Catalysis in a Refinery

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PCK Raffinerie GmbH

Boiling Range of Crude Oil (REB)

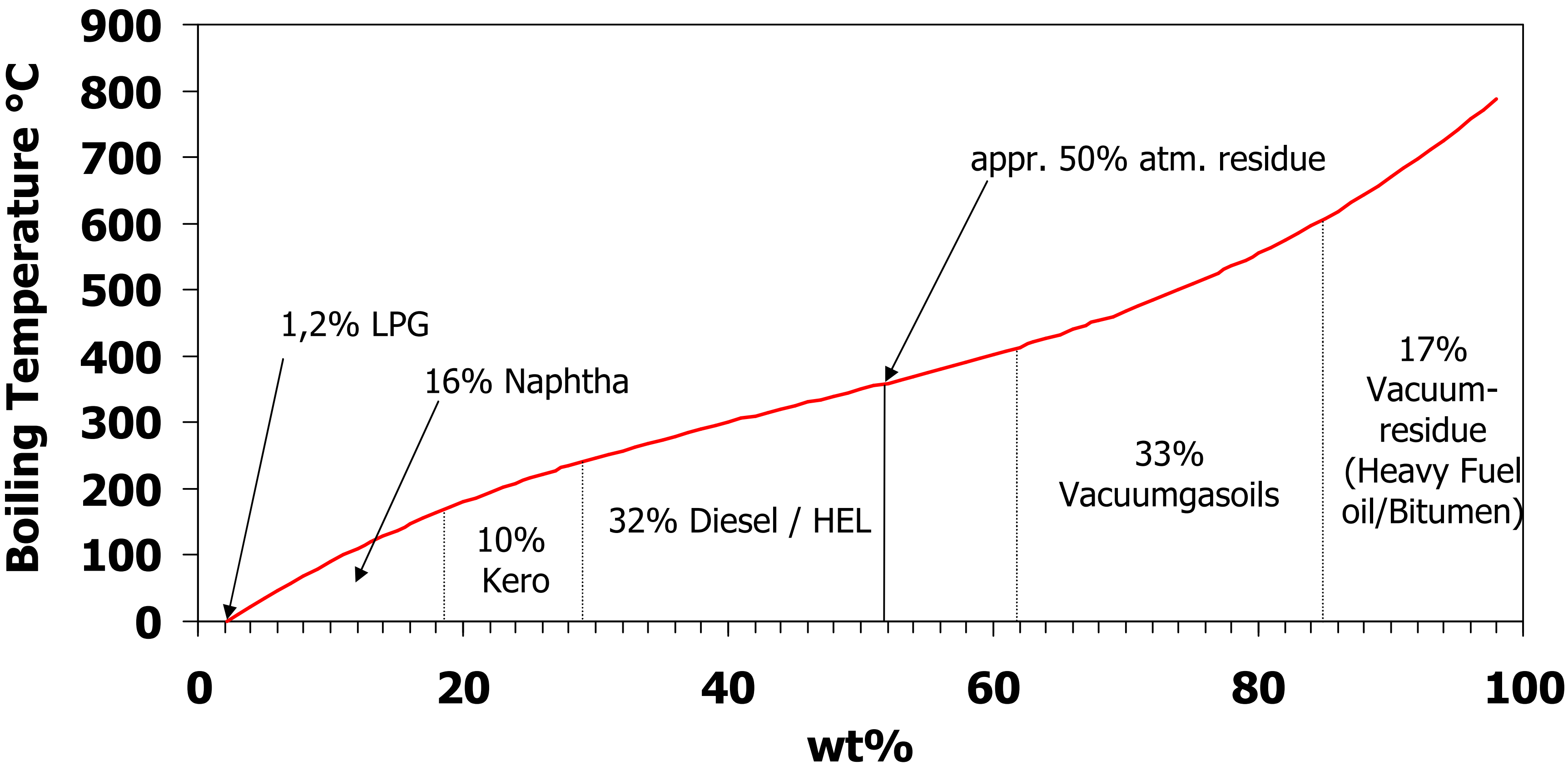

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Figure 1

Crude Oil Distillation

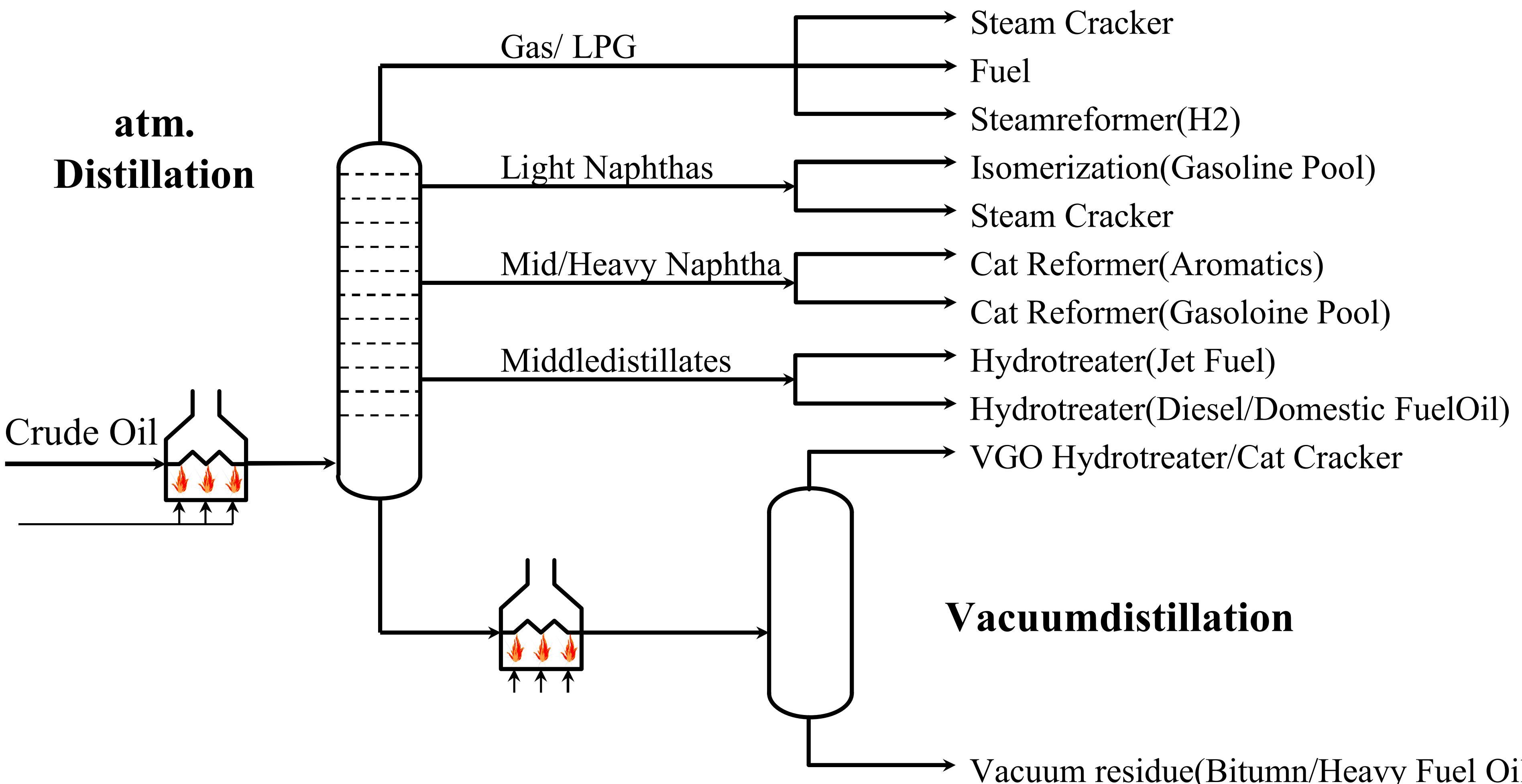

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Figure 2

Demand of Oil Products differs from Composition of Crude Oil

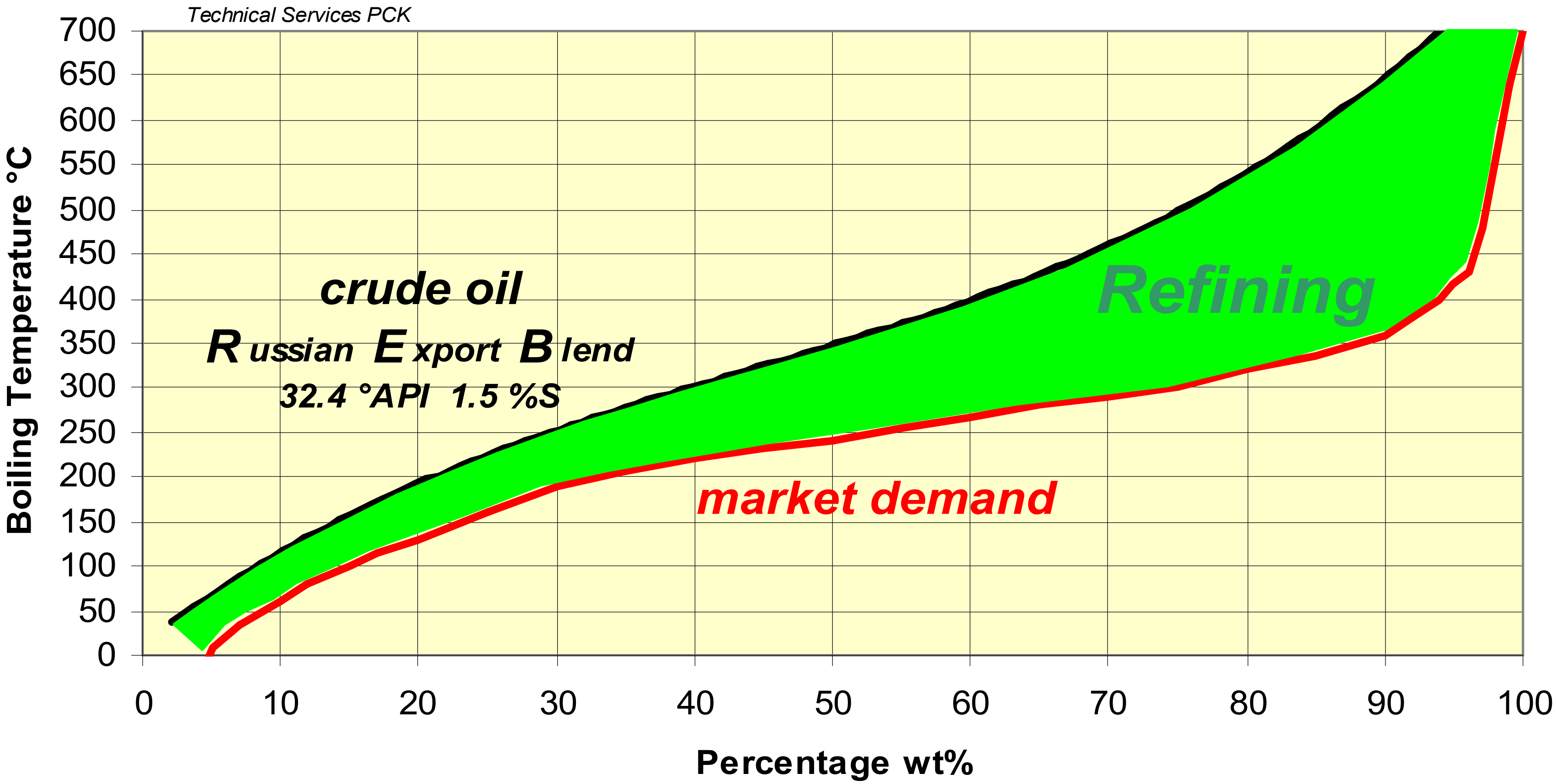

Figure 3

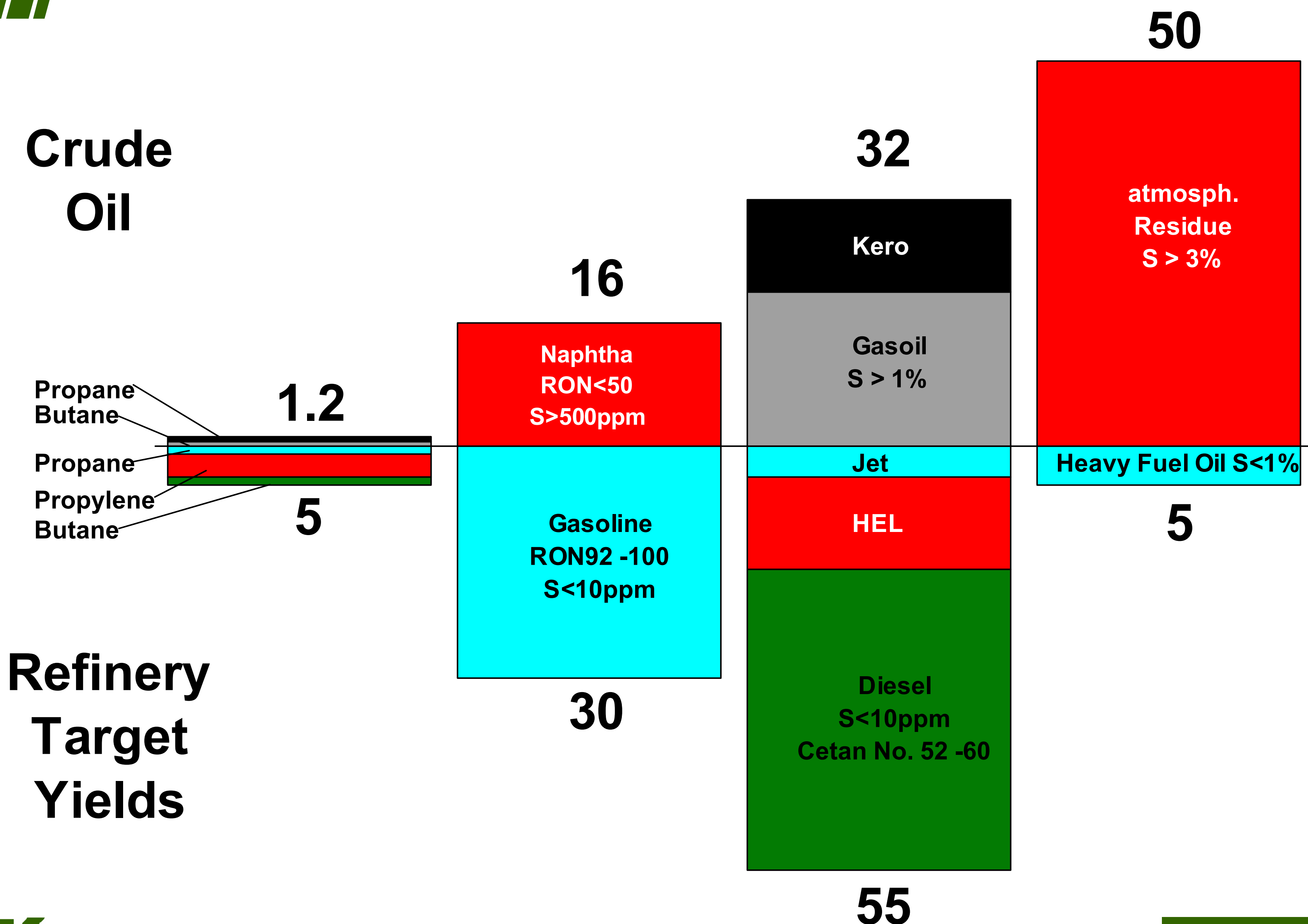

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Figure 4

Flow sheet

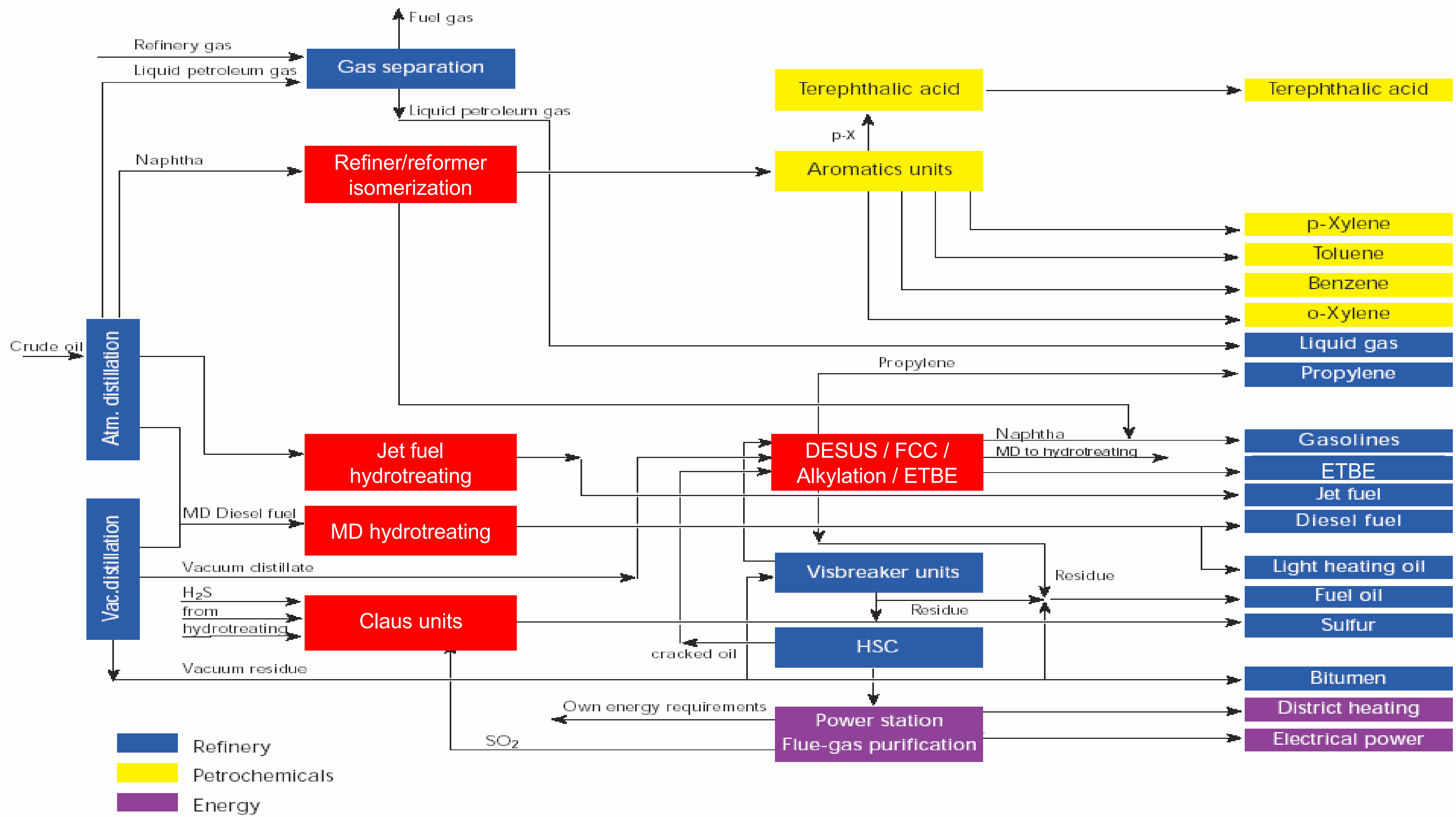

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Figure 5

Gasoline Upgrading

- Increasement of Octane number by Isomerization

  Conversion of normal C_5/C_6 Paraffins to iso Paraffins

- Increasement of Octane number by catalytic Reforming

  Aromatics from Dehydrogenation of Naphthenes as well as Dehydrocyclisation of Paraffins

- Increasement of Octane number by Alkylation

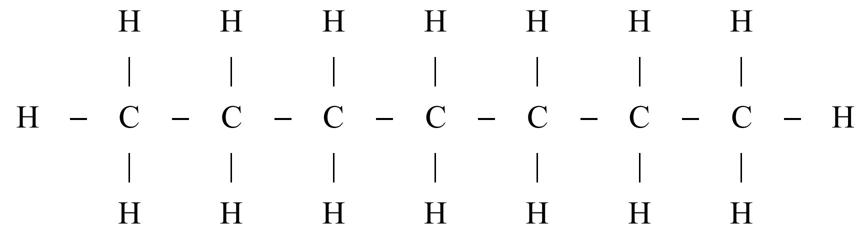
  Conversion of iso C_4 with Butenes to iso Octane

- Increasement of Octane number by Etherification

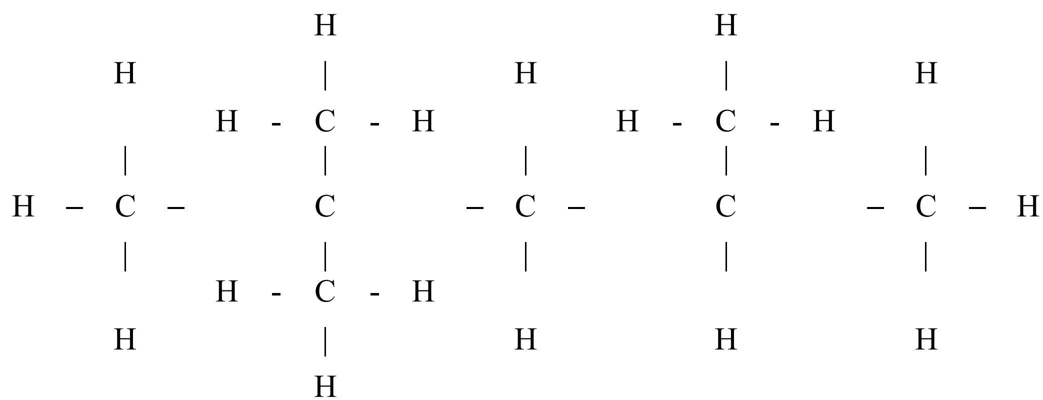
  Conversion of iso Butene with Ethanol to ETBE

Octane number

- **Antiknock Property**
  - **Octane number = 0**
    100 Vol% n-Heptane



  - **Octane number = 100**
    100 Vol% iso-Octane



Light Naphtha Isomerization

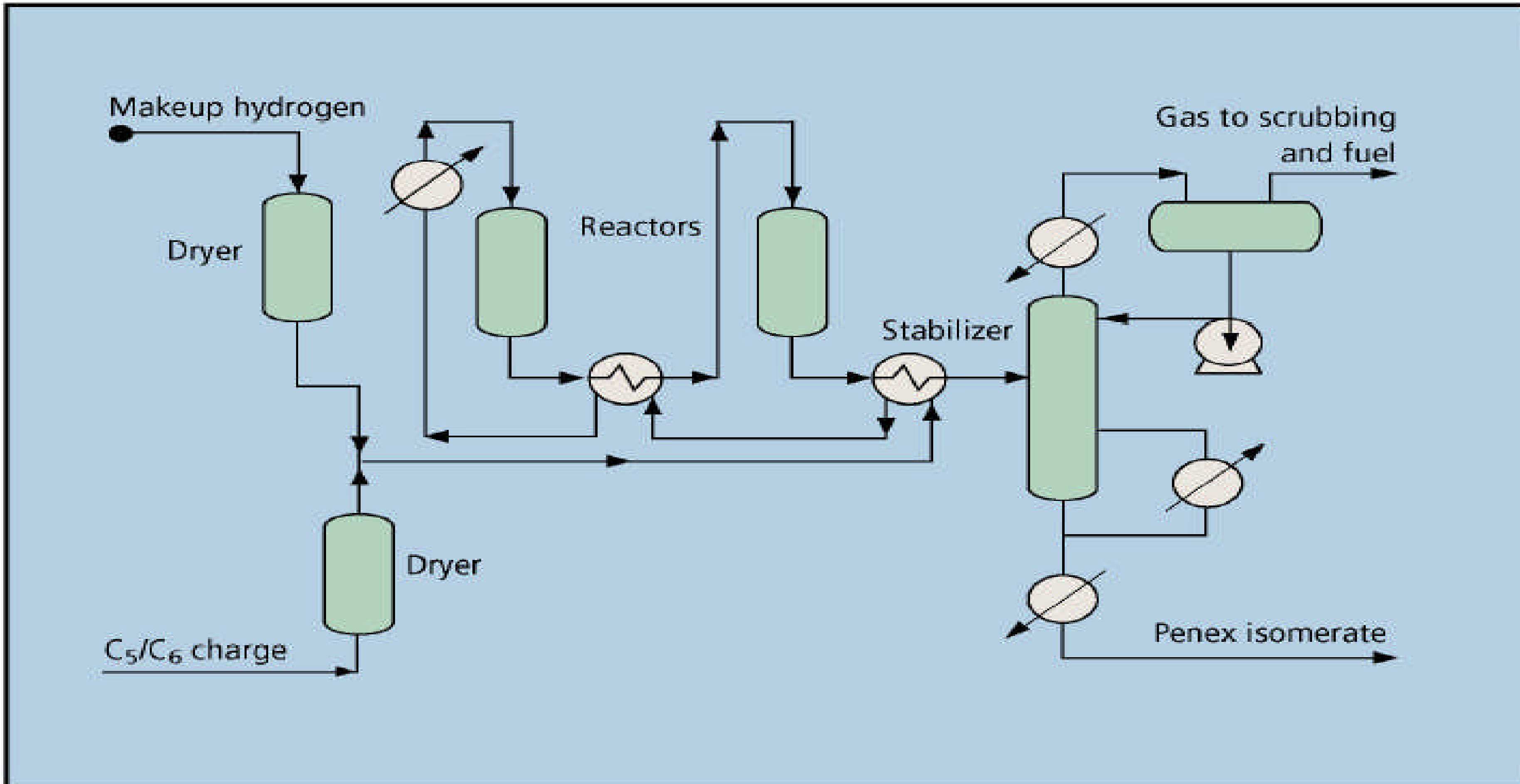


Figure 8

Catalytic Reforming

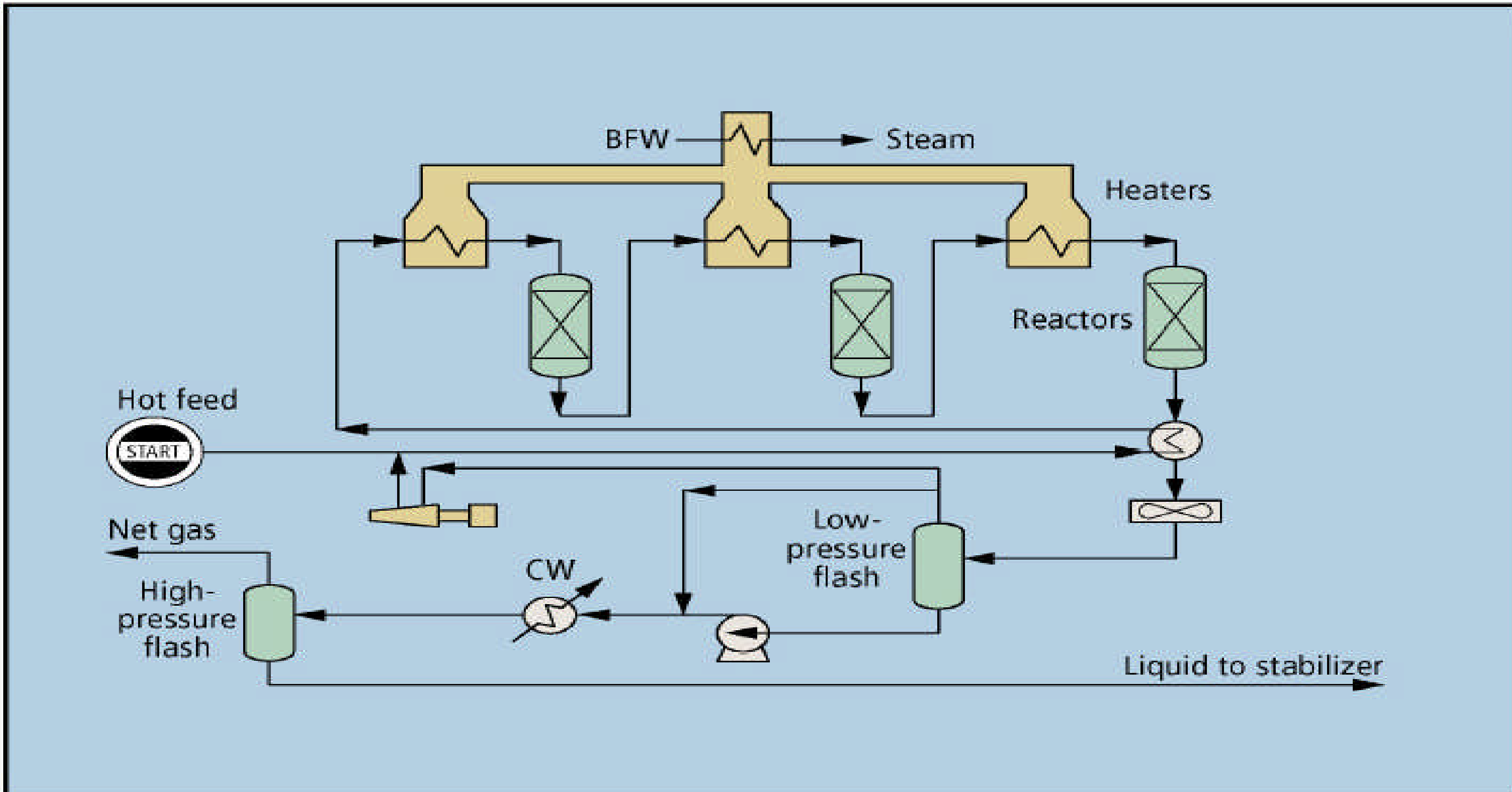
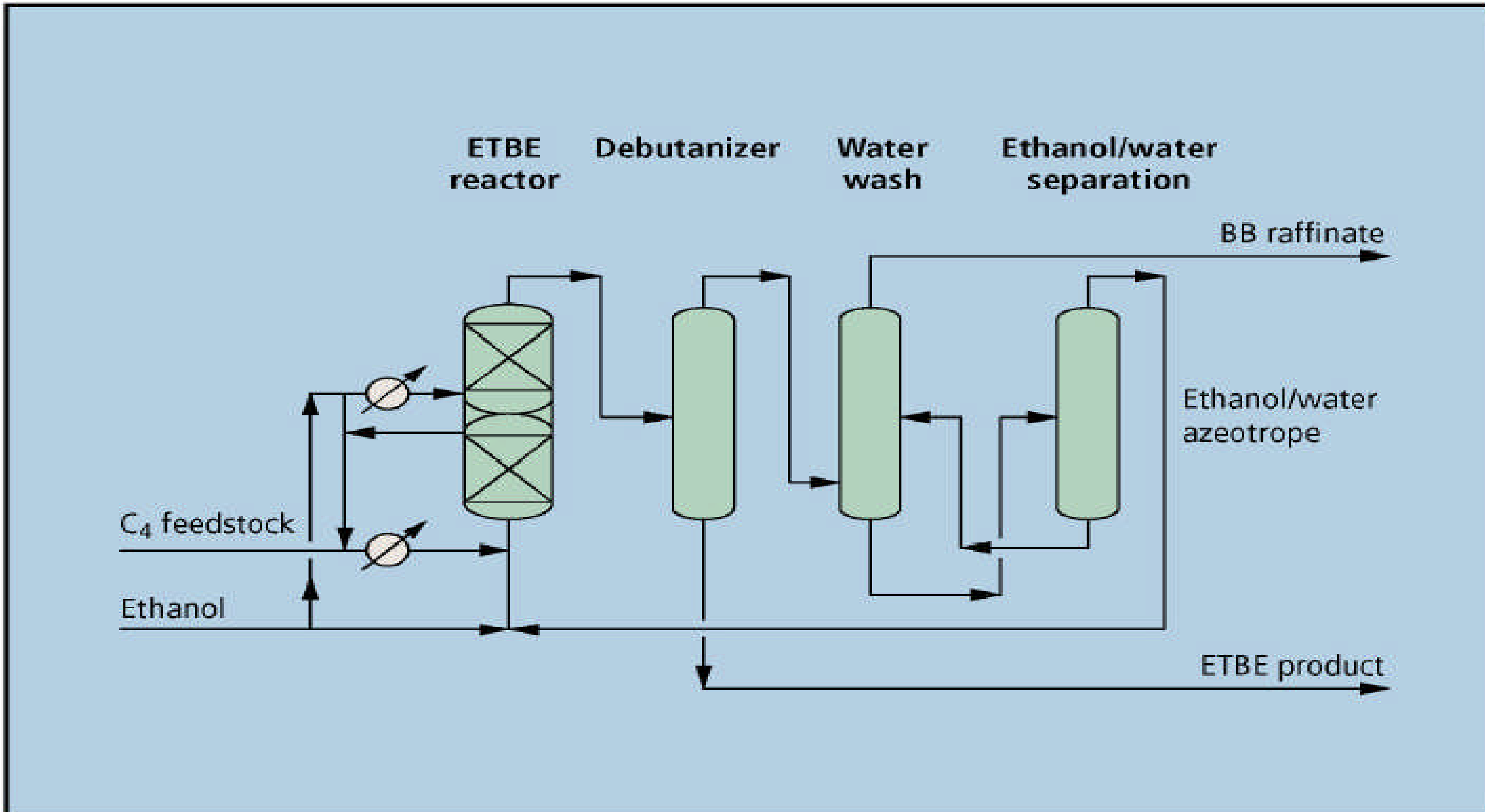


Figure 9

Ether



ETBE reactor
Debutanizer
Water wash
Ethanol/water separation
BB raffinate
Ethanol/water azeotrope
C4 feedstock
Ethanol
ETBE product

Flow sheet

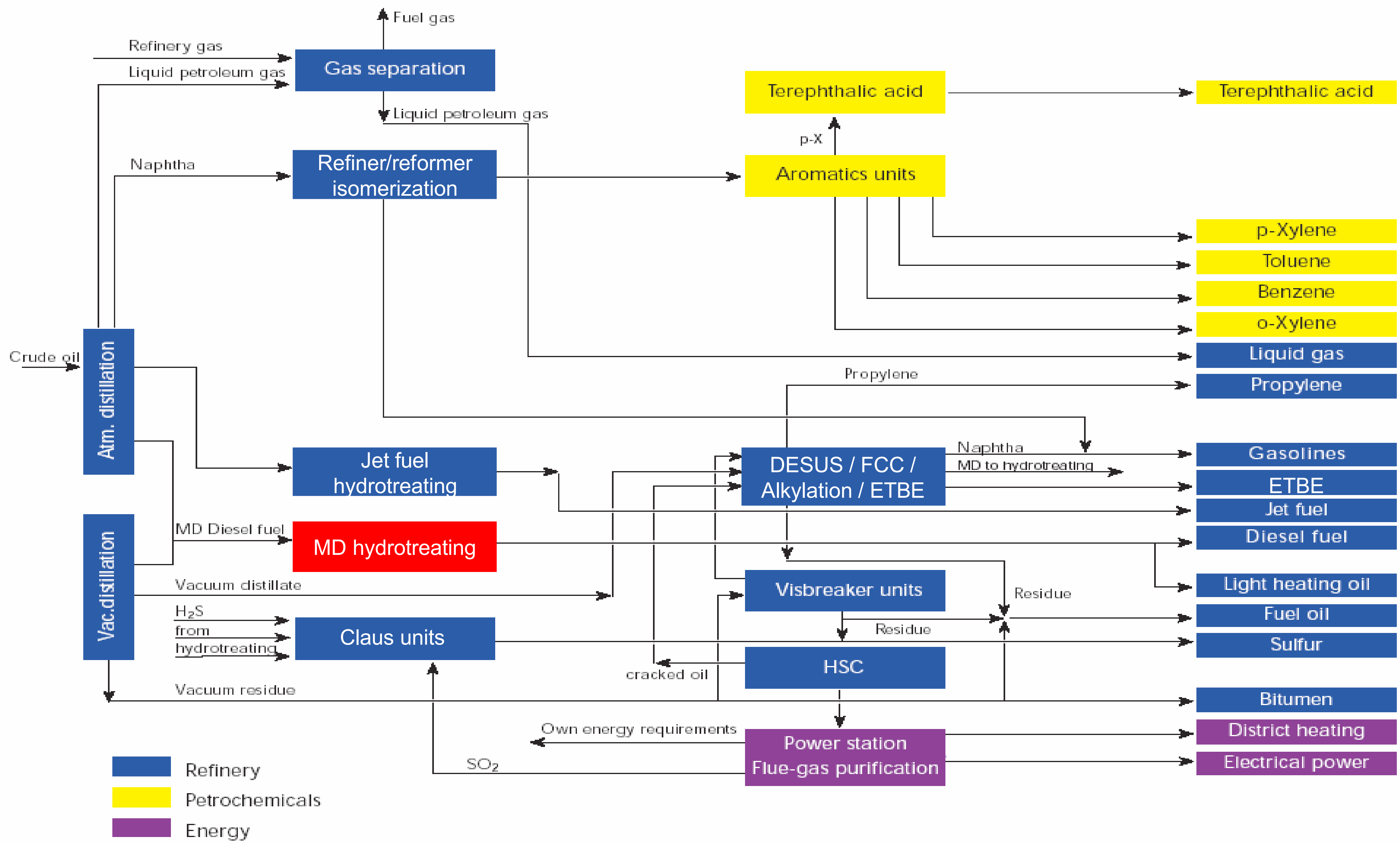


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Figure 11

Development of Sulfur Limit in Gasoline

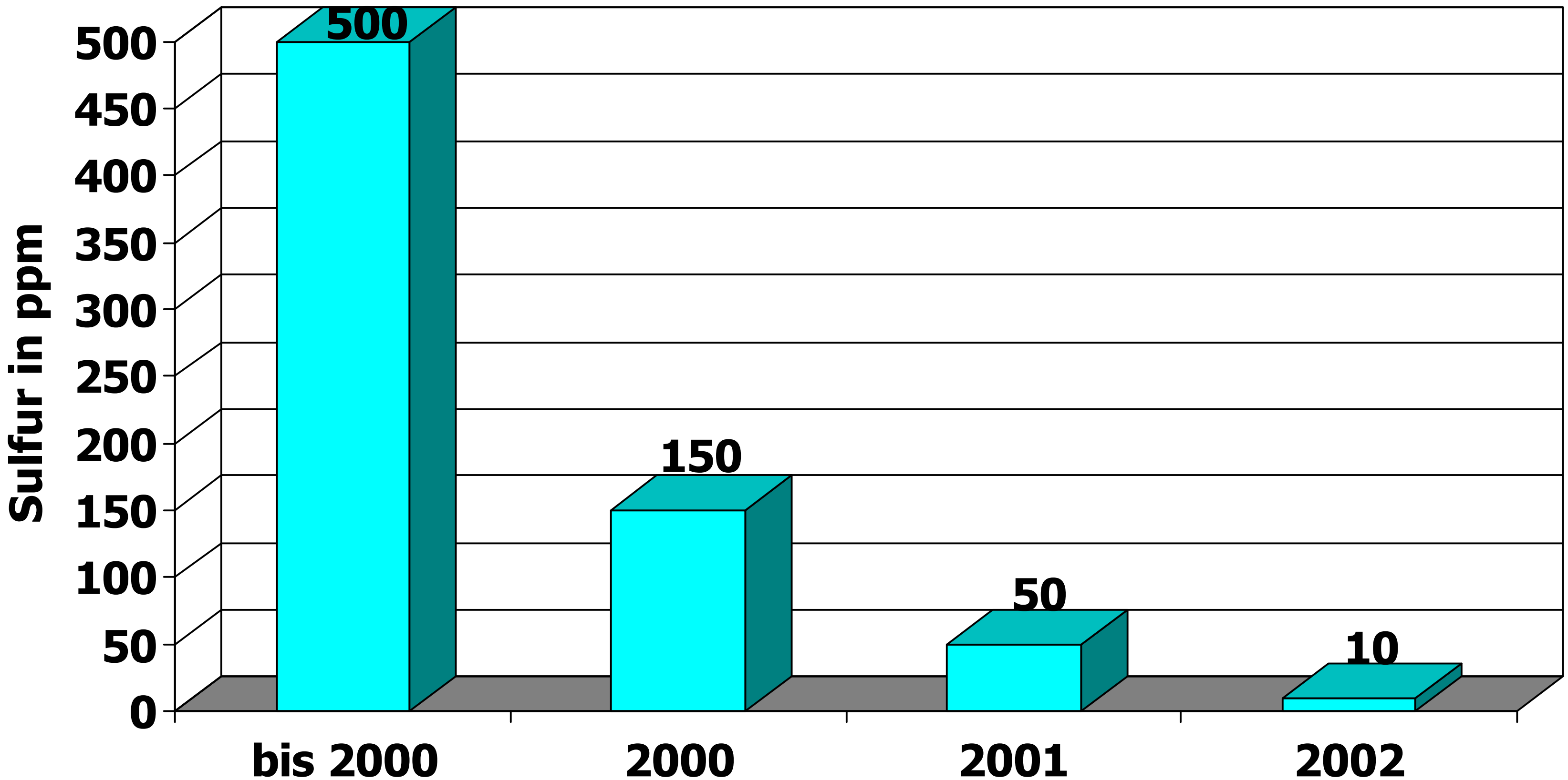
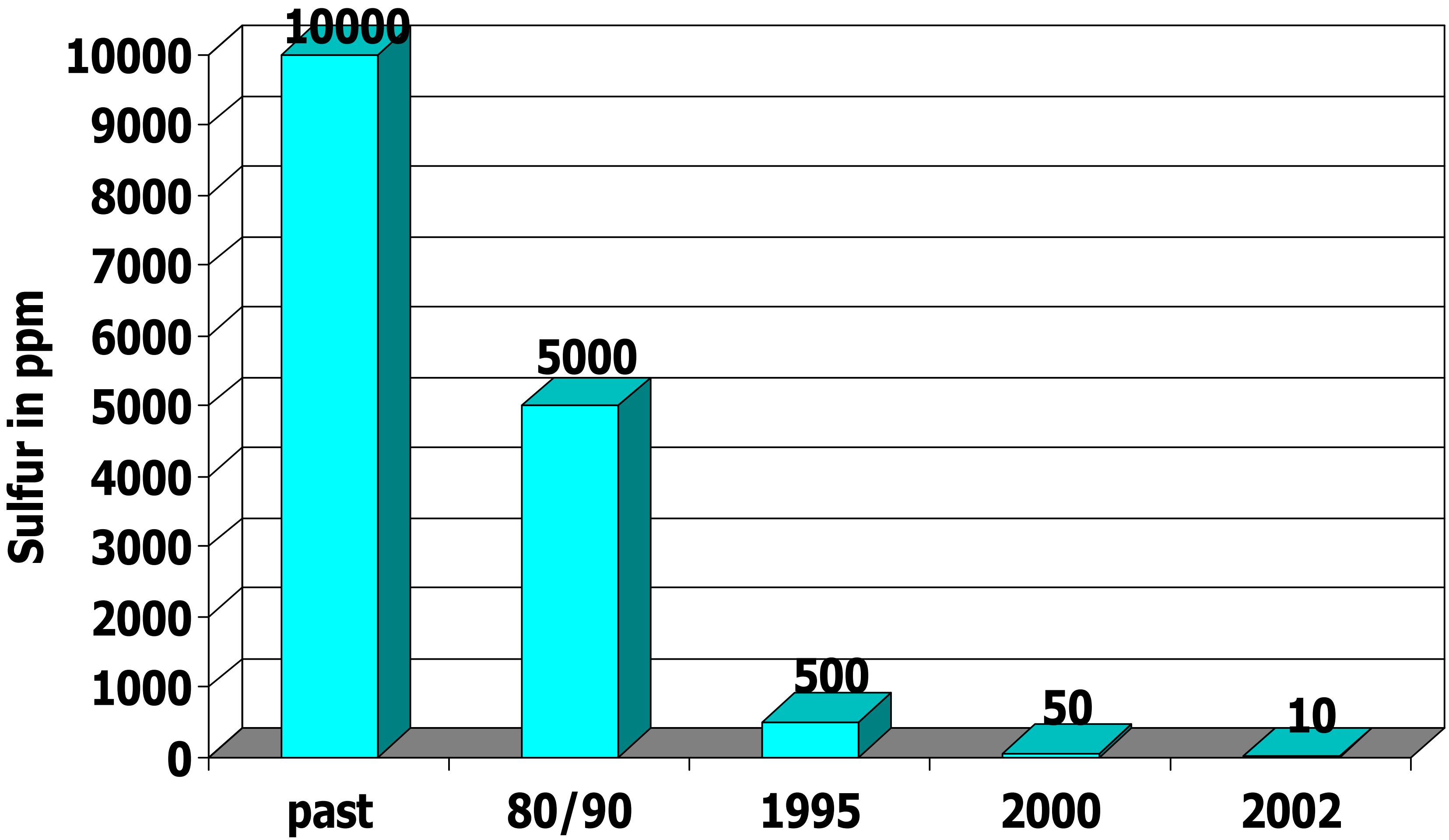


Figure 12

Development of Sulfur Limit in Diesel Fuels



Diesel Hydrotreating

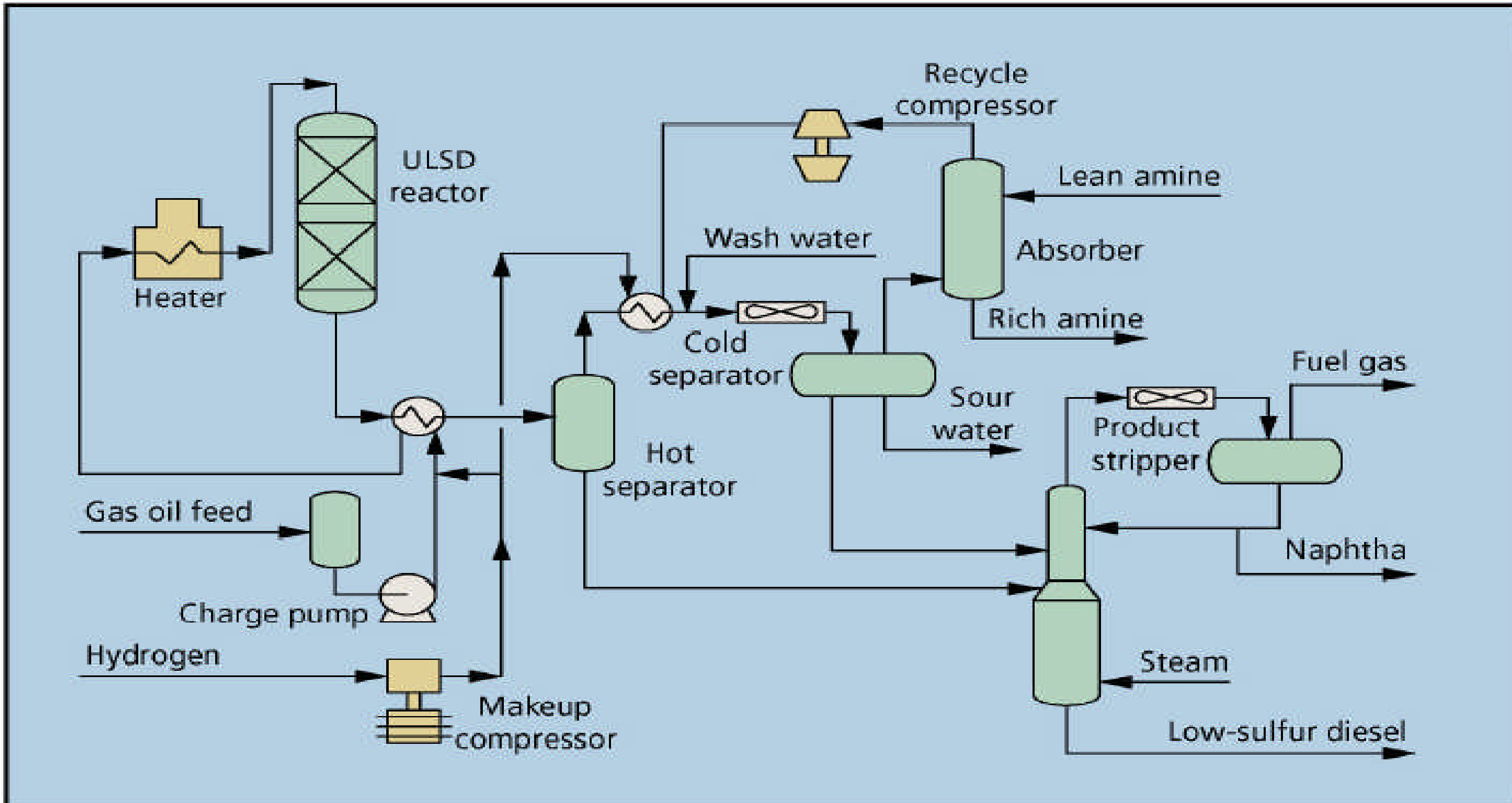


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Figure 14

Increasing of Desulfurization from 95 % up to more than **99.9 %** with existing Hydrotreaters by increasing of **Reactortemperature** only ?

⇒ > + 40 ° C WABT

⇒ Reactor outlet temperature > 400 °C

- material?
- Cycle length ↓↓↓
- Productstability (color, ox.stab.)
- target sulfur critical (10 ... 20 ppm → recombination to RSH, Thiophene)

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Figure 15

AOP - Targets

- Reliability
- Flexibility
- Potential to future
- Low opex (not lowest investment)
- Improved margin

Hydrogen partial pressure in the reactor

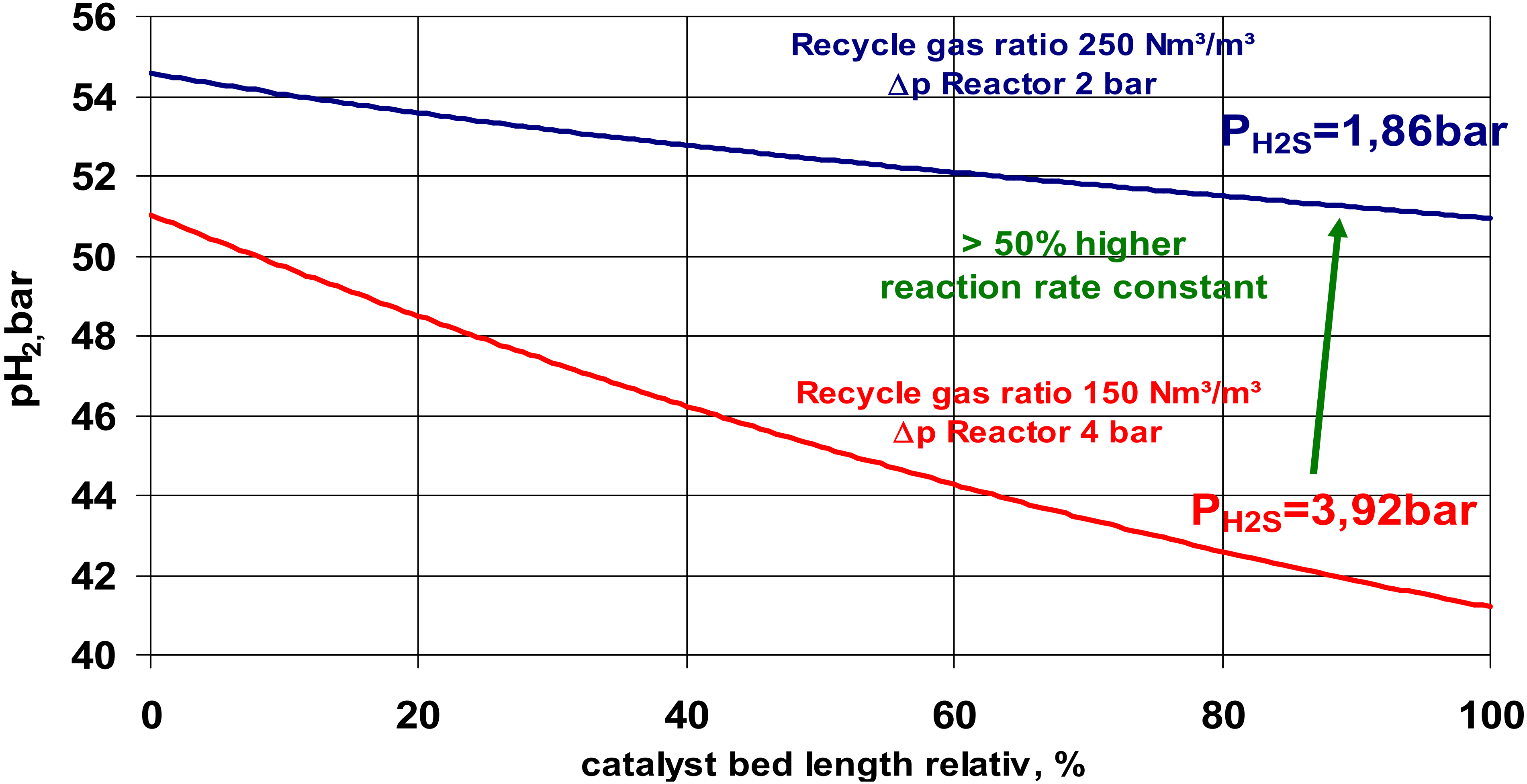

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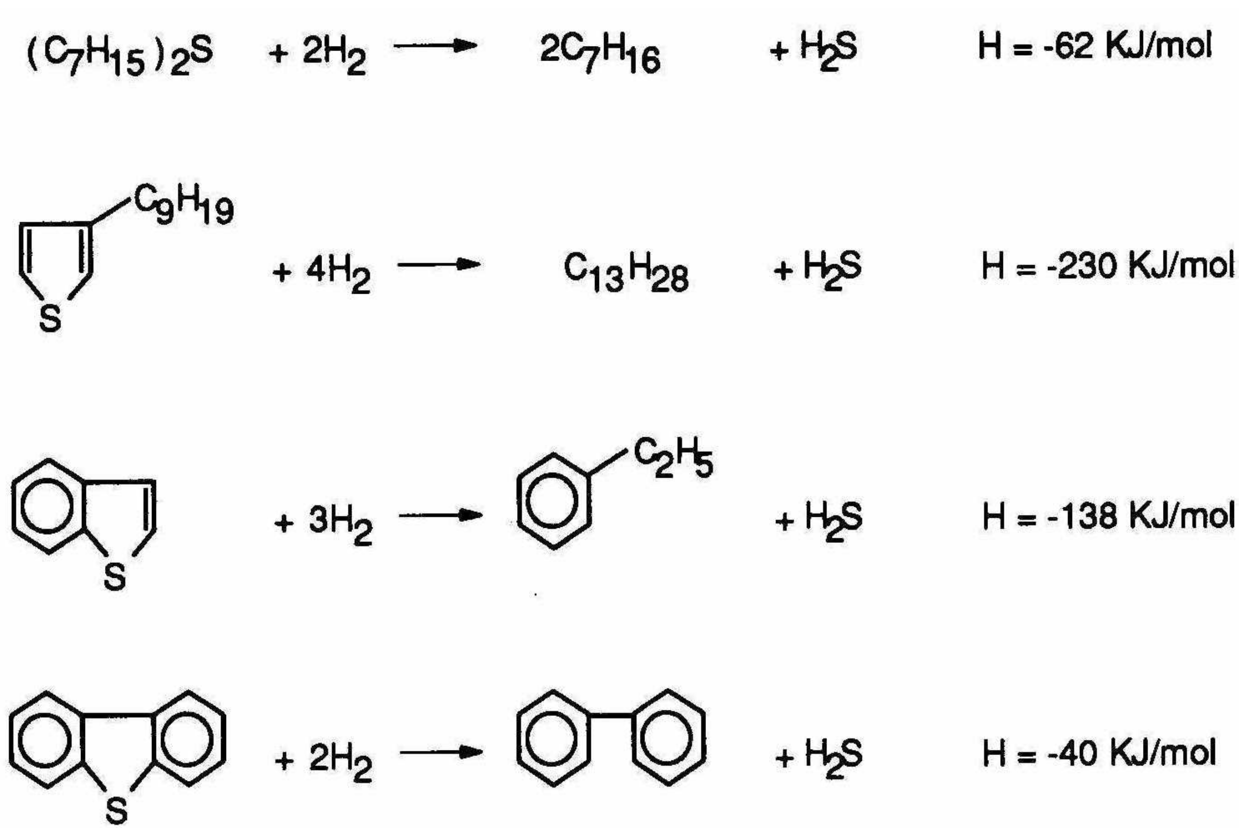
Figure 17

Basic desulfurization reactions



sulfides > thiophenes > benzothiophenes > dibenzothiophenes

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Figure 18

HDS - Kinetic

$$k = \frac{LHSV}{n-1} \cdot \left(\frac{1}{S^{n-1}} - \frac{1}{S_0^{n-1}} \right)$$

95,0% HDS $\rightarrow$ LHSV = 1·x
99,9% HDS $\rightarrow$ LHSV = 0.33·x

$\Rightarrow$ Cat requirement 3 times more

DK 4

R2
weight 535 t
d_a = 4.6 m
s = 98 mm
h = 43.5 m

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Figure 20

DK4 Reactors R-901 and R-902

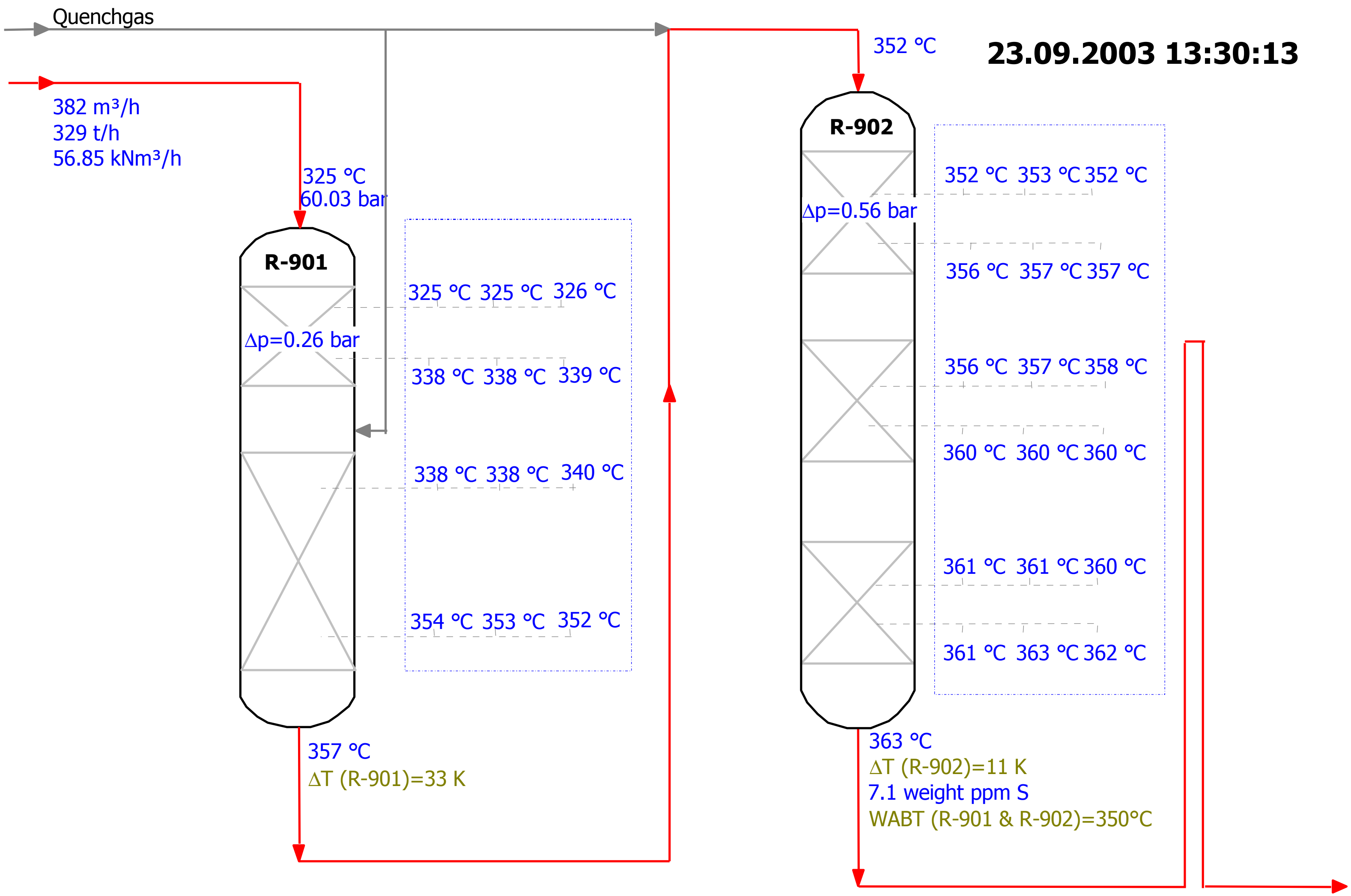

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Figure 21

DK 4 Reactor – pressure drop

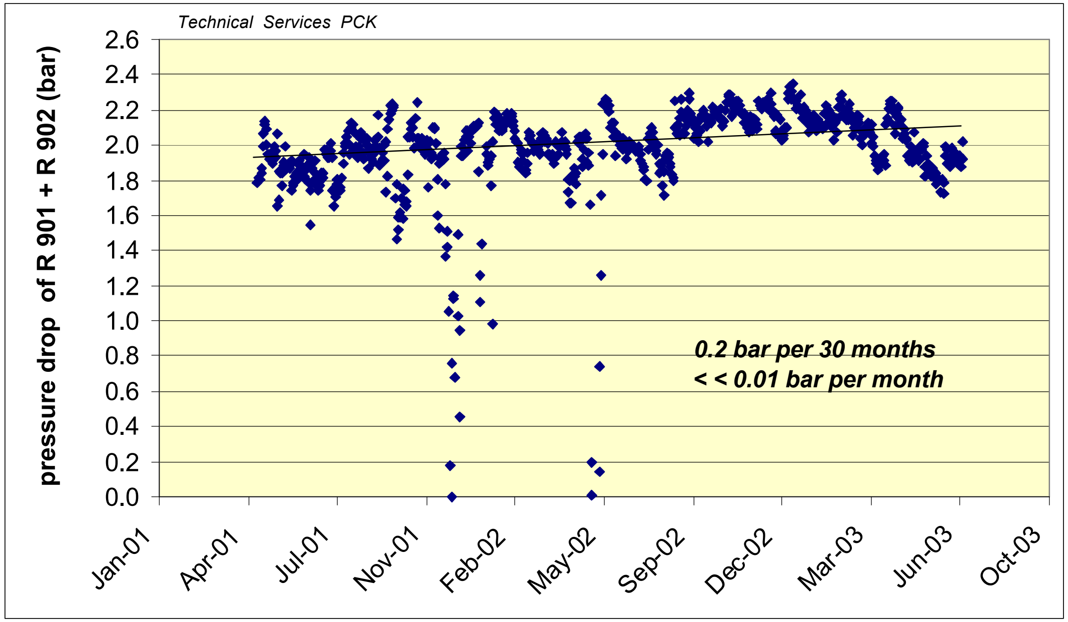

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Figure 22

R M P C T - DK4

(Robust Multivariable Predictive Control Technology)

03.12.2002 10:02:46

controlerstatus: ON

Set points (Sollwerte):		actual	vorausber.	min.	max.	Status
Feed	FC9011:	385 t/h	385 t/h	365 t/h	385 t/h	MV is ON
heater outlet temperature O-901	TC9027:	321°C	321°C	316°C	362°C	MV is ON

Monitored points:	aktuell	vorausber.	min.	max.	Status
pressure Feed – control valve FC9011	1 bar	1 bar	1 bar	6 bar	GOOD
Max. Skintemperature O-901	402°C	403°C	0°C	460°C	GOOD
Max. combustion chambertemperature O-901	643°C	644°C	0°C	700°C	GOOD
Opening control valve fuelgas to O-901	71%	71%	10%	95%	GOOD
Max. Reactortemperature	365°C	364°C	0°C	380°C	GOOD
Ampere V-901	1057 A	1059 A	0 A	1230 A	GOOD
Raffinate sulfur	6.81 ppm	7,20 ppm	0,00 ppm	7,20 ppm	GOOD

Comparison measurement/calculated:

Suflur analyzed:	6.82 ppm
Sulfur calculated (corr.):	6.81 ppm
Sulfur caculated (uncorr):	6.37 ppm

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Figure 23

DK 4 Advanced Control (RMPCT)

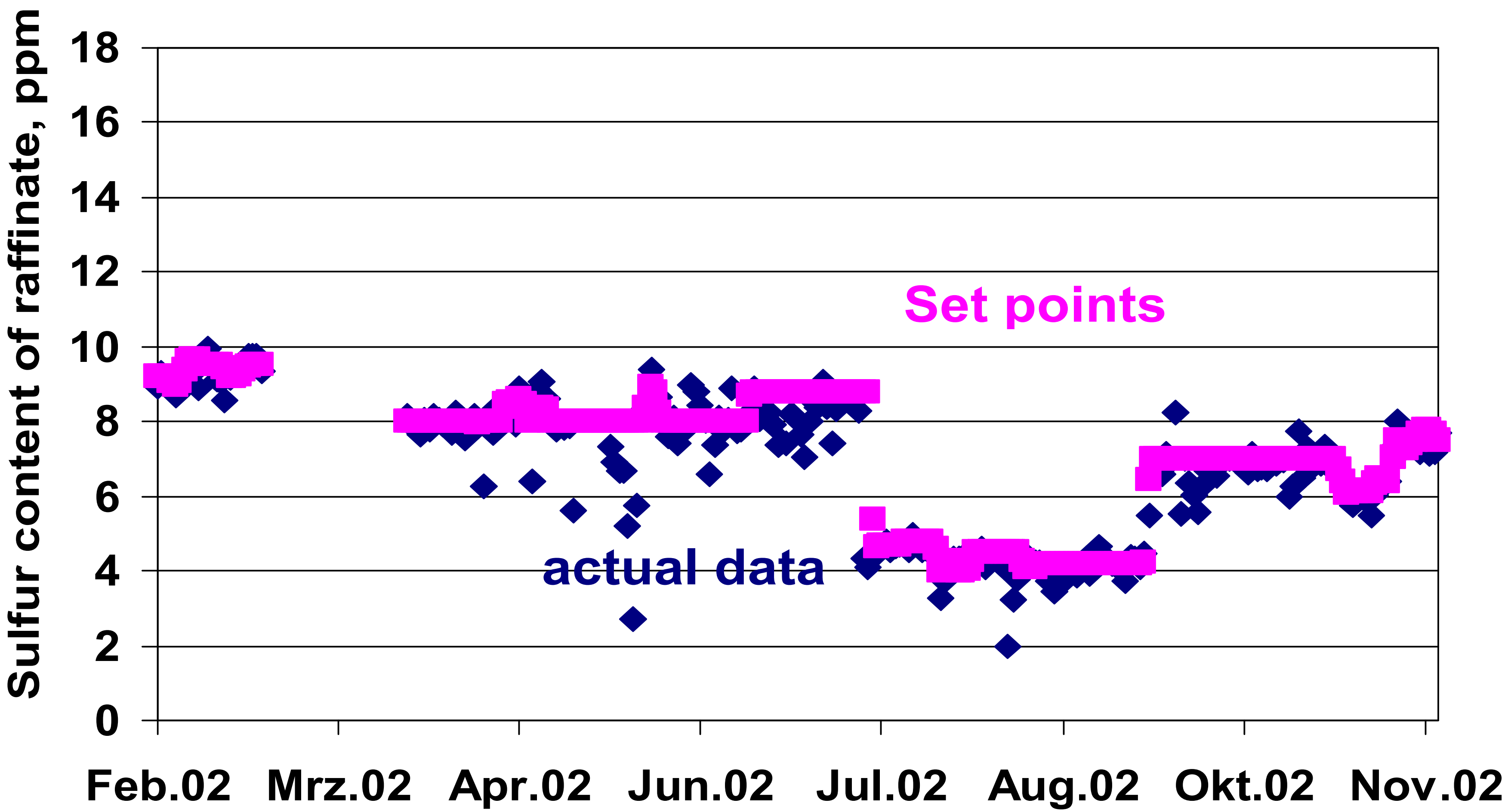

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Figure 24

Changeover fuel quality from 50 to < 10 ppm Sulfur

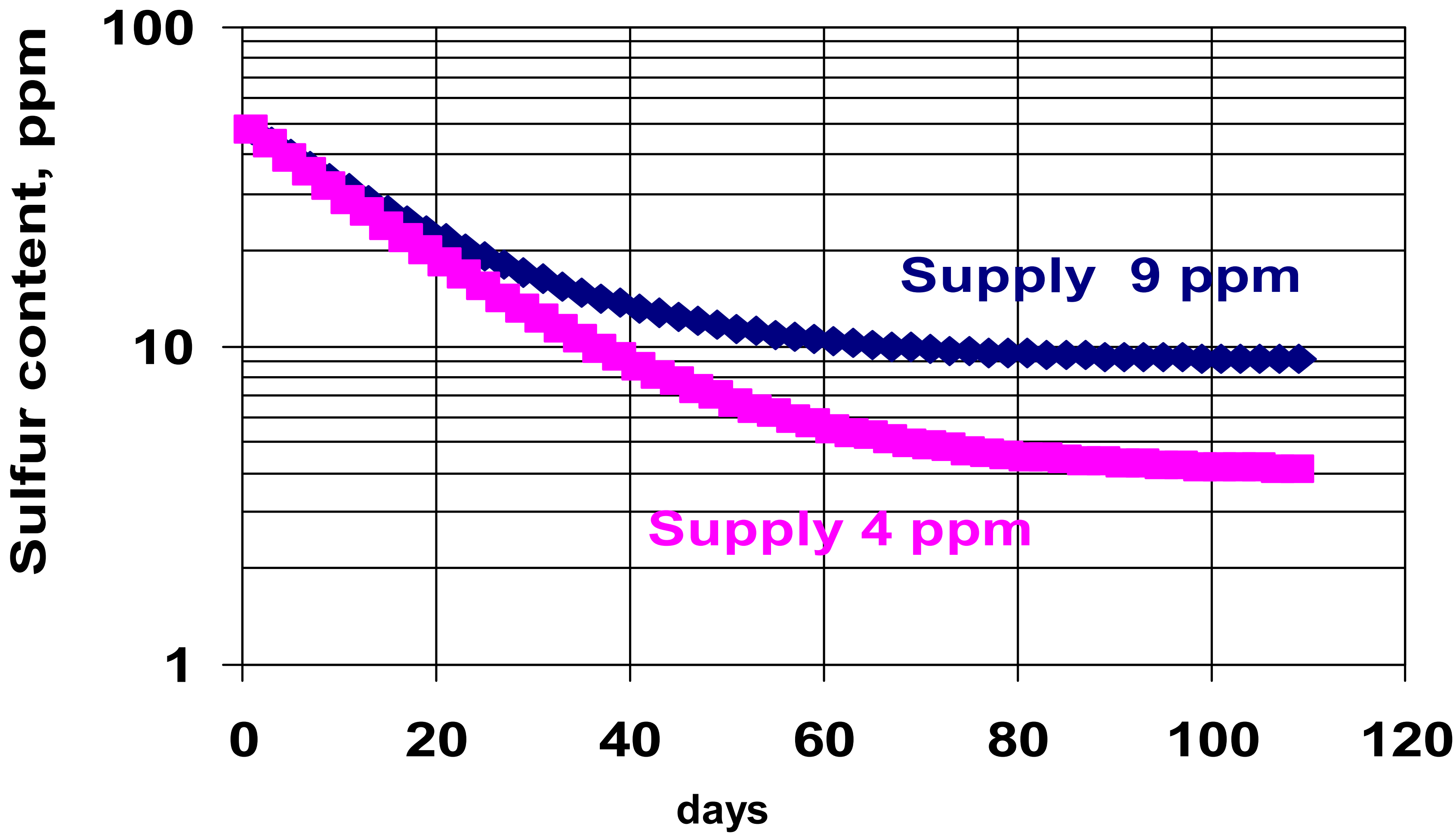

Figure 25

DK 4 Sulfur content of raffinate

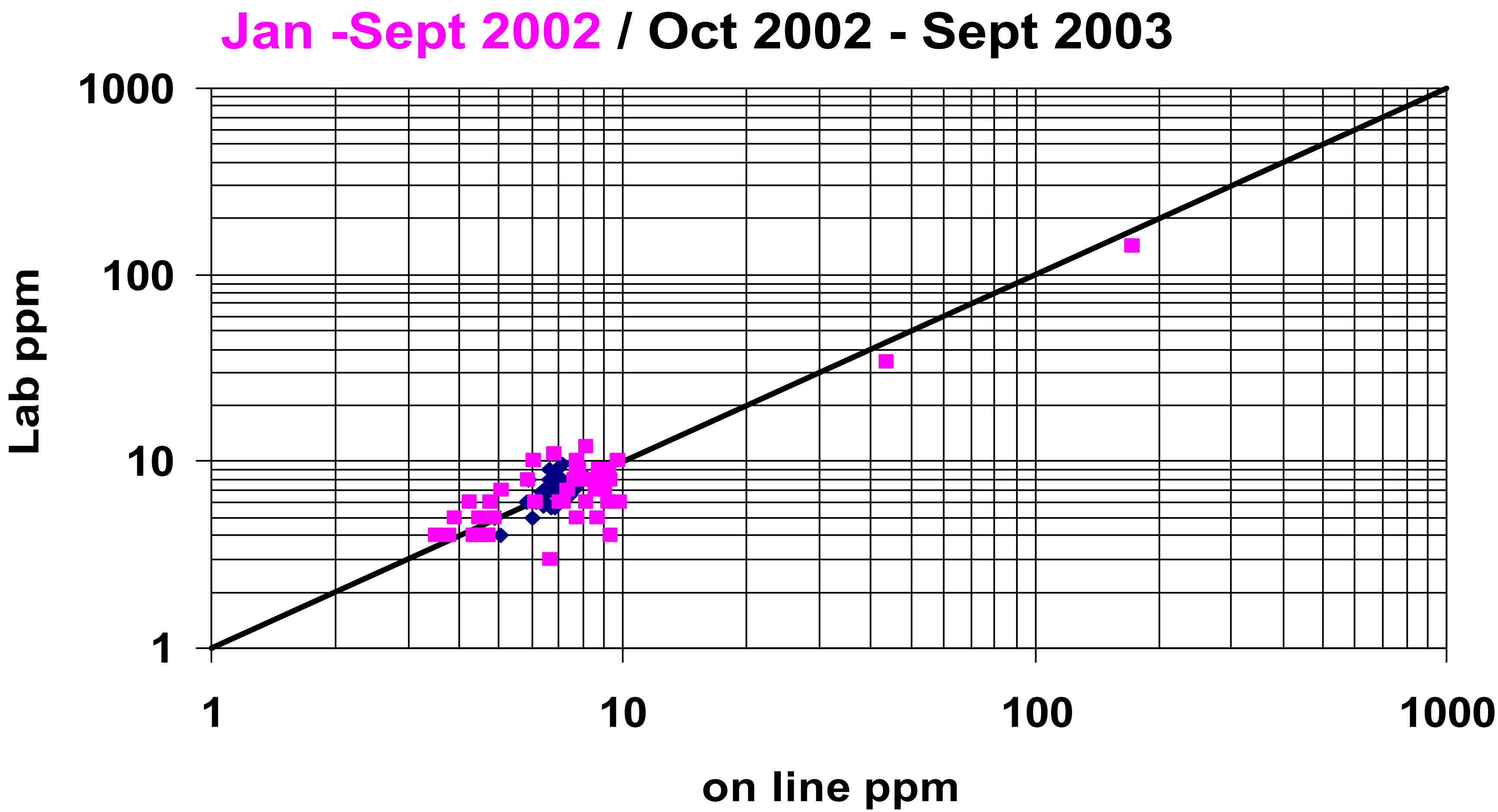

Figure 26

ULSD Hydrotreater DK 4 unit

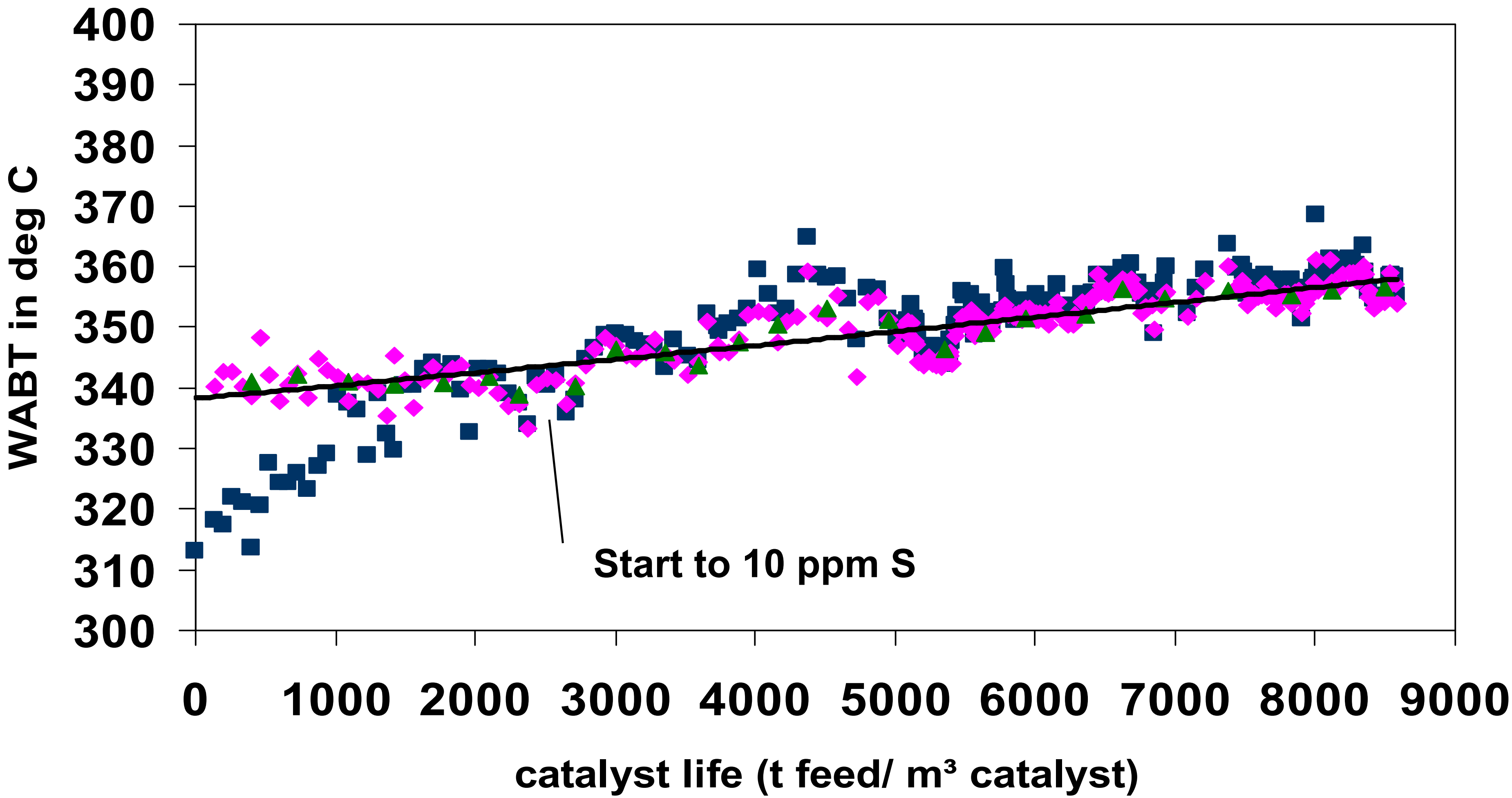

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Figure 27

Flow sheet

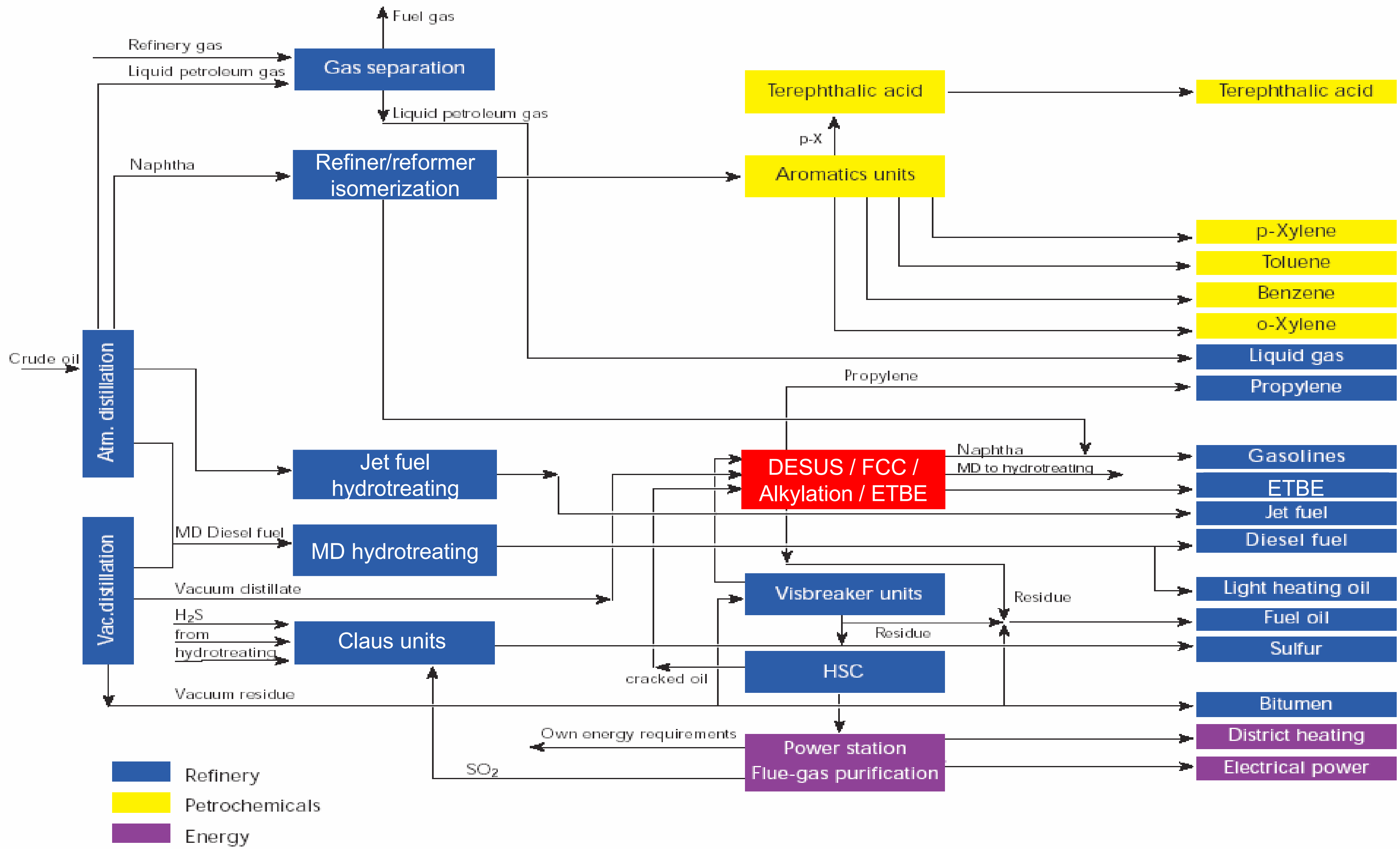

Figure 28

FCC History

Catalyst Research Associates
Agreement signed in London on 12 Oct 1938

- Standard Oil of New Jersey (Esso)
- Standard Oil of Indiana (Amoco)
- Kellogg
- IG Farben added by
- Anglo-Iranian Oil (BP)
- Royal Dutch/Shell
- Texaco
- UOP

FCC History

Group of 1000 Researchers

Massachusetts Institute of Technology

(W.K. Lewis and E. R. Gilliland)

⇒ Big Research program
(topped from Manhattan program only)

⇒ 25 May 1942: Start up of first commercial
Fluid Catalytic Cracking (FCC) Unit

- Capacity 500 000 t/yr

- Location Baton Rouge refinery of Standard Oil of Louisiana

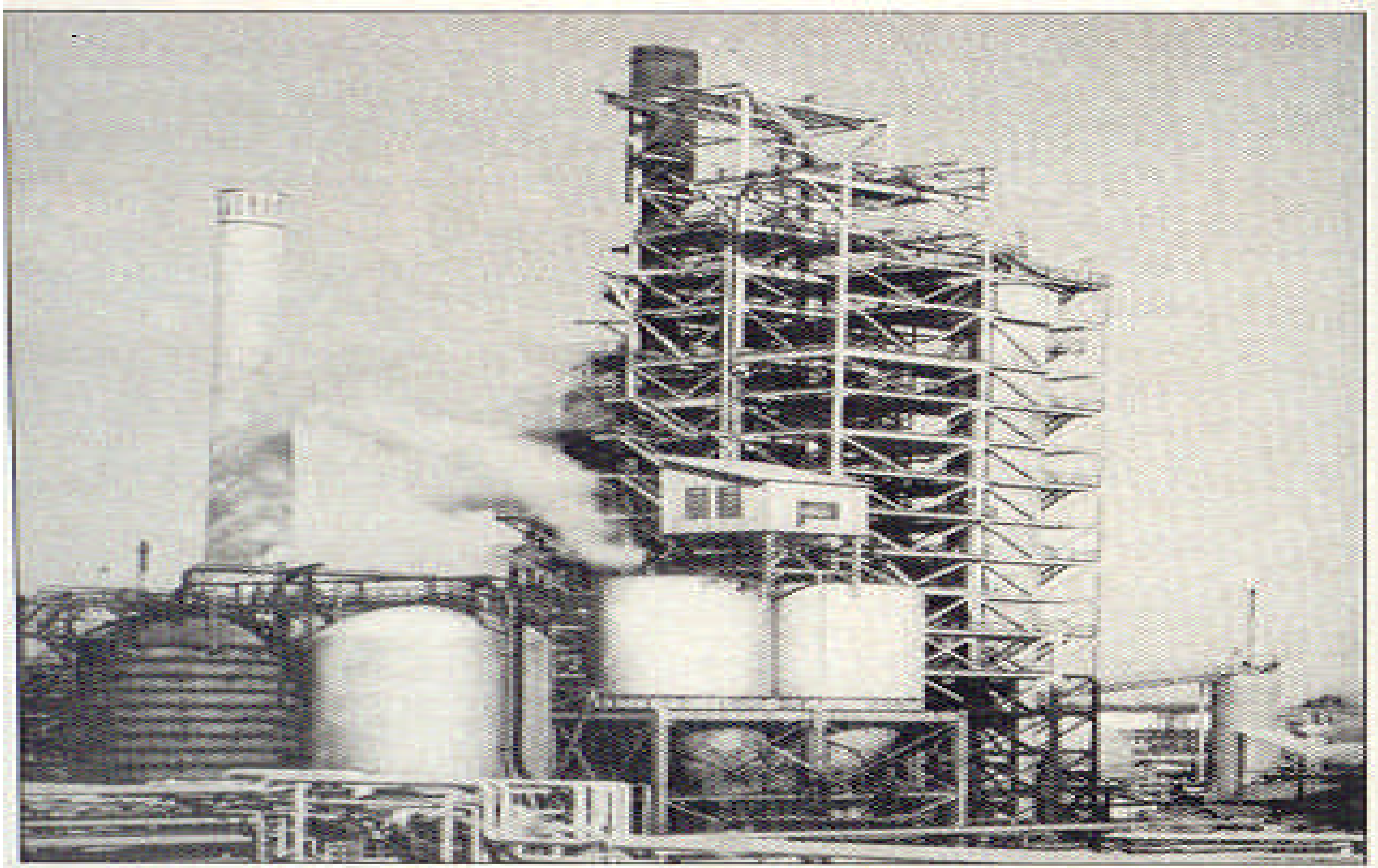

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Figure 31

FCC Features at the Beginning and Today (1)

early days of catalytic cracking	today
• synthetic catalyst era	• zeolitic catalyst era
• catalysts highly temperature sensitive → Reg.-temp. limited to 600 °C ⇒ residence time in regen. 10 -15 min ⇒ 0.6 % carbon on regenerated cat ⇒ CO_2/CO ratio ~ 1 ⇒ runaway afterburning → 1000 °C	• stable up to 800 °C ⇒ residence time in regen. 3 - 4 min ⇒ < 0.05 % carbon on regen. cat ⇒ complete combustion ⇒ no afterburning
• catalysts rel. low activity → high recycle → high coke yield	• high activity ⇒ no recycle ⇒ coke yield

FCC Features at the Beginning and Today (2)

early days of catalytic cracking	today
• Fluidized bed cracking - catalyst residence time 30 -120 sec - vapor residence time 10 - 60 sec - Temperatur 500 °C	• Riser cracking - cat residence time 5 - 15 sec - vapor residence time 1 - 5 sec - 540 °C

⇒ **Progress in** **Technology**
Equipment
Catalyst

FCC History

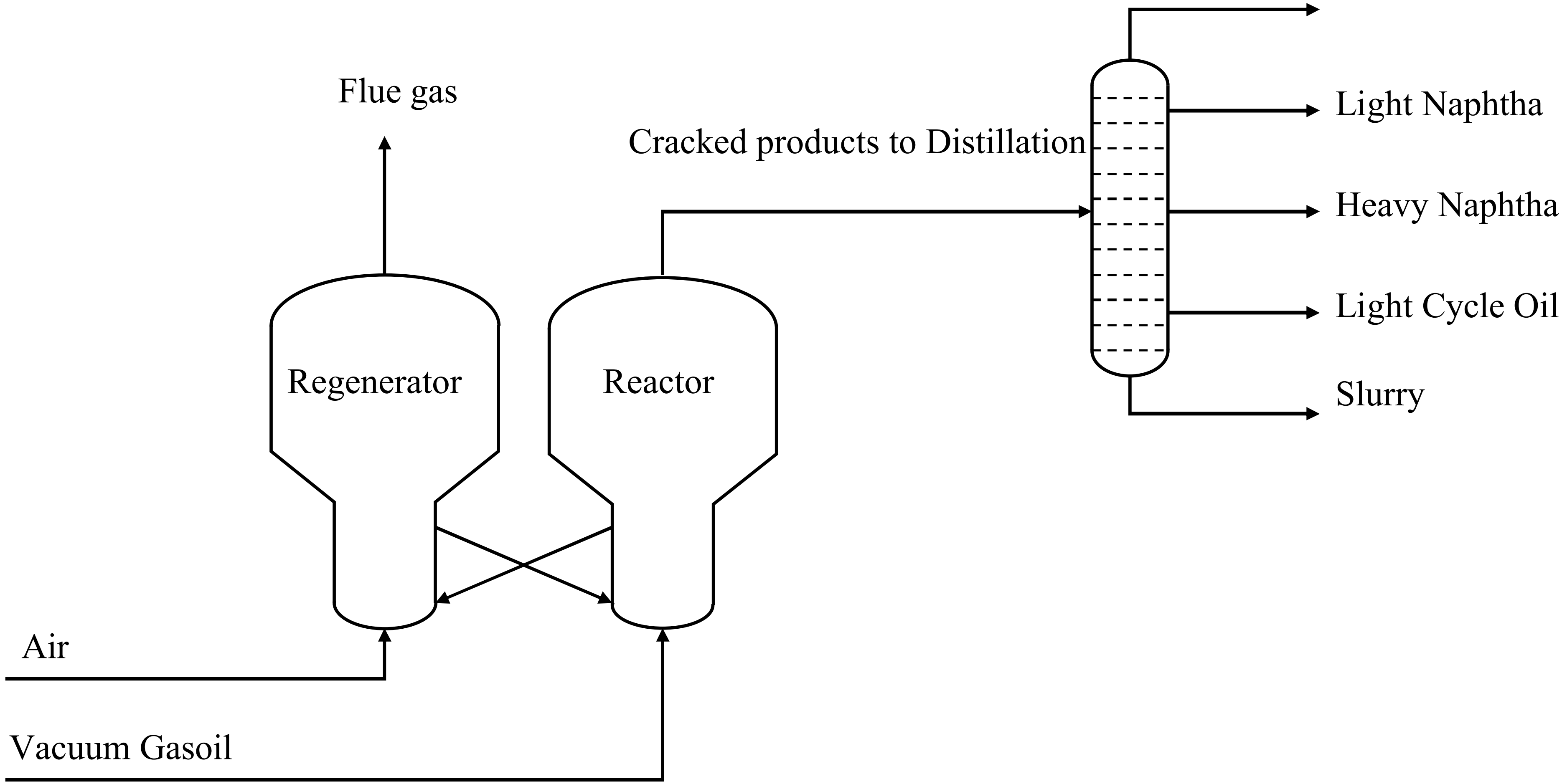
FCC Performance at the Begining and Today

		PCLA* No 1 May 1942	Today
Feedstock			
Boiling range,	°C	265 - 400	360 - 560
Catalyst natural day			Zeolite Re-H-Y ZSM 5
Cat/Oil		3.5	7.5
Cat losses	kg/t	1.5	0.15
Reactor Temp.	°C	490	540
Conversion	wt.-%	55	80
C_3/C_4	wt.-%	10	24
Gasoline	wt.-%	38	48

* Powdered Catalyst Louisiana No.1

... there have been so many changes in the ... FCC unit that its forefathers wouldn‘t recognize their offspring.

Cracking of VGO by FCC



FCC Unit PCK Schwedt

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Figure 37

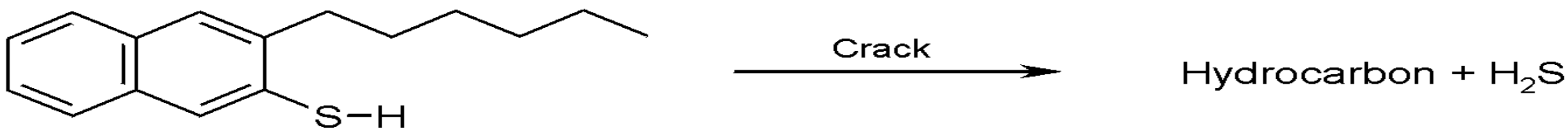
FCC Catalyst Additives

- for low sulfur gasoline

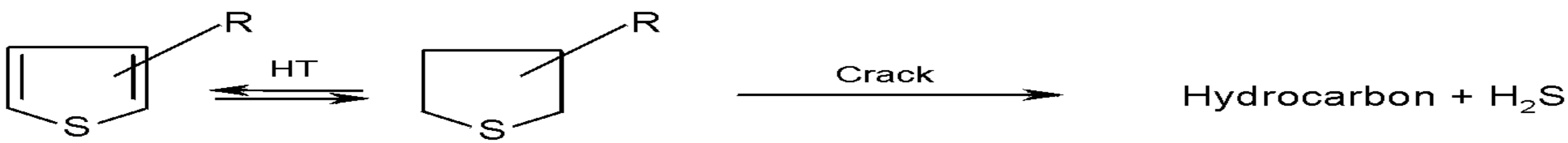
- for light olefines

Possible Gasoline Sulphur Reduction Mechanisms

A) Removal of S from gasoline precursors



B) Removal of S from gasoline range molecules



C) Conversion of heavy S species to coke

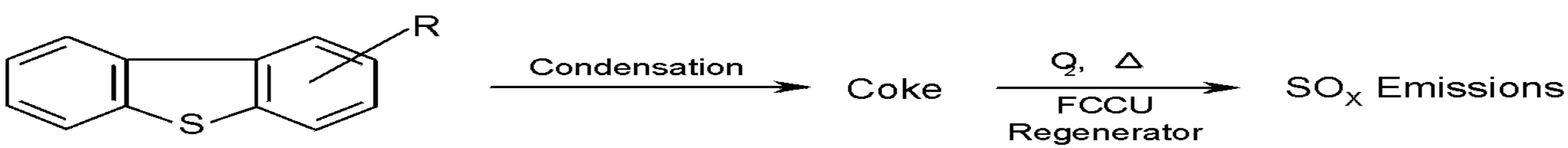


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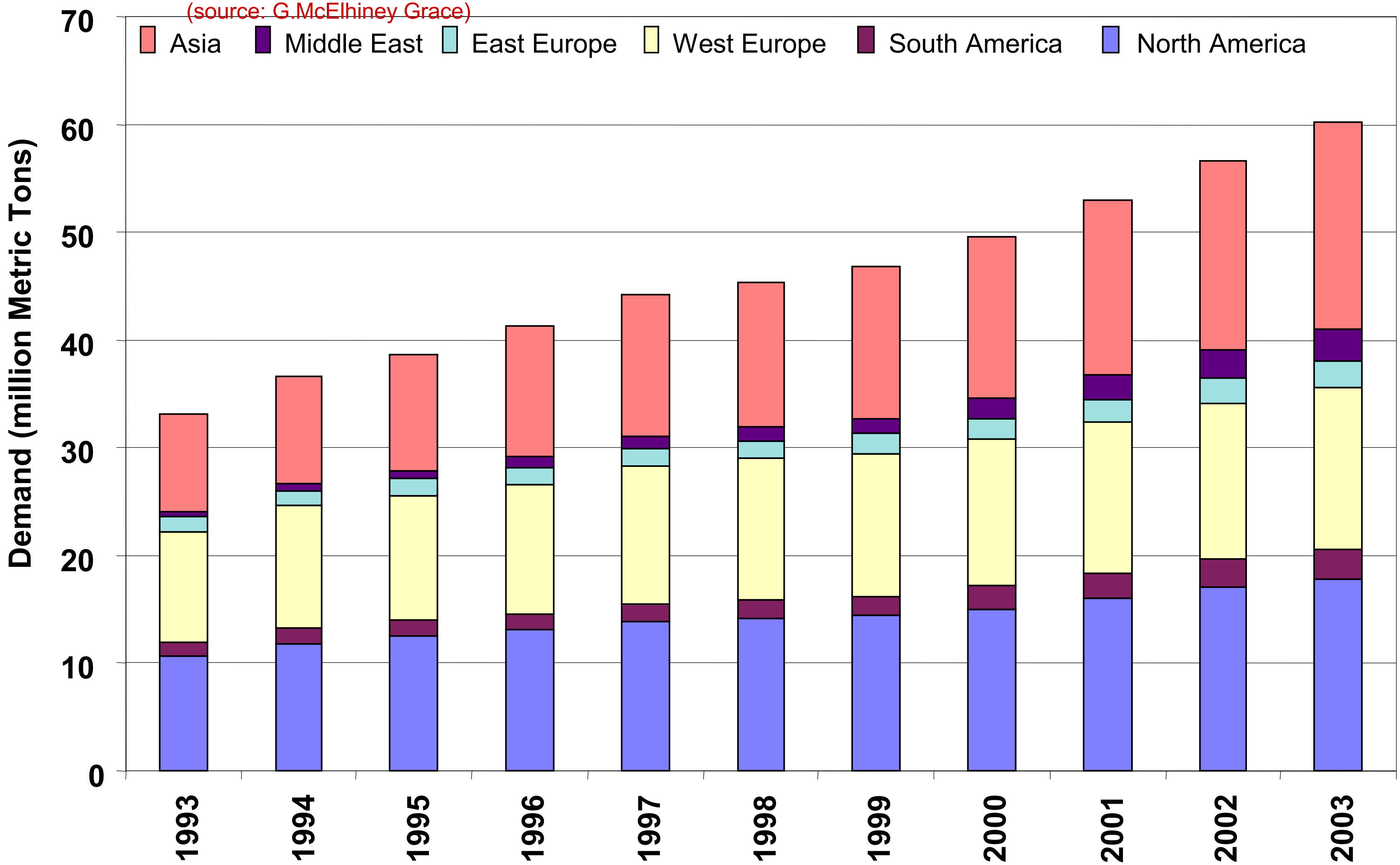
Figure 39

FCC Catalyst Additives

- for low sulfur gasoline

- for light olefines

World Propylene Demand by Region



- **World wide long term growth of 5-6 % per annum**

World-wide Propylene Production

- Use of ZSM-5 zeolite enables the FCC unit
  to make a valuable contribution
  to propylene production.

- This contribution is expected
  to increase significantly in the near future...

European refiners must

produce more diesel fuel

reduce gasoline yield

decrease production of heating oil.

Fuels are becoming
speciality chemicals
(Ultimate, V-Power)

⇒ there will be opportunities

for new catalyst formulations

to help control the composition

of these products at a molecular level.

Current catalyst market (~ 13 billion $/yr)

• environmental catalysts	27 %
• polymers	22 %
• refining	21 %
• petrochemicals	20 %
• fine chemicals and inter mediates	10 %

The refining catalyst market is the most competitive segment of the global catalyst market (bid contract basis).

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Figure 45

Sales of Refining Catalysts

- world wide -

~ 2.5 Billion $/yr

growth rate 75 Million$/yr

Capacities of catalytic units in Germany (Millions t/yr)

Fluid Catalytic Cracking	18
Hydrocracking	9
Catalytic Reforming	17
Alkylation	1
Isomerization	4
Ether	0.5
Hydrotreating (Naphtha 27/Kero 5/MD 43/VGO 12)	87
Total	**136.5**

$\Rightarrow$ $\approx$ **120 % of crude capacity**

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Figure 47

Catalysts in the Schwedt Refinery

	Inventory Kilograms	Annual Consumption kgs/yr
FCC	200 000	1 000 000
Hydrotreater	1 700 000	400 000
Mild Hydrocracker	65 000	30 000
Isomerization	90 000	10 000
Cat Reformer	105 000	10 000
Ether (ETBE)	60 000	10 000
Total	**2 220 000**	**1 460 000**

rule of **thumb**

added value by only 10 %

performance improvement

is much more than the

total catalyst cost

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Figure 49

Potentials for Improvement

- deep hydrotreated FCC feed
- new FCC catalysts (Low H-transfer)

} FCC Overcracking

→ Reduction of gasoline acc. market

→ Manufactoring of boosters (export)

→ Increasement of propylene yield

→ Increasement of biofuels
(etherification of tertiary C_4-/C_{5+}-Olefines)

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Figure 50

FCC Yields (wt.-% on feed)

	Base Y-Zeolith + ZSM5	Overcracking (enhanced Catalyst)
Propylene	7.0	13.0
Isobutane	4.7	8.8
n-Butanes	5.2	9.3
Isobutene	2.1	3.9
Isoamylenes (tert.)	1.7	3.1
Naphtha	45.7	26.9

Closing Comments

• Needs both
  Teamplayers & Individuals

• Is of interest to both
  Academe + Industry

• R&D in catalysis will remain
  challenging and rewarding

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Figure 53