The refinery of the future

A catalytic approach

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BRAZIL
There is a magic made by melody:
A spell of rest, and quiet breath, and cool
heart, that sinks through fading colors deep
to the subaqueous stillness of the sea,
and floats forever in a moon-green pool,
held in the arms of rhythm and of sleep.
Elizabeth Bishop
(American poetess)


http://go.to/funpic

Introduction

The main challenges of the refining industry nowadays are:

- More stringent environmental regulation;
- Growing demand for cleaner fuels;
-Traditional raw material (crude oil) of inferior quality;
-Uncertainties regarding the final choice of the customers;
- Growing pressure on the industries to reduce the emission of greenhouse gases;
-Globalisation;
-Maintenance of profitability.

Introduction

The increasing requirement for clean-burning fuels is drastically changing the traditional goals of the refining industry

The generation of cleaner fuels may be achieved by introducing further processing capacity in refineries, such as desulphurisation; however, these new units require energy and lower thermal efficiency

Hence, an improvement in air quality during the use of cleaner diesel may come at the expense of higher greenhouse-gas emissions during such diesel production

The refinery must search for intelligent alternative solutions to meet all those requirements.

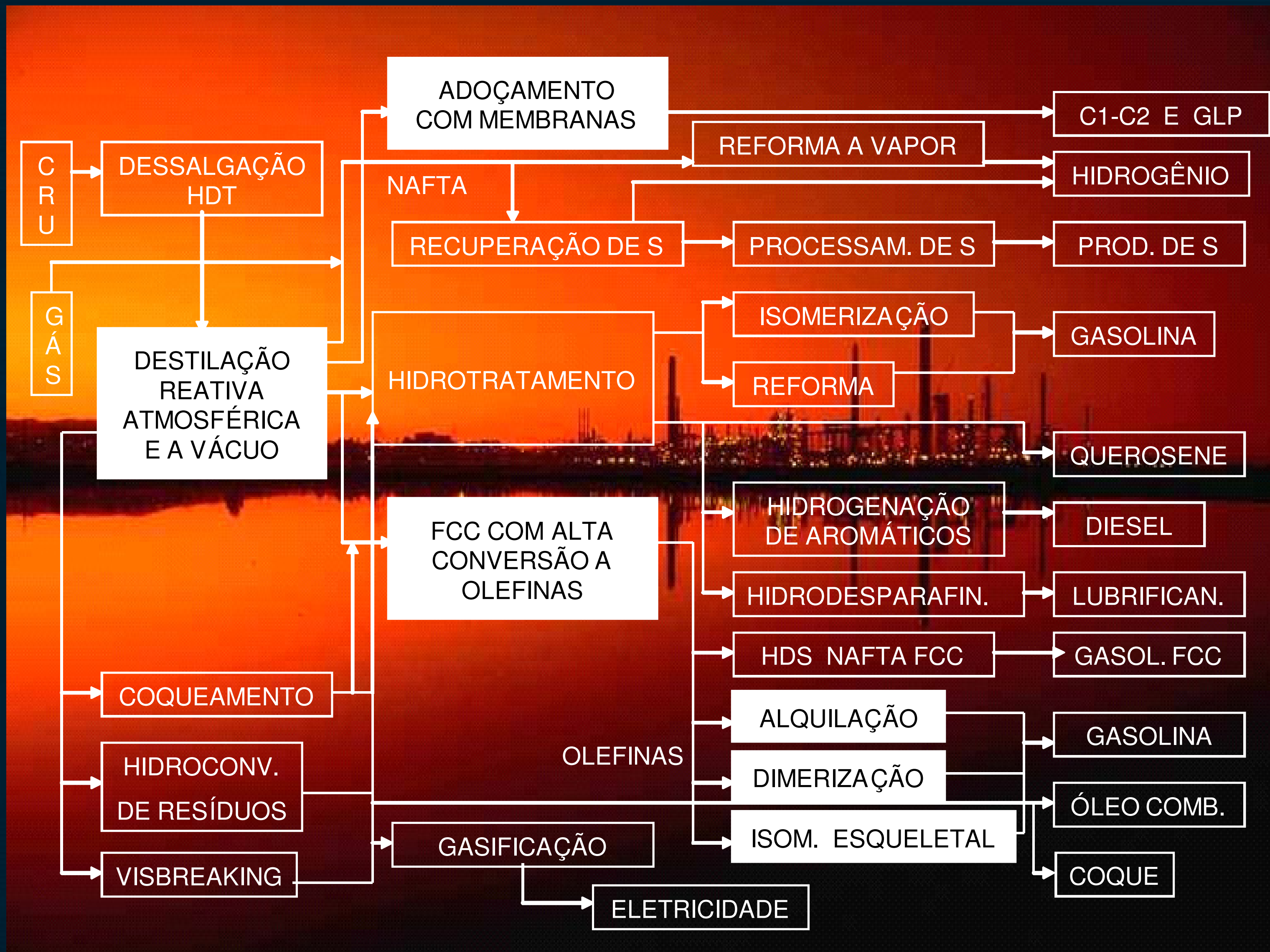
Therefore, the search for alternative feedstock such as natural gas or biomass has become a must in order to cope with more stringent regulations. Also, alternative refining routes such as synthetic fuels are striking back.

In this new peculiar scenario, catalysts play an outstanding role

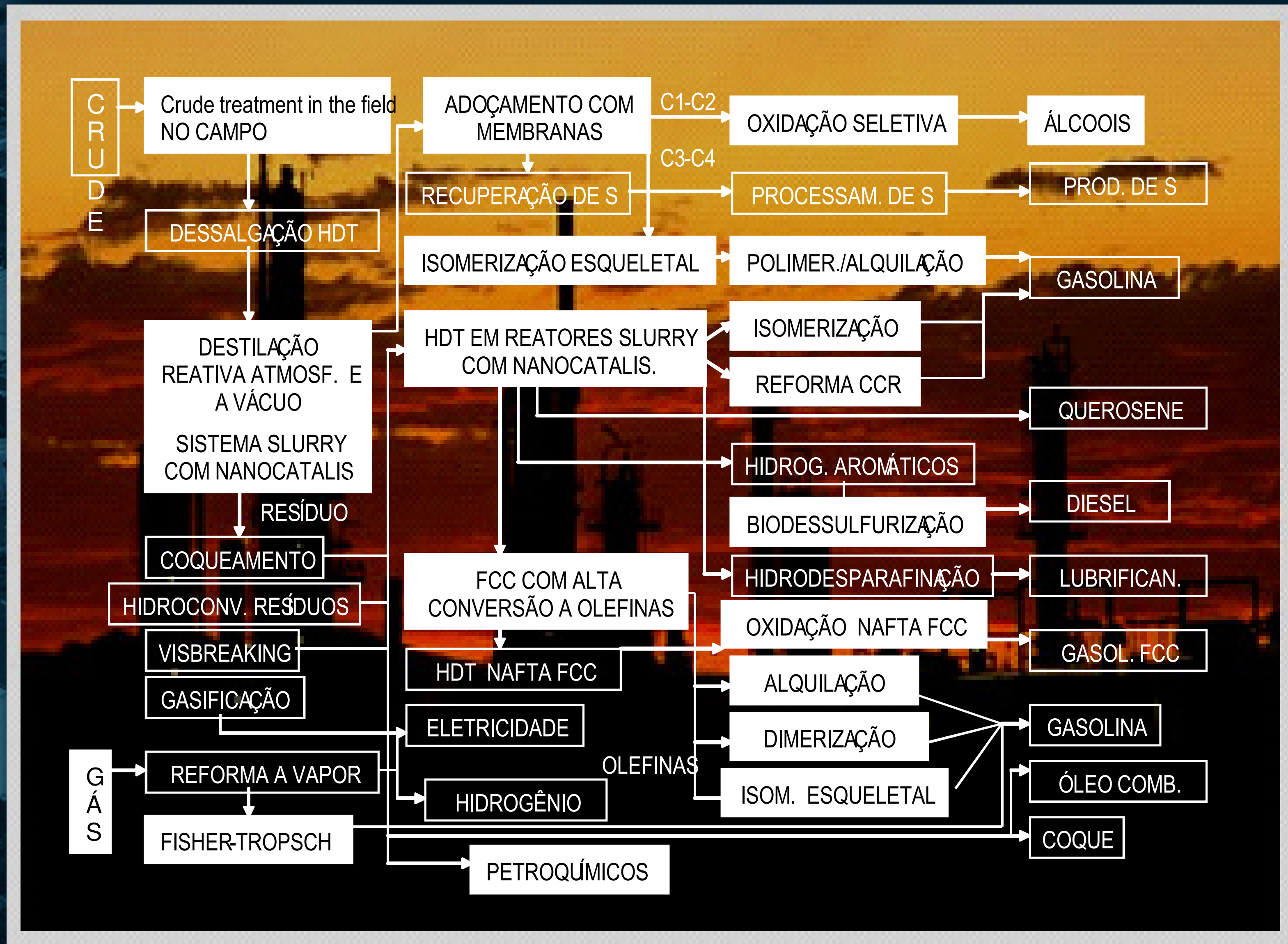
Scenarios

Scenario	Raw materials	Market	Process	Focus
Inertial (Prevailing vision among refiners)	Increasing proportion of heavy crude oils	- Traditional fuels with more stringent regulation - Growing market	Traditional	Higher profitability
Incremental (Refiners, contractors, catalyst industry, car industry and government)	- Heavy oils - Natural gas	- Potential use of Hydrogen as fuel - Growing market	- Use of traditional technologies; - More compact equipment - Oil pretreatment in the production fields	Integration with petrochemistry
Innovative	- Heavy oils - Natural gas - Coal - Biomass - Residues	Brand new automotive technologies	-Radical change in the technological paradigms -Renewable energy - Gasification of crude oil	Minimum environmental impact

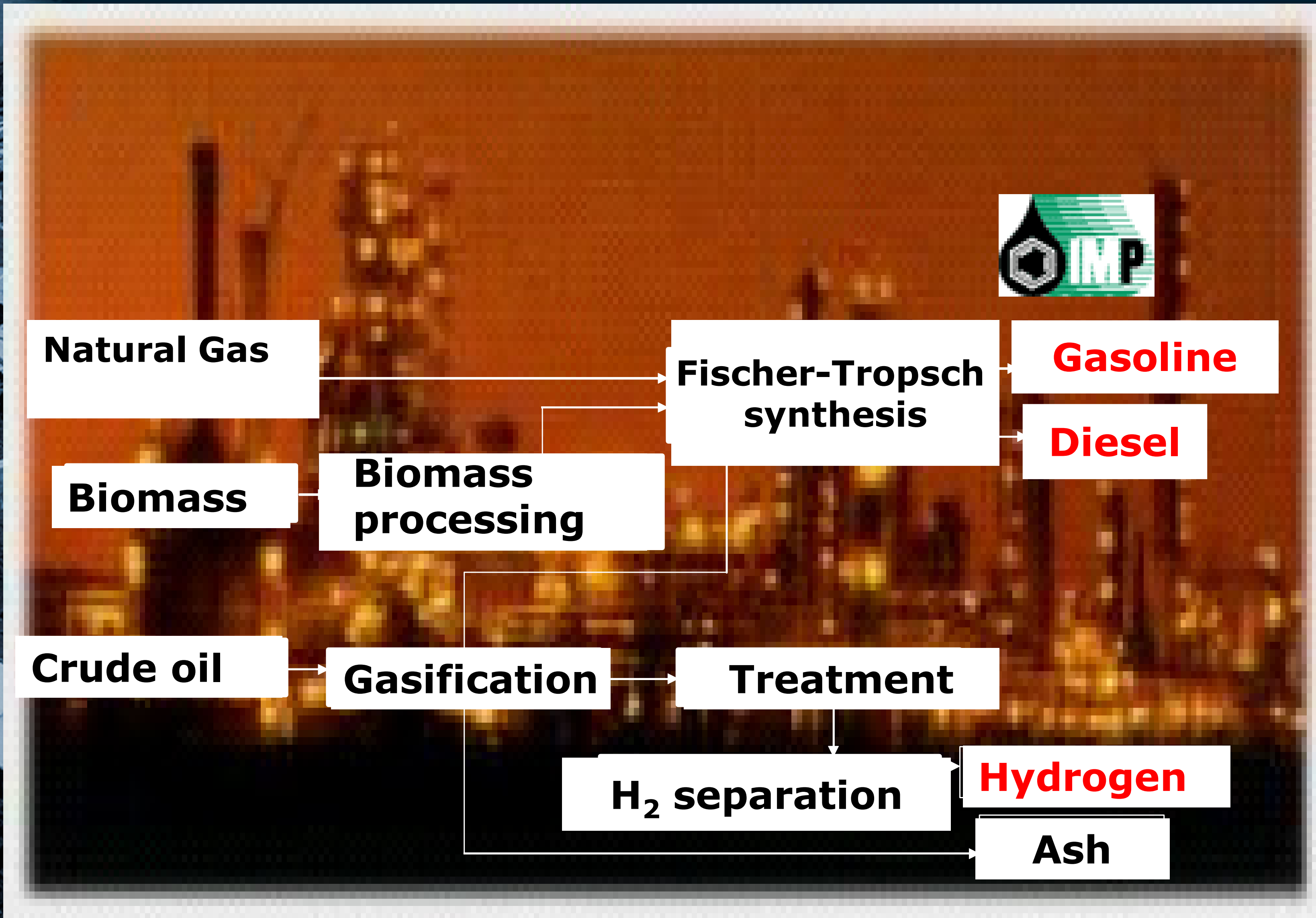
Refining Scheme for an Inertial Scenario



Refining Scheme for an Incremental Scenario



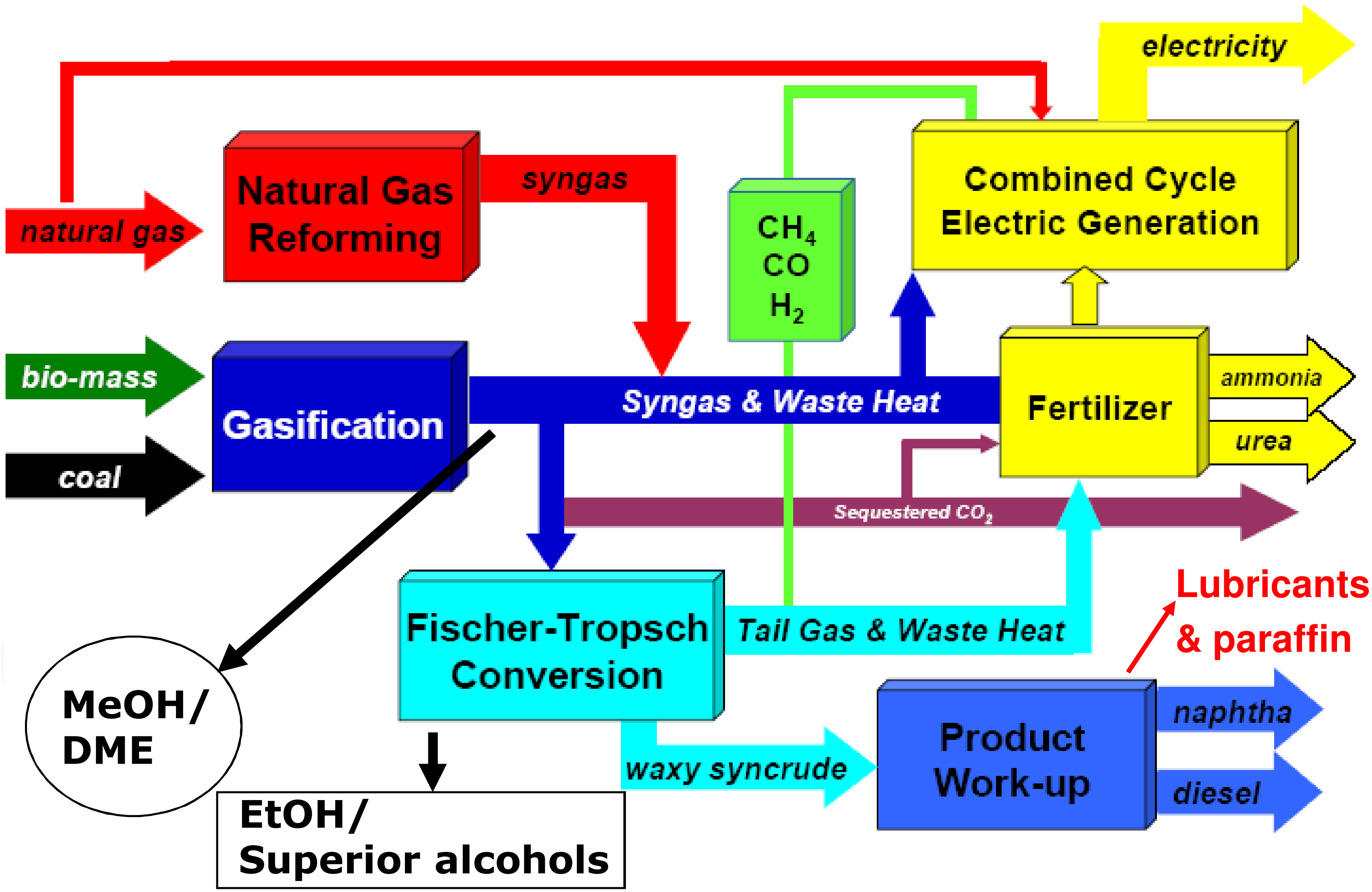
Refining scheme for an innovative scenario



Latin America: Refining schemes

	Raw material	Market	Process	Focus
	Increasing utilisation of heavy crudes, however with necessary modifications to process heavy oils and acidic oils without pre-treatment in the production fields.	Traditional fuels and growing market, however taking into account problems related to demand and new specifications.	Use of proven technologies, with special attention to hydrotreating and hydroconversion.	Integration with petrochemistry and minimum environmental impact.
Scenario	**Inertial**	**Inertial**	**Incremental**	**Incremental/ Innovative**

XTL (BTL, CTL, GTL) – the integrated concept



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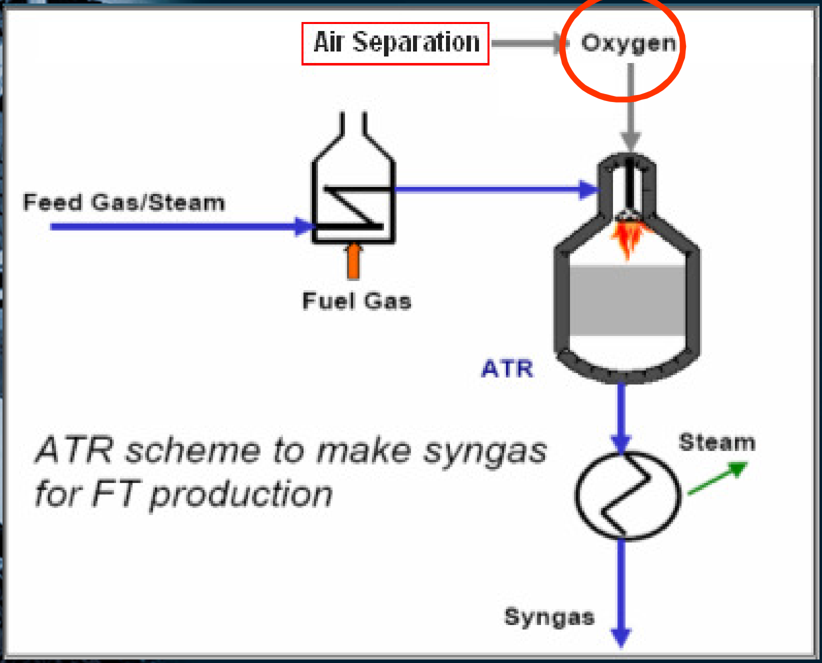
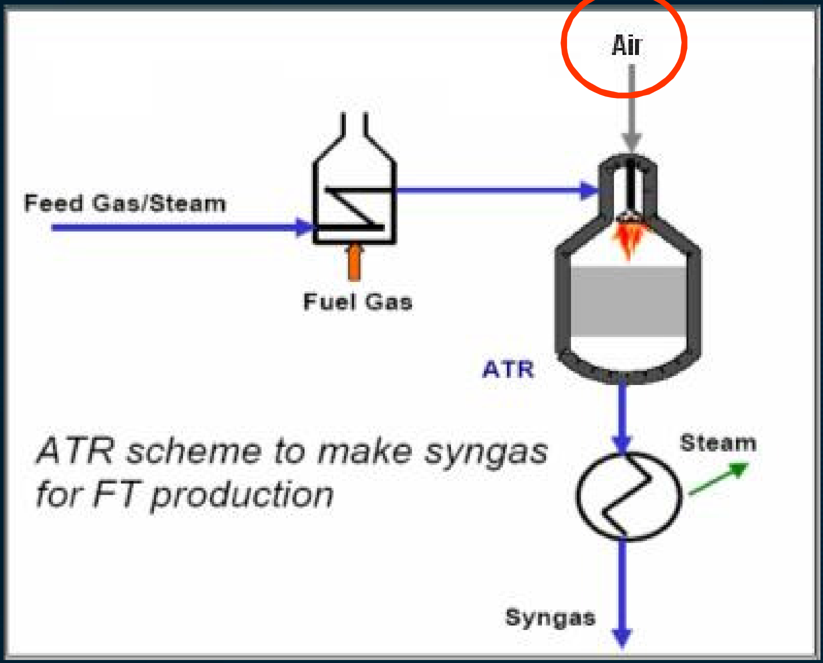
Regarding the integrated concept, some challenges in terms of traditional processes, new processes and break-trough processes deserve special attention

Autothermal reforming

Authothermal reforming is an industrial reality



ATR scheme to make syngas for FT production

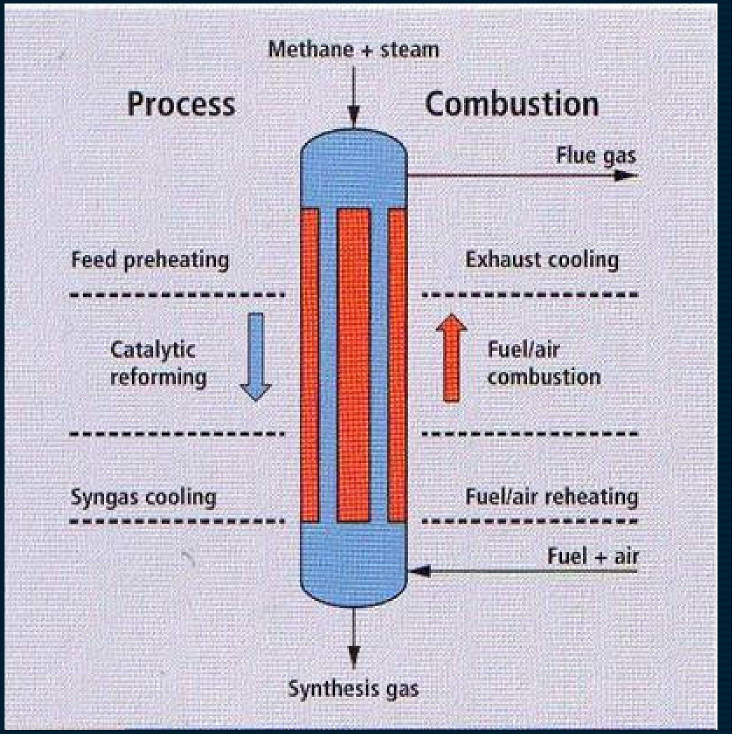


ATR scheme to make syngas for FT production

Autothermal reforming - the future

➲ *Compact reformers*

- *smaller size and capital costs;*
- *compact design → offshore and remote sites*
- *increased thermal efficiency;*
- *modular and scalable;*

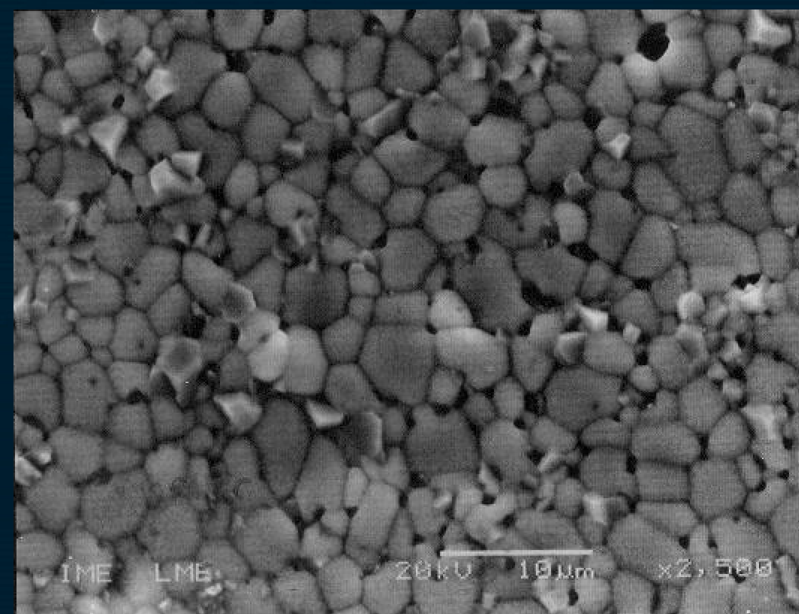


Source: BP compact reformer based on Steam methane reformer

Autothermal reforming - the future

➲ *Ceramic Membrane reactors*

- *combines air separation and synthesis gas generation*
- *processes into a single ceramic membrane reactor*
- *reduction of capital costs*
- *no need for a conventional oxygen plant*
- *challenges: material development*

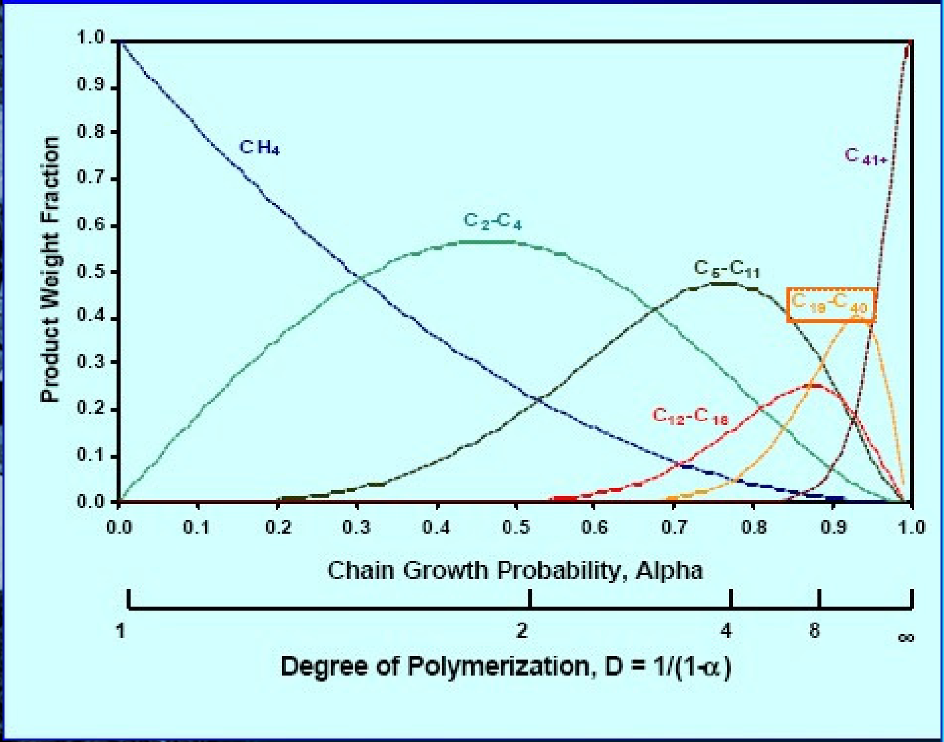


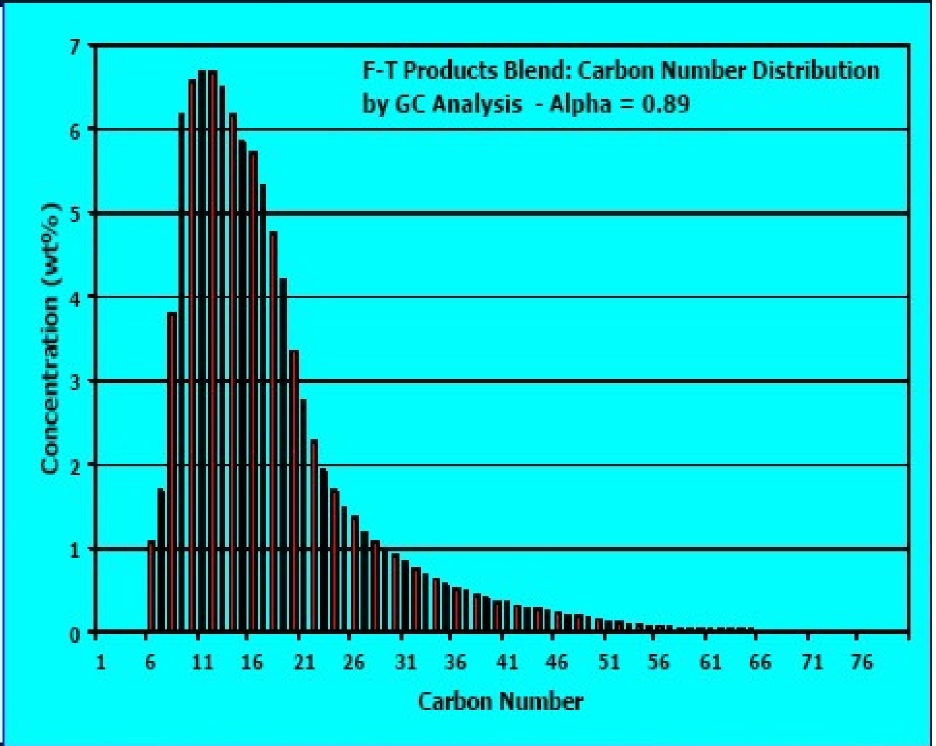
SEM of a ceramic membrane developed under a GTL-Petrobras Network project

Fischer-Tropsch synthesis

- Developed in 1920, at the Kaiser Wilhelm Institut für Kohlenforschung (Muhlheim-Ruhr)
- It produces hydrocarbons from synthesis gas (CO + H_2)
- It uses metallic catalysts from the pioneer work by Franz Fischer y Hans Tropsch
- Original Catalyst: precipitated Co

Products distribution versus alpha (degree of polymerisation)





Fischer-Tropsch catalyst

Fischer-Tropsch catalyst is still a challenge for those developing commercial catalysts.

a) Catalyst must improve metallic phase dispersion, or rather, smaller particles of cobalt on the support;

b) Smaller particles → more efficient use of cobalt → reduced costs.

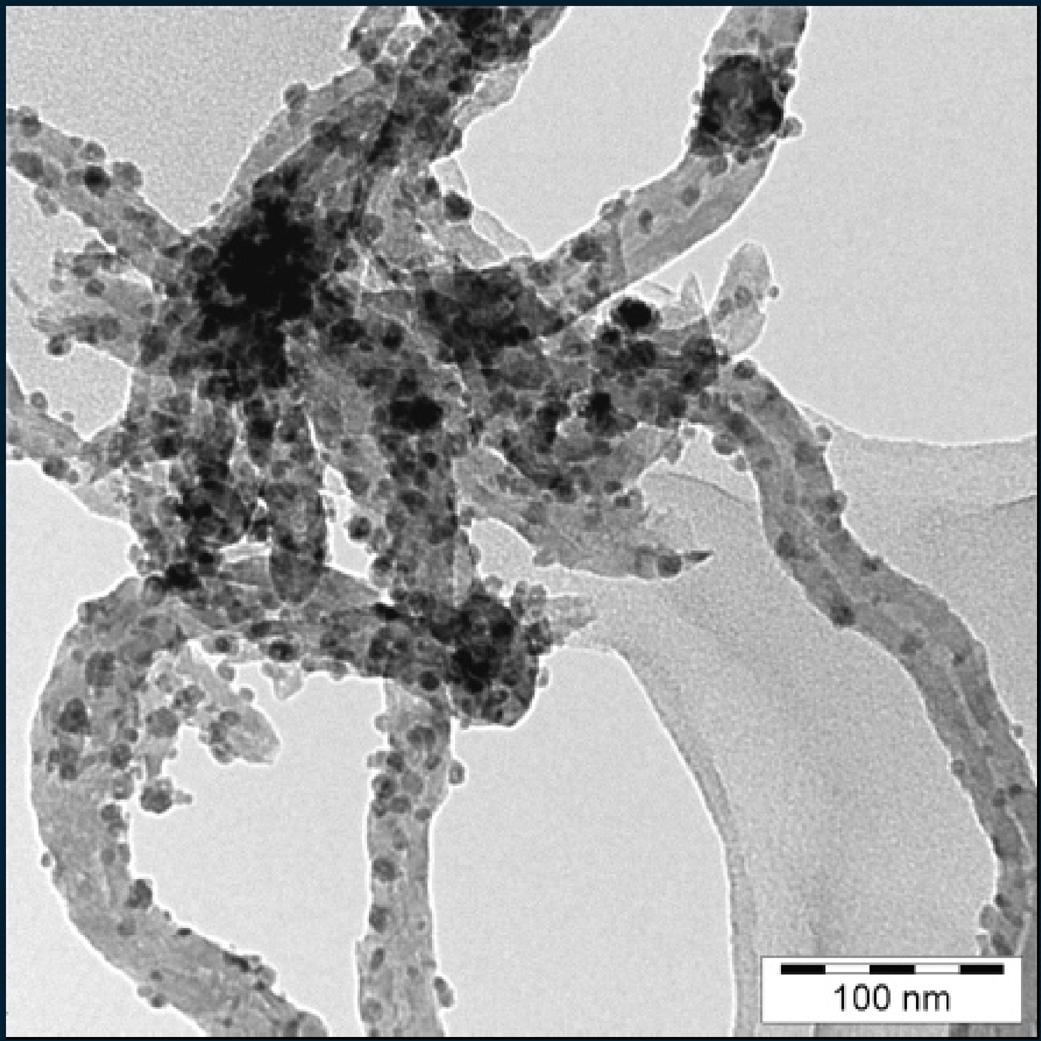
Fischer-Tropsch catalysts

a) FT catalysts - rather low cobalt dispersion (average cobalt particle sizes of about 20 nm);

b) Smaller particles → more efficient use of cobalt → lower costs;

c) The preparation of catalysts with smaller cobalt particle sizes is possible. Nevertheless, these catalysts are often not as active as expected. The phenomenon of lower activity for smaller particles has been referred to as the cobalt particle size effect ;

Fischer-Tropsch catalysts



TEM image of CNF showing Co particles with sizes of around 14 nm distributed over the fibers.

K. P. de Jong et al. J. AM. CHEM. SOC. 9 ,128, 12, 2006

Fischer-Tropsch catalysts

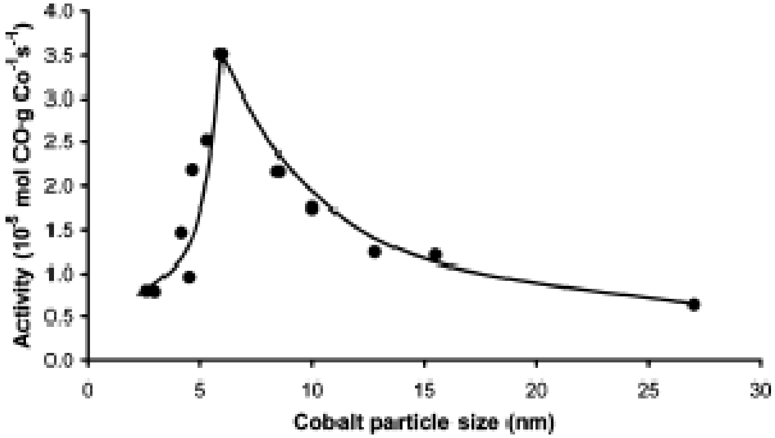


Figure 7. The influence of cobalt particle size on activity normalized to the cobalt loading (220 °C, H_2/CO = 2, 1 bar).

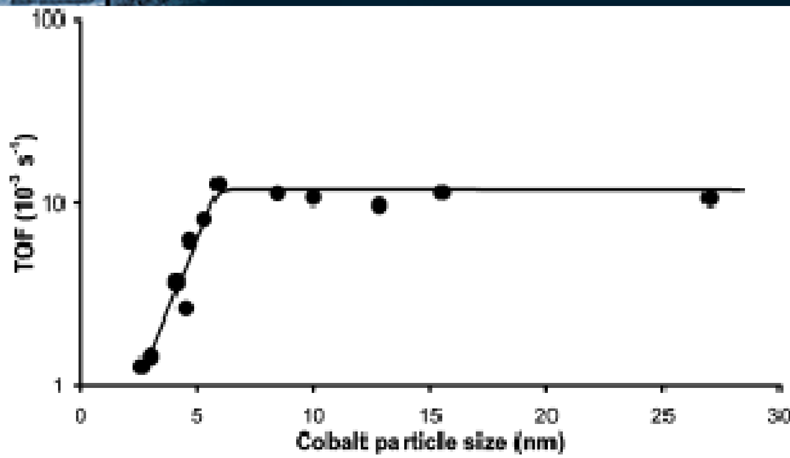


Figure 8. The influence of cobalt particle size on the TOF (220 °C, H_2/CO = 2, 1 bar).

Optimum → 6 to 8 nm average particle size

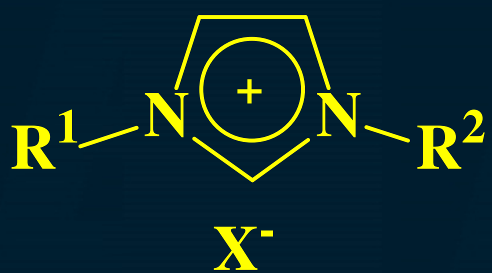
↓

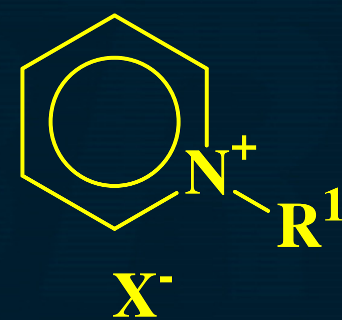
FT-catalysts are a good example of nanotechnology !

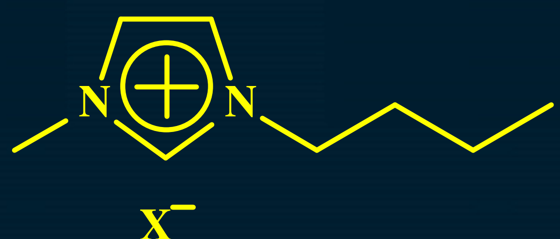
Fischer-Tropsch catalysts – the future

How can 6-8 nm Co particles be obtained ?

Ionic liquids are liquid compounds that present ionic-covalent crystalline structures or electrolites entirely composed of ions which are liquid at ambient temperature.



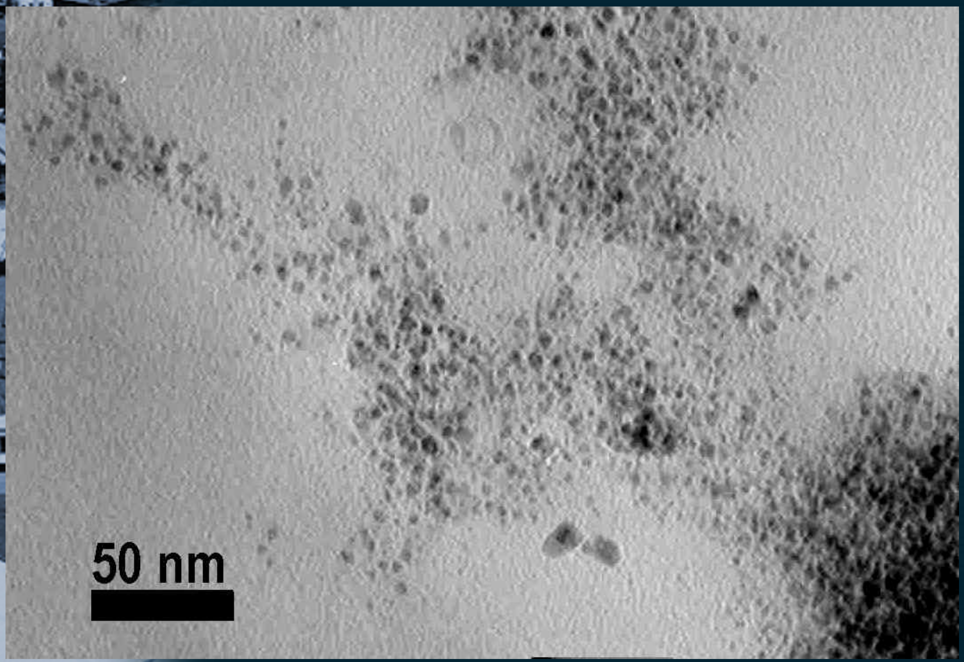




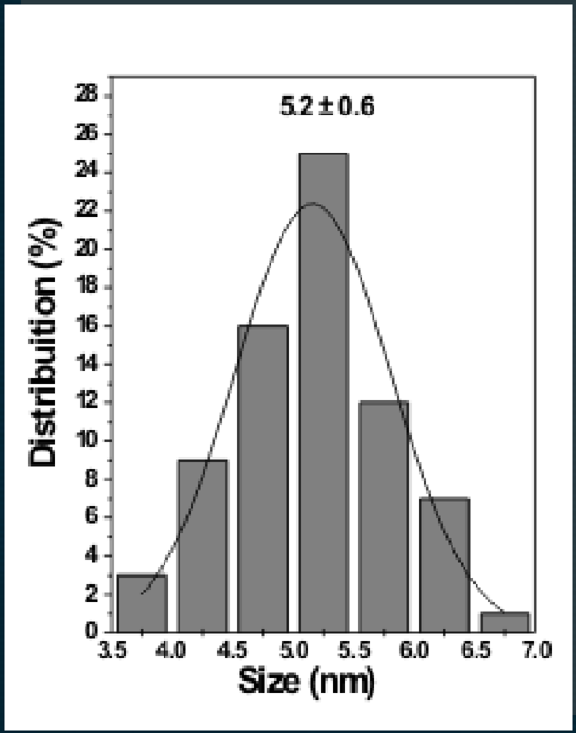
1-butyl-3-methyl imidazole (BMI)

Fischer-Tropsch catalysts – the future

Co nanoparticles can be stabilised by Ionic liquids via thermal decomposition of $Co(CO)_8$.



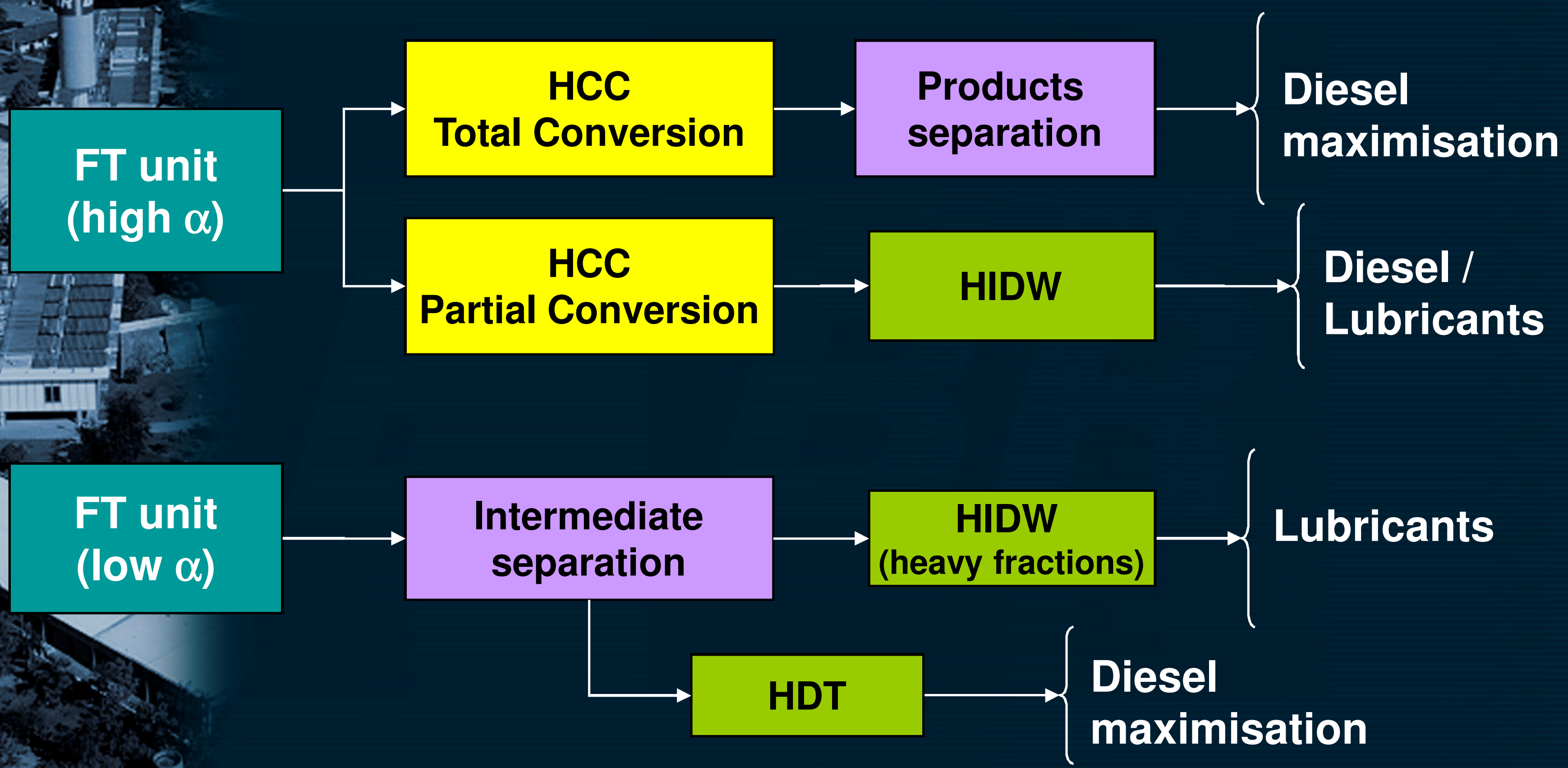
Co nanoparticules dispersed in BMI.BF4



E. Falabella, J. Dupont, A. C. Santos et al.
Disclosure request – NI06/023/2006

Upgrade

UPGRADING ROUTES



Upgrade – the future

- The removal of long-chain n-paraffin from lubricating oils is essential to obtain a product with good cold-flow properties.
- An attractive de-waxing procedure would result from catalytic de-waxing through isomerisation of the n-paraffin to branched isoparaffin, eliminating the yield loss associated with n-paraffin removal by cracking or solvent extraction

Challenge – a new catalyst capable of producing high quality products

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Upgrade – the future

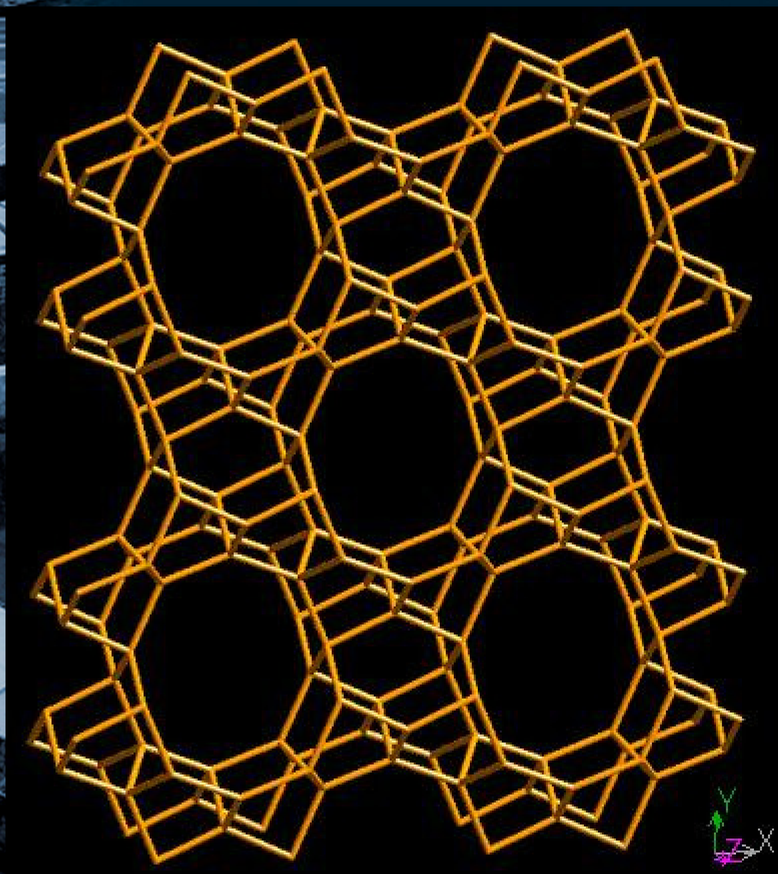
STRUCTURE	VISCOSITY (cSt@100°C)	VI	POUR POINT (°C)	"PRODUCT"
n-C26	3,24	188	+56,2	"Paraffin"
C4–C–C17 I C4	2,97	141	+20,8	"Paraffin"
C10–C–C10 I C5	2,68	126	-9,1	"Lube oil"
C10–C–C10 I C / \\ C2 C2	2,69	120	-40	"Lube Oil"

✓Branching impacts pour point – branch near the centre leads to lower pour point

✓Multiple branching impacts VI

Upgrade – the future

Pt/H-ZSM-22 seems to be the most promising catalyst to selectively isomerise FT-paraffin



ZSM-22 structure
a = 14.105Å   b = 17.842Å
c = 5.256Å

ZSM-22 contains parallel tubular pores with an almost uniform cross section of ca. 0.45X0.55 nm

Upgrade – the future

- On the Pt/H–ZSM-22 zeolite, the first methyl branching is formed preferentially at C2–C3 positions for decane and shorter n-alkanes and at C2–C3 or C5–C11 positions of longer alkanes

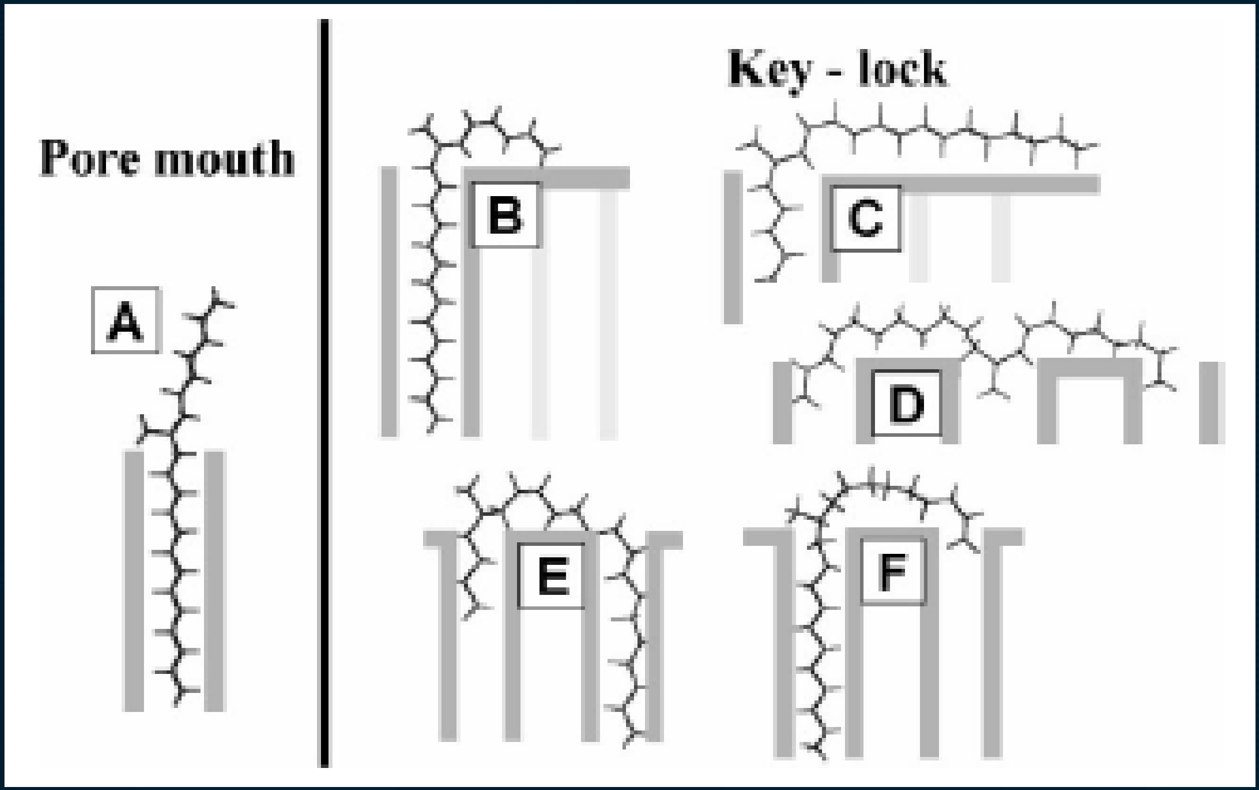
- The linear carbon chain penetrates with one end into a pore opening (pore mouth) or with both ends each into a different pore opening (key lock).

Upgrade – the future

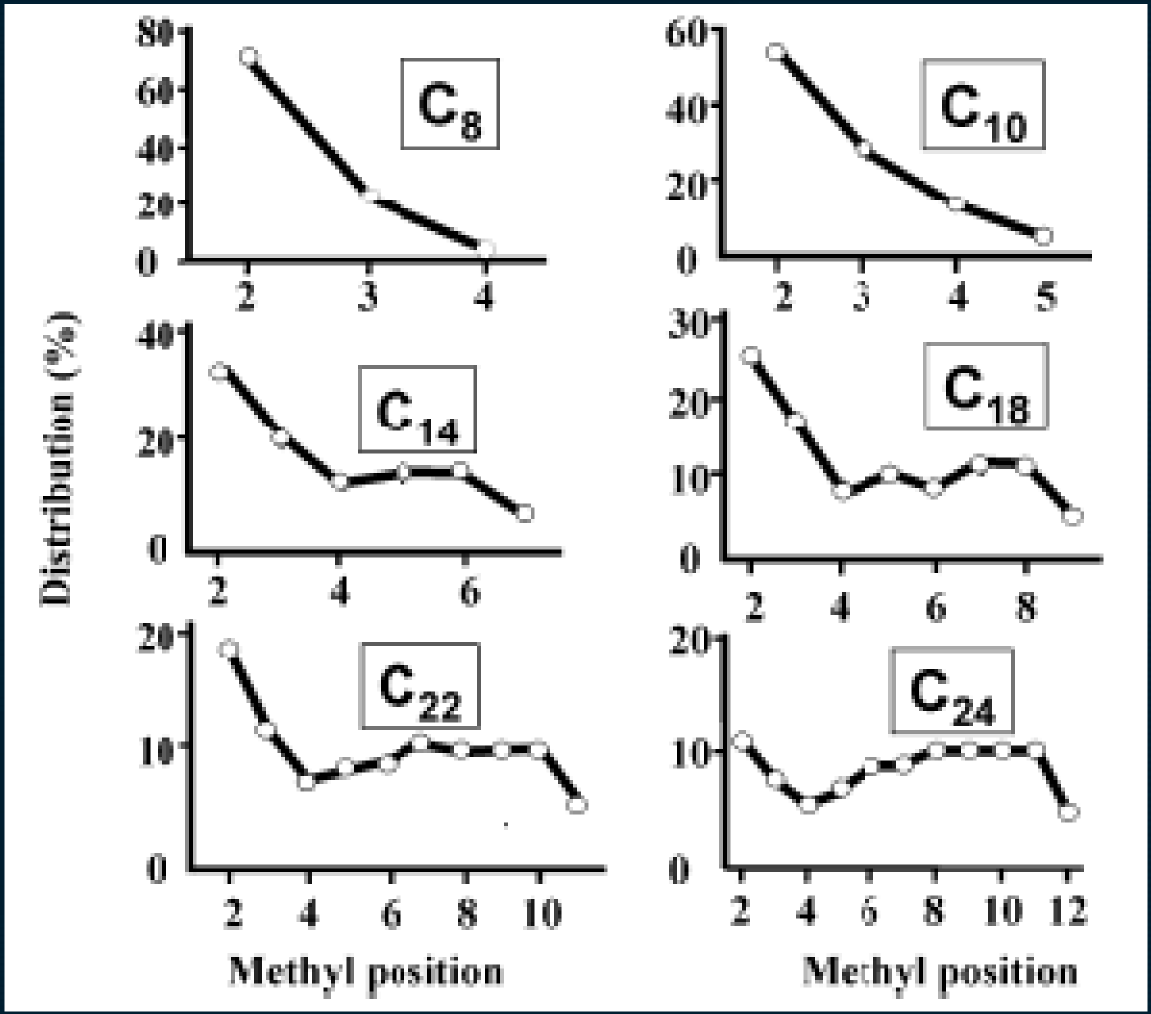
Pore mouth

- **n-alkanes enter the pore mouth**
- **Iso-alkanes do not**
- **Reactions occur only on the acid site at the pore mouth** (Martens *et al.* Catal. Today, 65 (2001))

Pore mouth versus key-lock mechanism



Pore mouth versus key-lock mechanism



J.A. Martens et al. / Catalysis Today 65 (2001) 111–116

Microreactors

Concept

Microreactors use the concept of *PI - process intensification* (reduction in plant size by at least a factor of 100) in which a given process is intensified whenever one enhances:

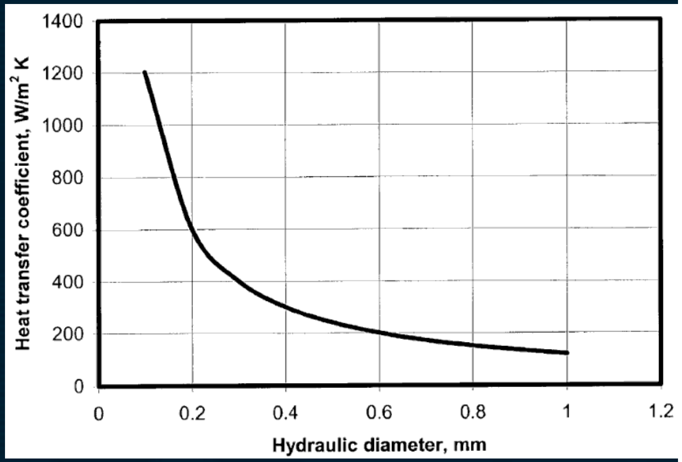
- Mass transfer
- Heat transfer
- Reaction rate

PI provides processes which are cleaner, safer, smaller and cheaper.

Main advantages of Microreactors

❖**Reduction in linear dimensions**

Heat transfer coefficient increases orders of magnitude



❖**Increase in the surface/volume ratio**

- Microchannels - 10.000 a 50.000 m^2/m^3
- Conventional lab equipment, 1000 m^2/m^3
- Industrial equipment, 100 m^2/m^3

❖ **Volume reduction**

Typical values are one or two orders of magnitude

Microreactors

The main reactions of the GTL process (Reforming and Fischer-Tropsch) seem to be very suitable for the technology of microchannels.

a) Reforming is a very *fast* and *endothermal* reaction which requires a very high heat flow and short contact times for the intensification thereof;

b) Fischer-Tropsch synthesis is *highly exothermal*, requiring a fine temperature control to improve its selectivity.

Furthermore, the existence of remote and off-shore natural gas fields calls for compact technologies, which should be located in space-restricted areas, such as on offshore platforms, Floating Production, Storage and Offloading (FPSO) vessels, or mobile skids.

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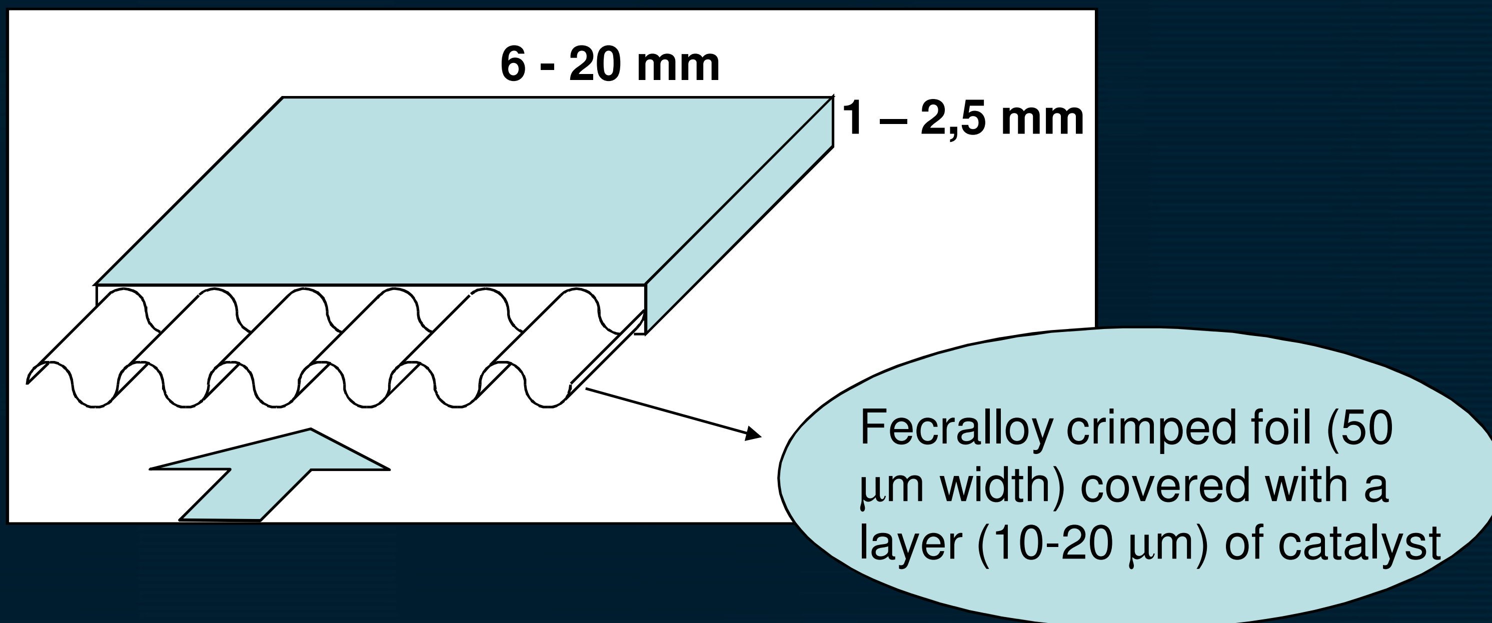
Microreactors – the catalyst

Reactor with milichannels or minichannels

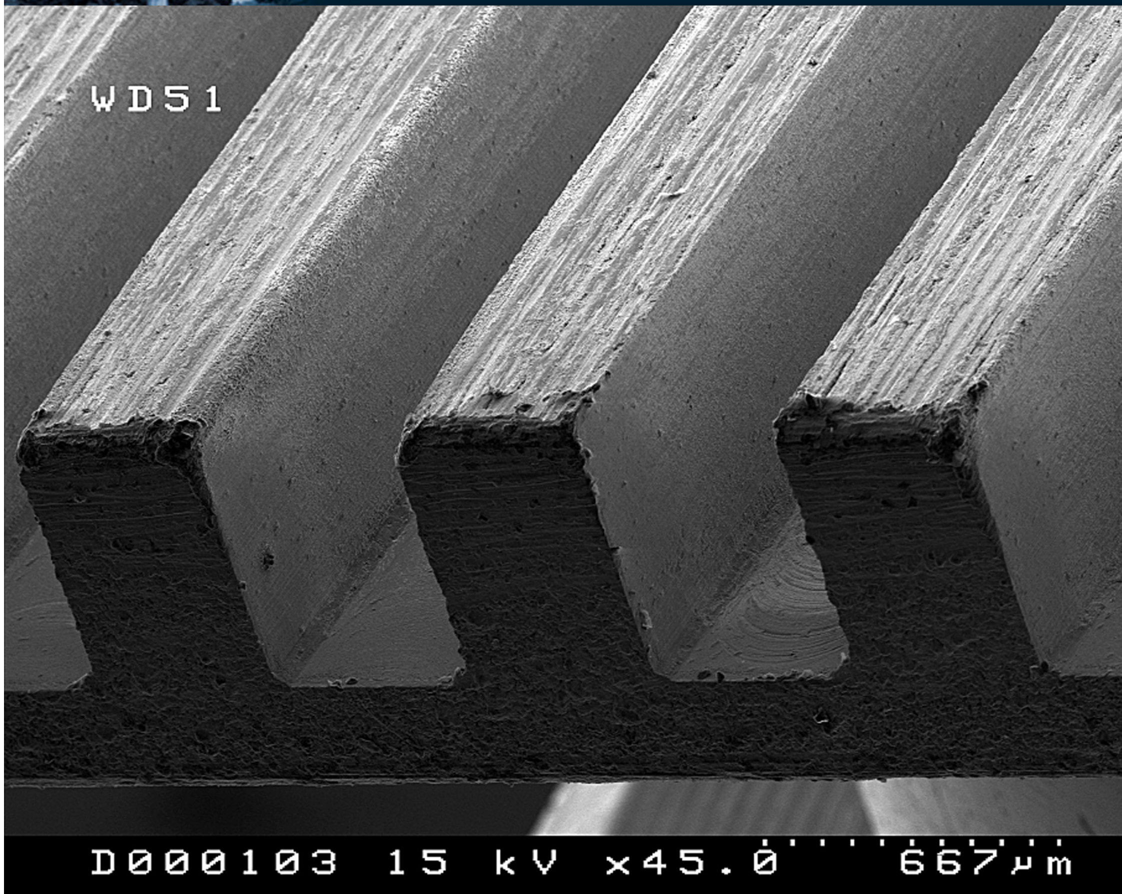
Minichannels are formed by stacking plates which are welded via “diffusion bonding”. Crimped foils containing the catalyst are added afterwards and may be replaced.

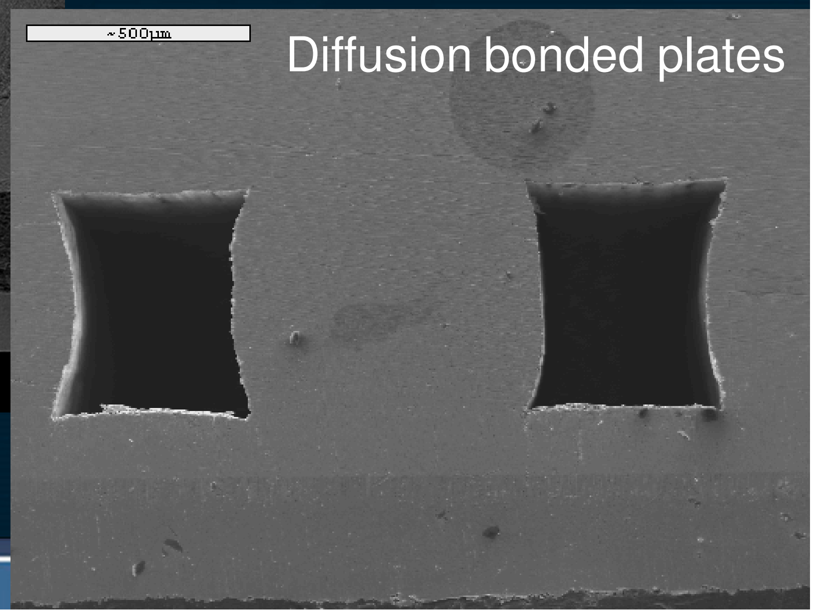


Source: CompactGTL patents

Microreactors

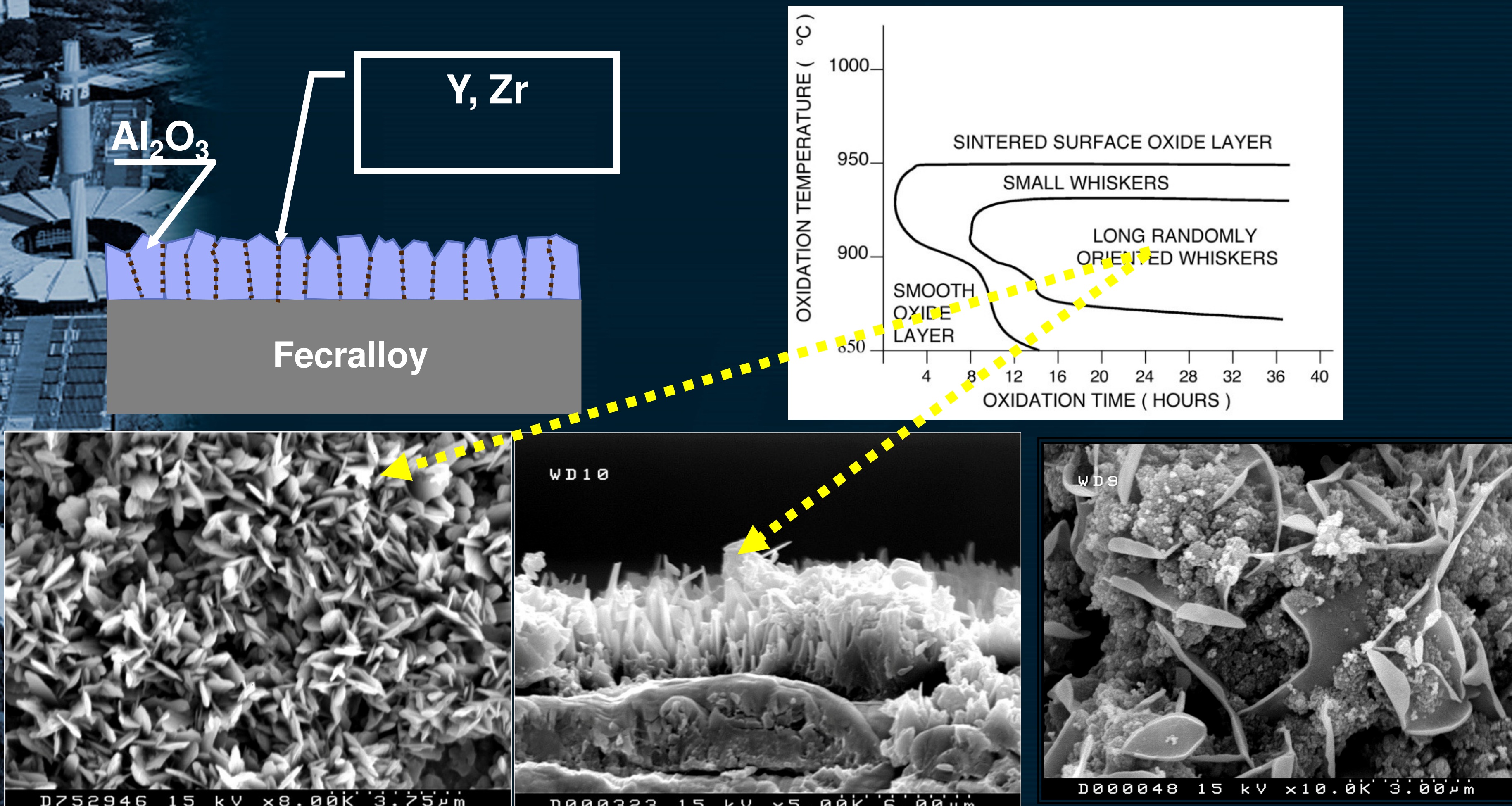
Microchannel plate





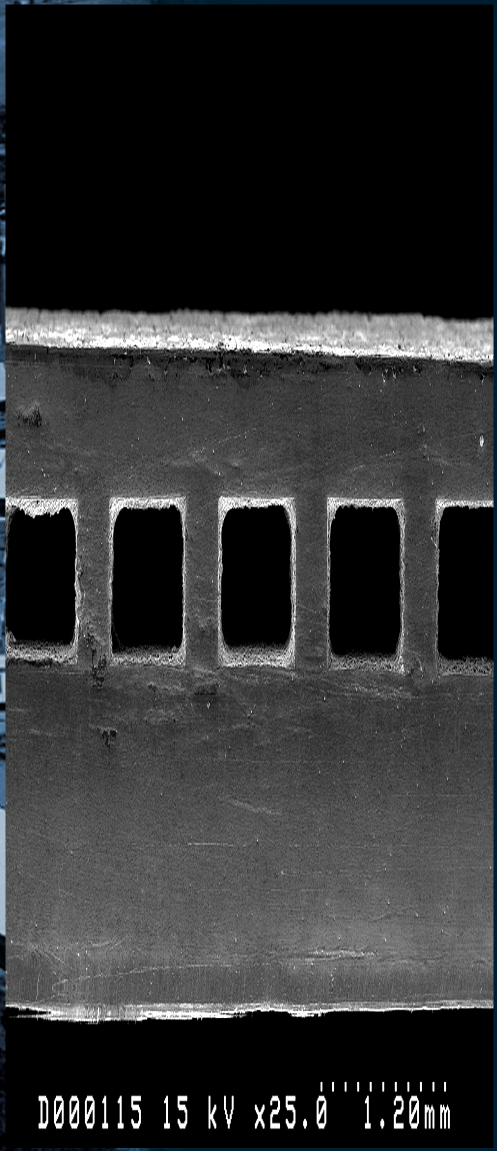
Microreactors – the catalyst

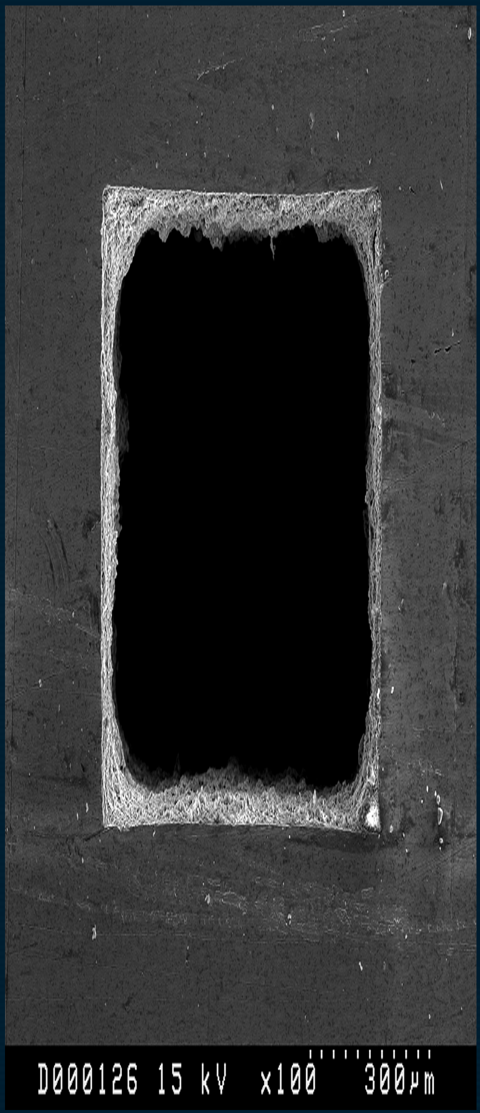
Fecralloy® Fe – stainless steel
Cr 22%, Al 4,8%, Si 0,3%, Y 0,3%, C 0,03%, Fe balance



α-alumina needles are generated from the Al-containing alloy

Microreactores





Microreactors

Space envelope for 1000 bpd GTL Plant – 20m x 30m x 23m

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Microreactors – the future of the future

Nanoreactors versus Microreactors

Reaction takes place in zeolite cages or nanotubes

Reaction occurs inside microchannels

	Characteristic Dimension	Performance	Effect on the process
Nanoreactor	Nanometers	Modifies electronic or esteric properties of the reactants	Alters reaction "**Chemistry**"
Microreactor	Micra	Intensifies mass and heat transfer phenomena	Alters process "**Engineering**"

The future **Nanoparticles of Co located inside microchannels**

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Conclusions

- The refinery of the future is a rather sophisticated technological concept, requiring innovative technologies for its implementation;

- Although inevitable, the introduction of such technologies will be carried out gradually;

- The different raw materials (Natural Gas, Coal, Biomass) will be used according to their availabilty and logistic characteristics;

Conclusions

- XTL processes will be the basis for the refinery of the future;
- New catalysts, using the concept of nanocatalysis/nanotechnology, as well as special zeolites, represent the future for XTL processes, mainly when Fischer-Tropsch and Hydroisomerisation are concerned;
- The future points towards new reaction systems such as microreactors;

Atom
Place yourself at our service
And instead of the fatal ashes
Instead of the unleashed infernos of your wrath
Instead of the menace of your terrible light
Deliver to us your amazing rebelliousness for our grain
Your unchained magnetism to found peace among men
And then your dazzling light will be happiness, not hell
Hope of morning, gift to earth…

Ode to the atom
Pablo Neruda