UNIVERSITÀ
DEGLI STUDI
DI PADOVA

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refining & marketing

The Eni Slurry Technology (EST) for the total conversion of the heavy feedstock and the oil residues.

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eni

Summary

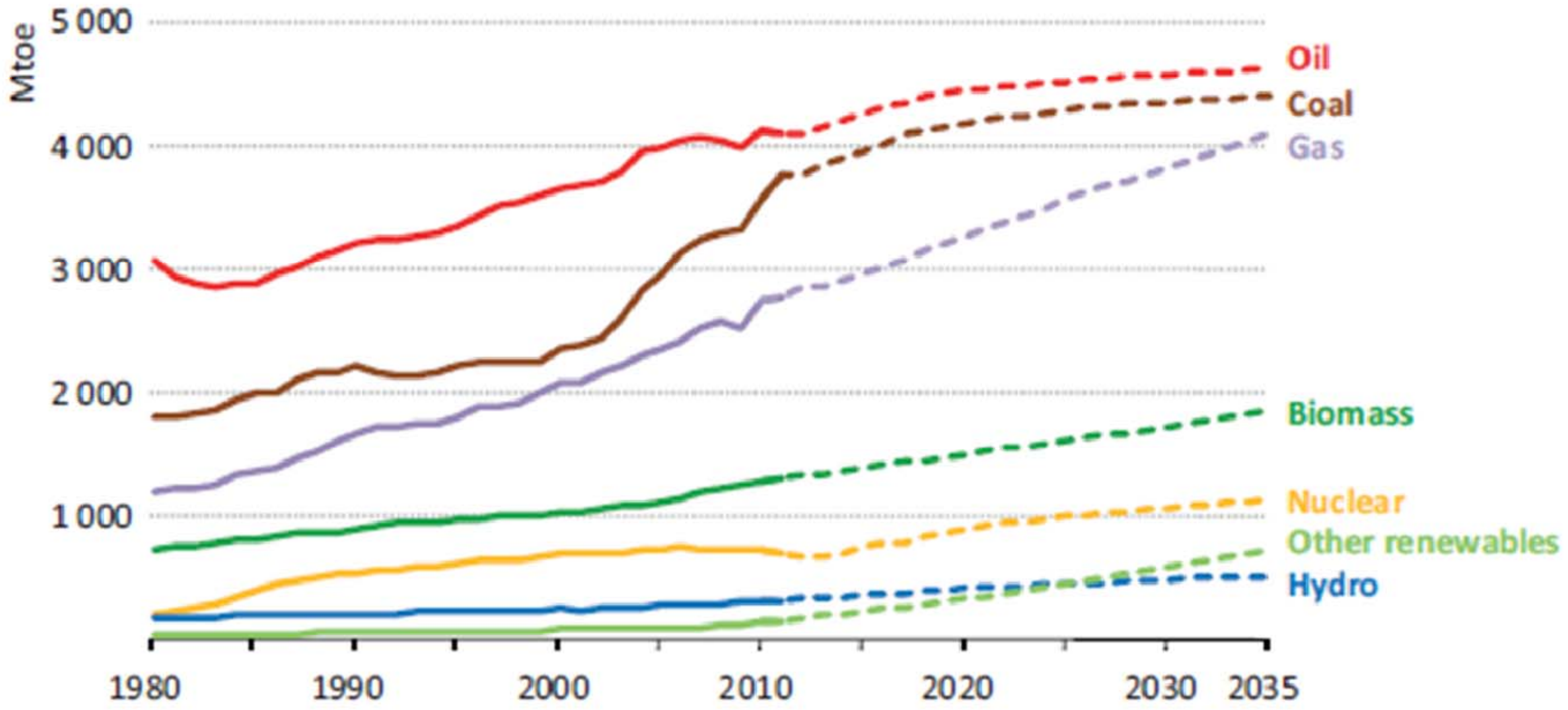
1 **Introduction**

2 **Eni Slurry Technology for residues and heavy oil upgrading**

3 **The “dual catalyst” system**

Outlook for energy demand

Figure 2.5 ▷ World primary energy demand by fuel in the New Policies Scenario



International Energy Agency: World Energy Outlook 2013

International Energy Agency: World Energy Outlook 2013

The needs

- Increase the availability of renewables energy sources.
- Secure the availability of fossil energy sources:
  - ✓ improve the energy saving;
  - ✓ improve the efficient use of energy;
  - ✓ debottleneck unconventional energy sources.

Total conversion of the barrel of conventional and heavy oils (Unconventional) to good quality distillates, avoiding the production of coke and fuel oil.

Improving the extra-heavy oils

OIL	S %	° API	H/C
WTI	0.43	39.1	$CH_{1.83}$
BRENT	0.31	38.7	$CH_{1.83}$
URAL ODESSA	1.57	30.9	$CH_{1.74}$
ARABIAN HEAVY	2.73	28.3	$CH_{1.70}$
PETROZUATA	2.76	20.5	$CH_{1.59}$
BACHAQUERO	2.50	16.2	$CH_{1.55}$
ATHABASKA BITUMEN	5.10	5.1	$CH_{1.40}$

35

26

10

+ H2 Addiction

- C Rejection

*API gravity: 141,5/d – 131,5 (d is the oil density respect to water at 60 °F)
sweet 35, medium 26, heavy 10, extra heavy < 10 (Sink in water)

Technologies currently available for converting the bottom of the barrel

- Several commercial technologies for converting vacuum residua to lighter products
- Increase of low H/C of residua to higher H/C of products via thermal or catalytic:

carbon rejection (thermal)

Coking offers high feedstock flexibility

but

⇩poorer quality of distillates
⇩loss of liquid yield,
⇩ca. 30% wt of low value coke

>90 M TPY petcoke produced worldwide

hydrogen addition (catalytic)

Fixed/Moving bed (low metals content feed)
Ebullating bed (relatively higher metals feed)

but

⇩limits the maximum conversion achievable
⇩fuel oil remains a fatal product

9 M BPSD fuel oil produced in the world

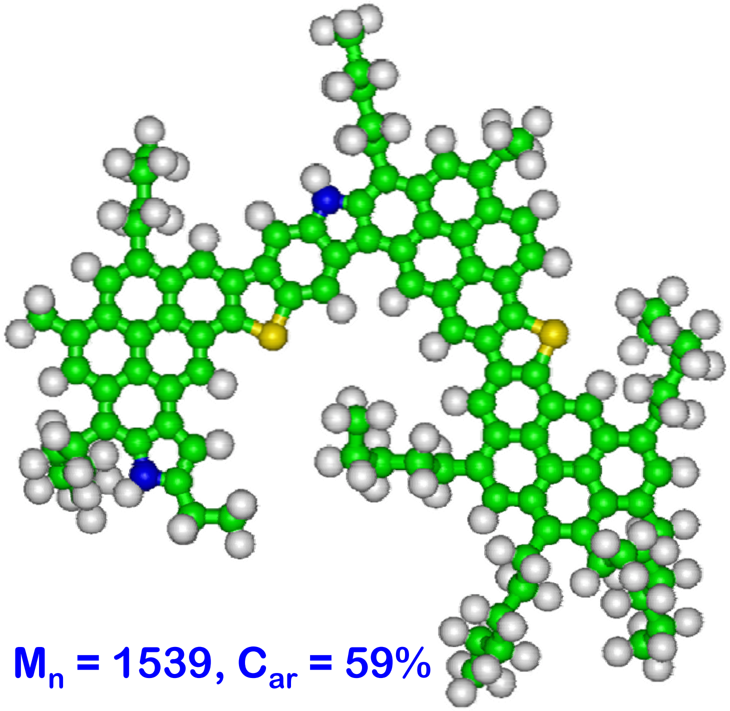
Summary

1. Introduction

2. Eni Slurry Technology for residues and heavy oil upgrading

3. The “dual catalyst” system

Is it possible achieve the total conversion of the oil to distillates ?



$M_n = 1539$, $C_{ar} = 59\%$

PROBLEM

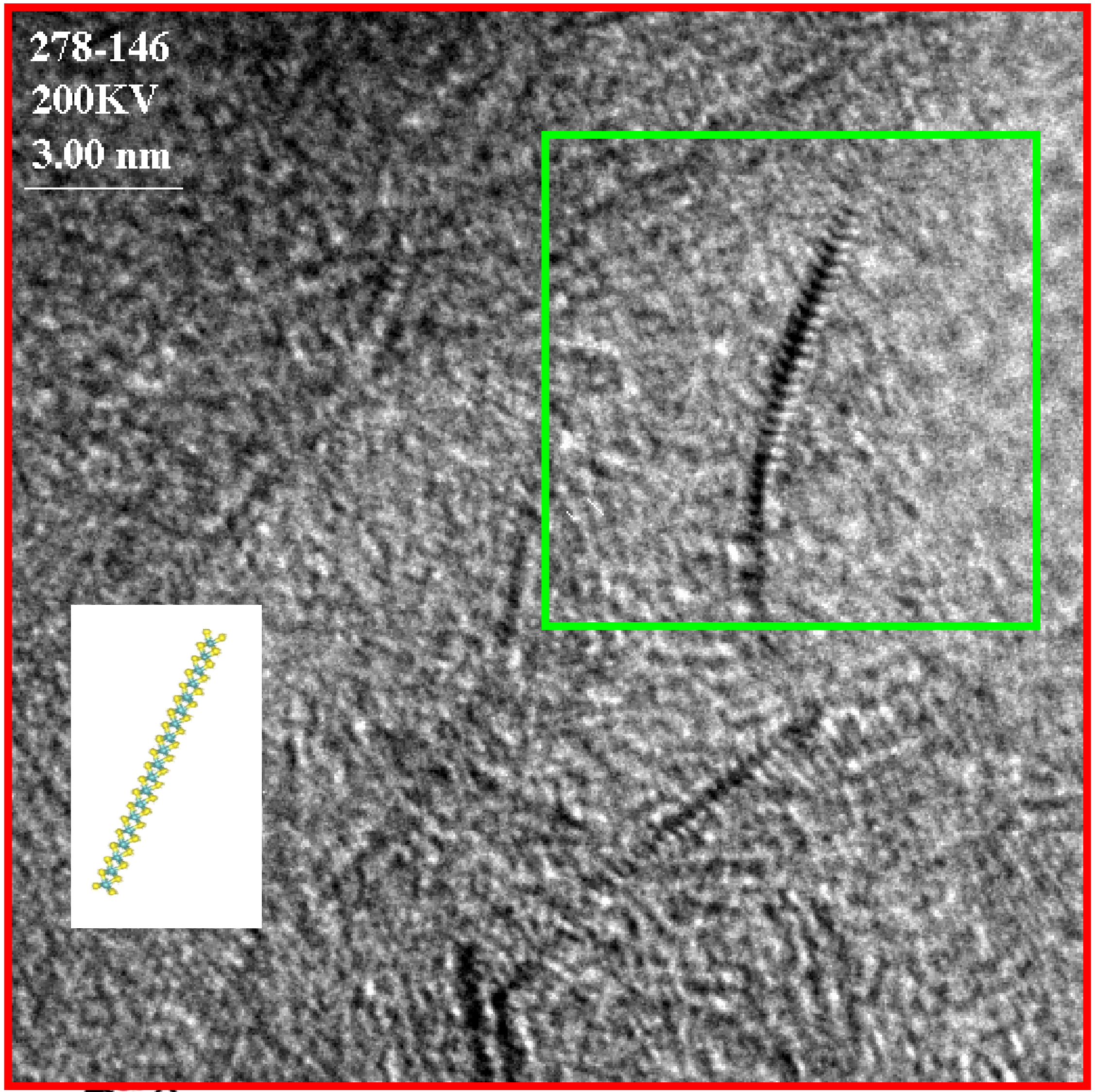
The total conversion requires long residence times; in this way, the more reactive species are converted to light (e.g. C1-C4) and heavy fractions (e.g. coke)

↓

SOLUTION

Minimize the gas and coke formation and **recycle back to the reactor** the heavier unconverted fraction, so that it remains in the reactor for longer residence times

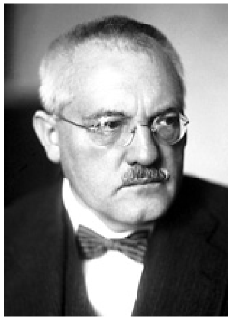
Conventional cracking catalyst are not stable under recycle...



... while nano-dispersed MoS_2 (Molybdenite) layers are very stable and can be integrally recycled back to the reactor, maintaining the original activity.

This catalyst used in a slurry reactor can therefore offer a solution for the total conversion of the barrel

The roots of slurry hydrogenation technology are in Germany….



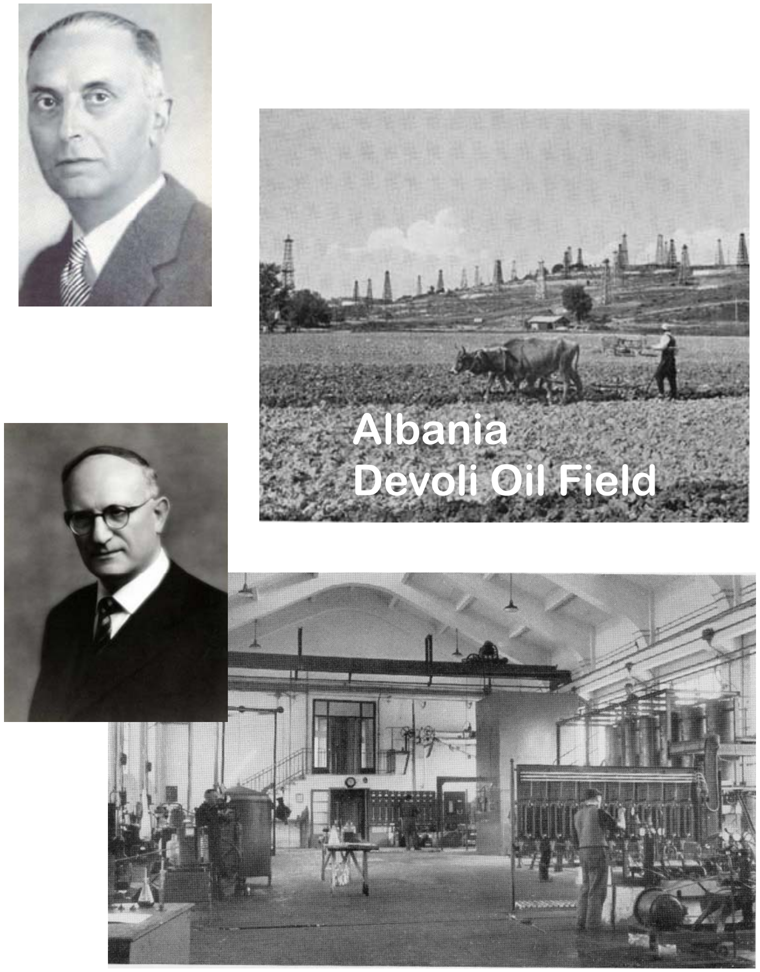
Gasoline from coal: In 1913, Friedrich Bergius had already succeeded in obtaining liquid reaction products from coal using hydrogen and high pressure.

In 1931 F. Bergius and C. Bosch are awarded with the Nobel prize for their studies on high pressure hydrogenation.

BASF chemist Matthias Pier picks up on Bergius idea and soon finds a way of translating the process to an industrial scale. At the end of **1927**, the first shipment of gasoline derived from coal leaves the Leuna site.

During WWII 12 hydrogenation plants were in operation in Germany. The catalyst was constituted by Iron or Tungsten Sulphide.

…. and in part in Italy.



On 8-13 april 1924, M. G. Levi (Bologna Univ.) visit the Bergius plants at Mannheim Rheinau site and start a research activity in Italy on heavy feedstocks hydrogenation.

In 1936 ANIC company was founded with the aim of producing fuels from hydrogenation of tarry products.

G. Fauser on the basis of early Levi's results build several pilots in Novara for hydrogenating heavy hydrocarbons and started-up the production of WS_2 hydrogenation catalyst.

1938: two refineries are built in Italy in Bari and Livorno to produce fuels mainly from tarry feedstocks from Albania.

During the WWII period Novara was supplying IG Farbenindustrie with 10 tons/month of "schwarzpulver" (WS_2)

More recent history

- Only two plants survived after the War and remained in operation for few years.
- In 1977 a coal liquids hydrogenation demo-plant was built in Bottrop (Nordrhein-Westfalen DE).
- In may 1987 this plant was converted to the hydrogenation of Vacuum residues by VEBA (Combi-cracking, 3500 bbl/day capacity).
- Since than several companies started-up R&D projects to develop heavy residues slurry upgrading technologies.

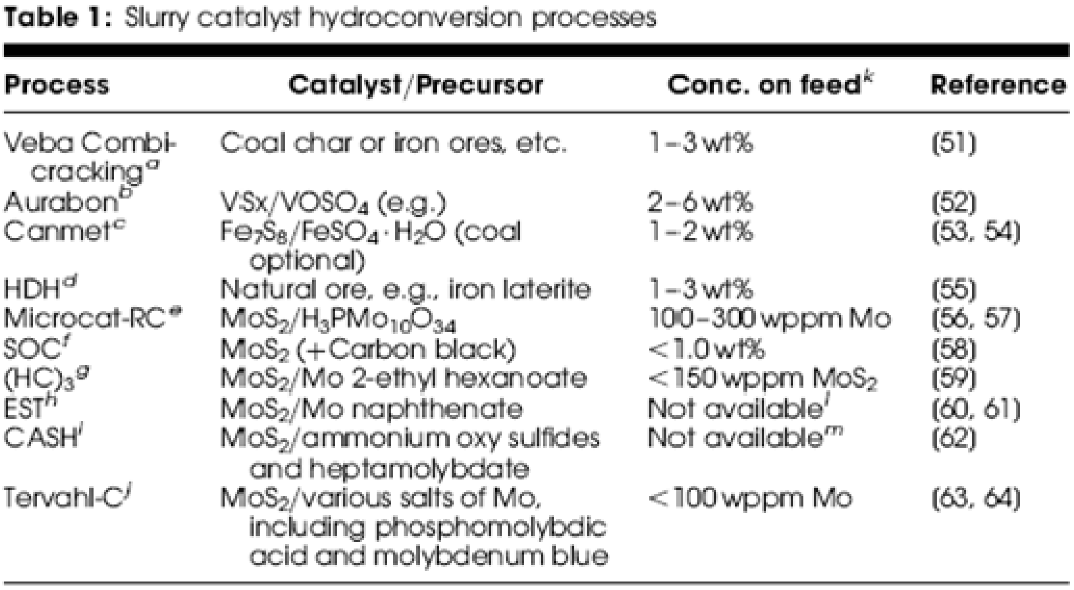


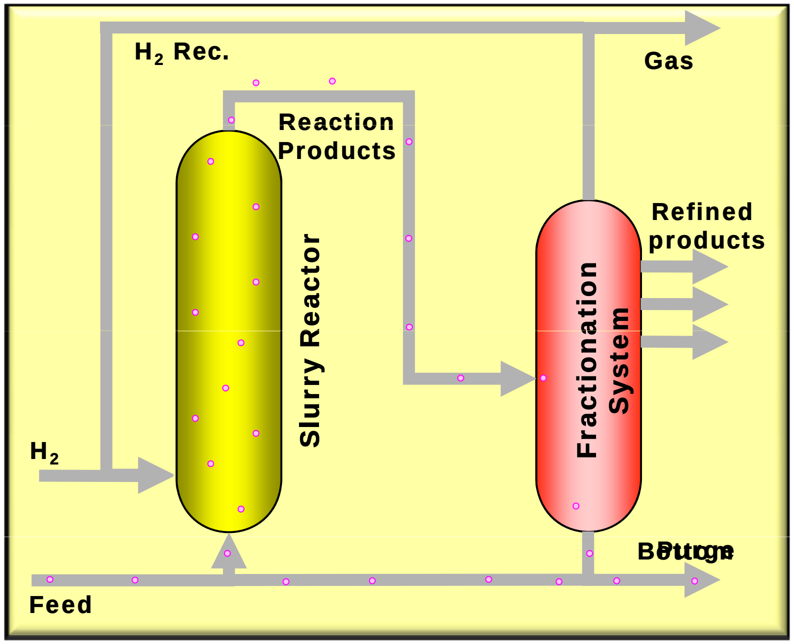
Table 1: Slurry catalyst hydroconversion processes

Process	Catalyst/Precursor	Conc. on feed[k]	Reference
Veba Combi-cracking[a]	Coal char or iron ores, etc.	1–3 wt%	(51)
Aurabon[b]	VSx/$VOSO_4$ (e.g.)	2–6 wt%	(52)
Canmet[c]	$Fe_7S_8/FeSO_4 \cdot H_2O$ (coal optional)	1–2 wt%	(53, 54)
HDH[d]	Natural ore, e.g., iron laterite	1–3 wt%	(55)
Microcat-RC[e]	$MoS_2/H_3PMo_{10}O_{34}$	100–300 wppm Mo	(56, 57)
SOC[f]	MoS_2 (+Carbon black)	<1.0 wt%	(58)
$(HC)_3$[g]	MoS_2/Mo 2-ethyl hexanoate	<150 wppm MoS_2	(59)
EST[h]	MoS_2/Mo naphthenate	Not available[l]	(60, 61)
CASH[i]	MoS_2/ammonium oxy sulfides and heptamolybdate	Not available[m]	(62)
Tervahl-C[j]	MoS_2/various salts of Mo, including phosphomolybdic acid and molybdenum blue	<100 wppm Mo	(63, 64)

R.R. Chianelli et al., Catalysis Reviews, 48 (2006) 1-41

Hydrogen addiction: slurry bed reactors

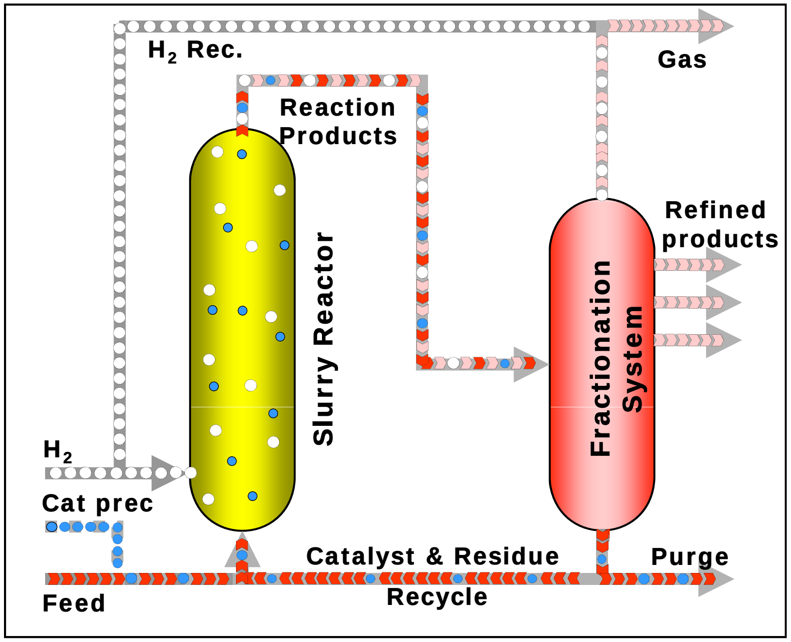
Molybdenite nanosized catalyst



EST: Eni Slurry Technology

The Eni Slurry Technology (EST)

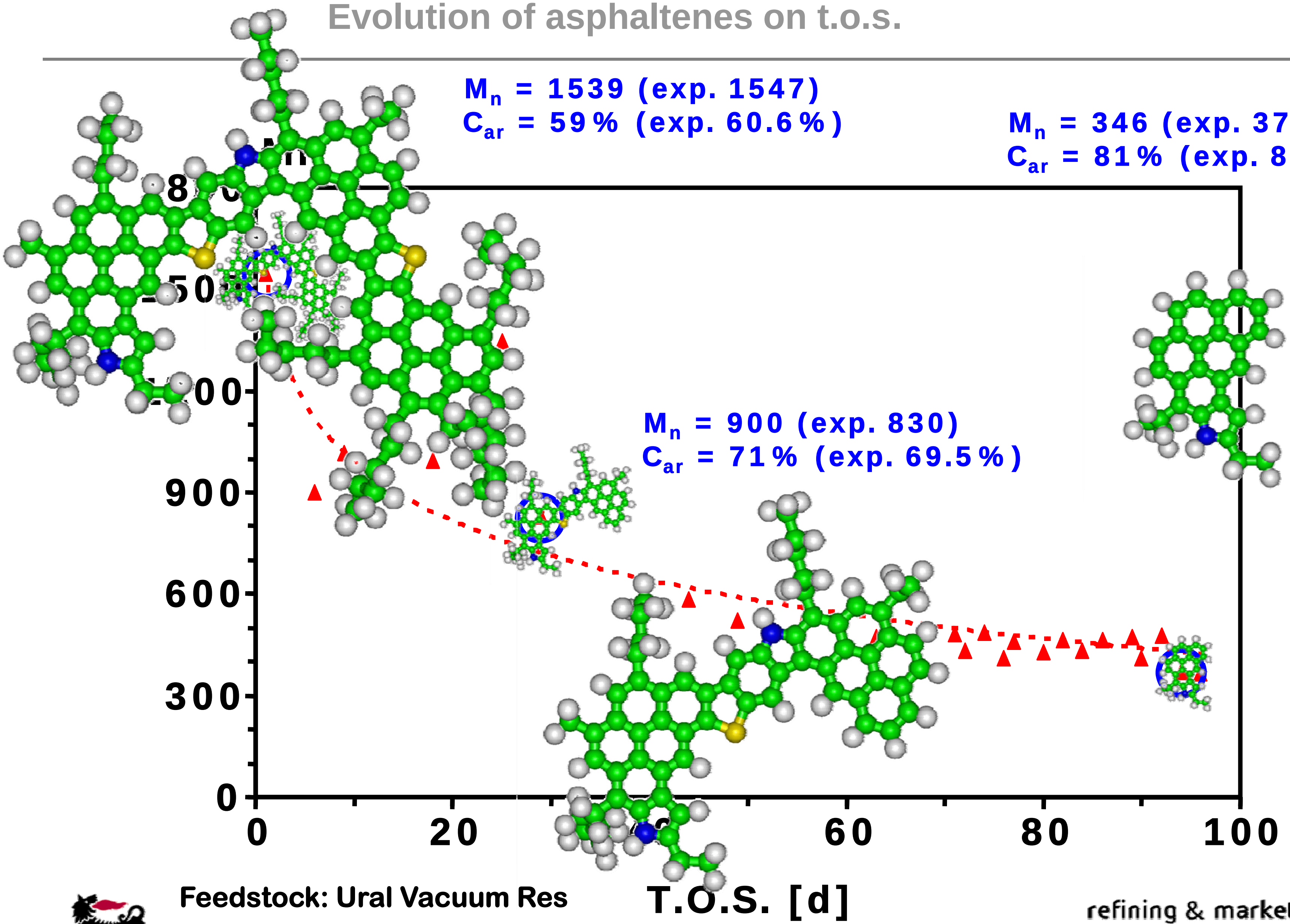
…is the evolution of the knowledge developed in Germany in the last century, on high pressure hydrogenation reactions.



CCR reduction > 97 %
HDM > 99 %
HDS > 85 %
HDN > 50 %

Feed: 500 °C+, t: 410-450 °C, p: 130-160 atm, purge: 1- 3 %

Evolution of asphaltenes on t.o.s.



M_n = 1539 (exp. 1547)
C_{ar} = 59% (exp. 60.6%)

M_n = 346 (exp. 370)
C_{ar} = 81% (exp. 80.6%)

M_n = 900 (exp. 830)
C_{ar} = 71% (exp. 69.5%)

Feedstock: Ural Vacuum Res

Eni Slurry Technology (EST) Development Phases

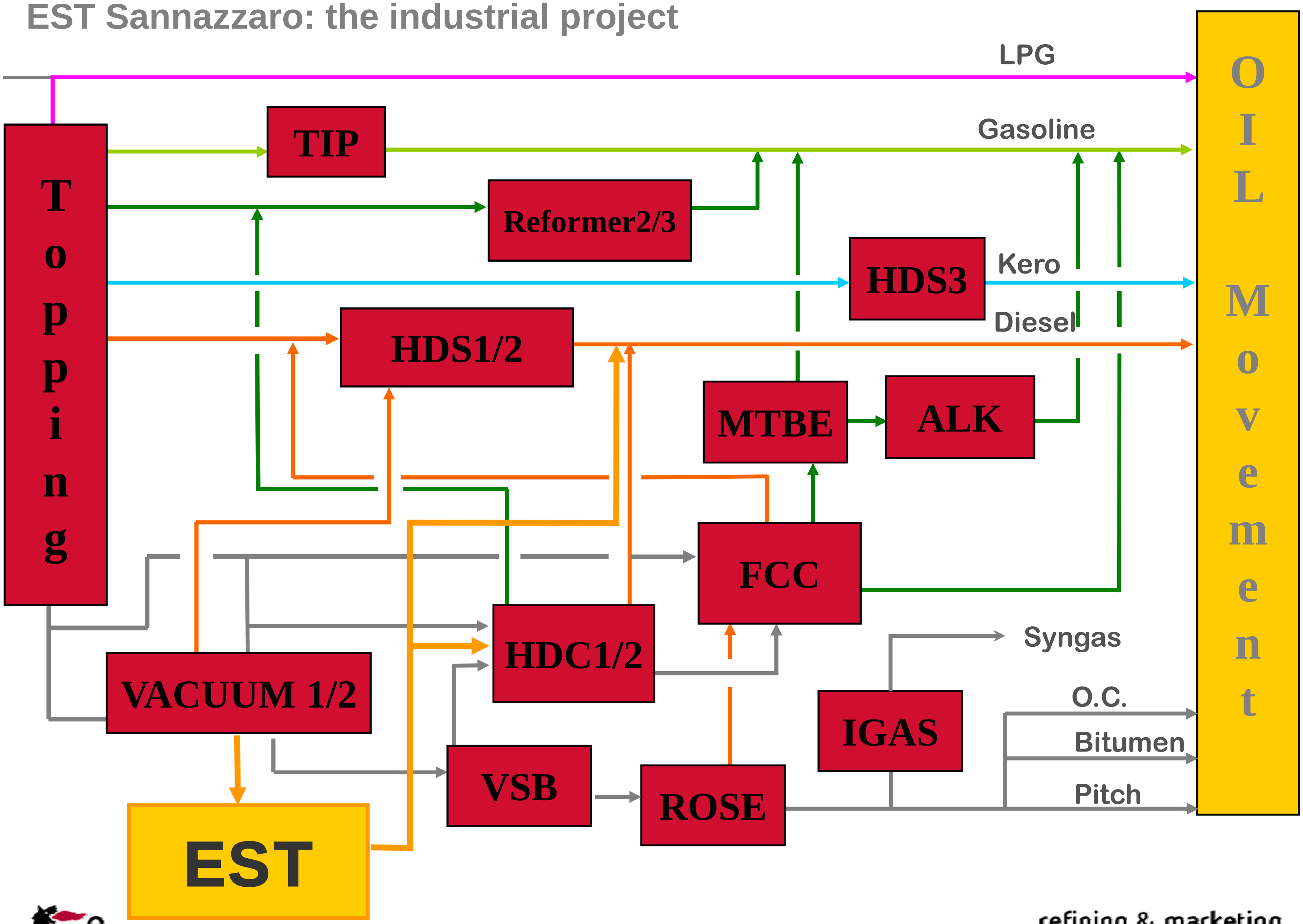
Early 90's
Start up of the R&D activity

2000-2003
Construction and running of a 0.3 bpd Pilot Plant

3Q 2005
Completion and start-up of a 1200 bpd demo plant

2013
Start-up of a 23000 bpd industrial plant

EST Sannazzaro: the industrial project



Topping

TIP

Reformer2/3

HDS3

HDS1/2

MTBE

ALK

FCC

HDC1/2

VACUUM 1/2

VSB

ROSE

IGAS

EST

OIL Movement

LPG

Gasoline

Kero

Diesel

Syngas

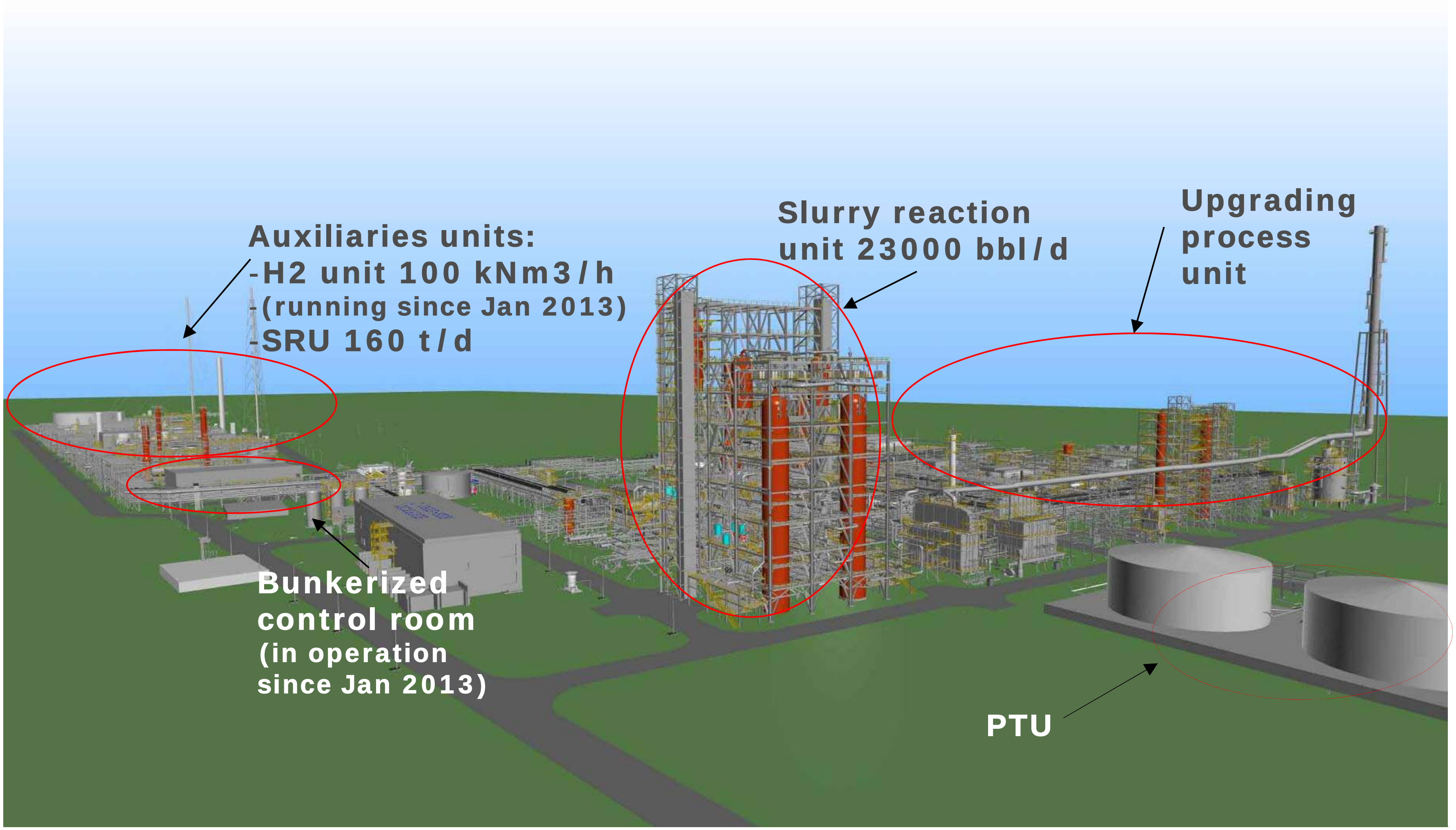
O.C.

Bitumen

Pitch

Integration of EST Complex in the Sannazzaro Refinery

EST Complex Lay-out



Auxiliaries units:

-H2 unit 100 kNm3/h

-(running since Jan 2013)

-SRU 160 t/d

Slurry reaction unit 23000 bbl/d

Upgrading process unit

Bunkerized control room

(in operation since Jan 2013)

PTU

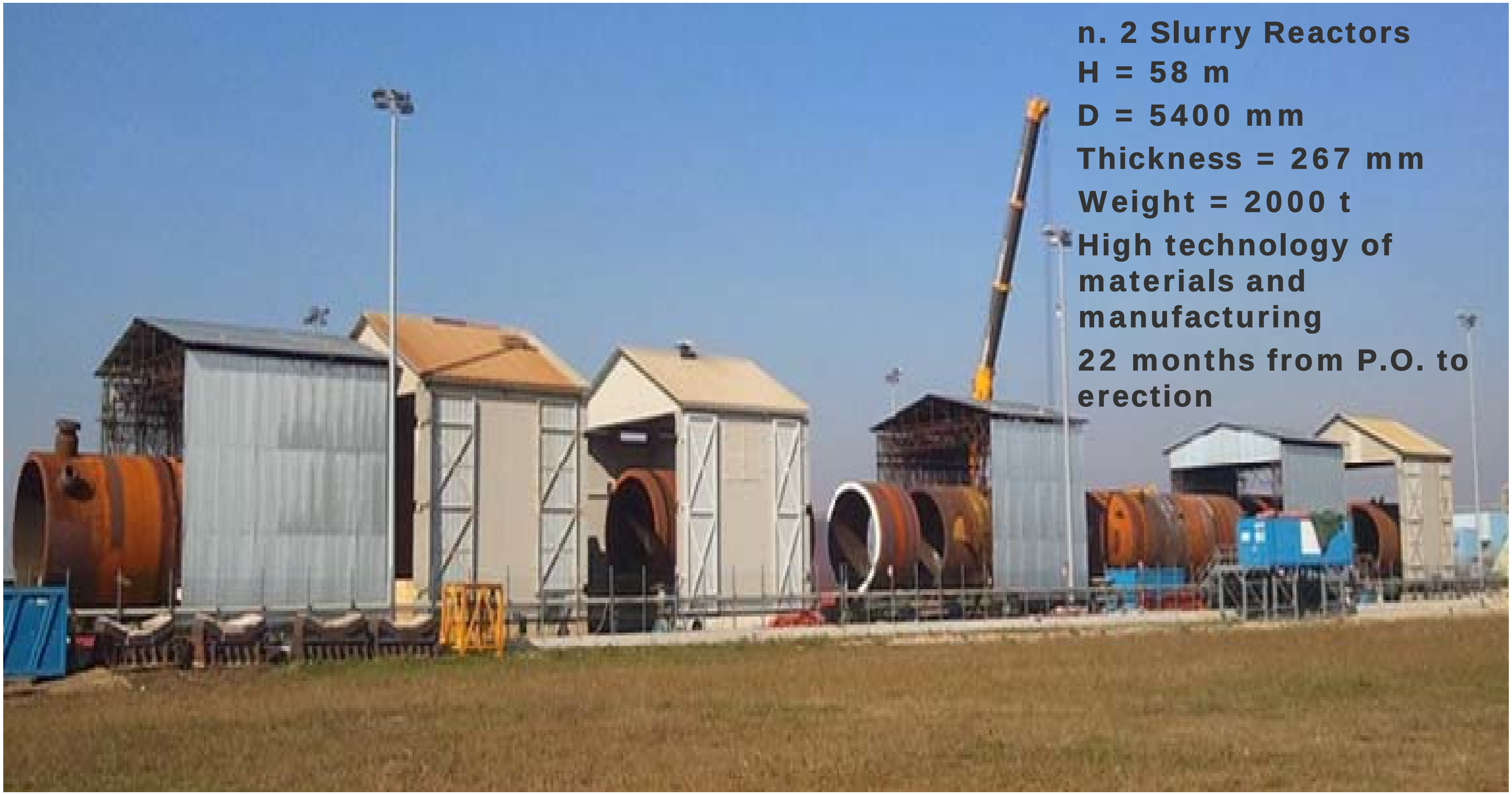
Sannazzaro EST Project –

Schedule of the main EST Project steps

- Engineering (Front End) started Jan 2009. Detailed engineering 9 months later
- Site Activities (earth movement and civil works) started in Nov 2010
- Steam Reforming unit and relevant utilities started-up in Jan 2013
- Pre-commissioning of EST started in Apr 2013
- Commissioning of EST started in Jul 2013
- **Oil in: Oct 14th, 2013**

Constructability – Slurry Reactors

Constructability – Slurry Reactors



n. 2 Slurry Reactors
H = 58 m
D = 5400 mm
Thickness = 267 mm
Weight = 2000 t
High technology of materials and manufacturing
22 months from P.O. to erection

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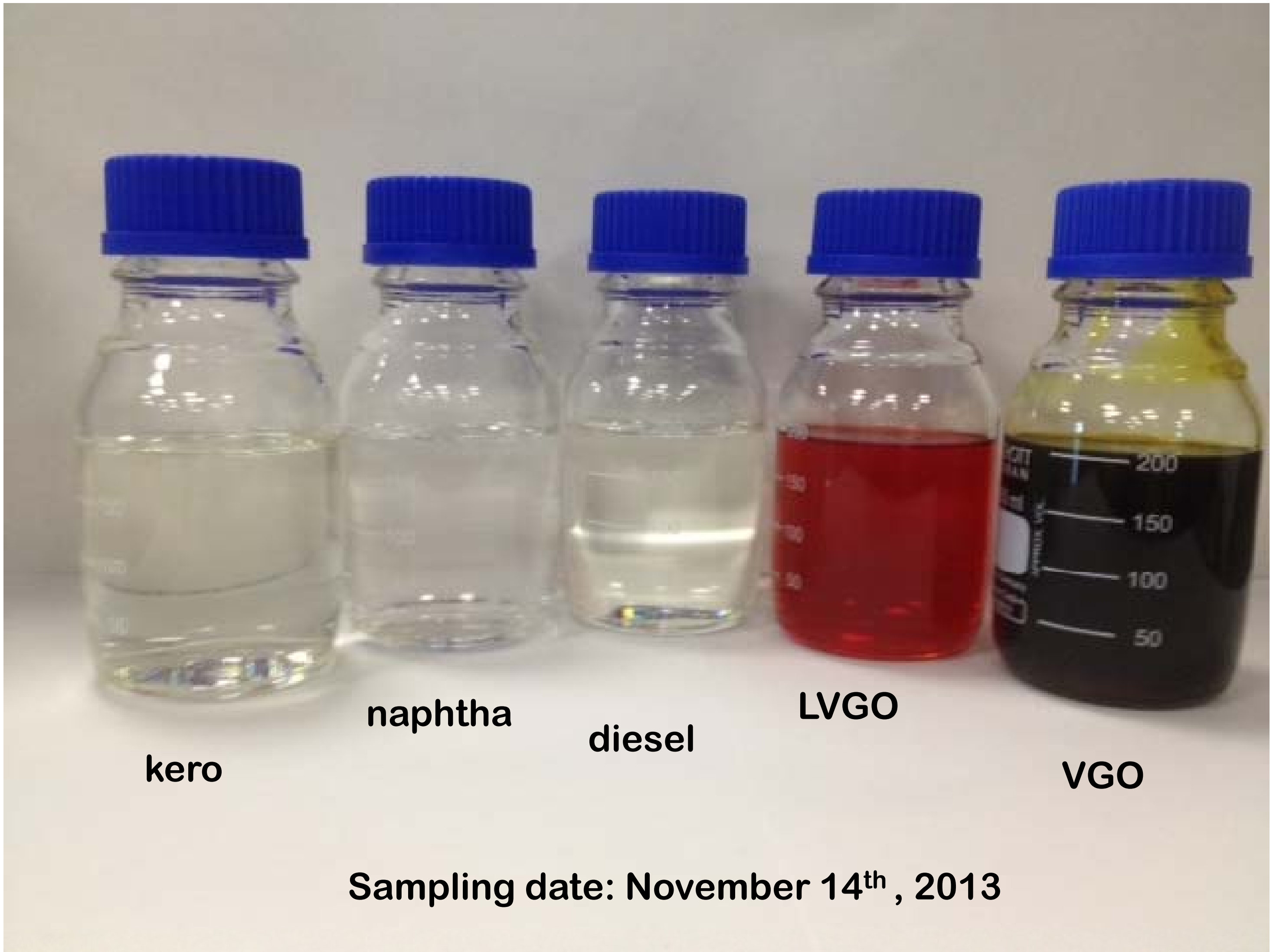
EST Sannazzaro today

EST Sannazzaro today



Sampling date: November 14th , 2013

Summary

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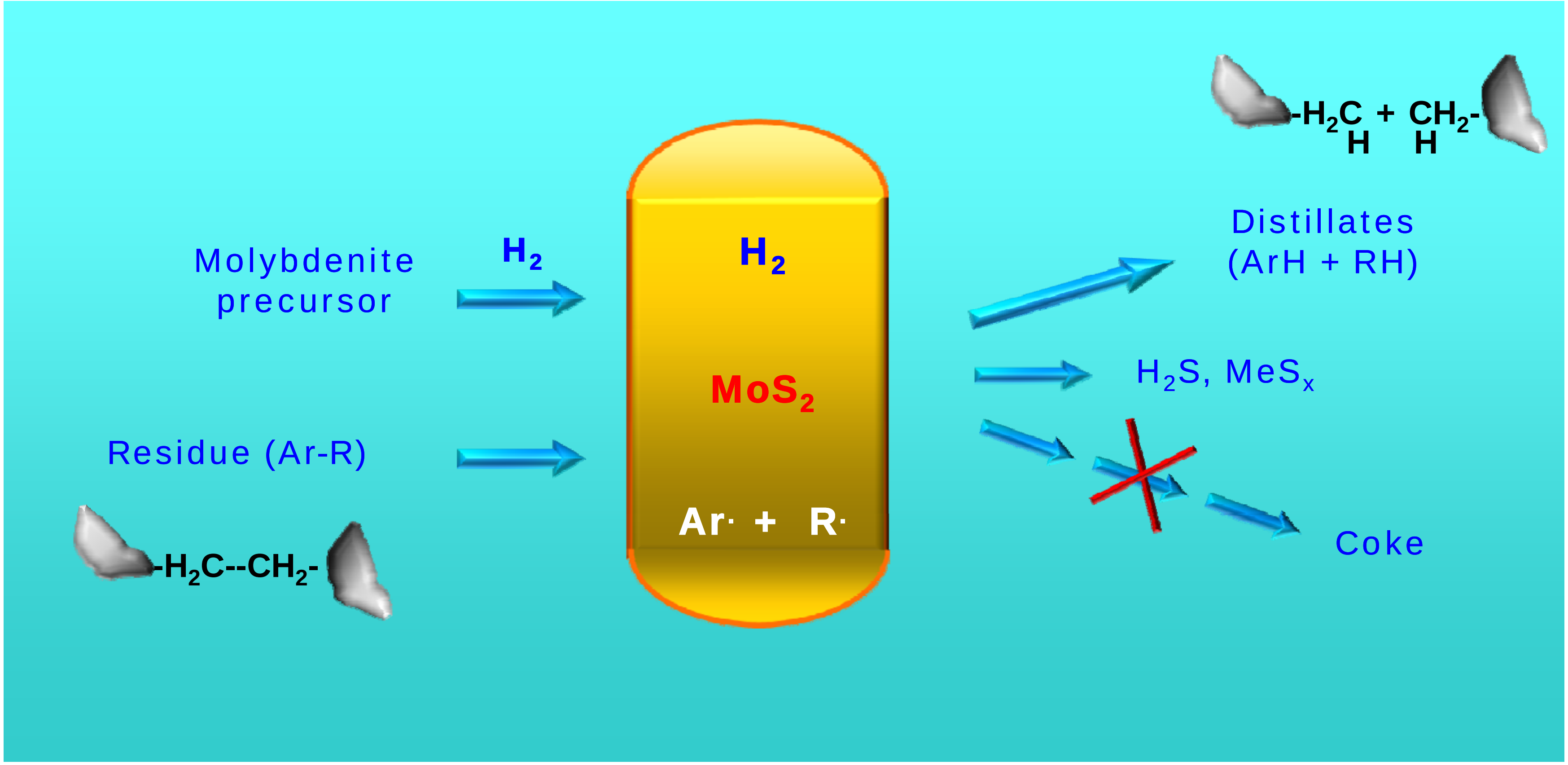
3 The “dual catalyst” system

Is it possible to improve the actual catalytic system ?



Molybdenite precursor

H_2

Residue (Ar-R)

$-H_2C--CH_2-$

H_2

MoS_2

Ar· + R·

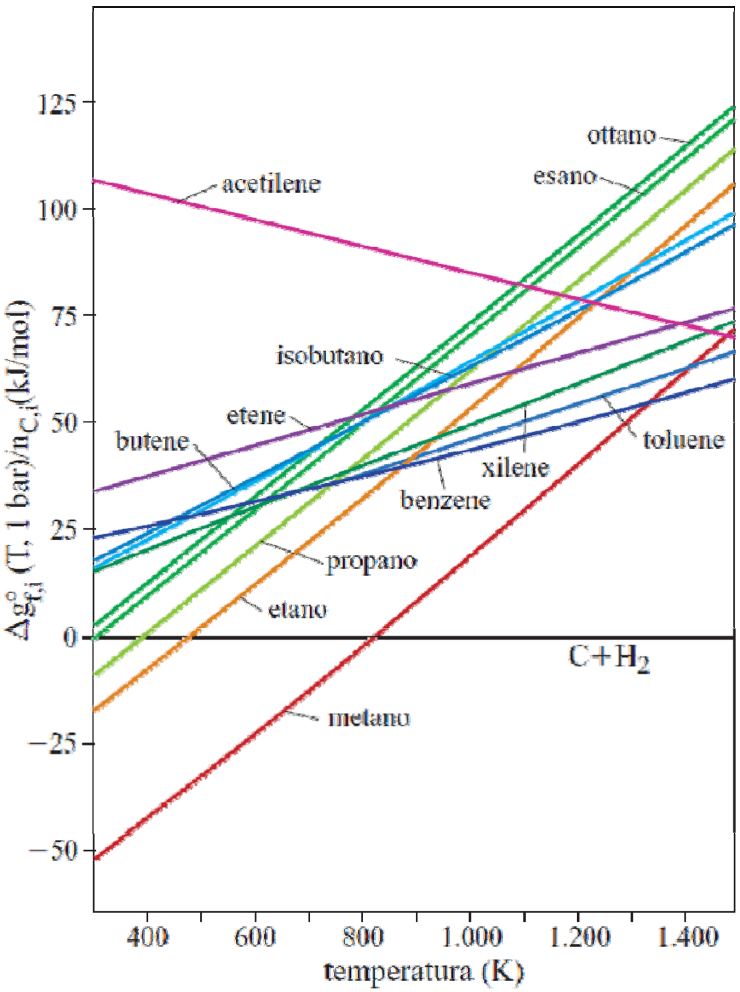
$-H_2C$ + CH_2-
H H

Distillates
(ArH + RH)

H_2S, MeS_x

Coke

Some chemistry for the cracking reaction



For the following equilibria:

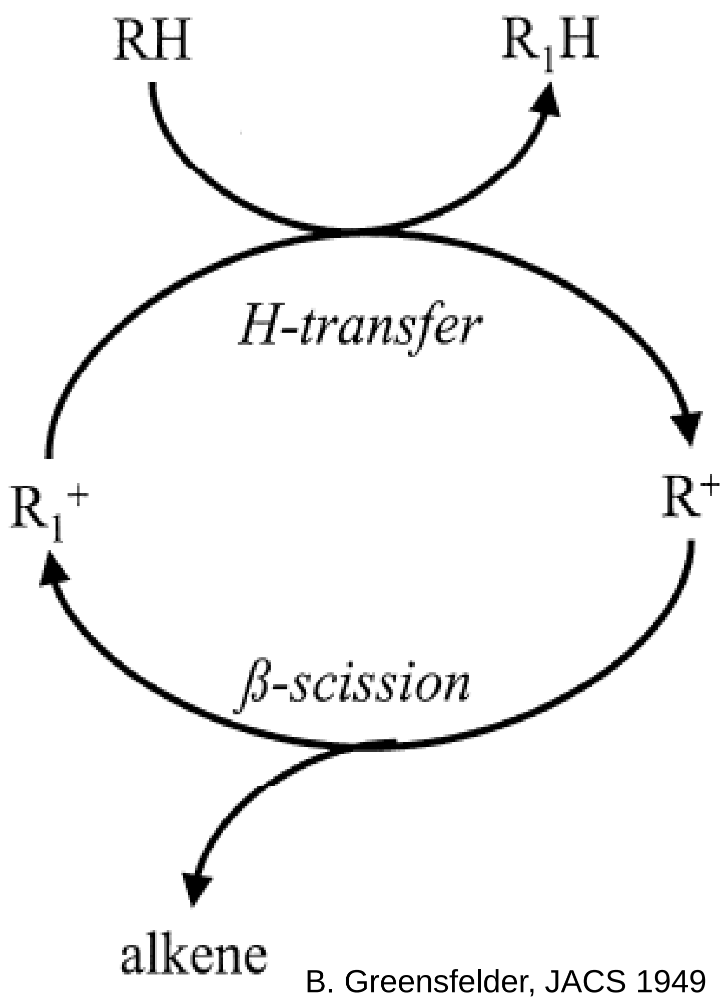
$$C_{(m+n)}H_{2(m+n)+2} \rightleftharpoons C_mH_{2m} + C_nH_{2n+2}$$

the Δ Gibbs free energy is $\Delta G = 0$ at 567 K and above this value, according to the thermodynamic, the reaction is favoured.

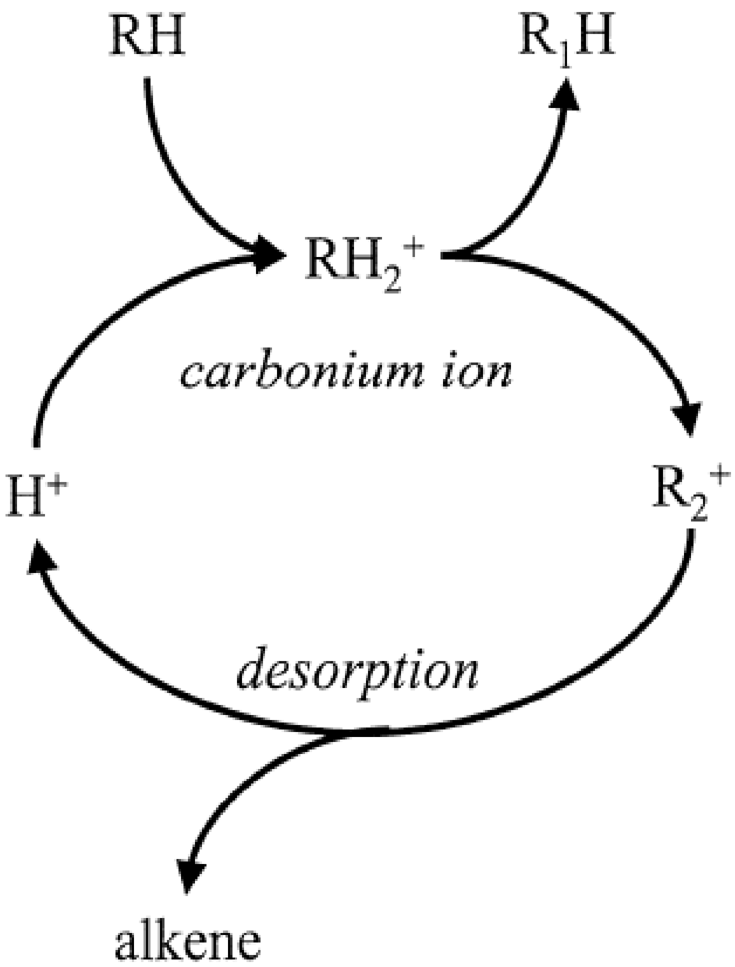
Kcal.mol^{-1}

$CH_3CH_2CH_2\dot{C}H_2$	0	0	$CH_3CH_2CH_2\overset{+}{C}H_2$
$CH_3CH_2\dot{C}HCH_3$	- 4.0	- 14.0	$CH_3CH_2\overset{+}{C}HCH_3$
$(CH_3)_3C\bullet$	- 7.7	- 26.7	$(CH_3)_3C^+$

Some chemistry for the cracking reaction

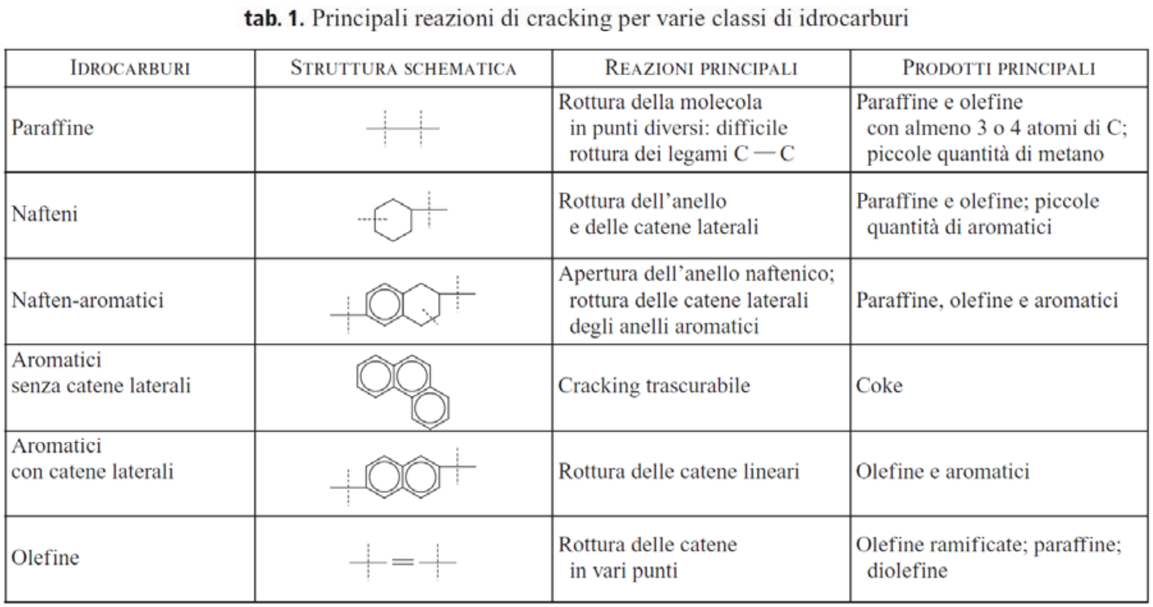


B. Greensfelder, JACS 1949



W. Haag, R.Dessau, 8th In. Cat. Conf. Berlin, 1984

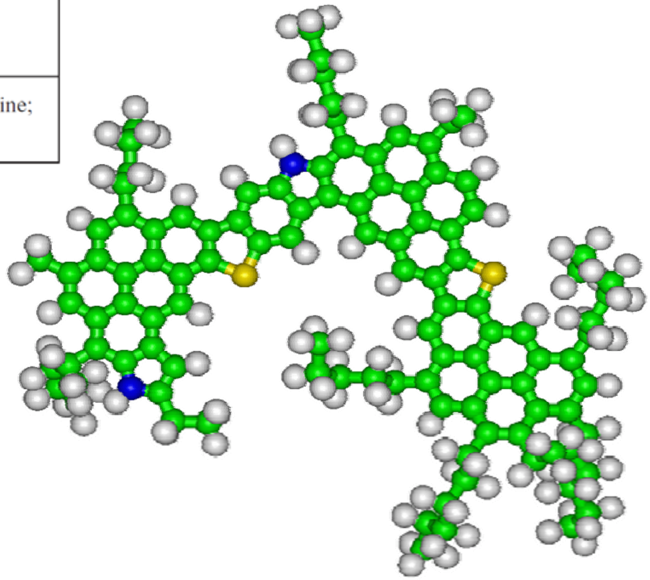
Some chemistry for the cracking reaction



tab. 1. Principali reazioni di cracking per varie classi di idrocarburi

Idrocarburi	Struttura schematica	Reazioni principali	Prodotti principali
Paraffine		Rottura della molecola in punti diversi: difficile rottura dei legami C — C	Paraffine e olefine con almeno 3 o 4 atomi di C; piccole quantità di metano
Nafteni		Rottura dell'anello e delle catene laterali	Paraffine e olefine; piccole quantità di aromatici
Naften-aromatici		Apertura dell'anello naftenico; rottura delle catene laterali degli anelli aromatici	Paraffine, olefine e aromatici
Aromatici senza catene laterali		Cracking trascurabile	Coke
Aromatici con catene laterali		Rottura delle catene lineari	Olefine e aromatici
Olefine		Rottura delle catene in vari punti	Olefine ramificate; paraffine; diolefine

Enciclopedia degli idrocarburi, Treccani,
“ Il cracking catalitico”, C. Giavarini, 2006, 247-262.



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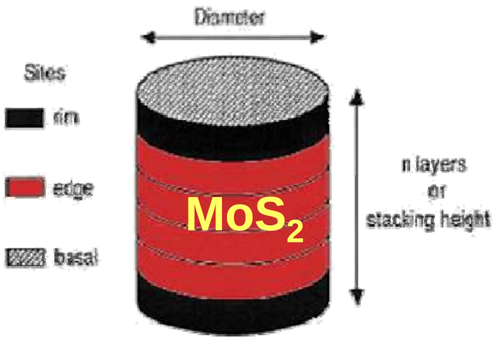
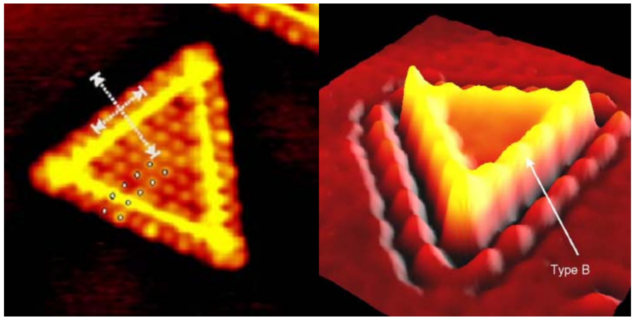
EST: the catalyst

The “Rim-Edge model”

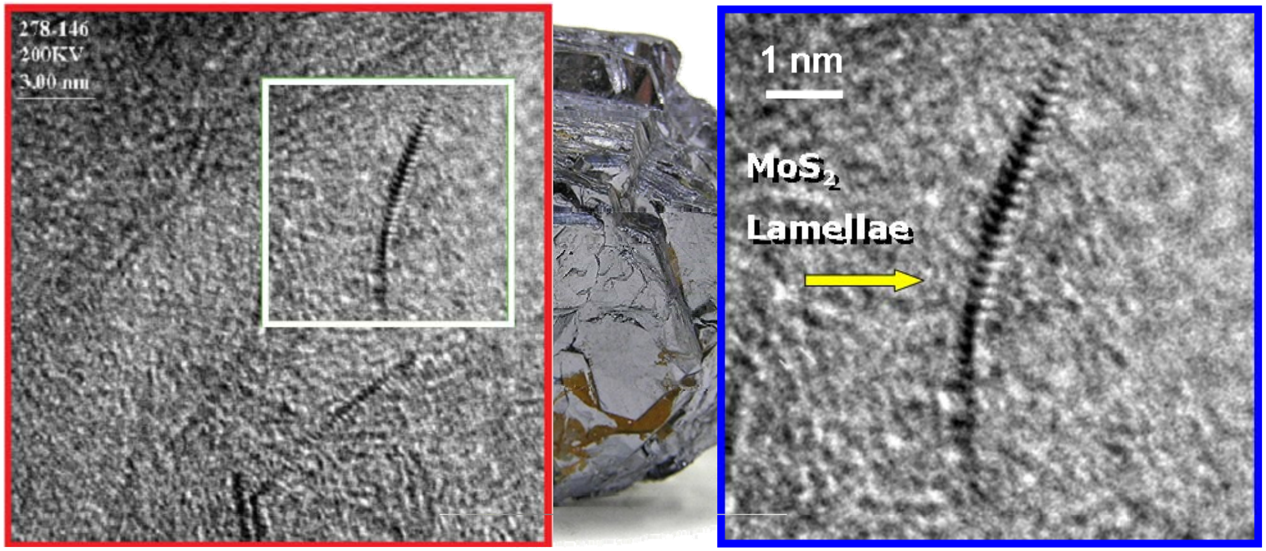


R.R. Chianelli et al., Catalysis Reviews, 48:1-41, 2006

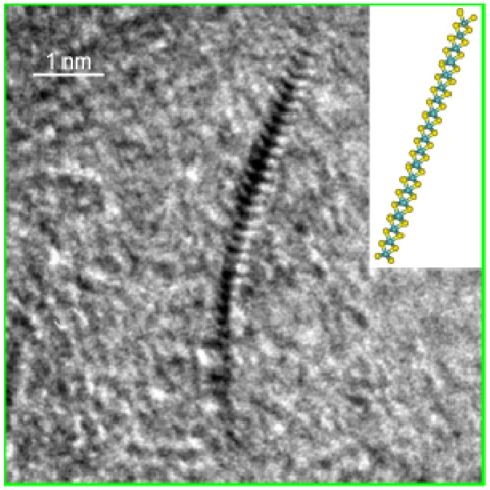
The “Brim model”



H. Topsoe et al., Catalysis Today, 107-108 (2005) 12-22.



Limits and perspectives for the EST catalytic system



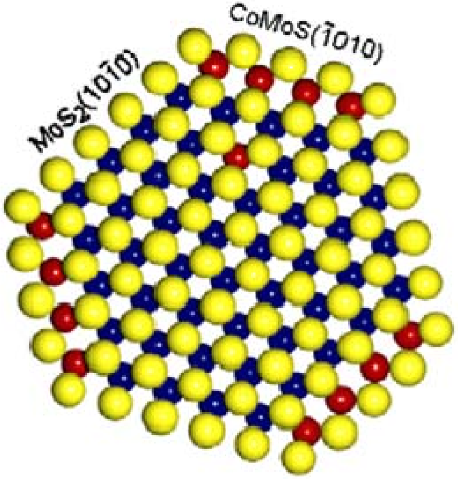
The main properties of this material are:

- 🙂 **the activation of molecular hydrogen;**
- 🙂 **the control of the coke formation ;**
- 🙂 **the conversion of organometallic Ni and V compounds to the correspondent sulphides;**
- 🙂 **the conversion of organic sulphur to H_2S;**

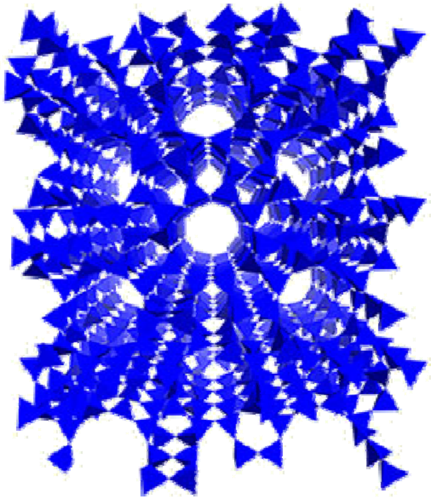
- ☹ **the cracking and HDN activity are low.**

How to improve the activity of MoS2

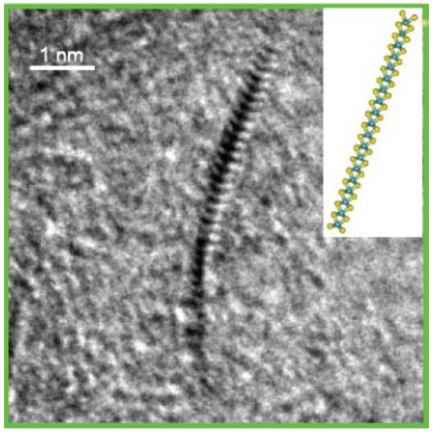
Partial substitution of Mo with Ni or Co



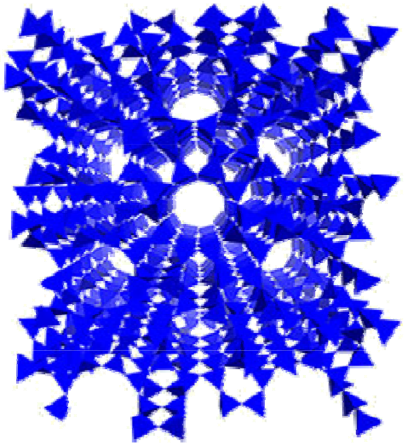
Addition of a cracking catalyst



Dual catalyst system



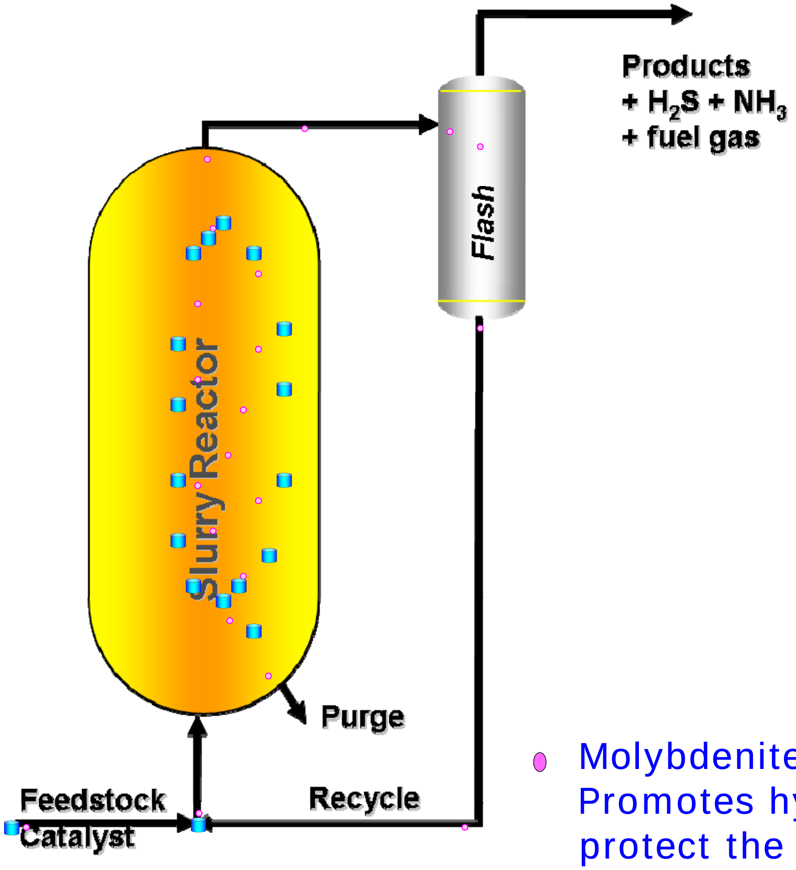
MoS_2 : very effective in promoting HDM and controlling coke formation.

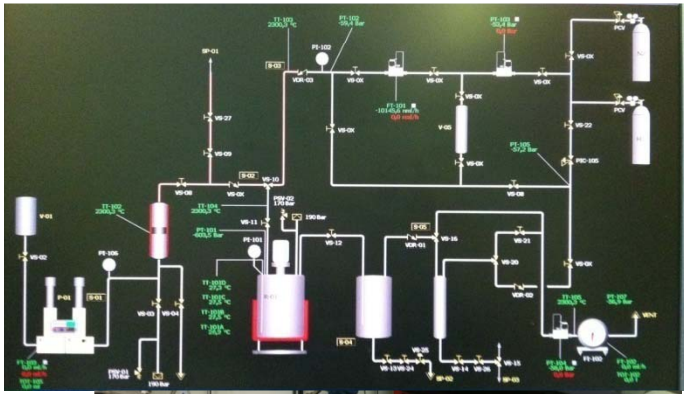


Cracking catalyst: fast decay due to the accumulation of metals and coke.

Can nano-dispersed Molybdenite be effective enough to protect a cracking catalyst from decay in a very aggressive environment under recycle conditions?

Dual Catalyst

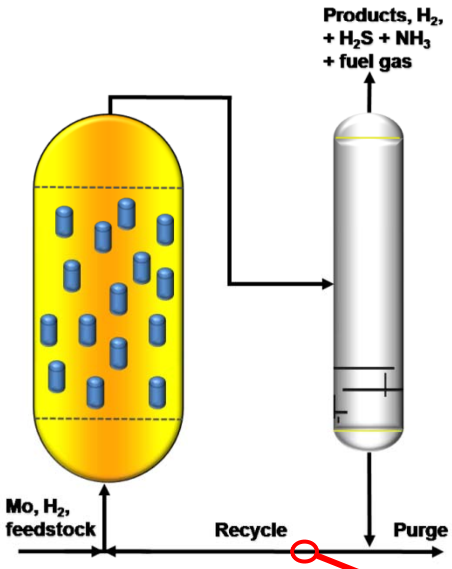




● Molybdenite:
Promotes hydrogenation and can protect the co-catalyst from metal poisoning and coke formation.

▮ Co-catalyst:
Promotes conversion and products quality

The metal poisoning



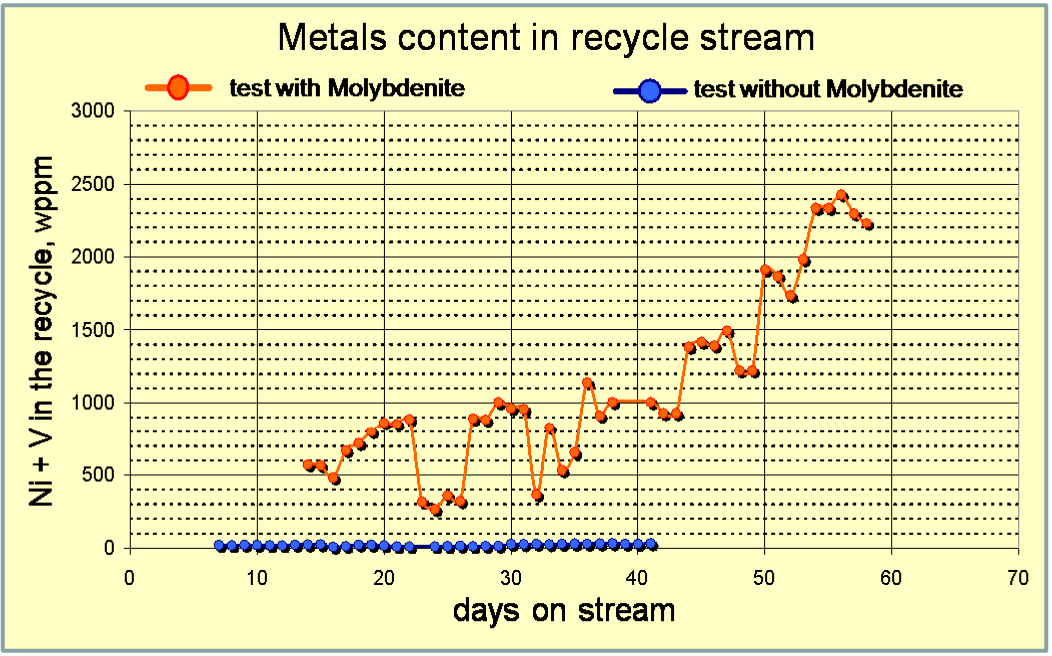
Catalyst:

hydroprocessing catalyst, 10% Mo, 4% Ni, γAl_2O_3 ; LHSV = 0.3-0.4;

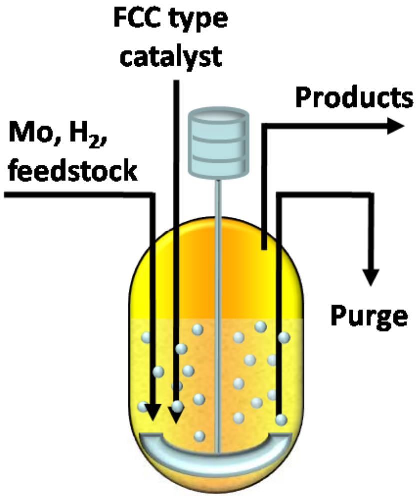
Molybdenite: equilibrated at 2000 ppmw;

Feedstock: vacuum resid Ural 550 °C +;

t: 430 °C, p: 130 barg



The formation of coke



Catalyst:

FCC-type catalyst , molar: SiO_2 : Al_2O_3 : La_2O_3 = 1 : 0,37 : 0,006;

Cat/oil = 0.1;

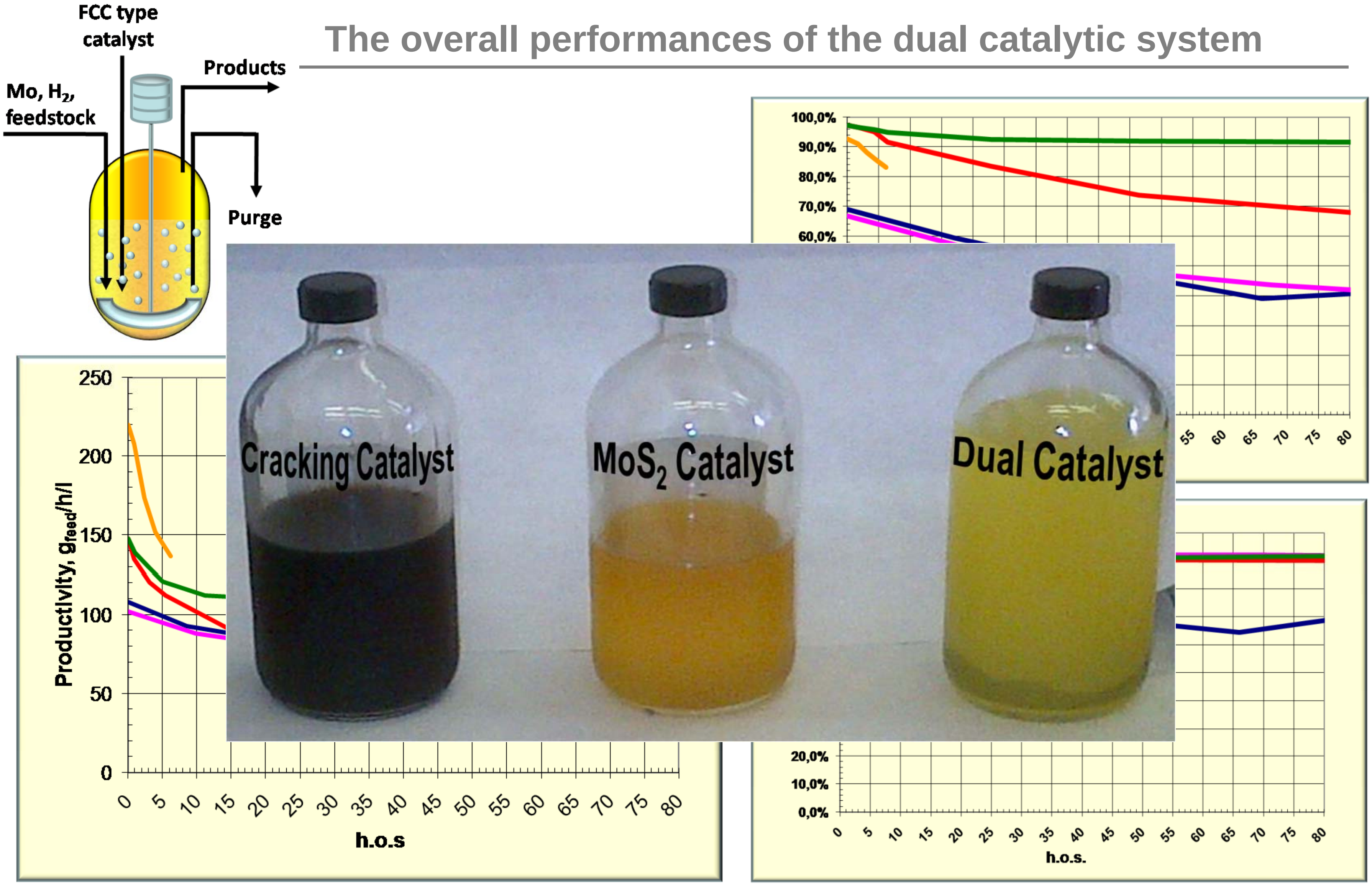
Molybdenite: equilibrated at 2000 ppmw;

Feedstock: vacuum resid Ural 550 °C +;

t: 430 °C, p: 130 barg

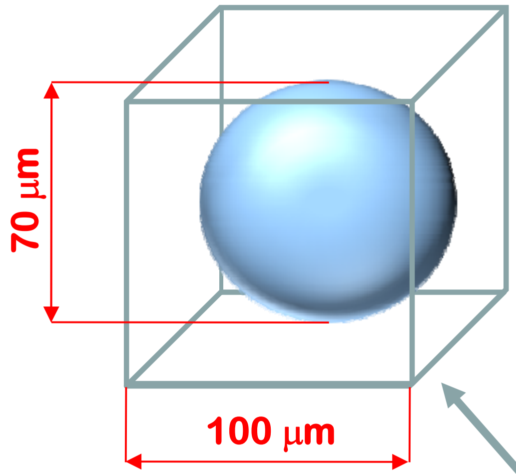
	t.o.s (h)	Solid yield (g/Kg feed)	Formation rate (g/h)
	h	g/Kg feed	g/h
No catalyst	120	57	1.2
Crack. Cat.	6	165	8.4
Dual Cat.	120	6	0,1

The overall performances of the dual catalytic system

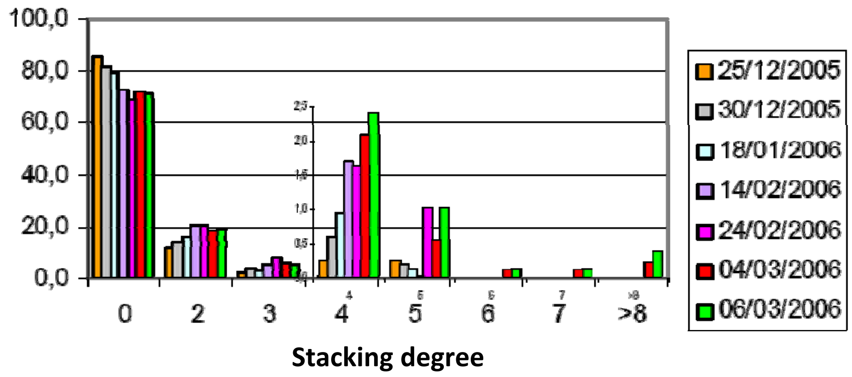


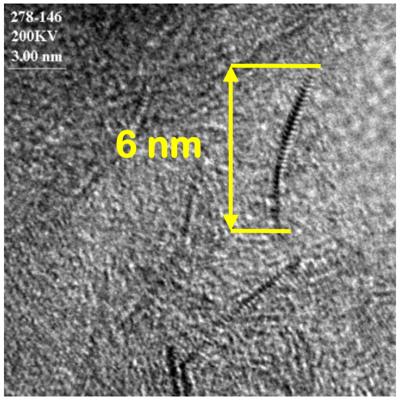
G. Bellussi et al., Catal. Sci. Technol., 3 (2013) 176-182.

Protection from metals deposition

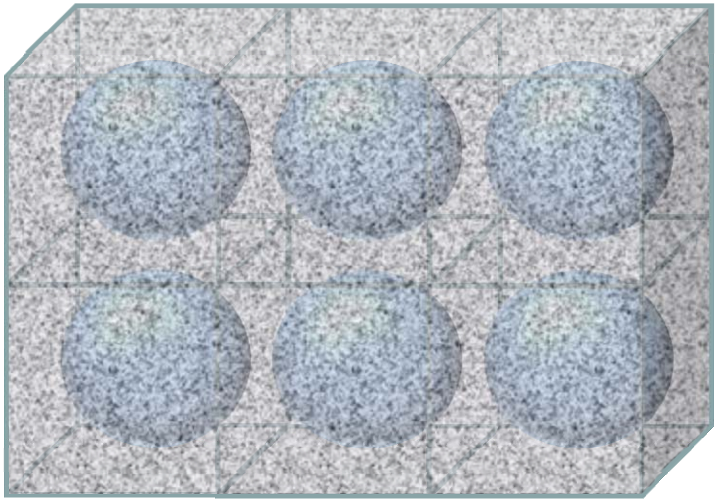


Distribution of average stacking of MoS_2





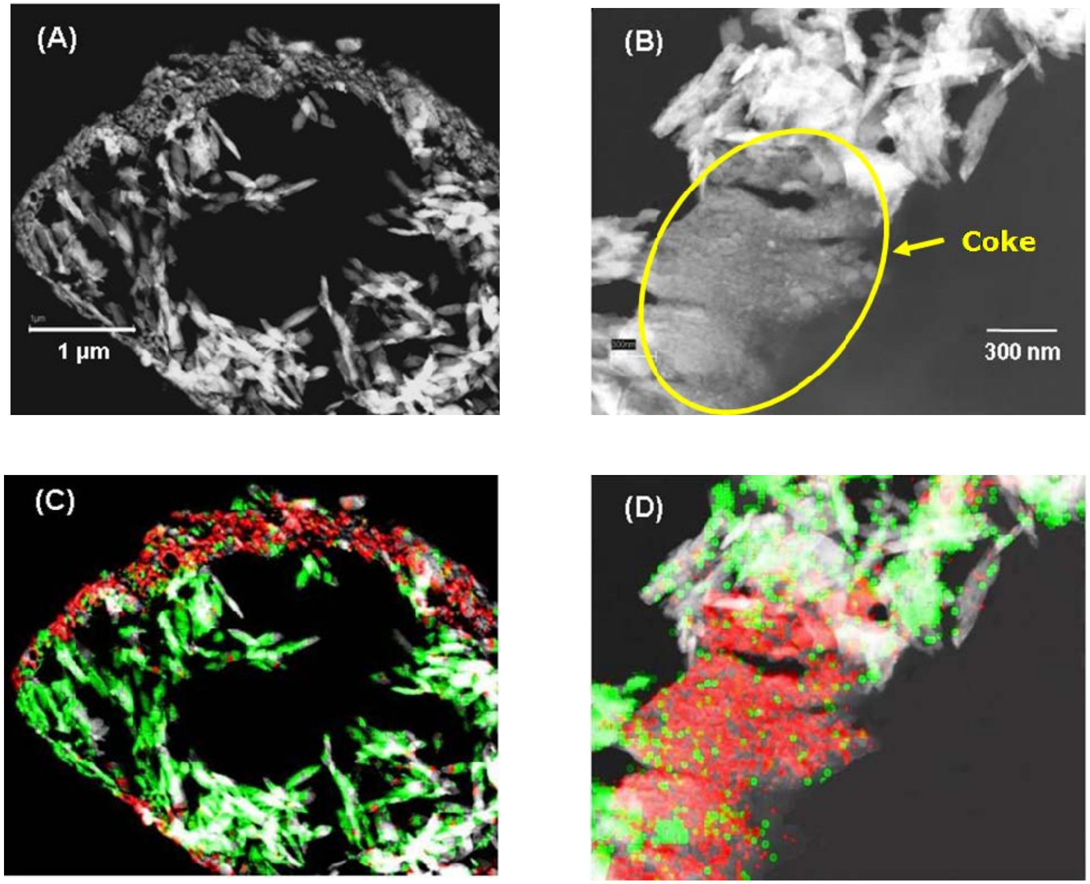
8 x 10^{10} particles



Average distance among cracking catalyst particles: 30 μm

Average distance among Molybdenite particles: 20 Å

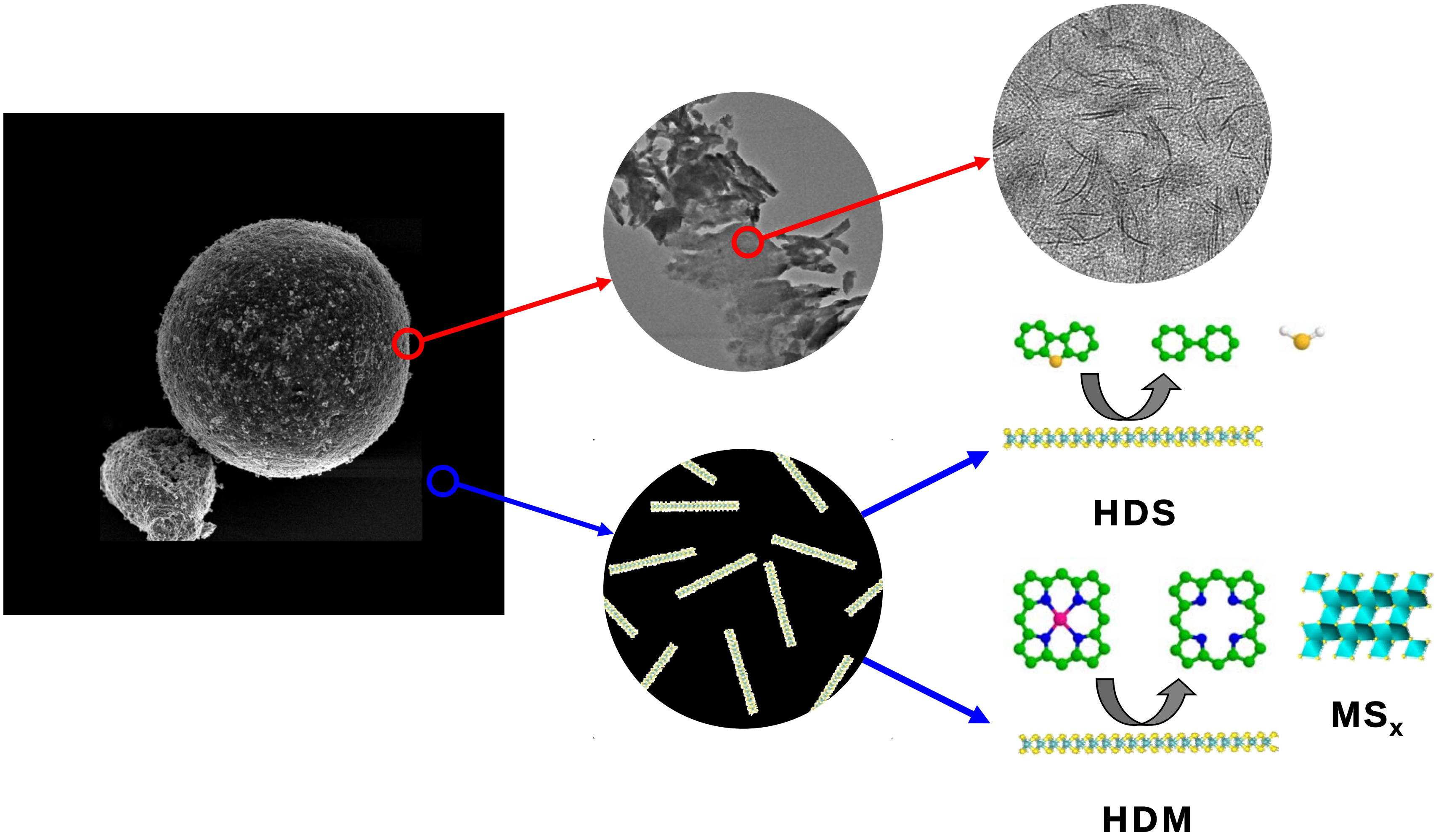
Protection from coke deposition



Jordisite: a C/MoS$_2$ mixed-layer phase (L-S Kao et al., Amer. Mineralogist, 86 (2001), 852-861.)

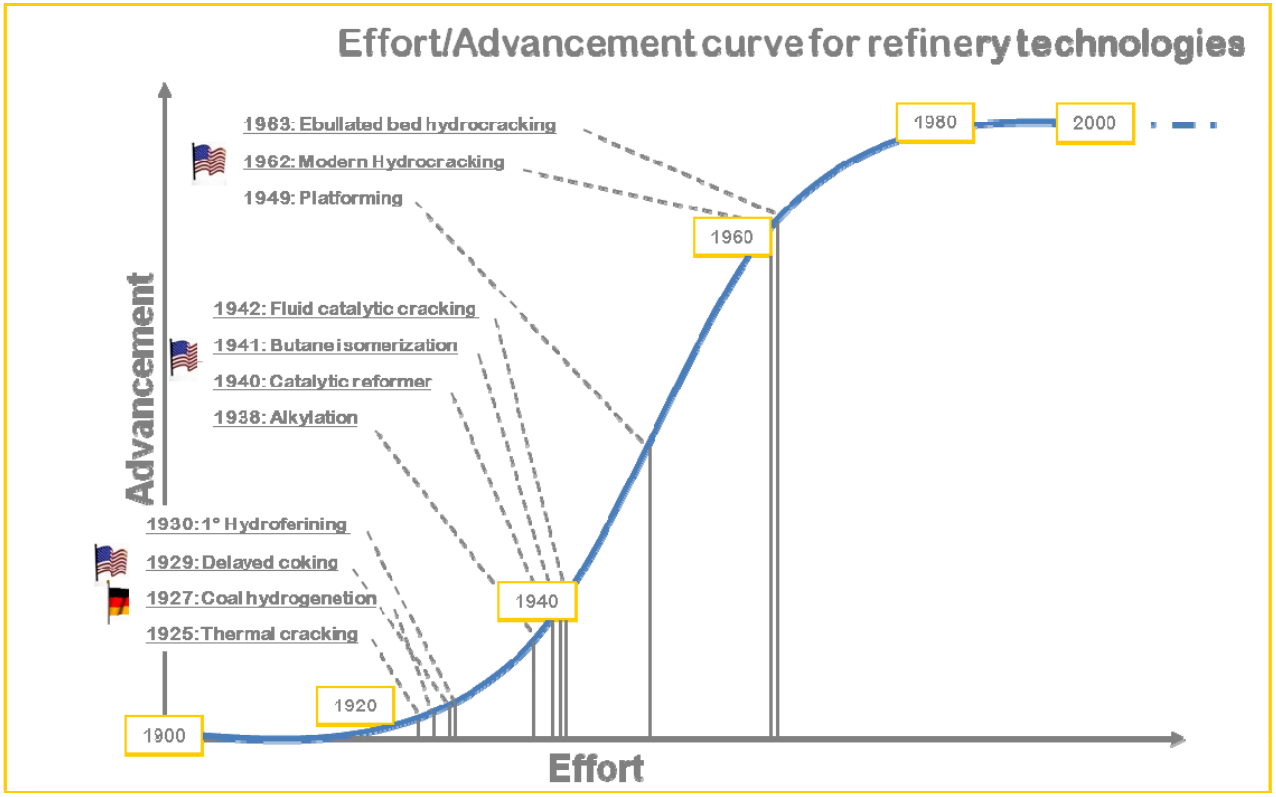
The general scheme

Inhibition of coke formation



Conclusion

Refinery is a mature technological sector where investement in R&D has been slowed down since several years by the oil companies and academic research center.



The rise in energy demand, the environmental concerns and the globalization, in the recent years have dramatically changed the scenario for refining business and introduced several urgent and important needs.

Conclusion

The EST technology is going to confirm the possibility of achieving the total conversion of the oil barrel to good quality middle distillates.

This technology breakthrough will provide an answer for the new needs of the refining and will open new perspectives in the oil business.

In the up-stream:

- ✓ a more effective use of unconventional oil resources;

In the downstream:

- ✓ increasing the use of sour, high sulphur, low-cost feedstocks and, were possible, taking advantage of the low cost natural gas from gas-shale;
- ✓ enabling the revamping of medium size refineries, simplifying the process scheme and reducing the specific energy cost