe and labelled molecule spectroscopies, HRTEM, XPS through collaboration with research groups with specific expertise outside our University

Facilities @ LCCP

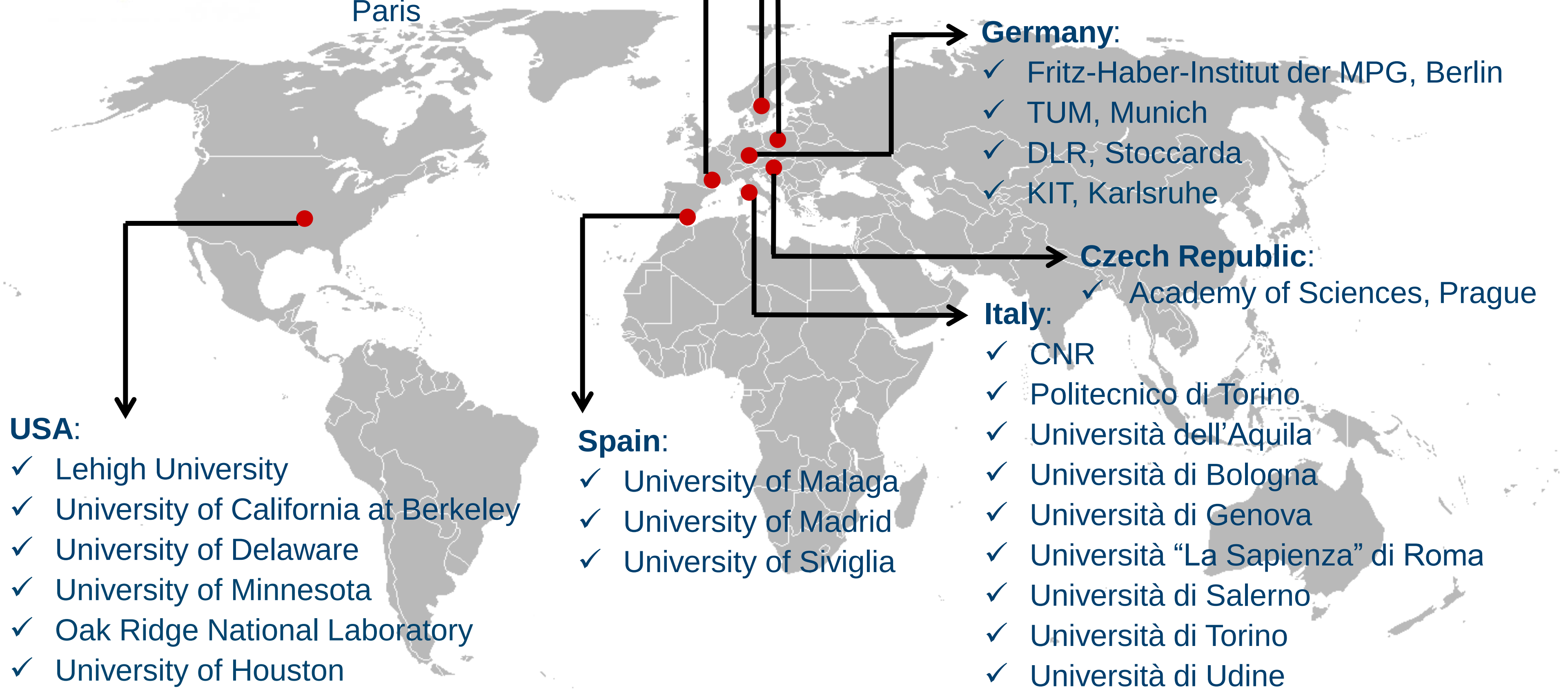
22 rigs for catalyst testing
(powder and structured catalysts,
steady state and transient conditions,
also operated under pressure)

Computational facilities
(computing time at supercomputer centers,
software for modelling and simulation)





Academic collaborations



France:
- ✓ University of Caen
- ✓ UPMC (Universitè Pierre et Marie Curie) Paris

Sweden:
- ✓ Chalmers University of Technology
- ✓ KTH Royal Institute of Technology

Poland:
- ✓ AGH-University of Science and Technology Kraków

Germany:
- ✓ Fritz-Haber-Institut der MPG, Berlin
- ✓ TUM, Munich
- ✓ DLR, Stoccarda
- ✓ KIT, Karlsruhe

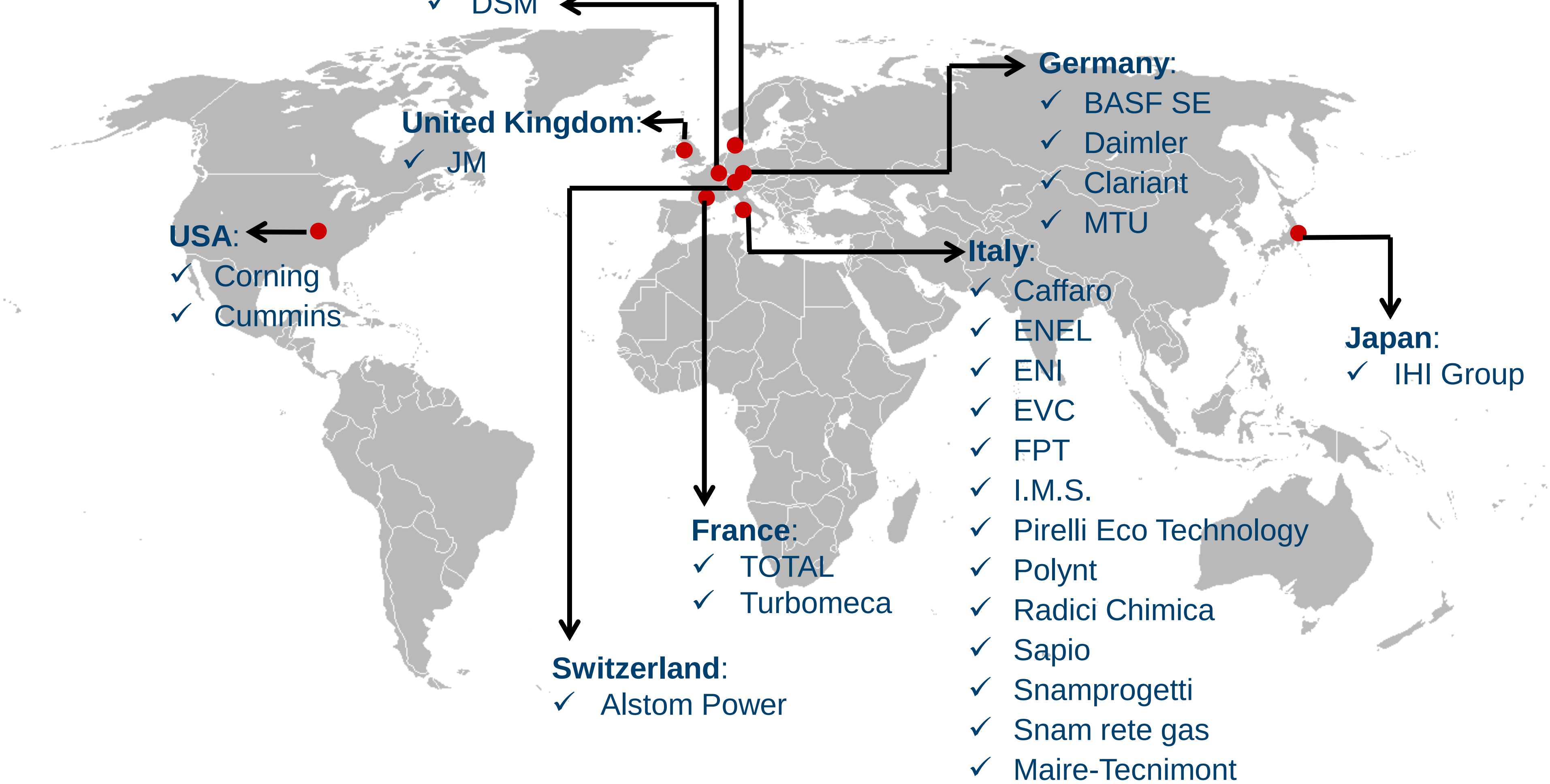
Czech Republic:
- ✓ Academy of Sciences, Prague

Italy:
- ✓ CNR
- ✓ Politecnico di Torino
- ✓ Università dell’Aquila
- ✓ Università di Bologna
- ✓ Università di Genova
- ✓ Università “La Sapienza” di Roma
- ✓ Università di Salerno
- ✓ Università di Torino
- ✓ Università di Udine
- ✓ Università di Cagliari

USA:
- ✓ Lehigh University
- ✓ University of California at Berkeley
- ✓ University of Delaware
- ✓ University of Minnesota
- ✓ Oak Ridge National Laboratory
- ✓ University of Houston
- ✓ University of Kentucky (CAER)
- ✓ University of Virginia

Spain:
- ✓ University of Malaga
- ✓ University of Madrid
- ✓ University of Siviglia

Industrial collaborations



Denmark:
- ✓ Haldor-Topsoe

The Netherlands:
- ✓ DSM

United Kingdom:
- ✓ JM

Germany:
- ✓ BASF SE
- ✓ Daimler
- ✓ Clariant
- ✓ MTU

USA:
- ✓ Corning
- ✓ Cummins

Italy:
- ✓ Caffaro
- ✓ ENEL
- ✓ ENI
- ✓ EVC
- ✓ FPT
- ✓ I.M.S.
- ✓ Pirelli Eco Technology
- ✓ Polynt
- ✓ Radici Chimica
- ✓ Sapio
- ✓ Snamprogetti
- ✓ Snam rete gas
- ✓ Maire-Tecnimont

Japan:
- ✓ IHI Group

France:
- ✓ TOTAL
- ✓ Turbomeca

Switzerland:
- ✓ Alstom Power

Current research focus

Energy conversion:

- Catalytic Partial Oxidation of NG/LPG to CO/H_2
- **Fischer-Tropsch Synthesis**
- Synthesis of DME, Methanol
- CO_2 activation

Advanced reactor design and modelling:

- Novel Structured Catalytic Reactors
- First-principles Guided Chemical Engineering

Electrocatalysis:

- Photo-electrochemical processes: Water Splitting
- Solid Oxide Fuel Cells

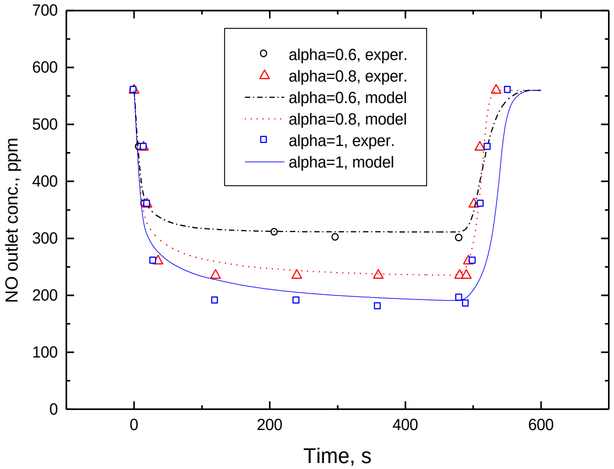
Environmental protection:

- Catalytic Combustion of Methane Emissions
- NO_x Storage-Reduction in Vehicles
- Combined Soot Combustion and NO_x Removal
- NH_3-SCR of NO_x for stationary sources
- NH_3-SCR of NO_x for mobile sources

NH_3-SCR of NOx for stationary sources

Chemistry: **Standard SCR**

$2\ NO + 2\ NH_3 + ½\ O_2 => 2\ N_2 + 3\ H_2O$



Experimental and simulated evolution of the NO outlet concentration during SCR reactor start-up and shut-down at T = 360 °C. C_{NO}^{0} = 560 ppm, AV = 33 Nm/h.

E. Tronconi, A. Cavanna, P. Forzatti, IEC Res. 37 (1998) 2341

Extensively investigated at POLIMI in the ‘90s

Commercial catalysts:

V_2O_5–WO_3/TiO_2 extruded honeycombs

Operating temperatures: 300 – 400 °C

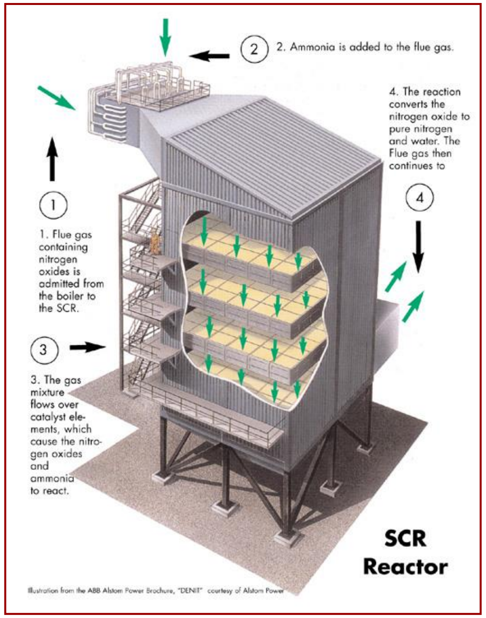
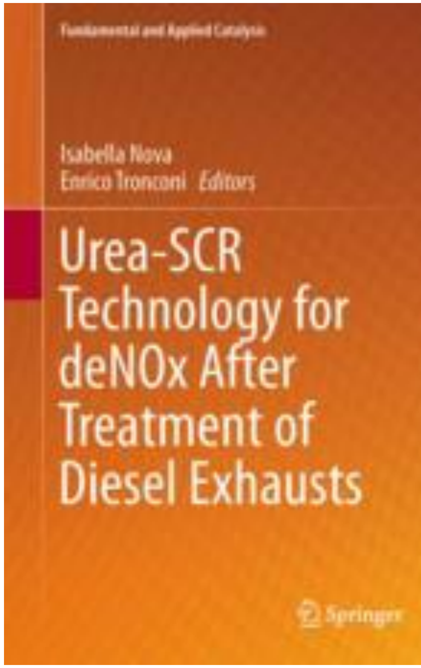


Illustration from the ABB Alstom Power Brochure, "DENIT" courtesy of Alstom Power

NH_3-SCR of NOx for automotive applications

BLUETEC

- Since 2001 collaboration with Daimler AG: Transient 1D+1D model of monolithic SCR converters used to design Euro 4, 5 and 6 compliant Mercedes-Benz Diesel vehicles



Fundamental and Applied Catalysis

Isabella Nova
Enrico Tronconi Editors

Urea-SCR Technology for deNOx After Treatment of Diesel Exhausts

Springer

DAIMLER

JM Johnson Matthey

mtu

Cummins

CORNING

ZHEJIANG UNIVERSITY

UNIVERSITY OF VIRGINIA

JUST

LAT
LABORATORY OF APPLIED THERMODYNAMICS

SEVENTH FRAMEWORK PROGRAMME

CO_2RE CO2 reduction for transport

•EU FP7 project «CO_2RE» (2012-2015)

HDGAS

•EU H2020 project “HDGAS” (2015 – 2017)

Thomson

•EU H2020 project “THOMSON” (2016-2018)

J. Heyrovský Institute of Physical Chemistry
Academy of Sciences of the Czech Republic

OAK RIDGE National Laboratory

KIT
Karlsruher Institut für Technologie

Fischer-Tropsch Synthesis

- Catalytic process for the conversion of natural gas, coal or biomasses into high-quality diesel fuels and chemicals

$$CO + 2\,H_2 \longrightarrow \begin{cases} C_nH_{2n+2} \\ C_nH_{2n} \\ C_nH_{2n+1}OH \end{cases} +\ H_2O$$

- Main achievements in the last years (in cooperation with Eni)

Main achievements

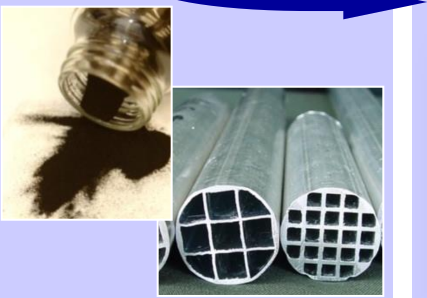
→ Development of lumped and detailed kinetic models, now used for the simulation of a pilot-scale demonstrative reactor (Sannazzar de’ Burgundi Eni’s refinery) and the design o industrial reactor units

→ Development of an innovative compact reactor technology, based on structured catalysts (WO2010/130399 & WO2014/102350) successfully tested at the pilot scale (Eni labs in San Donato)

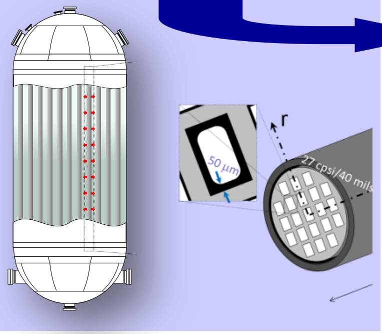
Small scale MT-FBR for FTS

DEVELOPMENT

Selection of materials, washcoating and testing at lab-scale (at PoliMi)

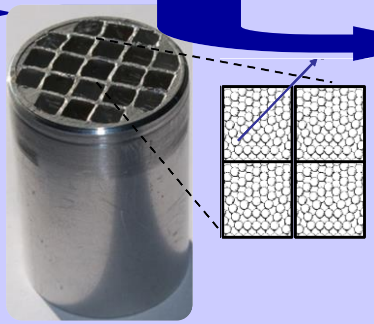


Industrial reactor modeling



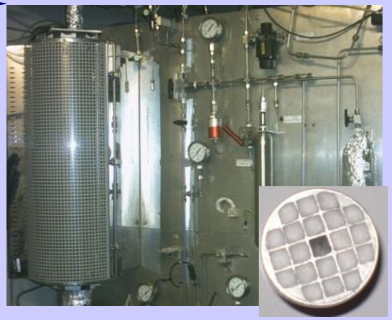
Chem. Eng. J. 171 (2011) 1294

Improved reactor config.: «Packed monolith» concept



WO/2010/130399

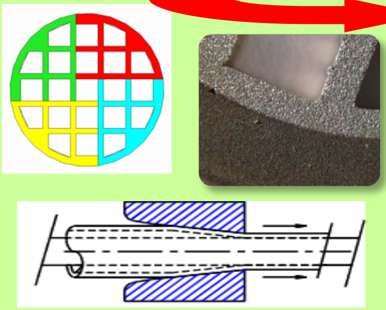
Lab-scale testing (at PoliMi)



DEMONSTRATION (and optimization)

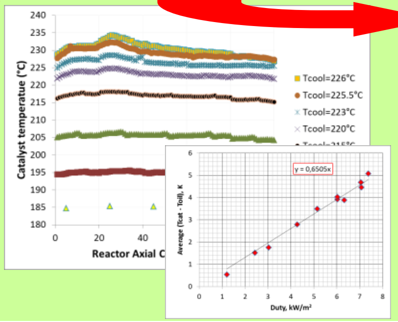
Proof of concept at the pilot scale (at Eni site)

Design & manufacturing of improved materials

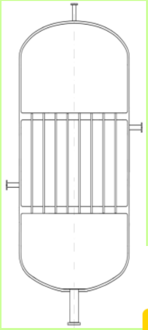


WO/2014/102350

Demonstration at the pilot scale (at Eni site)



Process analysis & scenarios



Presented at the 41° Eurokin Workshop – Milano, February 18th, 2015

ERC AdG Grant - INTENT

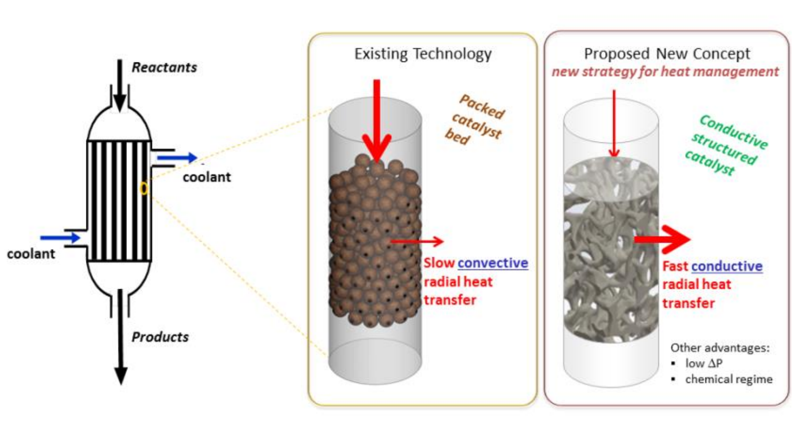
European Research Council
Established by the European Commission

POLITECNICO
MILANO 1863

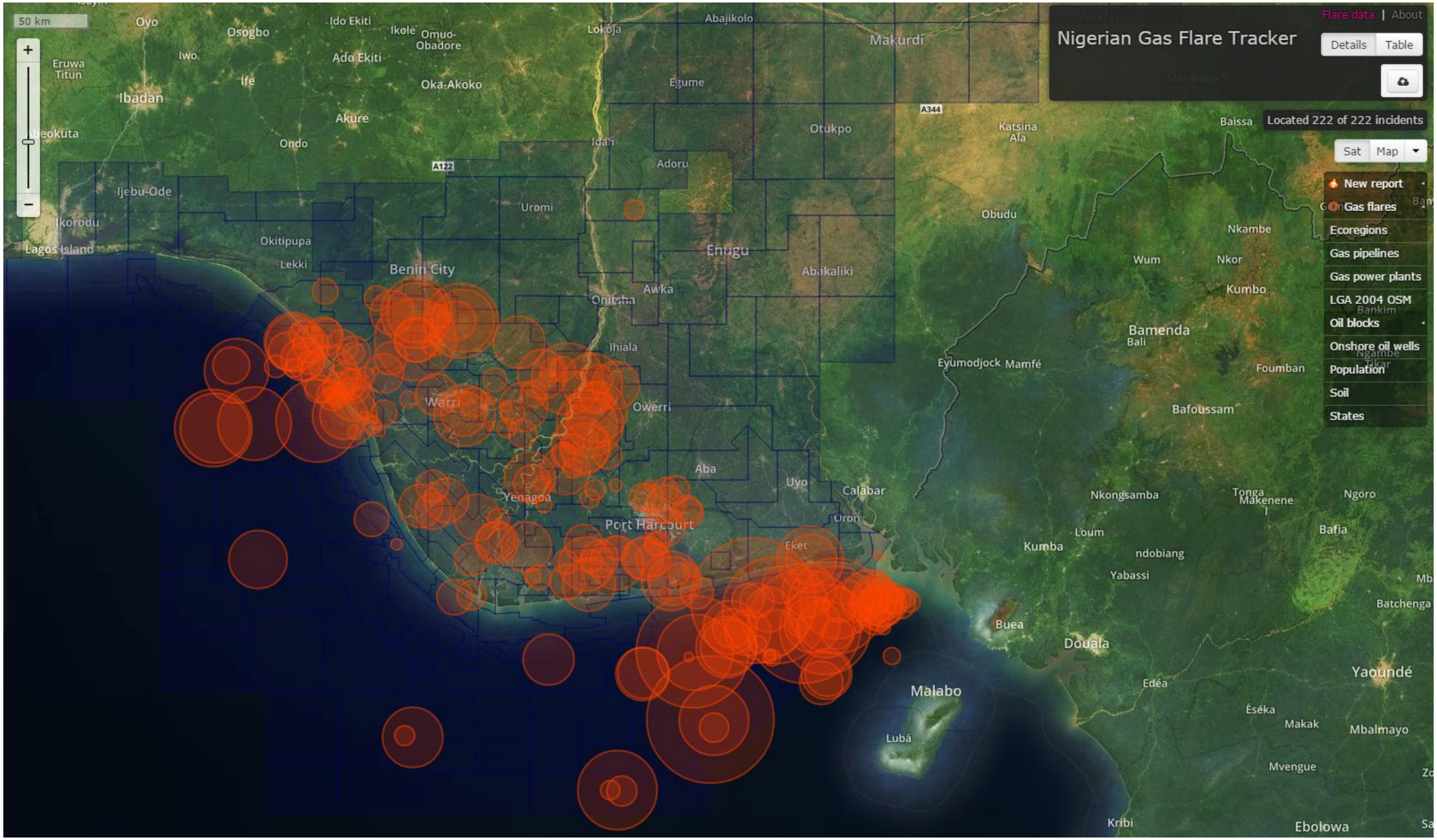
ERC Advanced Grant 2015
Action 694910: INTENT

“Structured Reactors with INTensified ENergy Transfer for Breakthrough Catalytic Technologies”

Principal Investigator: Enrico Tronconi
Host Institution: Politecnico di Milano
Duration: 60 months, started on Nov. 1st, 2016
Budget: 2 484 649 Euro

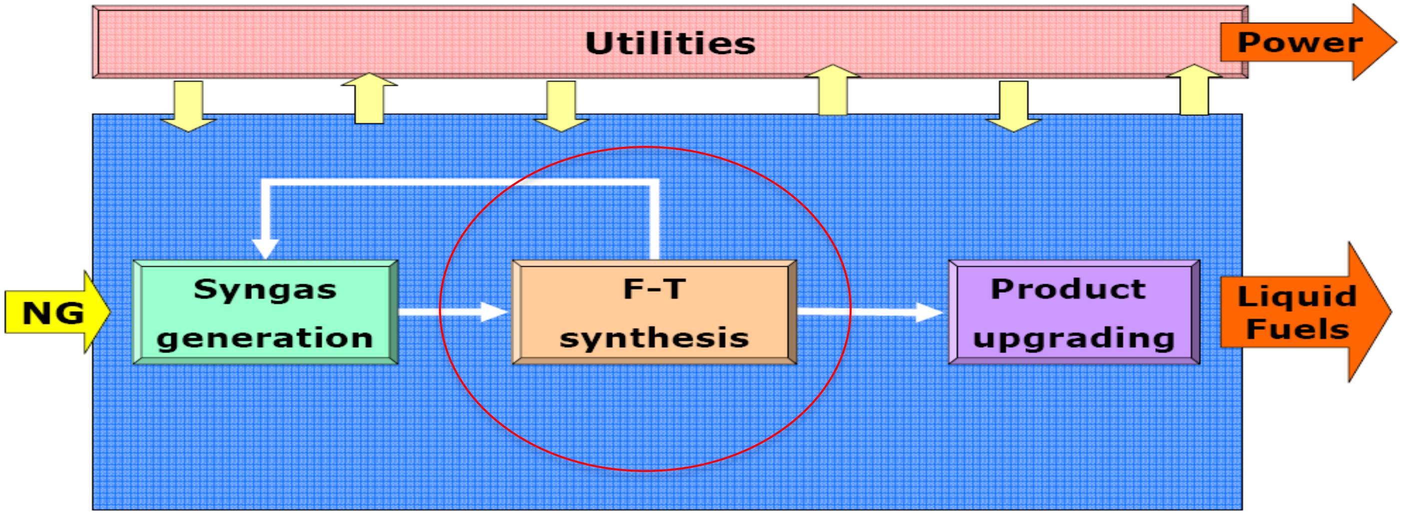


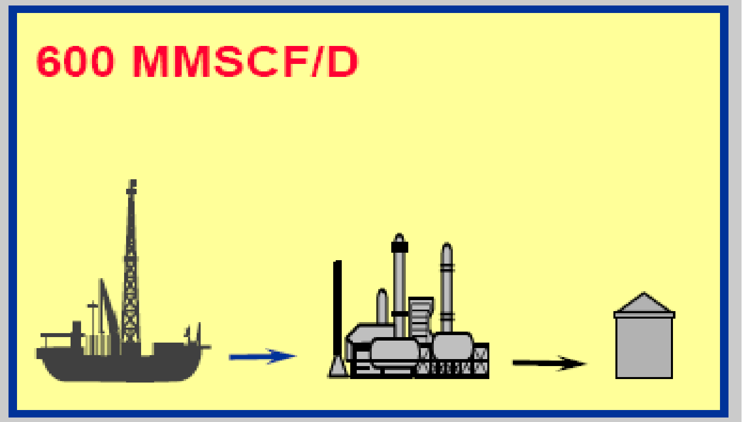
Natural Gas flaring in Nigeria



GTL = Gas-To-Liquids

Natural Gas conversion to clean fuels via Fischer-Tropsch Synthesis





MMSCF/D = million of million standard cubic feet per day

Why natural gas ?

- The maximum energy that is nowadays available from all the **alternative energy sources** (biomass, nuclear energy, wind energy, hydroelectric energy), would be only a little higher than the request of 2000 Mtep over the next 25 years.

- As the research aims at finding energy sources which are alternative or complementary to crude oil, a new trends is using **other fossil sources**, such as coal and **natural gas**.

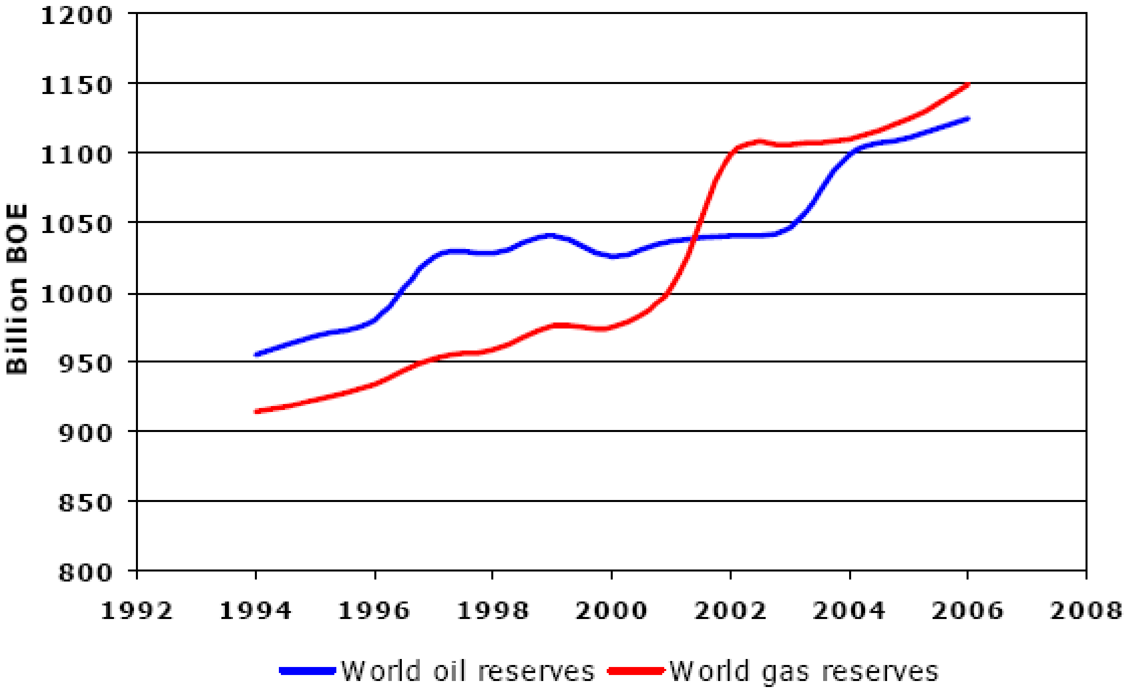
- Natural gas is considered **a better fossil fuel than coal**, as:
  - It is inherently **cleaner** than coal;
  - It can be purified already at the well-head.

- Large natural gas reserves

- How can we exploit natural gas ?

Sabato 31 Marzo, 2012 CORRIERE DELLA SERA
Gas naturale al posto del petrolio
Come cambierà il futuro del mondo
di FAREED ZAKARIA

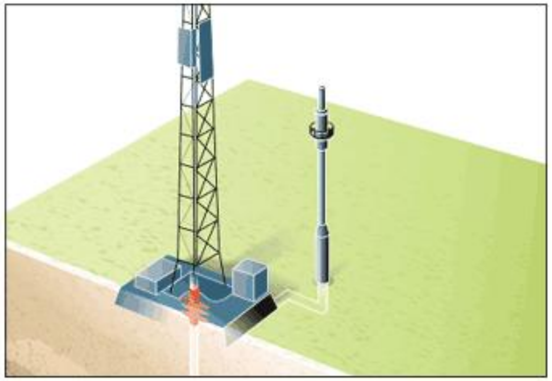
2005 Proven World Oil & Gas Reserves

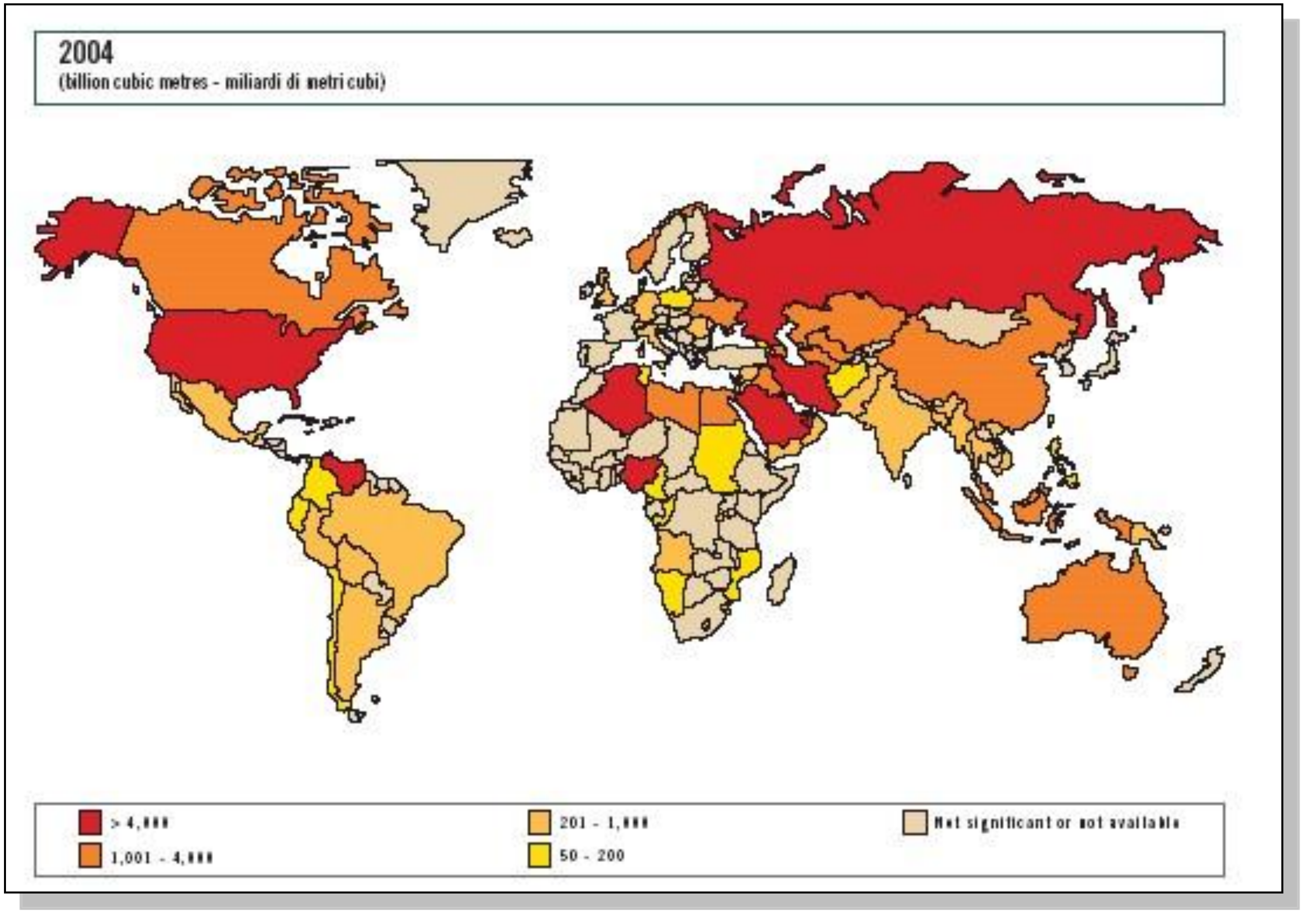


Source: Eni's World Oil & Gas Review 2006

How NG can be exploited? The «stranded gas» problem

- The main problem with NG is that about the 36% of it is located in **remote areas** (= Iran, Russia, Qatar) and/or in **small fields** (most of the times "**associated**" with oil fields – "flaring" = 15 bcfd), which are situated often **off-shore**





bcfd = *billion cubic feet per day*

How NG can be exploited? The «stranded gas» problem

Yellow dots= energy consumption

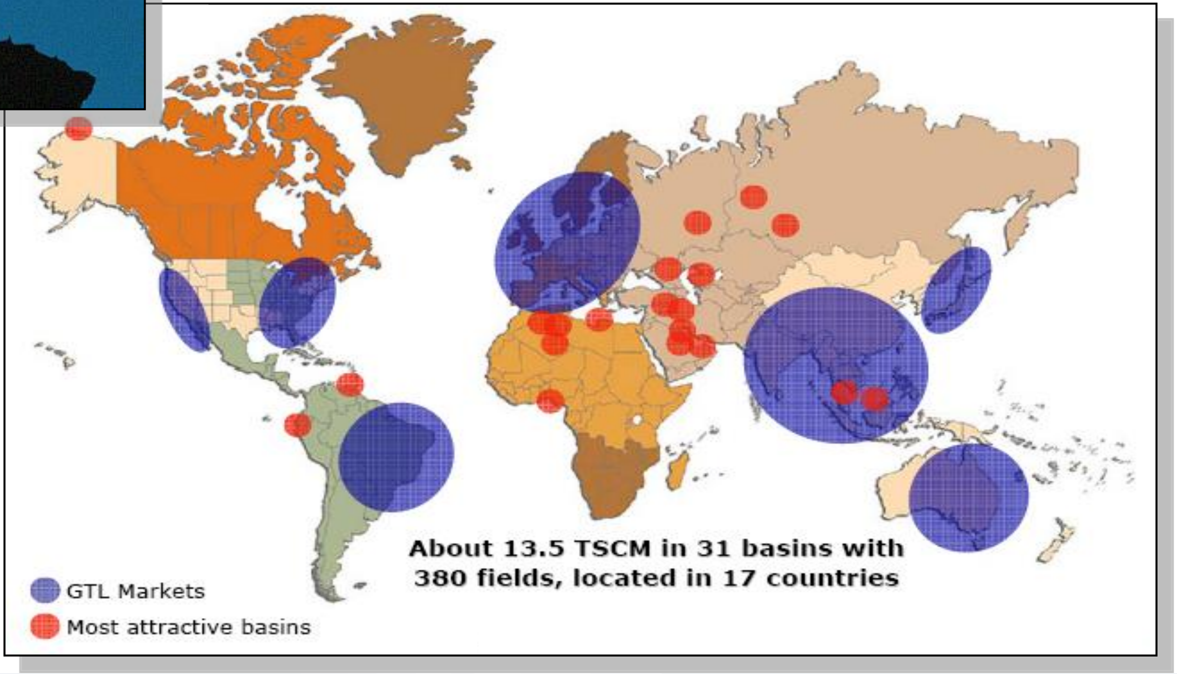
Red dots= flaring

Raw material cost:

<1.4 $/kJ

Product cost:

≈9.3 $/kJ

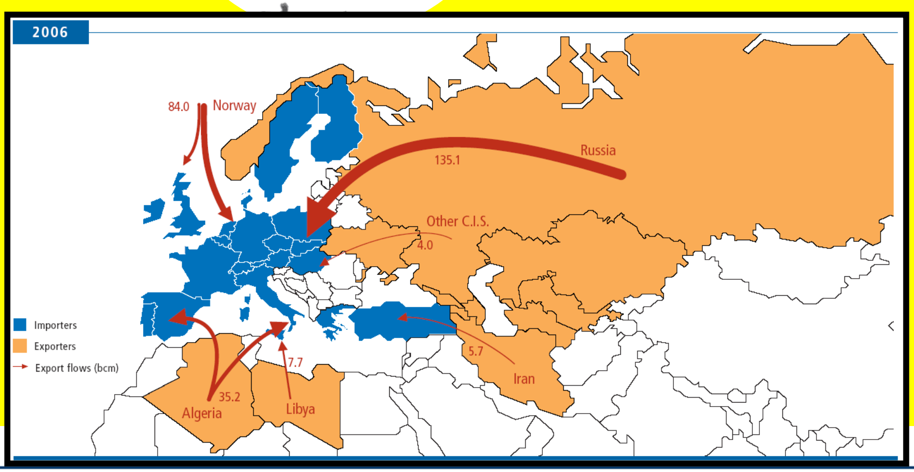


About 13.5 TSCM in 31 basins with 380 fields, located in 17 countries

bcfd = billion cubic feet per day

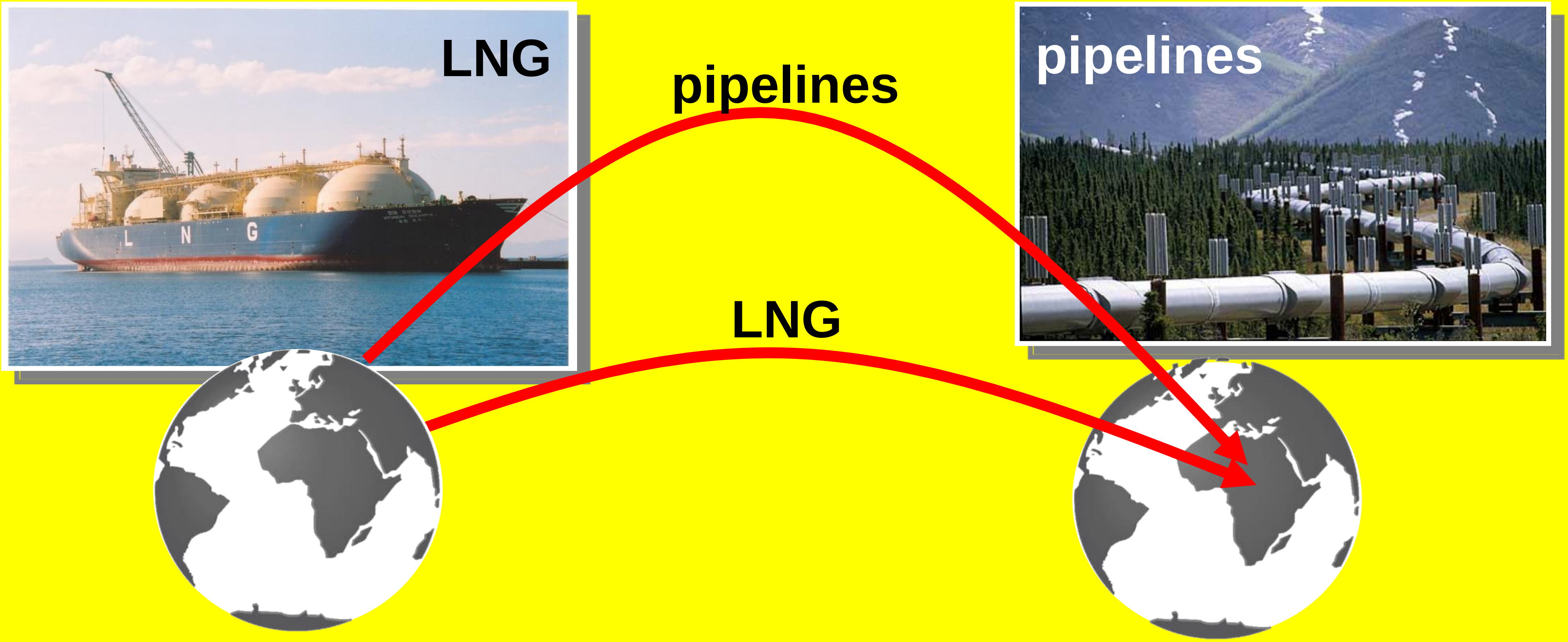
How remote NG can be exploited?

pipelines



✘ Energetic and economic costs restrict the pipeline length to max. 2500 km

How remote NG can be exploited?



LNG

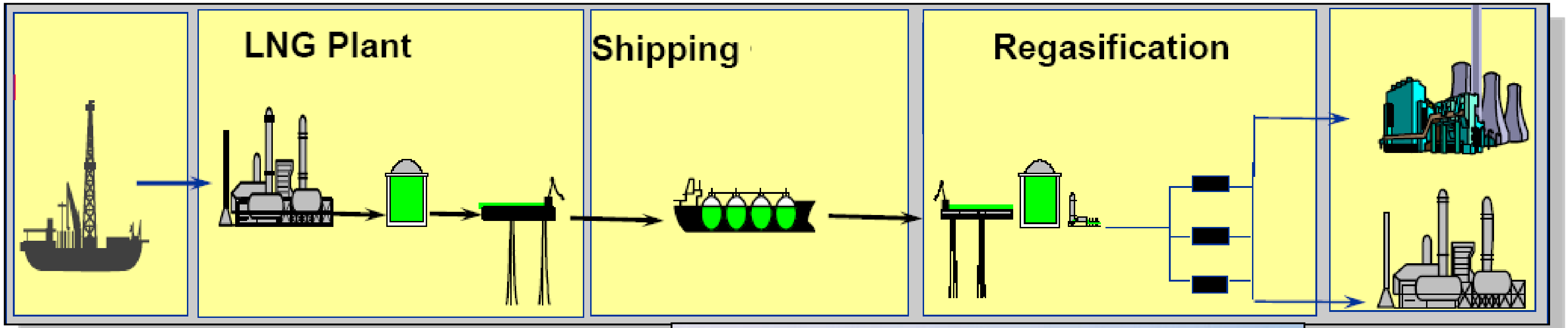
pipelines

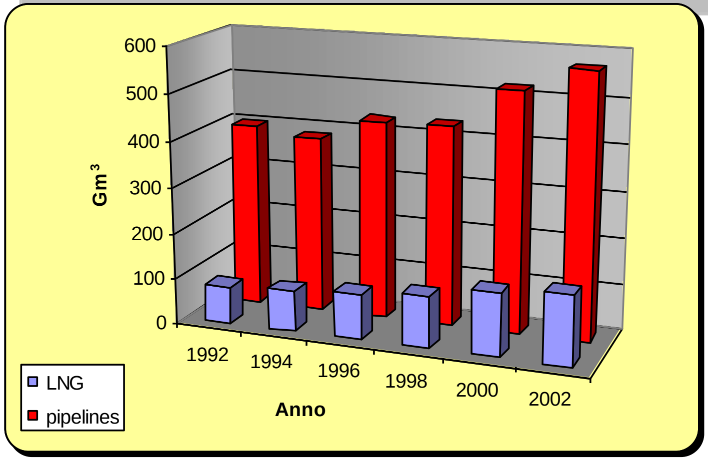
pipelines

LNG

How remote NG can be exploited?

- **LNG** = **L**iquified **N**atural **G**as → gas is liquefied with a cryogenic process (physical process) @ -162°C and transported using LNG tankers



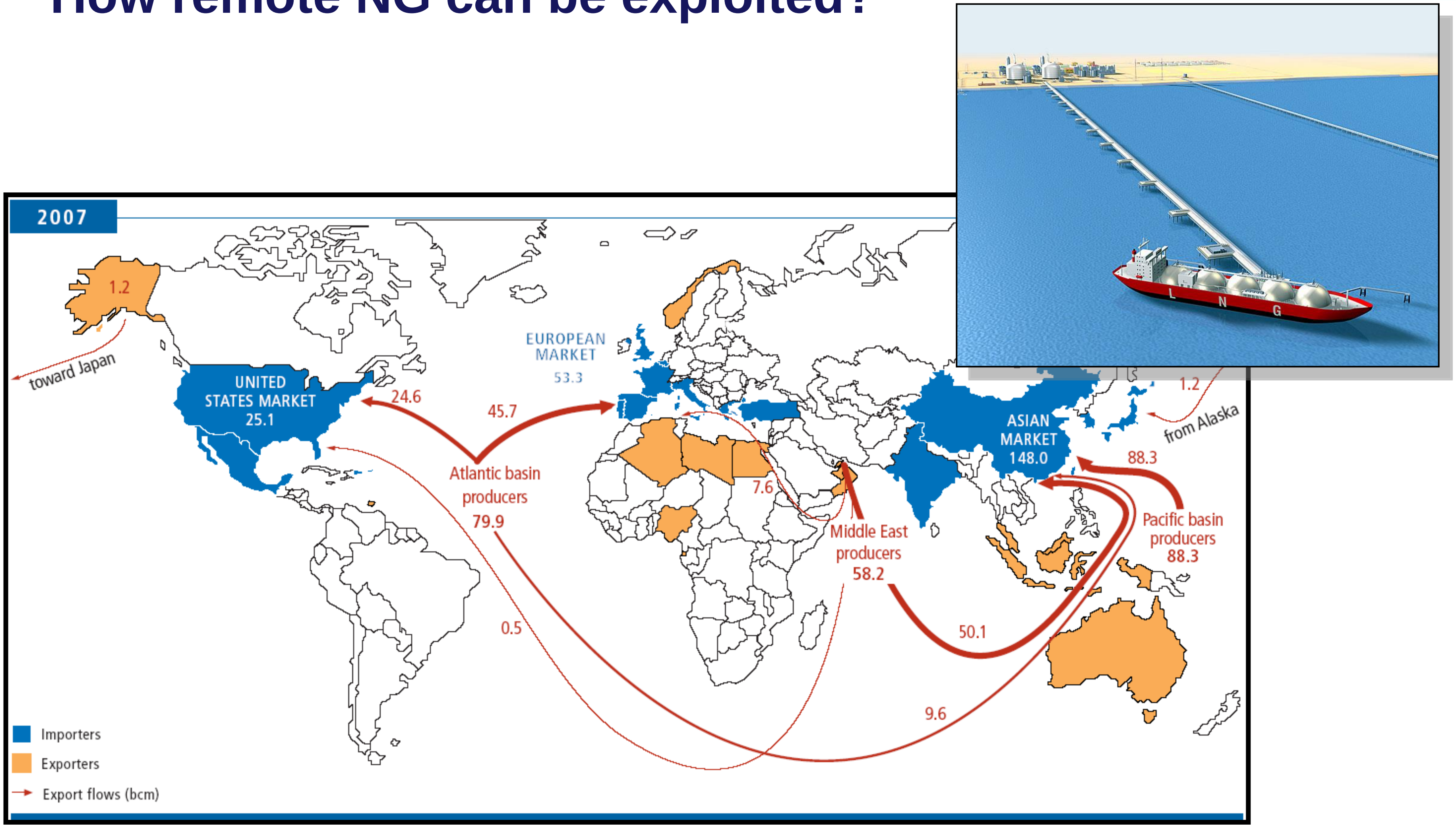


Liquefaction cost = 15% calorific power

MMSCF/D = million of million standard cubic feet per day

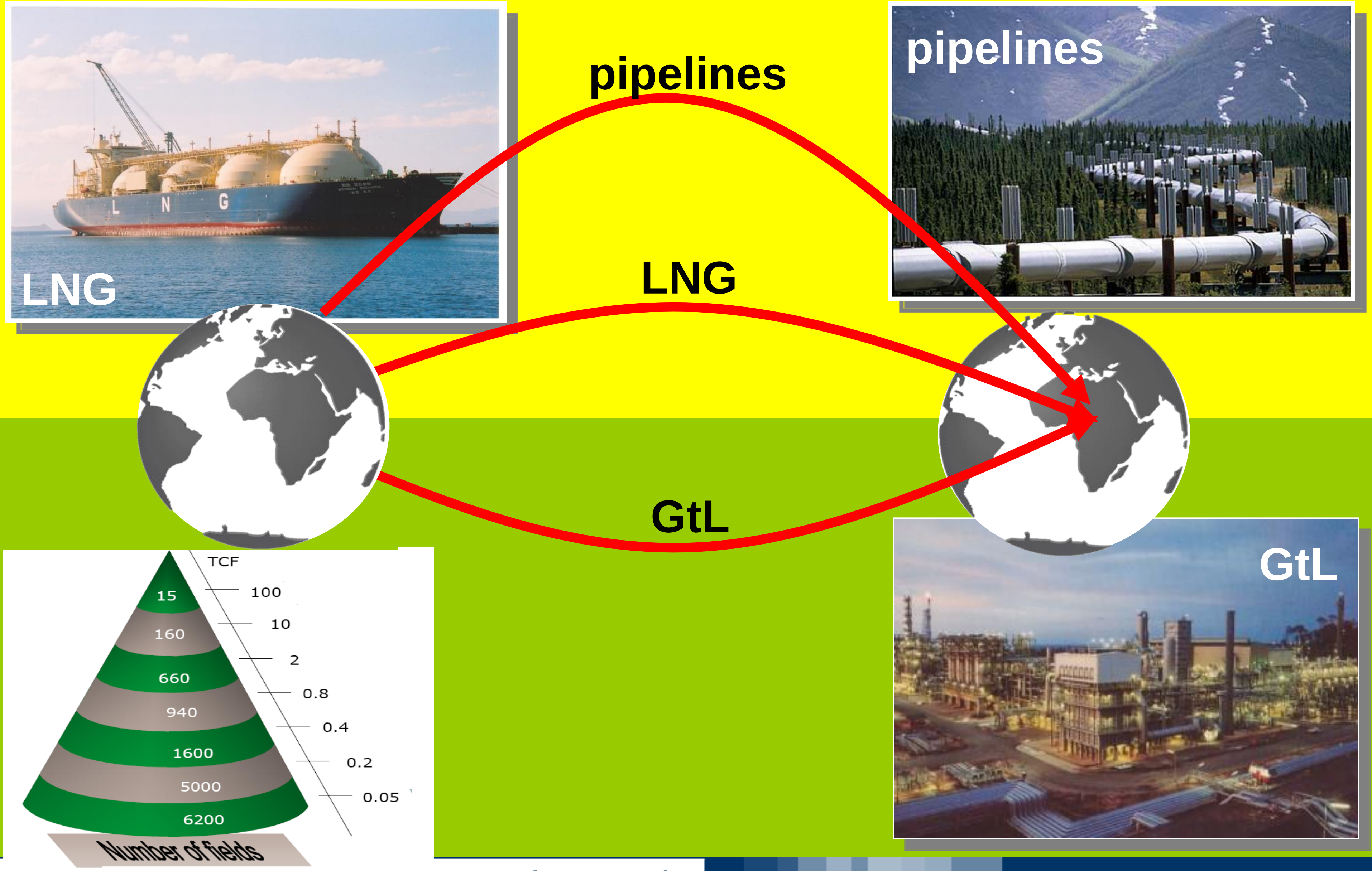
mtpa = million tons per annum 1 SCF = 2.83 x10^{-2} SCM

How remote NG can be exploited?

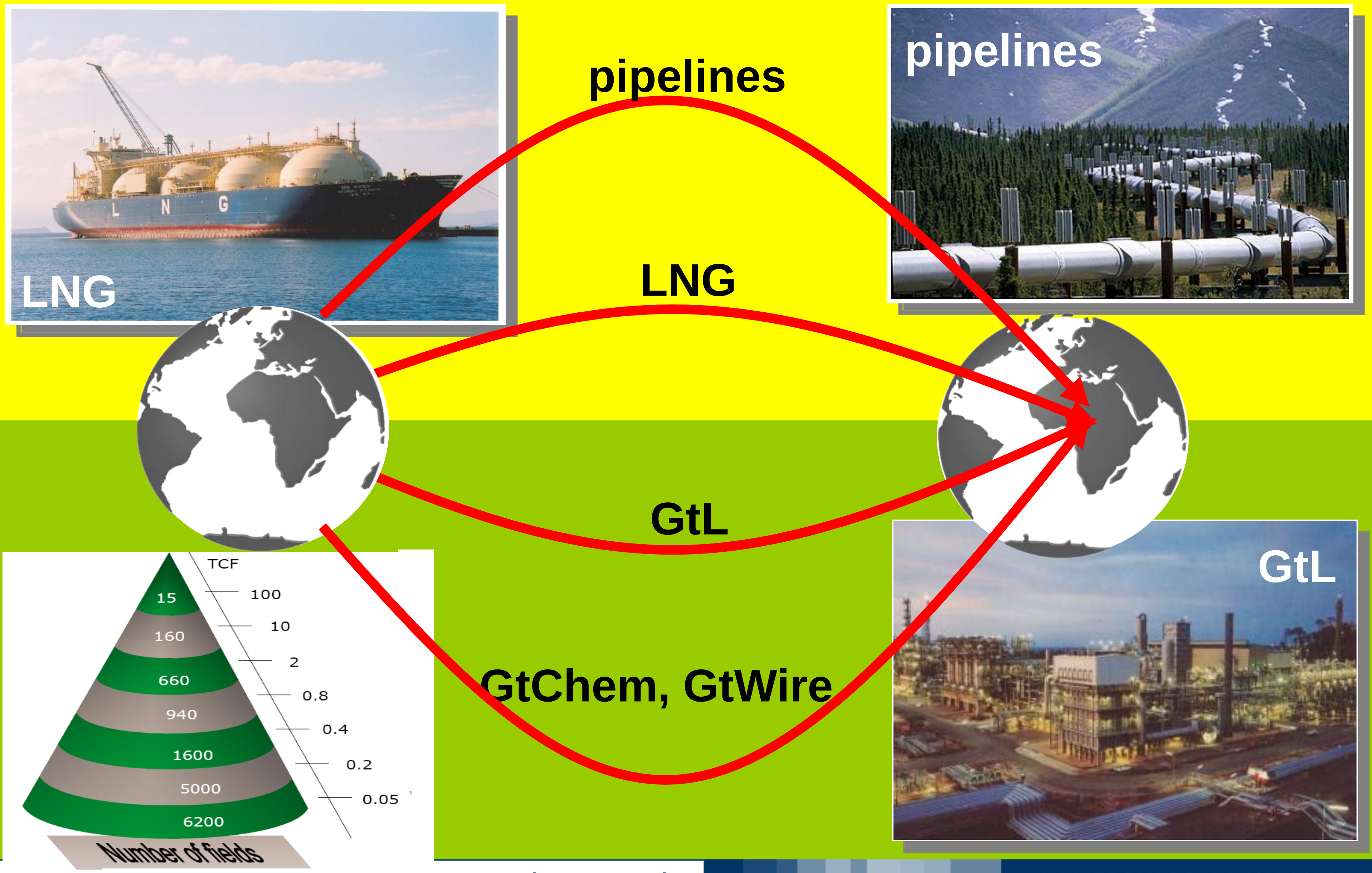


- LNG technology cannot be used for the exploitation of small fields of natural gas.

How remote NG can be exploited?

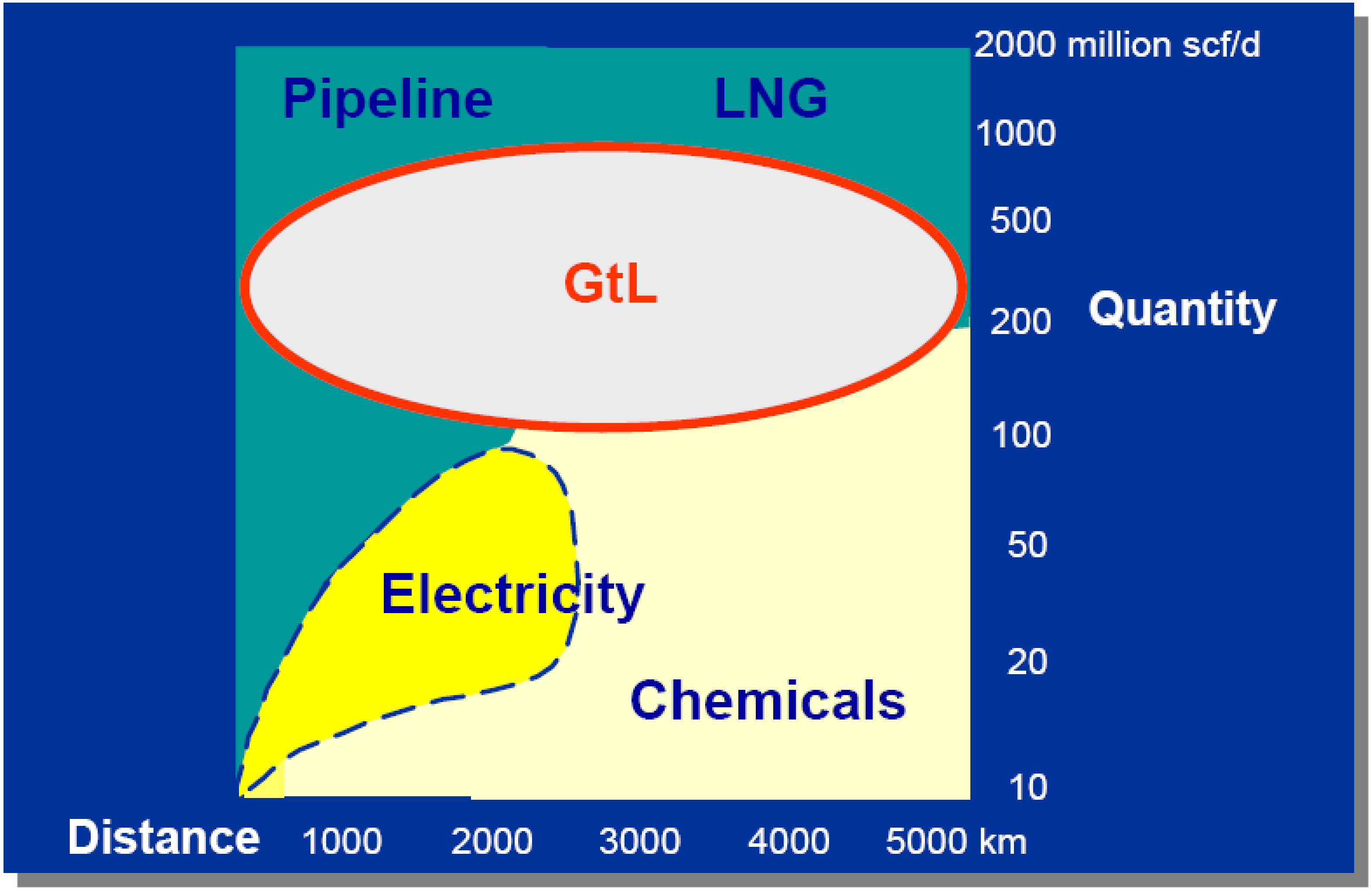


How remote NG can be exploited?



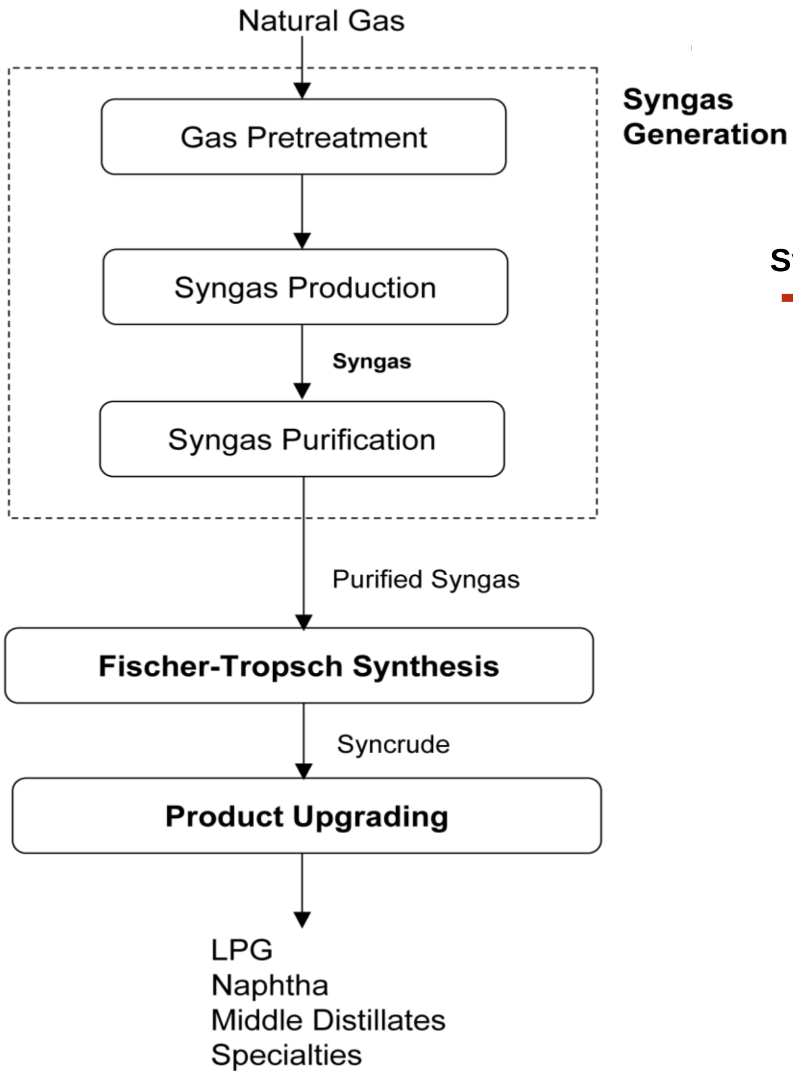
Pipeline, LNG, GtL, GtW or GtC ?

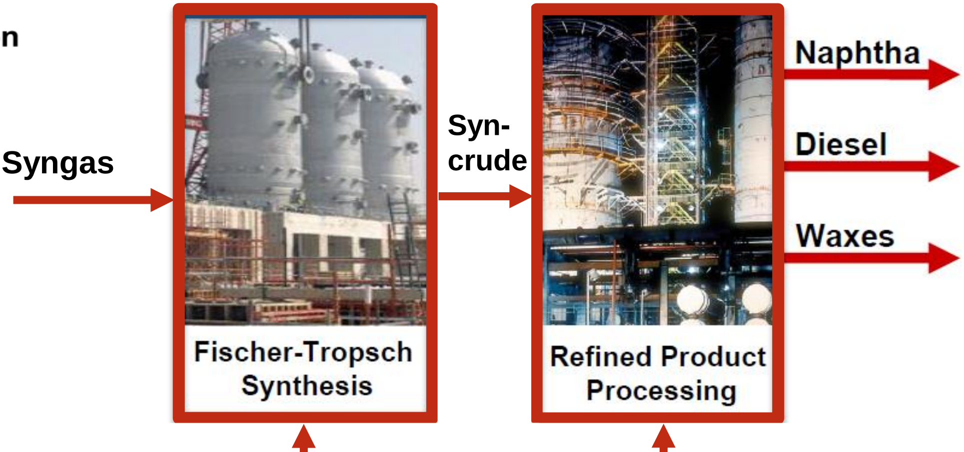
GtL is the best option for medium-size reservoirs



Hoek A., Oral Presentation, DGMK Conference “Synthesis Gas Chemistry”, Dresden October 4-6, 2006

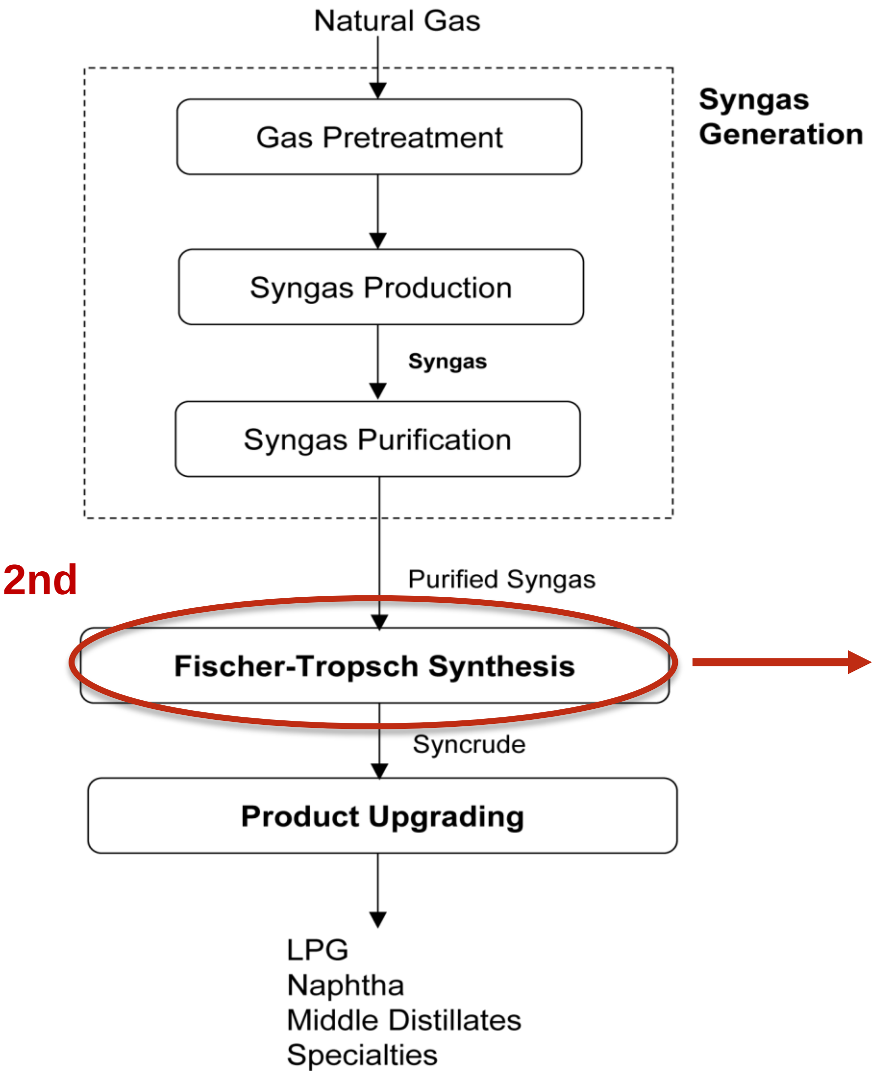
Gas to Liquid (GtL) process





Pearl GTL plant, Ras Laffan, Doha, Qatar.

Gas to Liquid (GtL) process


Natural Gas

Syngas Generation

Gas Pretreatment

Syngas Production

Syngas

Syngas Purification

Purified Syngas

2nd

Fischer-Tropsch Synthesis

Syncrude

Product Upgrading

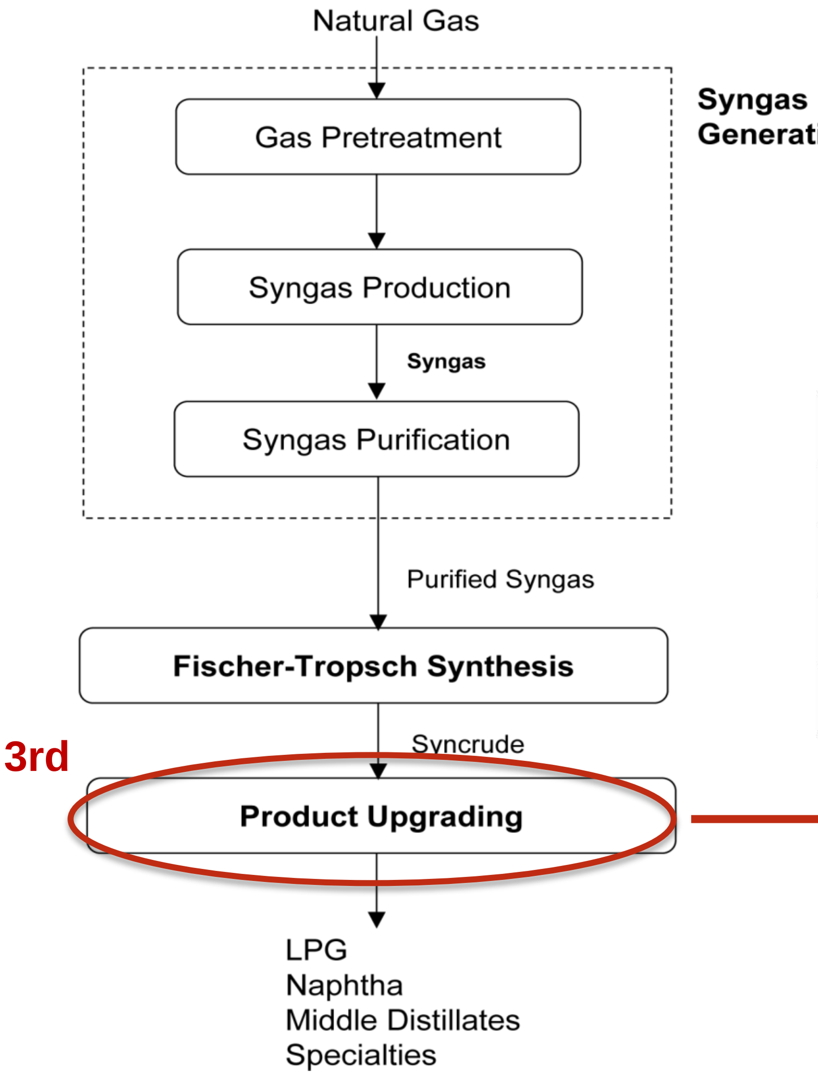
LPG
Naphtha
Middle Distillates
Specialties

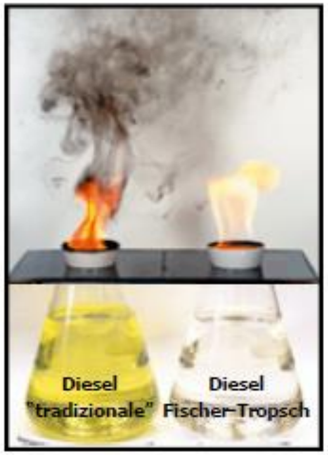
Fischer-Tropsch Synthesis

$$n\,CO + 2\,nH_2 \rightarrow -(CH_2)_n- + n\,H_2O$$

Highly exothermic reaction ($\Delta H^0_R \cong -165$ kJ/mol$_{CO}$)

Gas to Liquid (GtL) process





Characteristic	Refinery Diesel	GtL Diesel
Cetane number	51 (min)	>70
Sulphur (ppm)	50 (max)	<10
Aromatics (vol.%)	Not established	0
Relative density to H_2O	0,815 – 0,875	0,77 – 0,80

Hydrocracking

Hydrotreating

In summary: what are the advantages of the GtL process?

- It converts **remote gas** fields and **“flare” gas** to saleable products
- It leads to a strategic diversification of energy resources
- It causes the formation of **hydrocarbon products**:
  - of **high added value**:
    - » raw material: 0 – 1.5 $/MMBTU
    - » Products: 10 $/MMBTU
  - **environmentally friendly**, beacuse sulphur-free and aromatics-free

    ==> GtL diesel emissions, compared to the emissions of a conventional diesel:

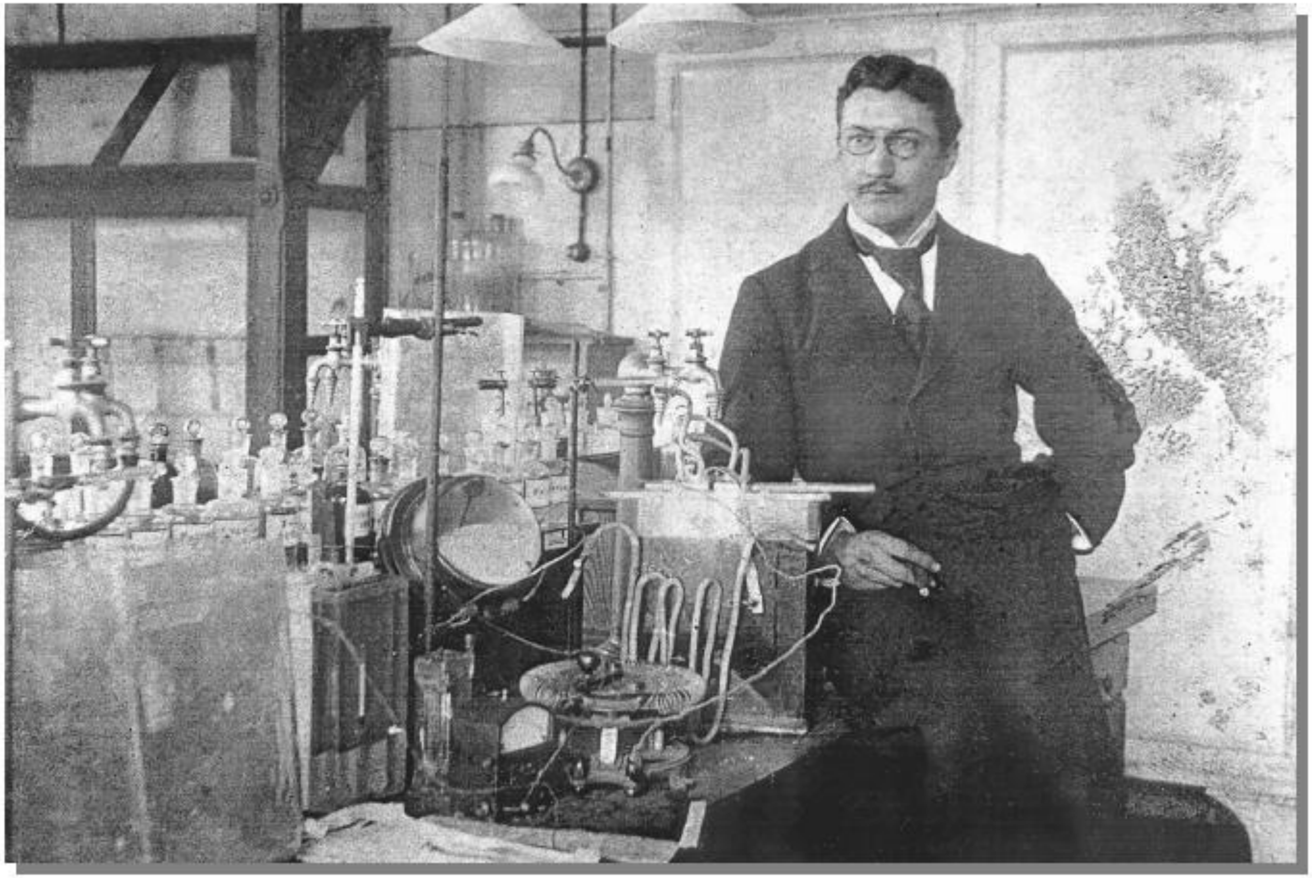
NO_x	-6%
PM_{10}	-20%
HC	-63%
CO	-71%

  - **high performance** (diesel with high cetane number) →

Diesel “tradizionale” **Diesel Fischer-Tropsch**

The Fischer-Tropsch Synthesis

Franz Fischer at Work in 1918

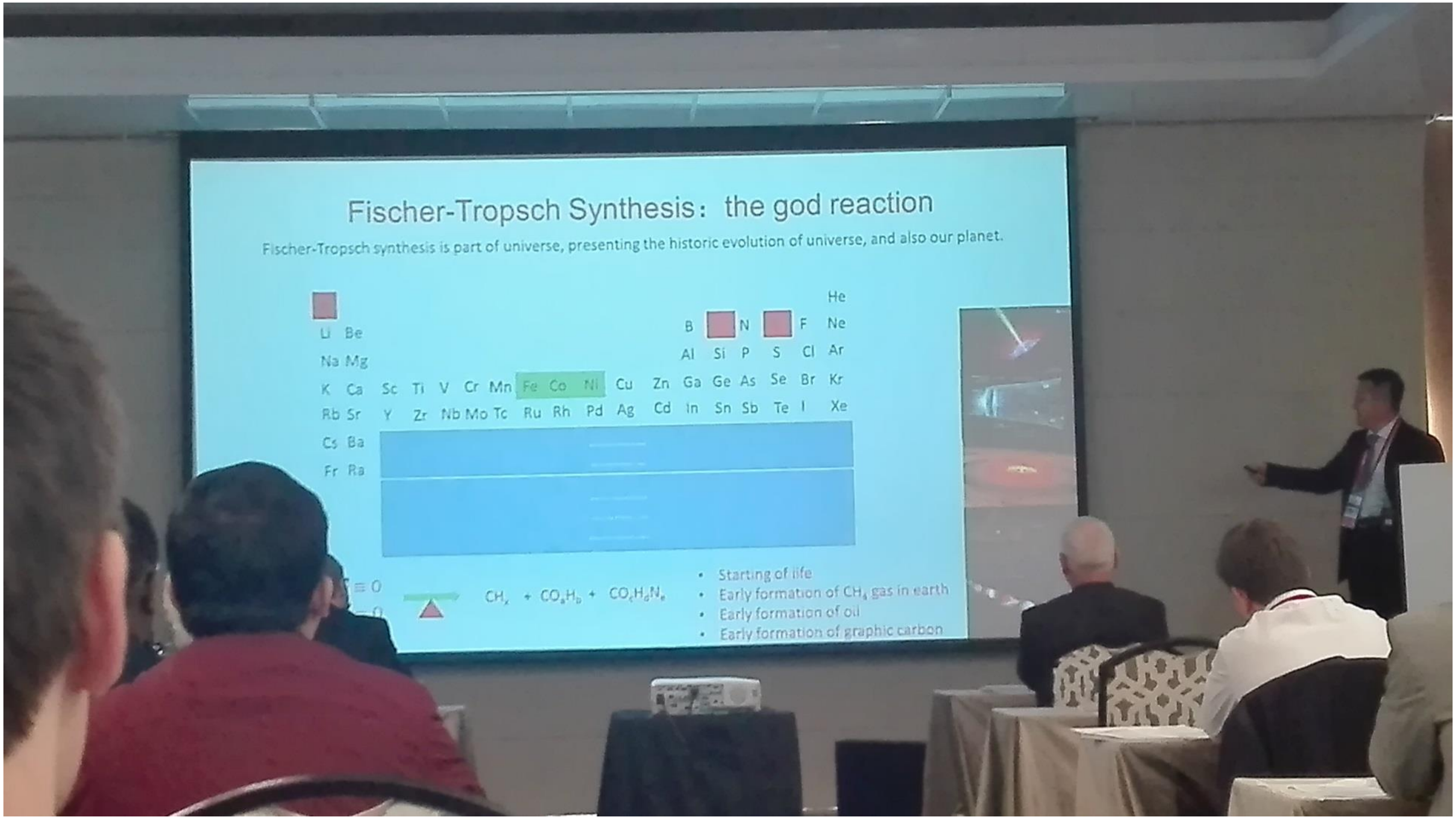


Financial Mail, 2000

www.fischer-tropsch.org

FTS: the God reaction?

3rd Syngas Convention
Cape Town, SA
March 2018



Fischer-Tropsch Synthesis: the god reaction

Fischer-Tropsch synthesis is part of universe, presenting the historic evolution of universe, and also our planet.

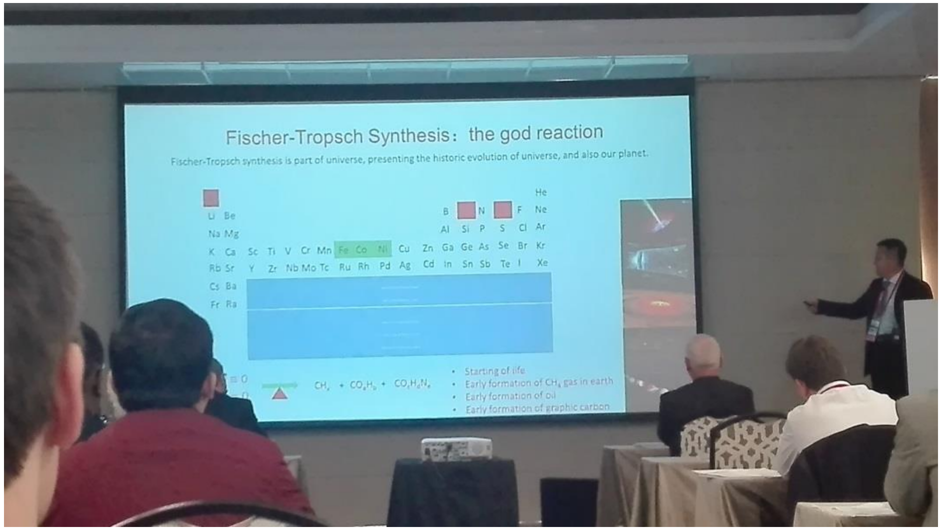
$CH_x + CO_aH_b + CO_cH_dN_e$

- Starting of life
- Early formation of CH_4 gas in earth
- Early formation of oil
- Early formation of graphic carbon

Fischer-Tropsch Synthesis: a brief history

FTS is one of the most important catalytic processes for energy and environment.

- Invention of the Bergius process (coal liquefaction, 1913) and FTS (1926)
- Germany's industrialization (1926 – 1945)



Fischer-Tropsch Synthesis：the god reaction

Fischer-Tropsch synthesis is part of universe, presenting the historic evolution of universe, and also our planet.

- Starting of life
- Early formation of CH_4 gas in earth
- Early formation of oil
- Early formation of graphic carbon

- Transfer of the technology to UK, US, South Africa … (1945 – 1990)
- New market drivers (2000 - ….):
  - need for cleaner fuels;
  - abundance of "stranded" natural gas

Fischer-Tropsch Synthesis: a brief history

- Studies on synthetic fuels (i.e. not from oil) began in early ‘900.
- Petroleum had become essential to the economy by the 1920s (cars, airplanes, ships required a shift from solid to liquid fuels).

- Germany had no petroleum but huge resources of coal. It was the first of industrialized nations to synthetize petroleum: Friedrich Bergius (1913) patented a process for coal liquefaction to produce a high-quality gasoline.
- (This process was briefly revived in the late ’70s due to the oil crises).

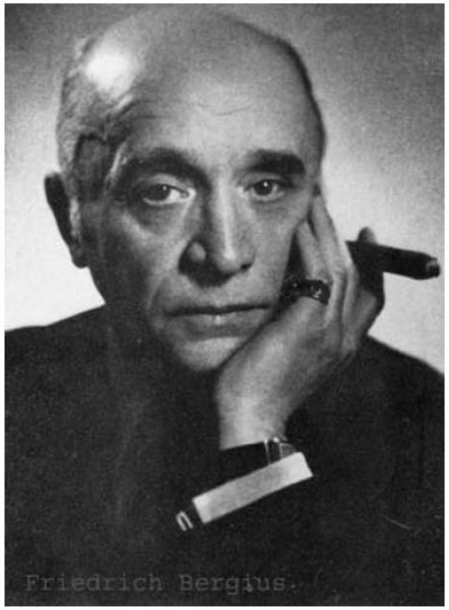


Figure 1. Friedrich Bergius

Fischer-Tropsch Synthesis: a brief history

- Invention of the FTS (1926) at the Kaiser Wilhelm Institute of Mülheim (Ruhr valley):

$C + H_2O \Longrightarrow CO + H_2$

$nCO + 2n\ H_2 \Longrightarrow (-CH_2-)_n + n\ H_2O$

over Co-Fe catalysts

German Patent 524,468 (2/11/1926)

Figure 2. Franz Fischer

Figure 3. Hans Tropsch

- First large plant (1934, Ruhrchemie AG): 1 kton/yr
- By 1937-38: four FTS plants, 300 kton/yr
- By 1939: nine FTS plants, peak = 576 kton/yr (1944)
- Contributed to ~ 15% of total synfuel production, which covered 95% of German Luftwaffe's gasoline and 50% of total liquid fuel consumption of Germany during WWII
- Plants destroyed by Allied bombing (March 1945)

Fischer-Tropsch Synthesis: a brief history

- After WWII: FTS plants, scientists and technicians transferred to USA.
- Technology acquired by USA: summary reported in H.H. Storch, N. Golumbic, R.B. Anderson, «The Fischer-Tropsch and related syntheses», J. Wiley, NY, 1951
- Development discontinued in the early ’50s due to very low oil price.

1955 SASOL I

Syntroleum

- FTS technology transferred in South Africa in the ’50s (oil embargo due to racial segregation).
- In 1950-1980: new large FTS plants erected in Sasolburg (SA) (coal gasification).

Fischer-Tropsch Synthesis: reactions

- The stoichiometry of the synthesis can be schematized as

$$n\,CO + 2n\,H_2 \rightarrow (-CH_2-)_n + n\,H_2O \qquad \Delta H = -40\ \text{kcal/mol CO}$$

- Actually the chemistry is more complex, possibly involving also the WGS reaction

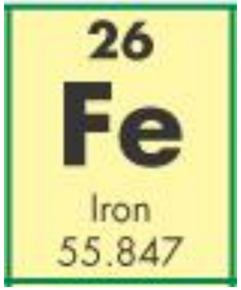
$$CO + H_2O \rightarrow CO_2 + H_2$$

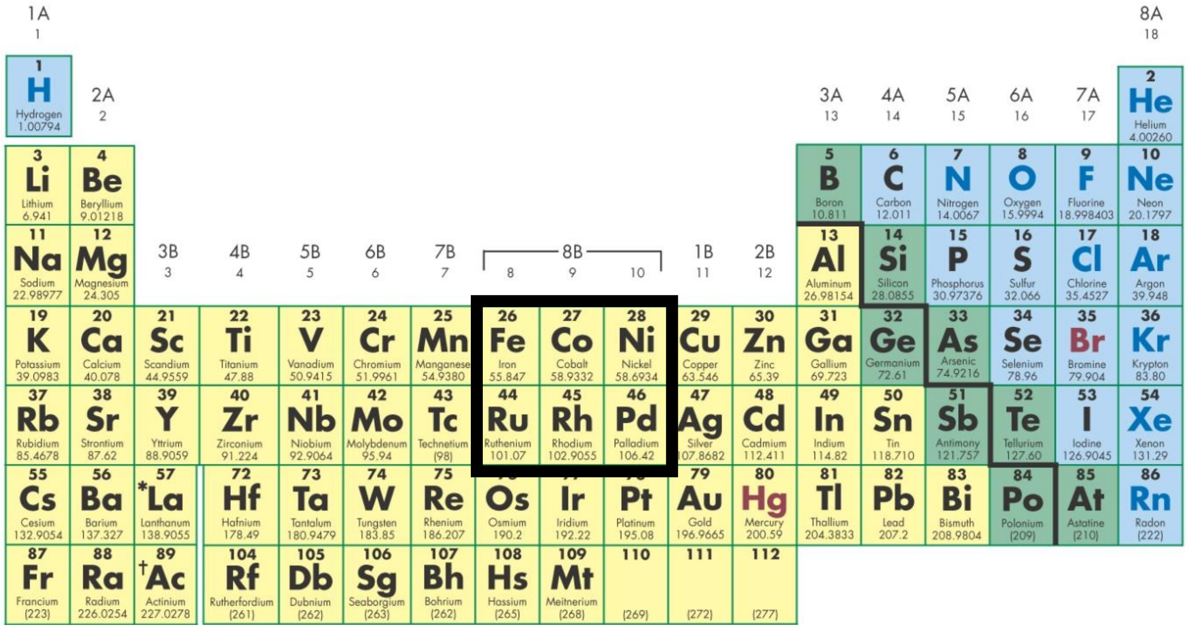
and the synthesis of straight chain oxygenates (C_{2+}),

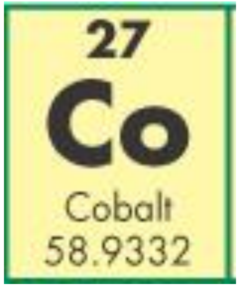
$$n\,CO + 2n\,H_2 \rightarrow H(-CH_2-)_nOH + (n-1)\,H_2O$$

- The choice of catalyst and operating conditions influences the products distribution (n_C, olefins vs. paraffins, oxygenates vs. hydrocarbons….).

Fischer-Tropsch Synthesis: catalysts







- ✓ economic
- ✗ low activity⇨HTFT (250<T<350°C)
- ✗ high selectivity for olefines and alcohols
- ✗ promotes WGS reaction

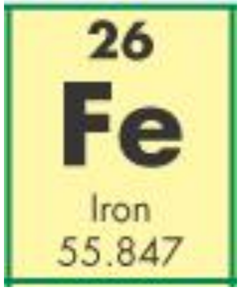
⇨ **appropriate for the production of syngas from coal or from biomass**

- ✗ expensive
- ✓ high activity⇨LTFT (T<250°C)
- ✓ high selectivity for paraffins
- ✓ no WGS reaction

⇨ **appropriate for the production of syngas from natural gas**

Fischer-Tropsch Synthesis: reaction products

Species	**Selectivity [%]**	
	HTFT	**LTFT**
CH_4	7	4
Olefins C_2-C_4	24	4
Paraffins C_2-C_4	6	4
Gasoline	**36**	18
Diesel	12	19
Lubricant oils and waxes	9	**48**
Oxygenated	6	3



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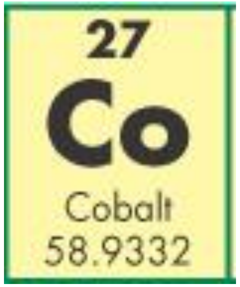


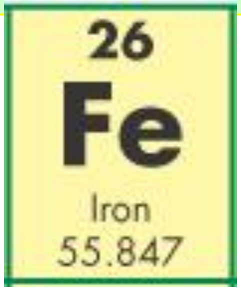
- ✗ expensive
- ✓ high activity ⇨ LTFT (T<250°C)
- ✓ high selectivity for paraffins
- ✓ no WGS reaction

⇨ **appropriate for the production of syngas from natural gas**

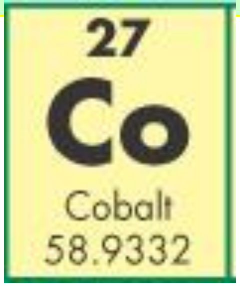
Fischer-Tropsch Synthesis: catalysts

Support materials:
SiO_2, Al_2O_3, TiO_2, mix
They act actually like structural promoters
They are able to start secondary reactions (e.g.: acid sites)

Promoters:
Structural: they increase the active phase dispersion (**Re, Zr, Ce**)
of **Reduction**: they increase the active phase reducibility (**Ru, Pd, Pt, Cu**)
of **Activity**: they prevent coke deposition (**noble metals**)
of **Selectivity**: they change the product distribution (**Na, K, Cs**)



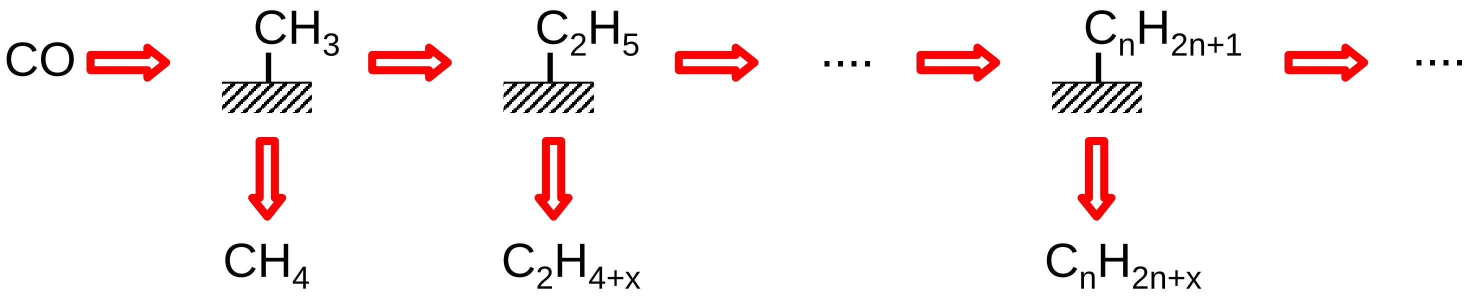
- ✓ economic
- ✗ low activity⇨HTFT (250<T<350°C)
- ✗ high selectivity for olefines and alcohols
- ✗ promotes WGS reaction
- ⇨ **appropriate for FTS with syngas from coal or biomass**



- ✗ expensive
- ✓ high activity⇨LTFT (T<250°C)
- ✓ high selectivity for paraffins
- ✓ no WGS reaction
- ⇨ **appropriate for FTS with syngas from natural gas**

Fischer-Tropsch Synthesis: product distribution

x =0,2



CO ⇒ CH_3 ⇒ C_2H_5 ⇒ .... ⇒ C_nH_{2n+1} ⇒ ....

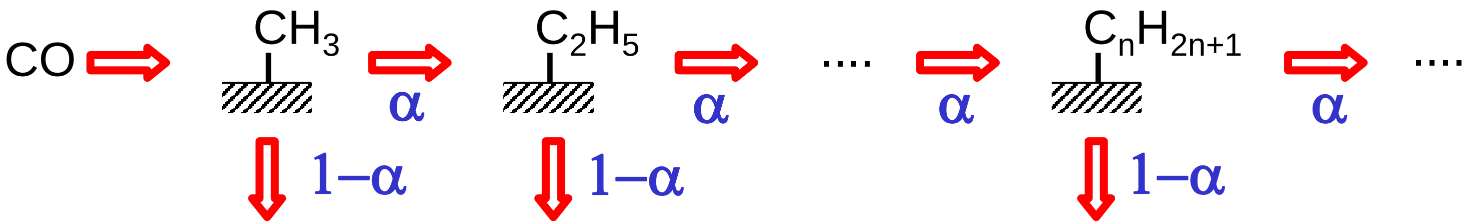
CH_4

C_2H_{4+x}

C_nH_{2n+x}

Fischer-Tropsch Synthesis: product distribution

x =0,2



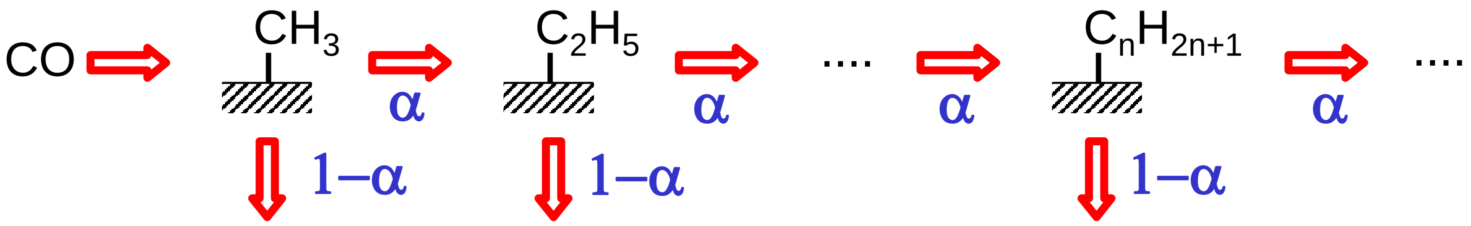
$$CO \Rightarrow CH_3 \xrightarrow{\alpha} C_2H_5 \xrightarrow{\alpha} \ldots \xrightarrow{\alpha} C_nH_{2n+1} \xrightarrow{\alpha} \ldots$$

$$CH_3 \xrightarrow{1-\alpha} CH_4 \qquad C_2H_5 \xrightarrow{1-\alpha} C_2H_{4+x} \qquad C_nH_{2n+1} \xrightarrow{1-\alpha} C_nH_{2n+x}$$

	CH_4	C_2H_{4+x}		C_nH_{2n+x}	
Probability	$1-\alpha$	$\alpha\,(1-\alpha)$	...	$\alpha^{n-1}\,(1-\alpha)$	

Fischer-Tropsch Synthesis: product distribution

x =0,2



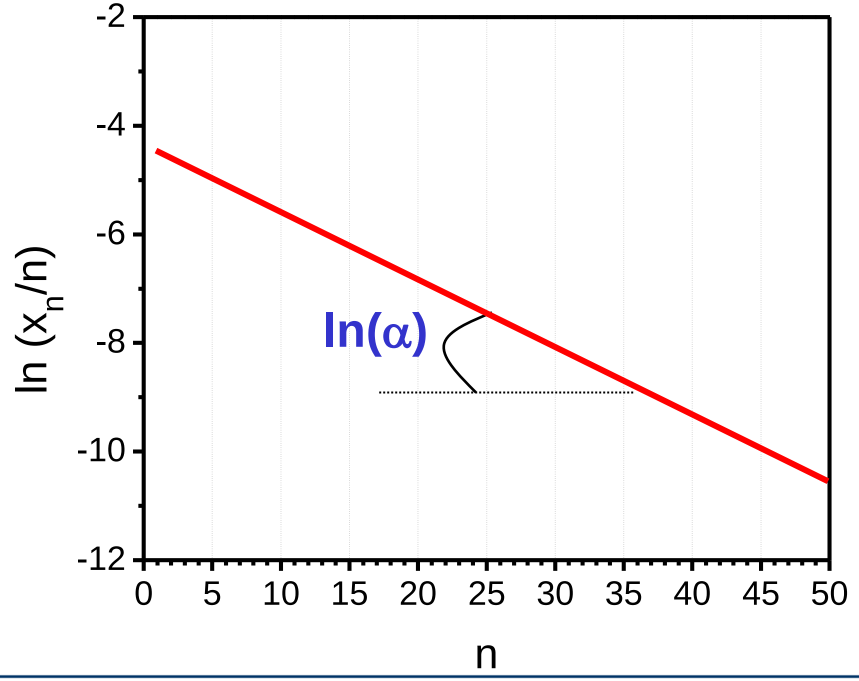
CO $\Rightarrow$ CH_3 $\xrightarrow{\alpha}$ C_2H_5 $\xrightarrow{\alpha}$ .... $\xrightarrow{\alpha}$ C_nH_{2n+1} $\xrightarrow{\alpha}$ ....

$CH_3 \xrightarrow{1-\alpha} CH_4$

$C_2H_5 \xrightarrow{1-\alpha} C_2H_{4+x}$

$C_nH_{2n+1} \xrightarrow{1-\alpha} C_nH_{2n+x}$

	CH_4	C_2H_{4+x}		C_nH_{2n+x}
Probability	$1-\alpha$	$\alpha\,(1-\alpha)$	...	$\alpha^{n-1}\,(1-\alpha)$



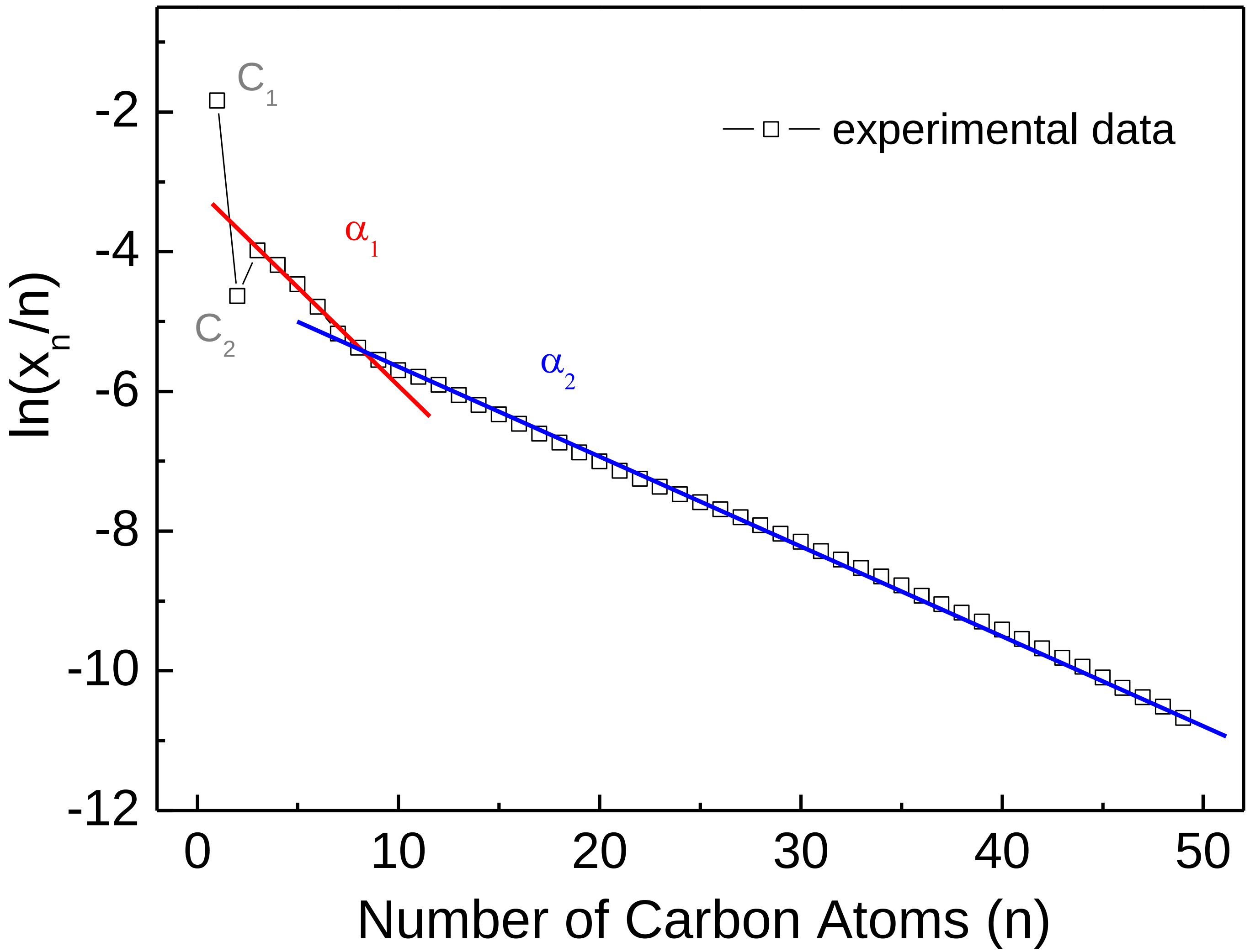
$$\ln\left(\frac{x_n}{n}\right) = \ln\alpha \cdot n + \ln\left[\frac{(1-\alpha)^2}{\alpha}\right]$$

ASF (Anderson Schulz Flory) distribution

α = chain growth probability

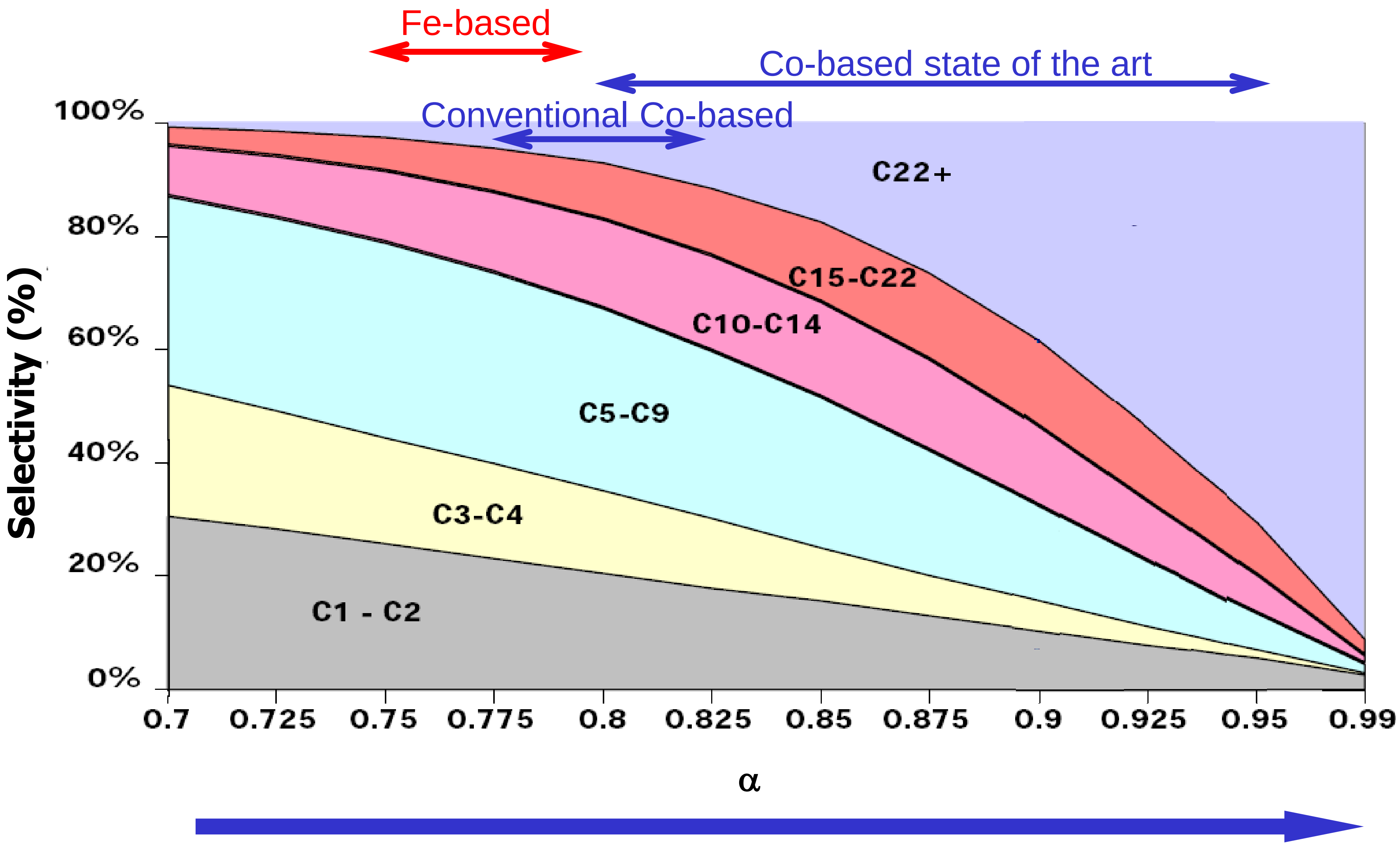
1–α = chain termination probability

Anderson-Schulz-Flory Distribution



C.G. Visconti, E. Tronconi, L. Lietti, R. Zennaro, P. Forzatti, ”Development of a complete kinetic model for the Fischer-Tropsch Synthesis over Co/Al_2O_3 catalysts”, Chem. Eng. Sci., 62, 5038-5043 (2007)

Fischer-Tropsch Synthesis: selectivity

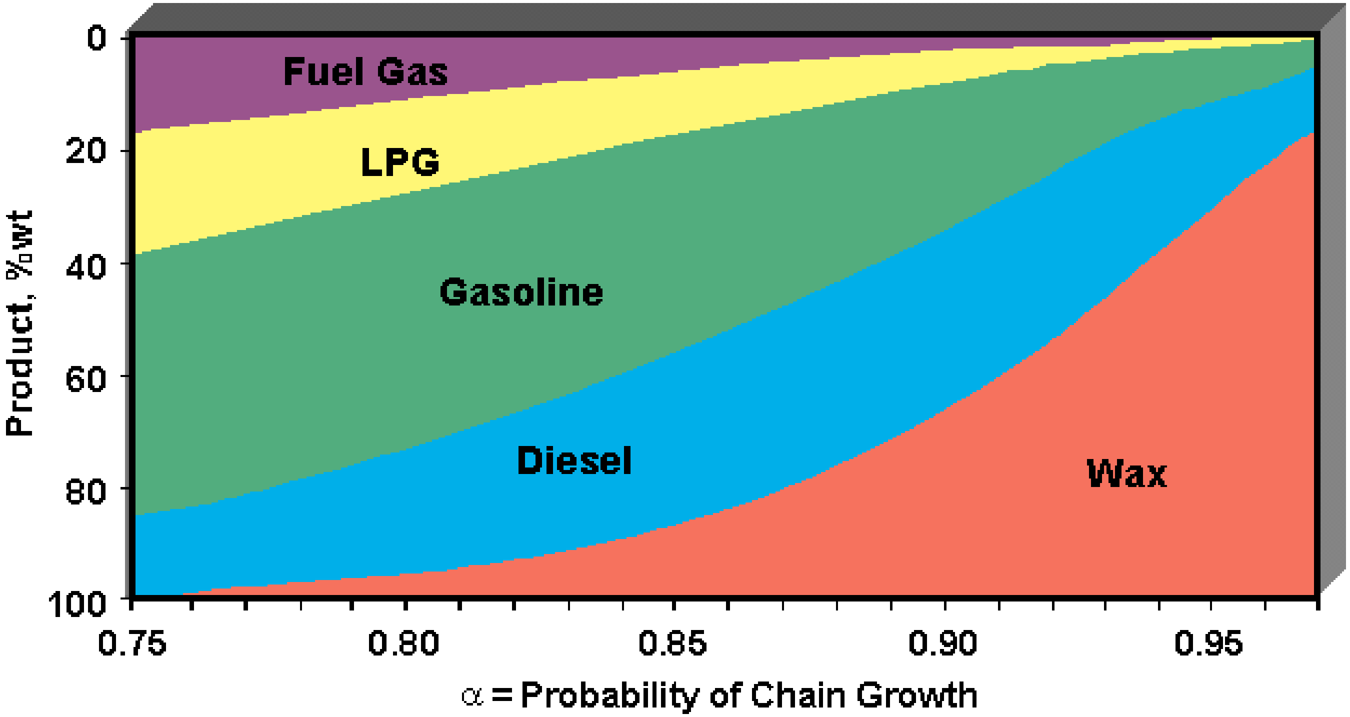


High molecular weight linear paraffins

Products distribution

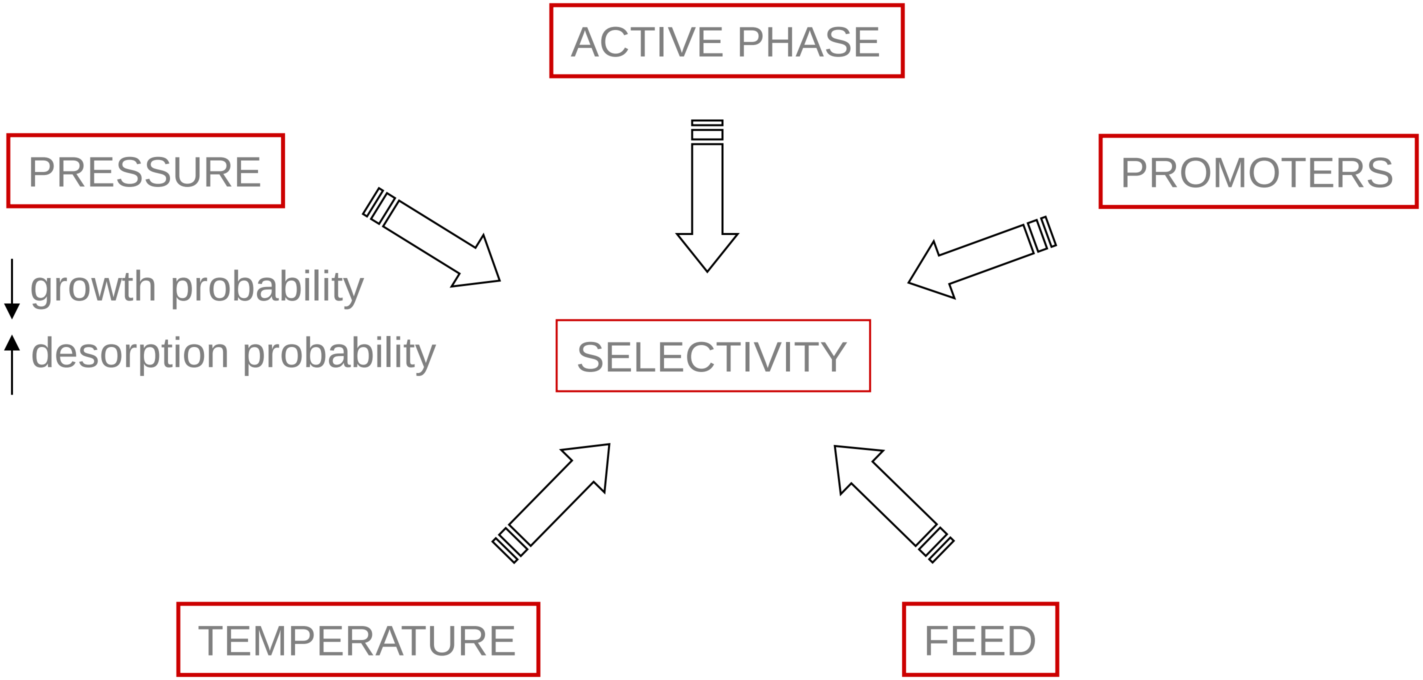
Higher values of the probability factor lead to products with longer carbon chain

The current trend is to work with α between 0.9 and 0.95 in order to obtain higher fractions of diesel and lubricants



FT products distribution as a function of chain growth factor α

Fischer-Tropsch Synthesis: selectivity



ACTIVE PHASE

PRESSURE

PROMOTERS

SELECTIVITY

TEMPERATURE

FEED

P_{CO}↓ ↓ growth probability

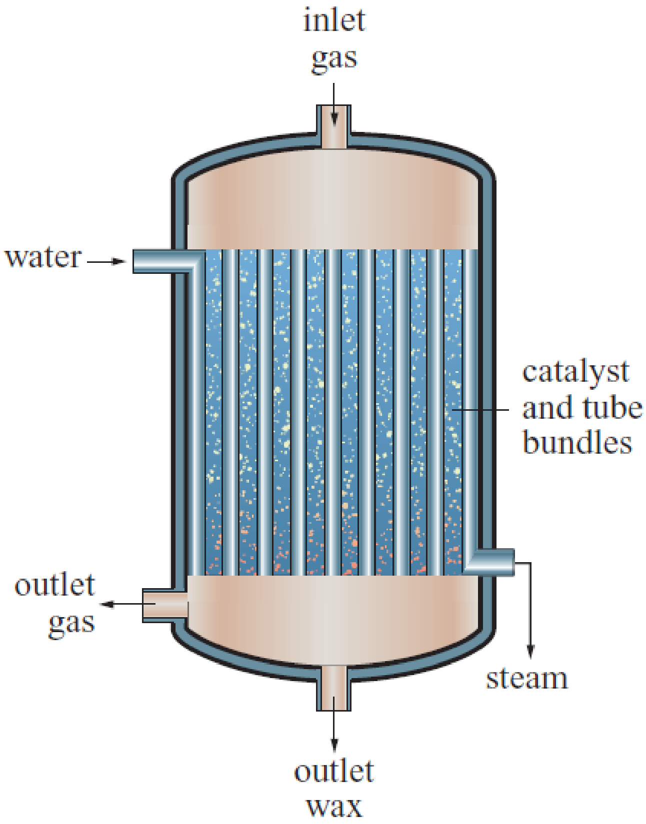
↑ desorption probability

T↑ hydrogenated products with lower MW

carbon deposits

- H_2/CO ratio

Fischer-Tropsch Synthesis: reactors



MTFBR = **M**ulti **T**ubolar **F**ixed **B**ed **R**eactor

- up to 30’000 tubes (lenght up to 12 m, I.D. 1-2”)
- up to 5’800 bpd per reactor

1) It has been used in the past for the Fe-LTFT from coal:
   - in Germany during the second world war
   - Sasol I (Arge), Sud Africa, 1950-1985 (700 bpd/reactor)

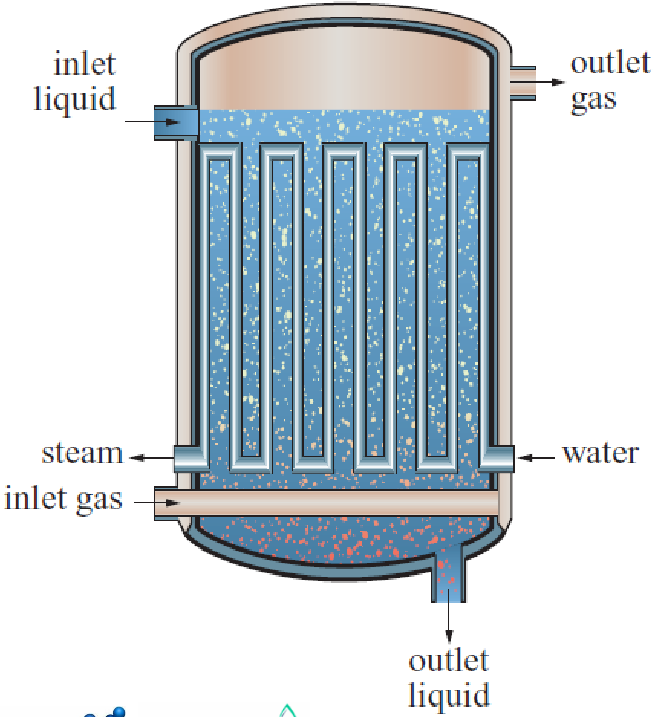
2) Currently operating, since 1993, Shell Bintulu (Malaysia)
Co-LTFT from gas, 3’675 bpd/reactor (tot: 4 reactors)

3) Currently operating, Shell Pearl (Qatar)
Co-LTFT from gas, 5’800 bpd/reactor (tot 24 reactors)

DISADVANTAGES:

a) poor heat dissipation from the reaction zone
---for Co-LTFT a liquid phase recycle is requested---
b) high pressure drop
c) material diffusion limitations
d) difficulty in catalyst charge and dischrge operations
e) Elaborated (trickle-bed) and expensive

Fischer-Tropsch Synthesis: reactors



SBCR = **S**lurry **B**ubble **C**olumn **R**eactor

- height up to 60m, O.D. up to 10m
- up to 17’000 bpd/reactor

Currently operating:

- Sasol I, Sud Africa, since 1993

- Qatar Petroleum and Sasol (Oryx), since 2008
17’000 bpd/reactor (2 reactors)

ADVANTAGES:

a) isothermicity
b) reduced pressure drop
c) catalyst can be replaced on-line
d) more economic than MTFBR

DISADVANTAGES:

a) catalyst crushing
b) Backmixing
c) only for large-scale application

GtL initiatives in the world

Property owner	Project	Location	FT Technology	Capacity (kbpd)	Cost (G$)	Cost ($/bpd)	Status
Chevron (75%) NNPC (25%)	Escravos EGTL	Nigeria	**SBCR**	34	1.7	50	under construction since 2005 expected to end in 2011 commissioning since 2012/13
Qatar Petroleum (70%) Shell (30%)	Pearl GTL	**Qatar**	MTFBR	70+70	6	43	under contruction since 2005 ended in 2010
Qatar Petroleum ExxonMobil	-	**Qatar**	**SBCR**	154	7	45	project announced in 2004 expected to end in 2011 **cancelled in 2007**
Qatar Petroleum (51%) SasolChevron (49%)	Oryx II Oryx III	**Qatar**	**SBCR**	130	4.5	**35**	expected to end in 2009 commissioning not before 2012
Qatar Petroleum Marathon Oil	-	**Qatar**	**SBCR**	120	-		project delayed for three years
Qatar Petroleum ConocoPhillips	-	**Qatar**	**SBCR**	80+80	-		expected to end in 2010 commissioning not before 2013


Escravos EGTL


Pearl GTL

Existing commercial GtL plants

PetroSA
StatoilHydro

Start up: 1992
Location: South Africa
Capacity (bbl/d): 22’500
Catalyst: Fe
Process: HTFT
Reactor: CFBR

Start up: 1993
Location: Malaysia
Capacity (bbl/d): 14’500
Catalyst: Co
Process: LTFT
Reactor: MTFBR

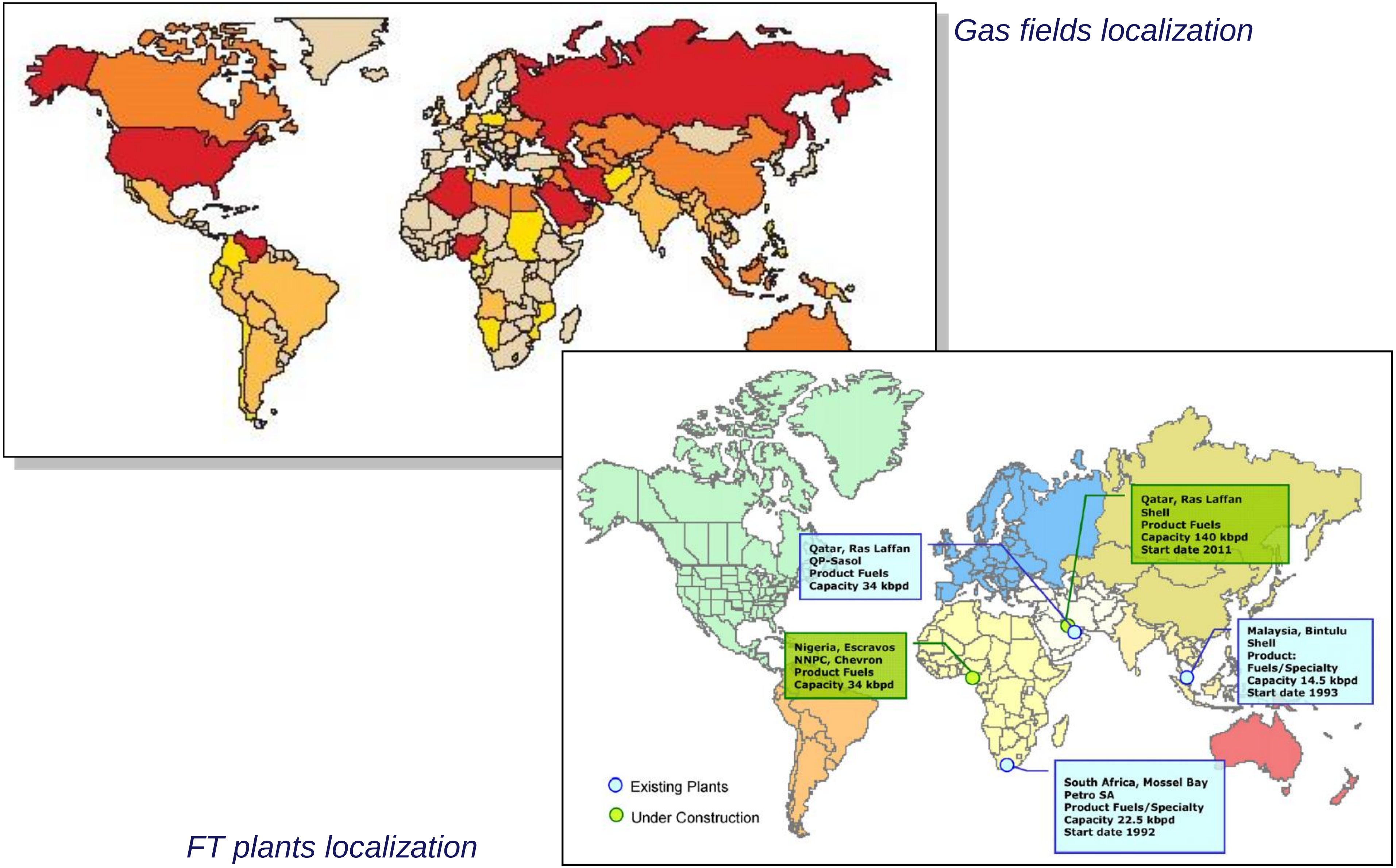
sasol
reaching new frontiers

قطر للبترول
Qatar Petroleum

ORYX GTL
QP - SASOL joint venture

Start up: 2007
Location: Qatar
Capacity (bbl/d): 34’000
Catalyst: Co
Process: LTFT
Reactor: SBCR

A close correspondence…



Gas fields localization

FT plants localization

Qatar, Ras Laffan
QP-Sasol
Product Fuels
Capacity 34 kbpd

Qatar, Ras Laffan
Shell
Product Fuels
Capacity 140 kbpd
Start date 2011

Nigeria, Escravos
NNPC, Chevron
Product Fuels
Capacity 34 kbpd

Malaysia, Bintulu
Shell
Product:
Fuels/Specialty
Capacity 14.5 kbpd
Start date 1993

South Africa, Mossel Bay
Petro SA
Product Fuels/Specialty
Capacity 22.5 kbpd
Start date 1992

The Shell case

- **SMDS = Shell Middle Distillate Synthesis**

1973 *Start of SMDS research*

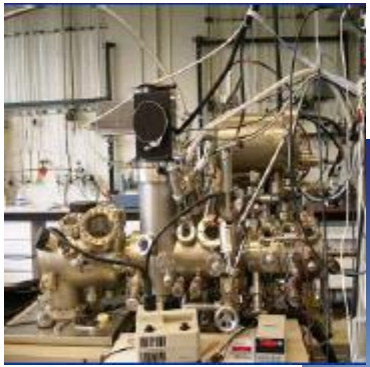
1983 *Pilot plant construction*

1993 *Start-up of the industrial plant in Malaysia*

1997 *ASU Explosion*

2003 *New “Debottlenecking”*

2011 *Start-up of the industrial plant in Qatar*



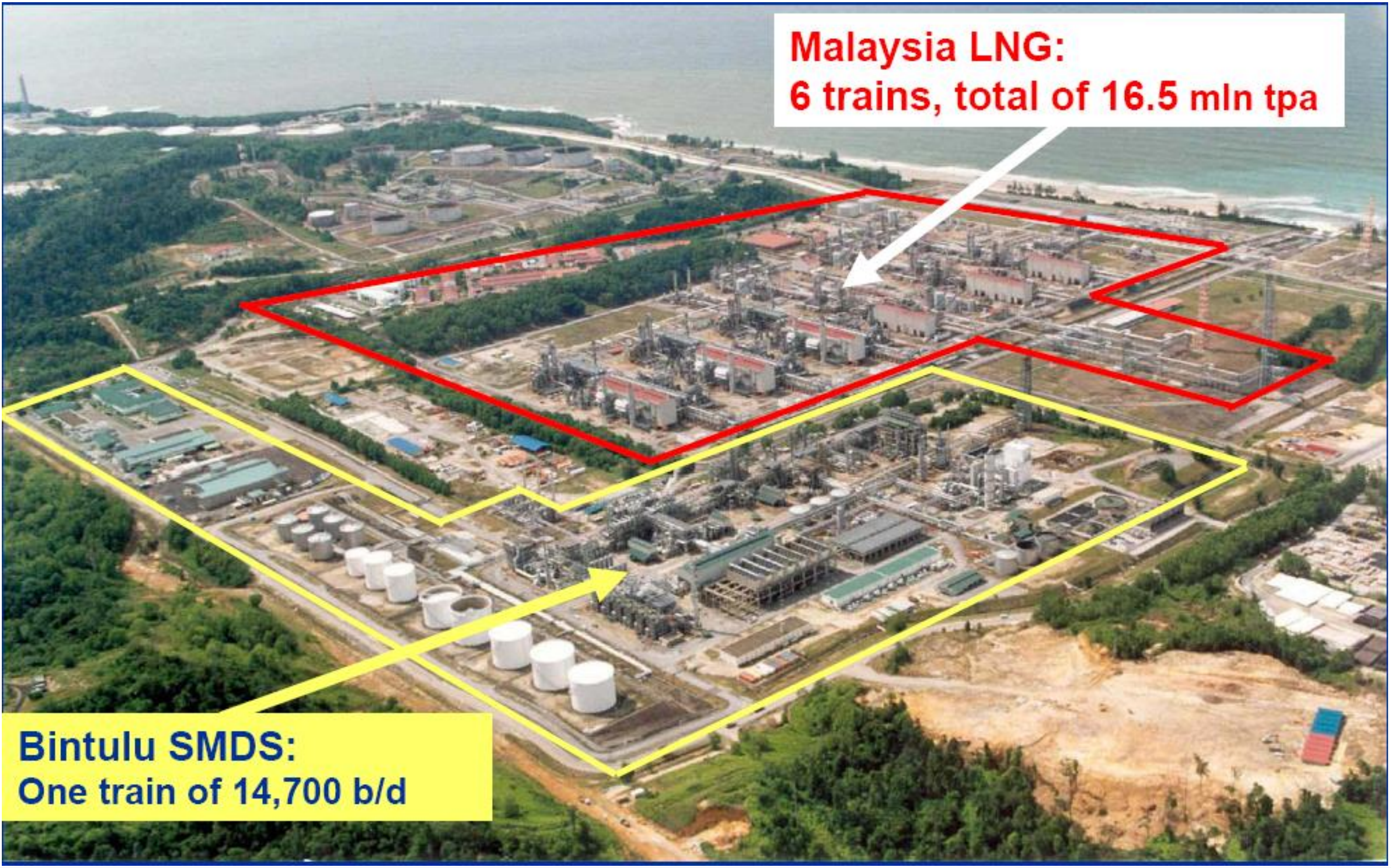
1973

1983

1993

ASU = *Air Separation Unit*

Shell in Malaysia



Launch of Shell-VW GTL Test : Berlin, 6th May 2003

Synthetic diesel based on SMDS Gasoil - Bintulu

FTS Pearl plant

Aerial view of Shell’s Pearl GtL plant, built in Qatar in 2010

Pearl GtL: quantitative data

Shell finished to build Pearl GtL plant in the Qatar desert in 2010, while the full production started in 2012.

It was built to exploit a $2.5\cdot10^{14}$ m^3 natural gas well in Qatar gulf.

28 Mm^3 of natural gas are daily fed to the two trains of the plant, where they are converted into 140’000 barrels of GtL products and 120’000 barrels of LNG and ethane.

The specific area of catalyst contained in all 24 reactors is more than 200 Mm^2, 18 times the surface of Qatar.

Water system treats 45000 m^3 of water per day, the equivalent of a city with 140,000 persons.

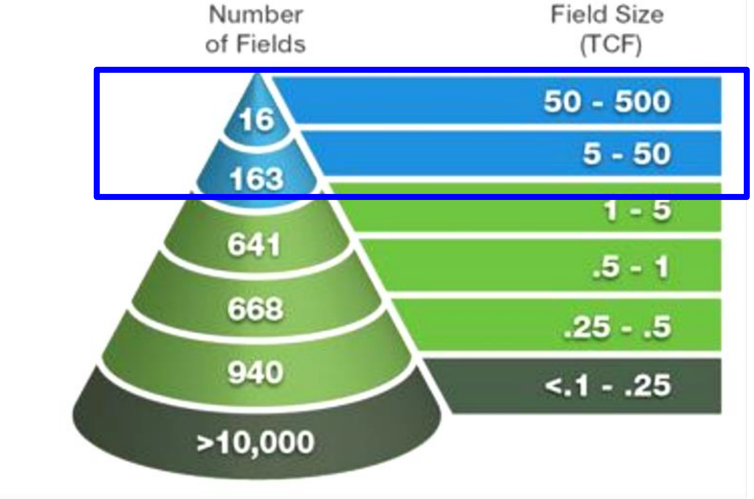
Initial investment has been in the order of 19 billion US$. The only fuel market, assuming an average price for Shell V-Power=2€/L, grants revenues higher than 33 M€/d.

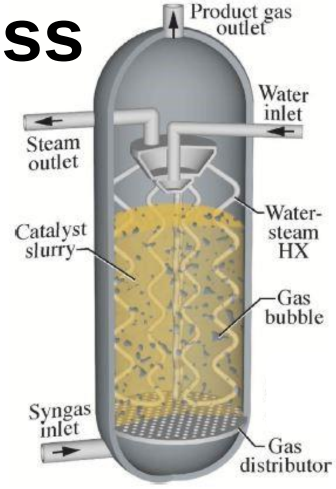
Shell in Qatar

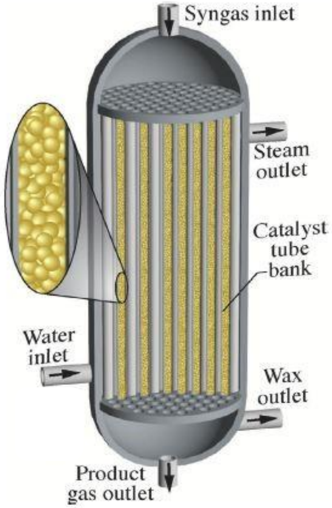
Pearl 1   Pearl 2

Gas to Liquid (GtL) process

≈6% of the total gas fields in the world





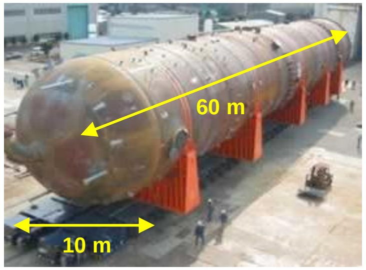


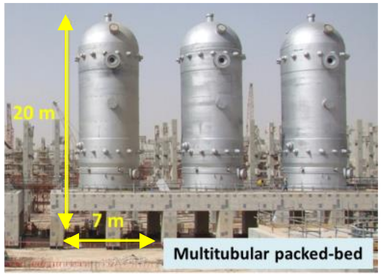
Isothermal, no intraporous resistances

Modular, egg-shell catalyst

Slurry Bubble Column Reactor

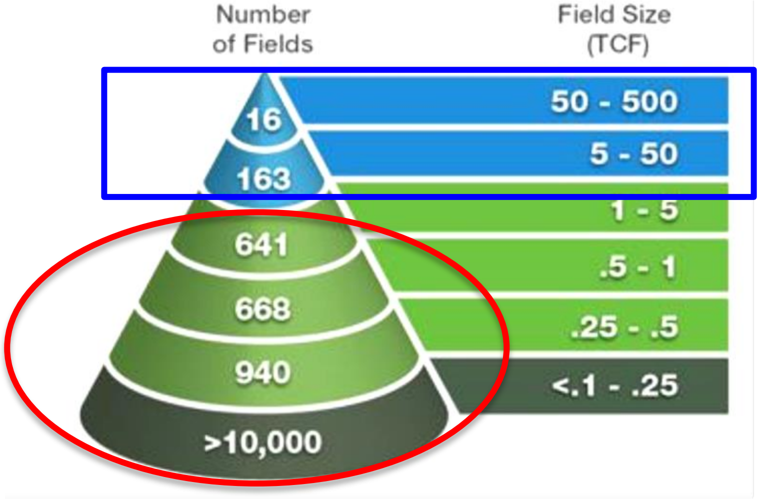
Multitubular Fixed Bed Reactor



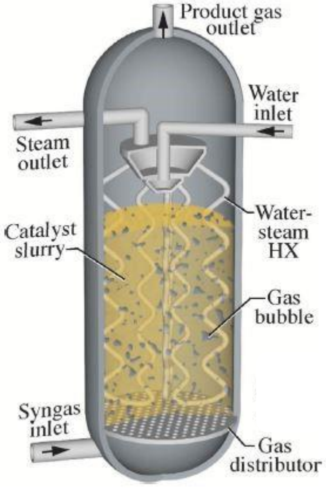


Compact GtL?

≈6% of the total gas fields in the world



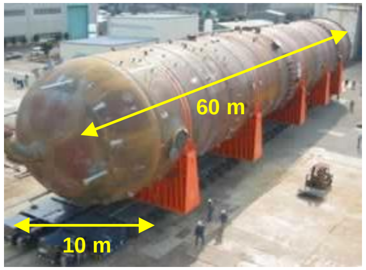
«compact-scale GTL» for associated & remote natural gas reserves

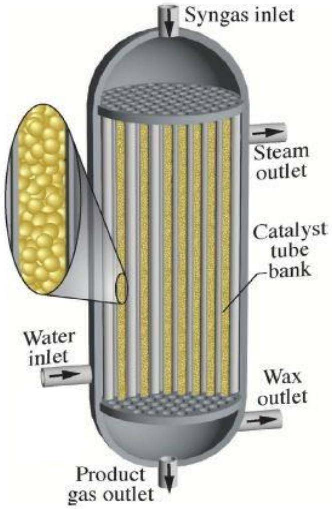


Not modular and not suitable for small-scale, low productivity

Isothermal, no intraporous resistances

Slurry Bubble Column Reactor

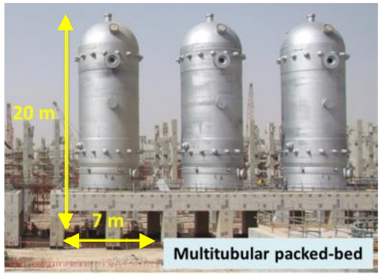




Thermally unmanageable on small-scale

Modular, egg-shell catalyst

Multitubular Fixed Bed Reactor

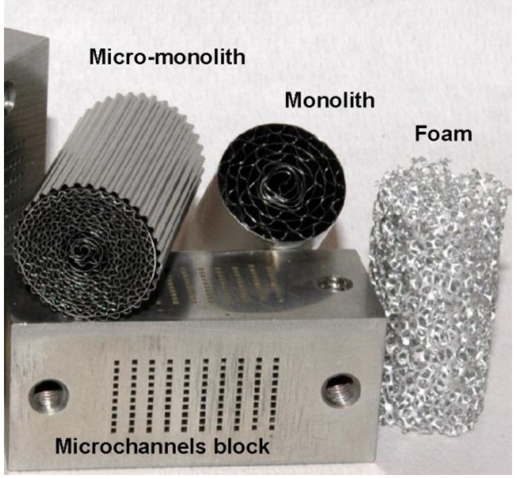


How to manage the heat removal in compact PBR??

The FTS is highly exothermal ($\Delta H^0_R \cong -165$ kJ/mol$_{CO}$) an inefficient T-control would lead to:

- Presence of hot-spots
- Strong axial and radial T-gradients

- Worsening of the catalyst selectivity
- Fast catalyst deactivation
- Thermal runaway of the reactor!



Improved Heat Transfer
☺

Conductive Structured Catalysts:
From slow convective mechanism to the fast heat conduction in the solid matrix

Almeida et al. Cat. Today 215(2013)103

Visconti et al. Chem. Eng. J. 171 (2011)1294

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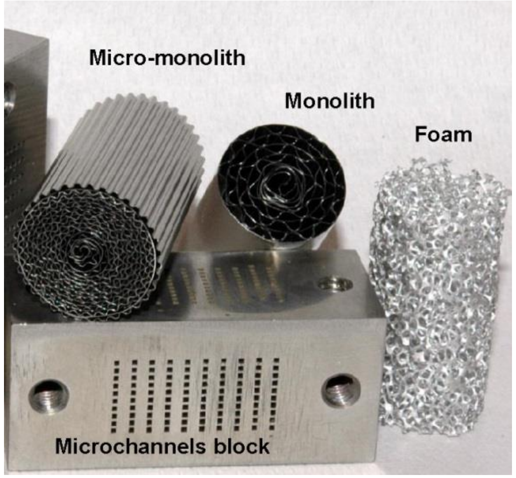


Improved Heat Transfer

☺

Conductive Structured Catalysts:

From slow convective mechanism to the fast heat conduction in the solid matrix

Washcoated systems

☹

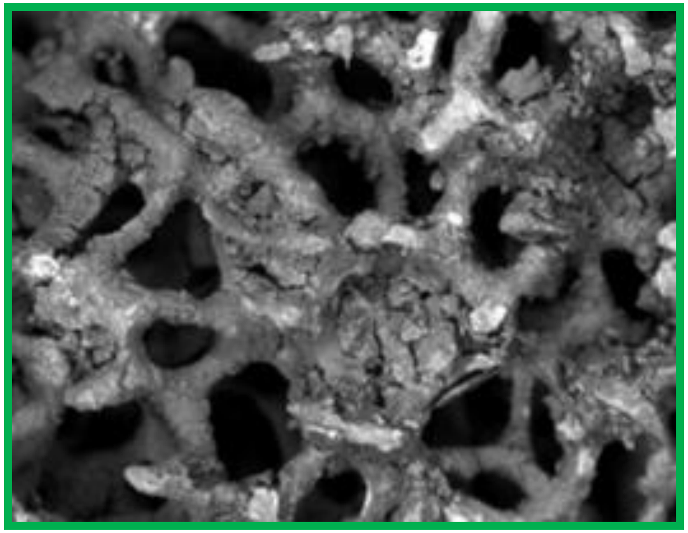
The catalyst inventory is much less than in a packed bed of catalyst pellets

Almeida et al. Cat. Today 215(2013)103

Visconti et al. Chem. Eng. J. 171 (2011)1294

How to manage the heat removal in compact PB??

Development of more appropriate washcoating techniques:
the macropores of the foam may be partially occluded



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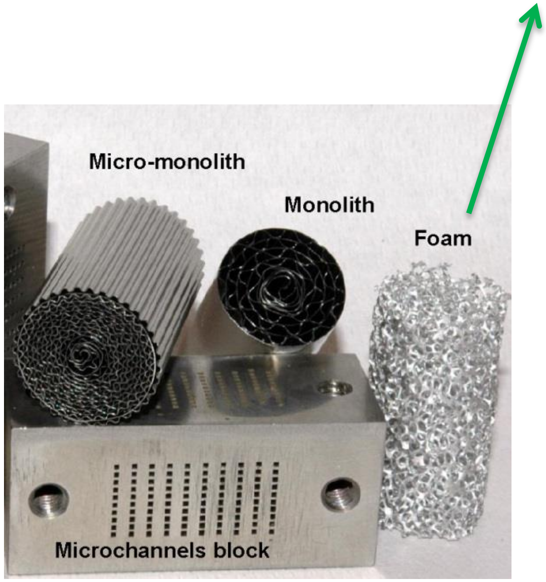

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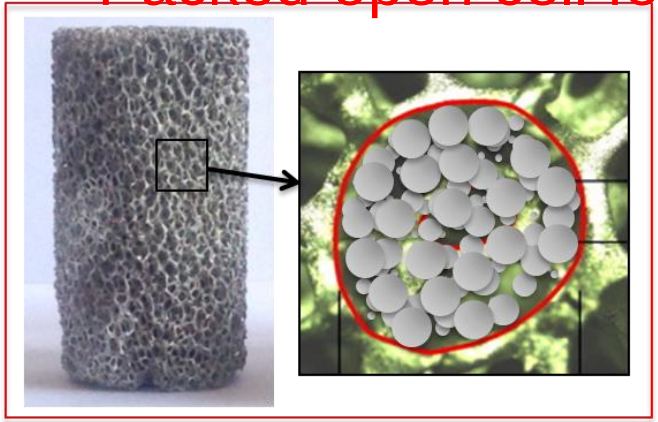
How to manage the heat removal in compact PB??

Packed-open cell foams



Improved Heat Transfer

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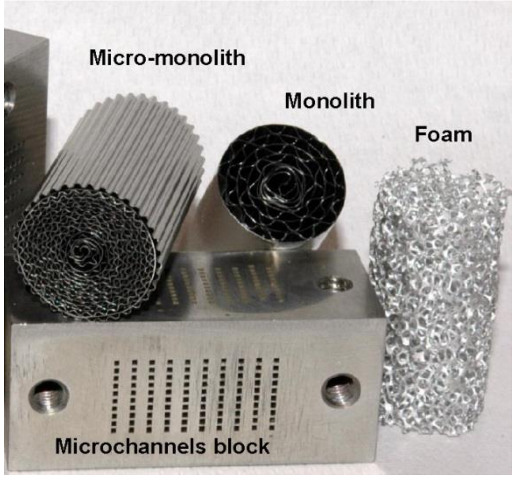
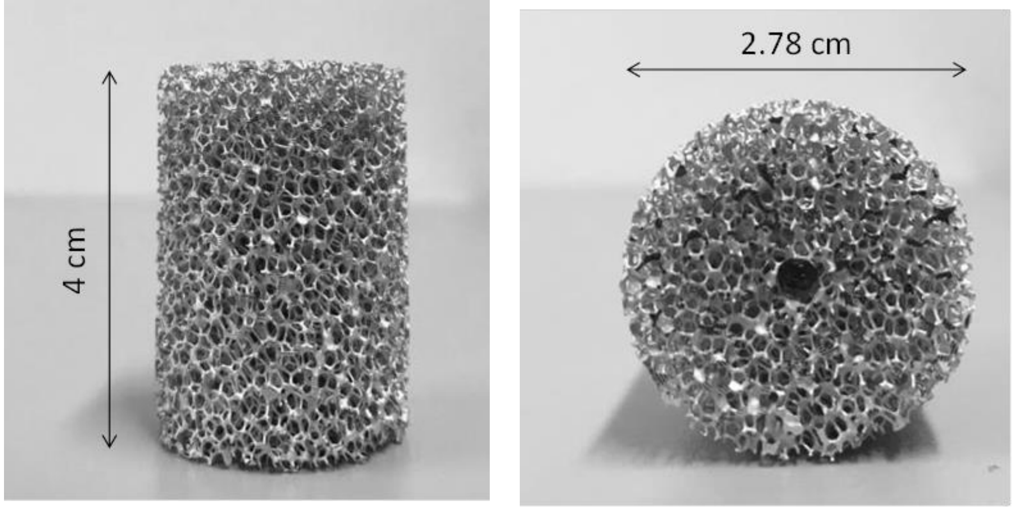


Patent application WO/2015/033266

Almeida et al. Cat. Today 215(2013)103

Visconti et al. Chem. Eng. J. 171 (2011)1294

Open cell Al-foams packed with cat.pellets for the FTS



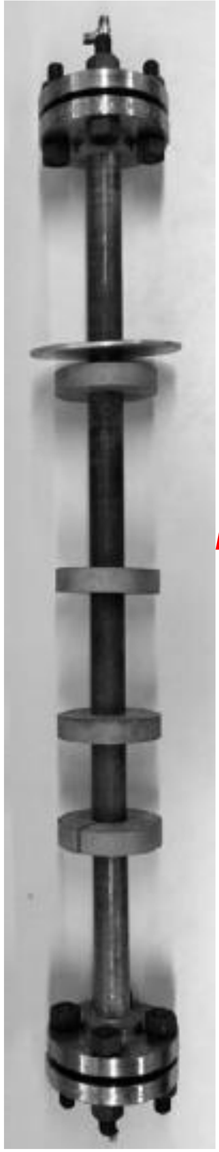
40 ppi ($\varepsilon_{foam} \approx 0.906$; $d_{cell} \approx 2$ mm) provided by ERG

Packed with Pt-promoted highly active Co-based catalyst (d_{pellet}= 300 μm)
23wt.%Co/0.1wt.%Pt/$Al_2O_3$$^{(s)}$

Comparison of the catalytic performances with the packed bed reactor

European Research Council
Established by the European Commission

Experimental:



Packed-foam reactor

Catalyst weight: 7.2 g

Cat.Vol.Den.= 0.63 g/cm^3

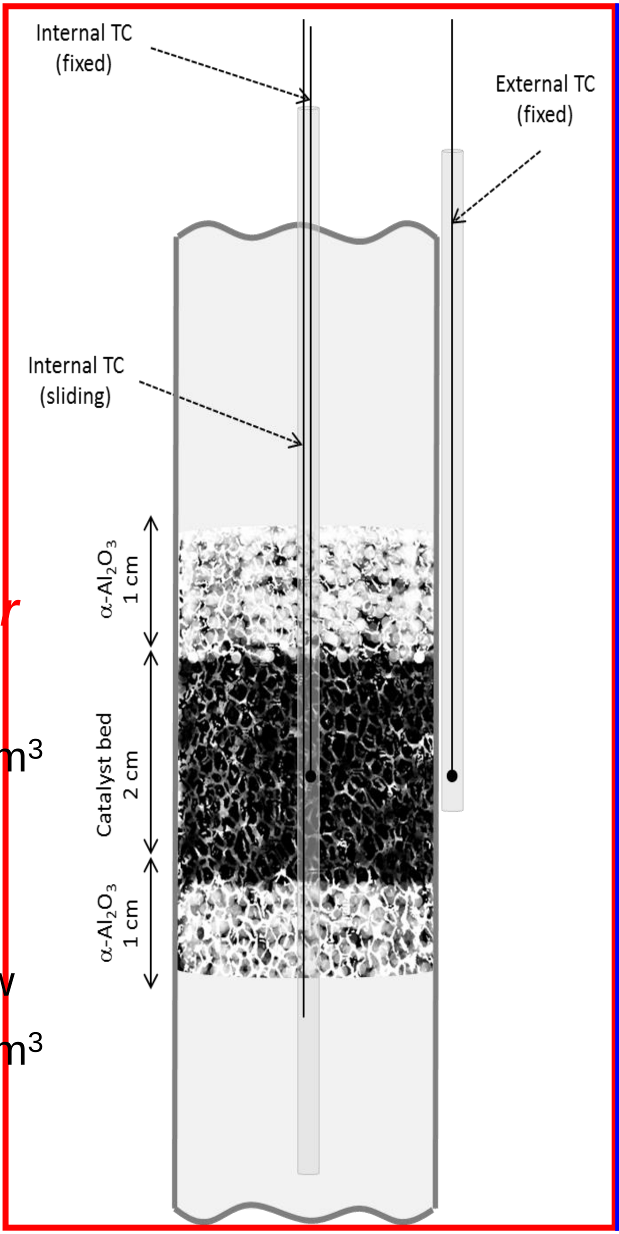
Packed-bed reactor

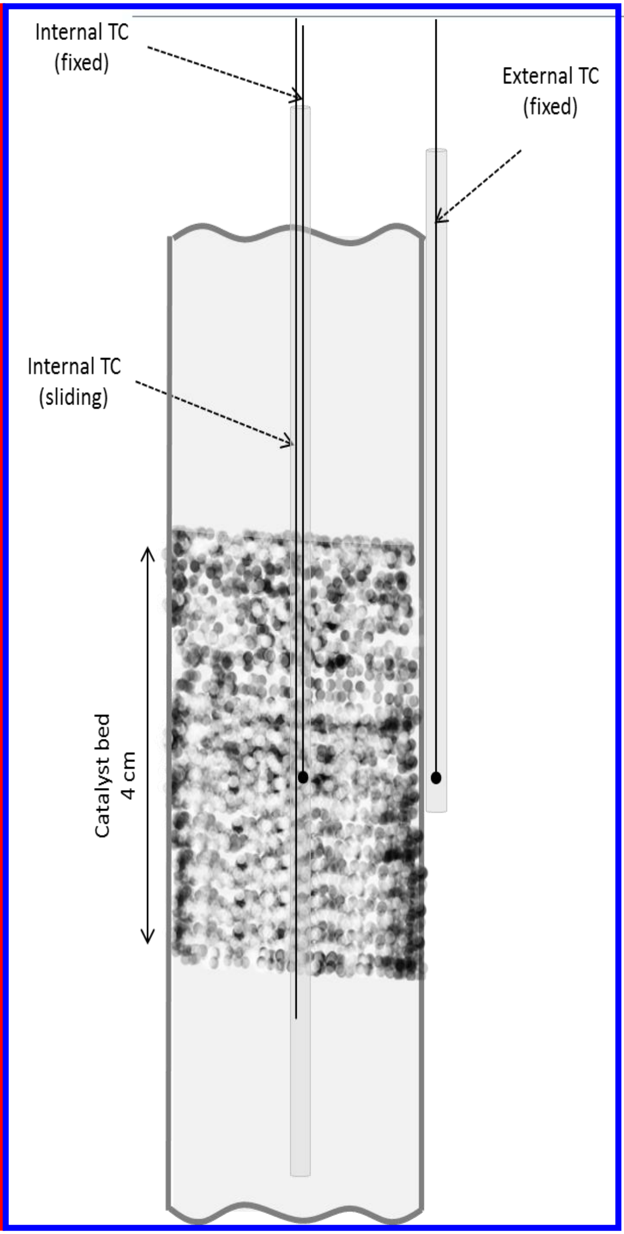
Cat:α-Al_2O_3 = 1:1.7 w/w

Cat.Vol.Den.= 0.29 g/cm^3

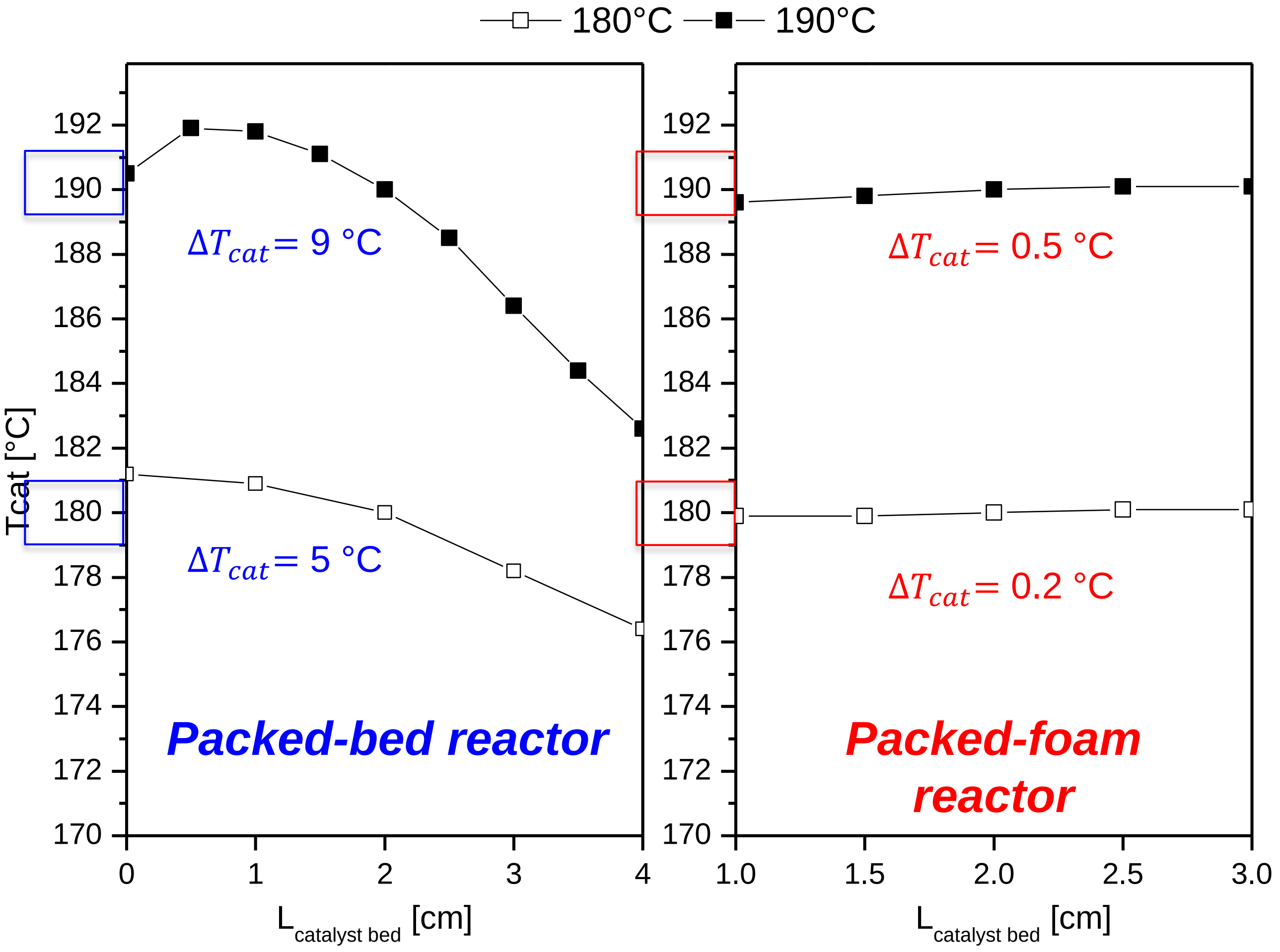
European Research Council

Established by the European Commission

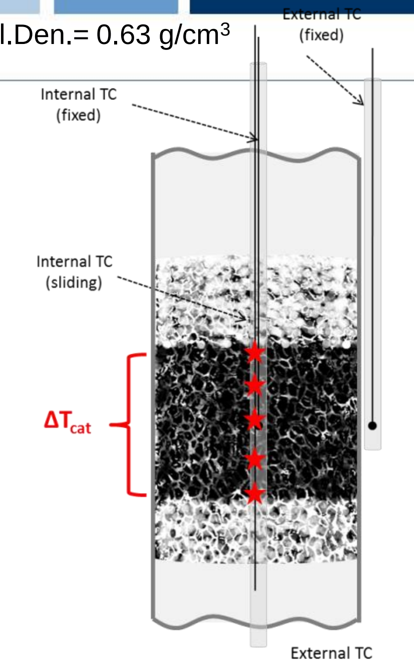




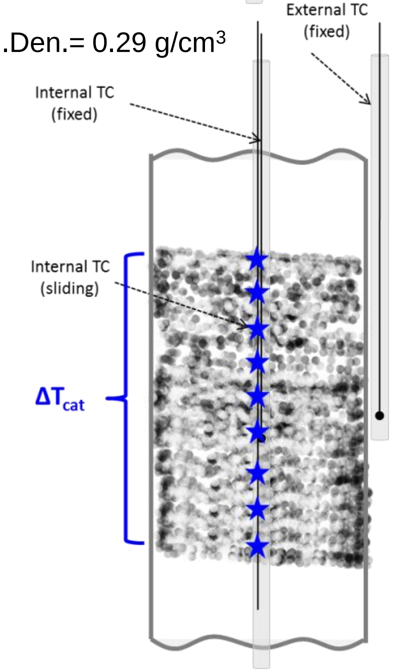
T-Profiles: Packed-foam vs Packed-bed



Cat.Vol.Den.= 0.63 g/cm^3



Cat.Vol.Den.= 0.29 g/cm^3



P= 25 bar, H_2/CO^{in}= 2 mol/mol, GHSV= 6410 cm^3(STP)/h/g_{cat}, inerts= 24 vol.%. T = 180-190°C

$$\Delta T_{cat} = T_{max} - T_{min}$$

European Research Council

Established by the European Commission

Fischer-Tropsch synthesis: lessons learnt

✓ Fischer-Tropsch Synthesis:

- can help us to exploit efficiently the best available fossil fuel (NG)
- can help us to make clean Diesel & transportation fuels
- can help us to reduce gas flaring and related pollution

but also:

- supported Hitler’s war efforts during WWII
- supported South Africa’s economy during the Apartheid regime

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✓

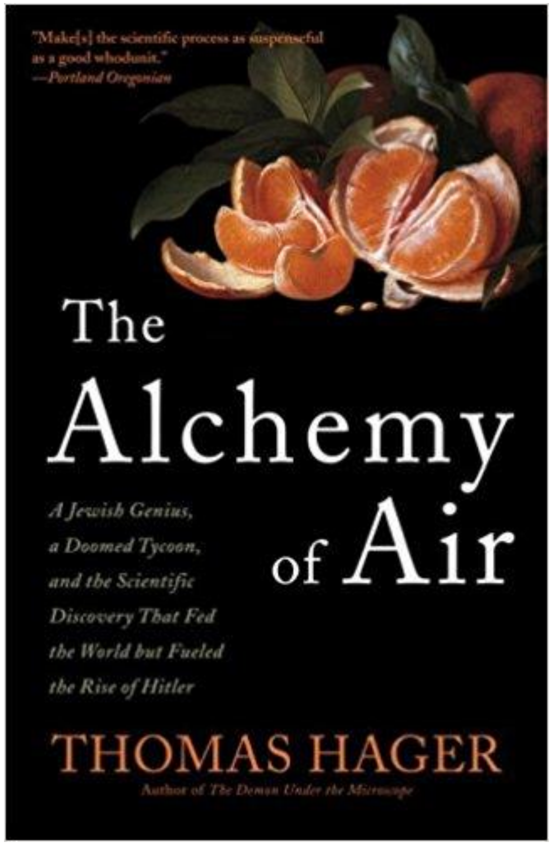
✓ Catalysis is crucially important!

✓

FTS: Recommended reading

- H. Schulz, «Short history and present trends of Fischer-Tropsch synthesis», Appl. Catal. A: General 186 (1999) 3
- A.N. Stranges, «A History of the Fischer-Tropsch Synthesis in Germany 1926-45», Studies in Surf. Sci. & Catalysis (B.H: Davis and M.L. Occelli, Ed.s), 2007
- H.H. Storch, N. Golumbic, R.B. Anderson, «The Fischer-Tropsch and related syntheses», J. Wiley, NY, 1951
- F. Zakaria, «Gas naturale al posto del petrolio: Come cambierà il futuro del mondo», Corriere della Sera, 31 marzo 2012
- W. Liss, “A Golden Age of Natural Gas”, Chem. Eng.ng Progress, August 2012, p. 35

Another German catalytic process that changed the world



The Alchemy of Air: A Jewish Genius, a Doomed Tycoon, and the Scientific Discovery That Fed the World but Fueled the Rise of Hitler

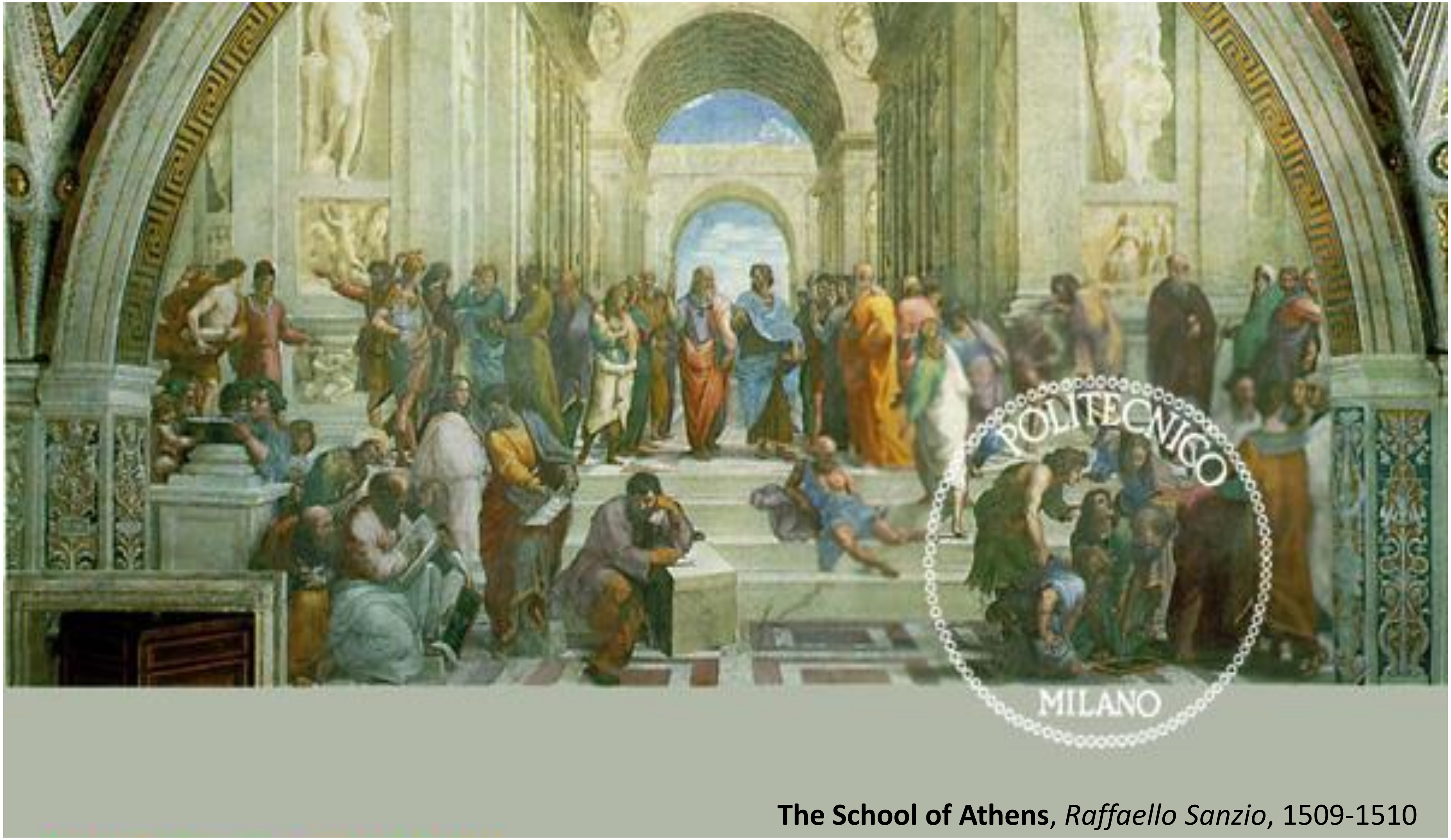
by Thomas Hager
Broadway Books, New York (2009)

$$\boxed{N_2 + 3\,H_2 <==> 2\,NH_3}$$

«… the story of two men who invented a way to turn air into bread…»

The discovery of the **Haber-Bosch** process for ammonia synthesis (1913) saved the world from starvation, but was used also to make explosives that killed millions of people during WW1.

Thank you for your kind attention!



The School of Athens, *Raffaello Sanzio*, 1509-1510