Catalysis in a Refinery

Hartmut Schütter
Boiling Range of Crude Oil (REB)

Figure 1

Boiling Temperature °C

wt%

0 100 200 300 400 500 600 700 800 900

1,2% LPG
16% Naphtha
10% Kero
32% Diesel / HEL

33% Vacuumgasoils

appr. 50% atm. residue

17% Vacuum residue
(Heavy Fuel oil/Bitumen)
Crude Oil Distillation

Crude Oil → atm. Distillation → Gas/ LPG → Steam Cracker → Fuel

Vacuum distillation

Vacuum residue (Bitumen/Heavy Fuel Oil)

Light Naphthas → Isomerization (Gasoline Pool)

Mid/Heavy Naphtha → Steam Cracker

Mid/Heavy Naphtha → Cat Reformer (Aromatics)

Mid/Heavy Naphtha → Cat Reformer (Gasoline Pool)

Mid/Heavy Naphtha → Hydrotreater (Jet Fuel)

Mid/Heavy Naphtha → Hydrotreater (Diesel/Domestic Fuel Oil)

Mid/Heavy Naphtha → VGO Hydrotreater/Cat Cracker

Middledistillates

Steamreformer (H2)

Figure 2
Demand of Oil Products differs from Composition of Crude Oil

**Figure 3**

- **crude oil**
- **Russian Export Blend**
  - 32.4 °API 1.5 %S
- **market demand**
- **Refining**

Boiling Temperature °C vs. Percentage wt%
Crude Oil

Refinery Target Yields

Propane
Butane
Propane
Propylene
Butane

1.2

5

16

Naphtha
RON<50
S>500ppm

Gasoline
RON92 -100
S<10ppm

Jet

HEL

Diesel
S<10ppm
Cetan No. 52 -60

Gasoil
S > 1%

Kero

atmosph. Residue
S > 3%

Heavy Fuel Oil S<1%

50

5

32

55

30
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

    \[
    \begin{array}{cccccccccc}
    \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \\
    \mid & \mid & \mid & \mid & \mid & \mid & \mid & \mid \\
    \text{H} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{H} \\
    \mid & \mid & \mid & \mid & \mid & \mid & \mid & \mid \\
    \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \\
    \end{array}
    \]

  - Octane number = 100  
    100 Vol% iso-Octane

    \[
    \begin{array}{cccccccccc}
    \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \\
    \mid & \mid & \mid & \mid & \mid & \mid & \mid & \mid \\
    \text{H} - \text{C} - \text{H} & \text{H} - \text{C} - \text{H} \\
    \mid & \mid & \mid & \mid & \mid & \mid & \mid & \mid \\
    \text{H} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{H} \\
    \mid & \mid & \mid & \mid & \mid & \mid & \mid & \mid \\
    \text{H} - \text{C} - \text{H} \\
    \mid & \mid & \mid & \mid & \mid & \mid & \mid & \mid \\
    \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \\
    \end{array}
    \]
Light Naphtha Isomerization
Catalytic Reforming

Figure 9
Ether

Figure 10
Flow sheet

Figure 11
Development of Sulfur Limit in Gasoline

Figure 12

Sulfur in ppm

- bis 2000: 500 ppm
- 2000: 150 ppm
- 2001: 50 ppm
- 2002: 10 ppm
Development of Sulfur Limit in Diesel Fuels

Figure 13

Sulfur in ppm

past  80/90  1995  2000  2002

10000  5000  500  50  10

past 80/90 1995 2000 2002
Diesel Hydrotreating

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)
AOP - Targets

- Reliability
- Flexibility
- Potential to future
- Low opex (not lowest investment)
- Improved margin
Hydrogen partial pressure in the reactor

Recycle gas ratio 250 Nm³/m³
Δp Reactor 2 bar

Recycle gas ratio 150 Nm³/m³
Δp Reactor 4 bar

P_{H2S}=1,86bar

> 50% higher
reaction rate constant

P_{H2S}=3,92bar
Basic desulfurization reactions

\[
\begin{align*}
(C_7H_{15})_2S + 2H_2 & \rightarrow 2C_7H_{16} + H_2S & H = -62 \text{ KJ/mol} \\
\text{C}_9H_{19} + 4H_2 & \rightarrow C_{13}H_{28} + H_2S & H = -230 \text{ KJ/mol} \\
\text{C}_7H_7S + 3H_2 & \rightarrow \text{C}_7H_7(C_2H_5) + H_2S & H = -138 \text{ KJ/mol} \\
\text{C}_7H_7S(S)C_7H_7 & + 2H_2 & \rightarrow \text{C}_7H_7(C_7H_7) + H_2S & H = -40 \text{ KJ/mol}
\end{align*}
\]

sulfides > thiophenes > benzothiophenes > dibenzothiophenes
**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

⇒ Cat requirement 3 times more
DK 4

Figure 20

R2
weight 535 t
\( d_a = 4.6 \text{ m} \)
\( s = 98 \text{ mm} \)
\( h = 43.5 \text{ m} \)
DK4 Reactors R-901 and R-902

Figure 21

Quenchgas

382 m³/h
329 t/h
56.85 kNm³/h

Δp=0.26 bar
Δp=0.56 bar

325 °C 326 °C
338 °C 339 °C
354 °C 352 °C
357 °C

ΔT (R-901)=33 K

325 °C 325 °C 326 °C
338 °C 338 °C 339 °C
354 °C 353 °C 352 °C
357 °C

ΔT (R-902)=11 K
7.1 weight ppm S
WABT (R-901 & R-902)=350°C

23.09.2003 13:30:13
Figure 22

DK 4 Reactor – pressure drop

The diagram shows the pressure drop of R 901 + R 902 (bar) over time from January 2001 to October 2003. The pressure drop is measured in bars. The technical services PCK report a decrease of 0.2 bar per 30 months and less than 0.01 bar per month.
### Set points (Sollwerte):

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Actual</th>
<th>Vorausberechnet</th>
<th>Min.</th>
<th>Max.</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed FC9011</td>
<td>385 t/h</td>
<td>385 t/h</td>
<td>365 t/h</td>
<td>385 t/h</td>
<td>MV is ON</td>
</tr>
<tr>
<td>Heater outlet temperature O-901 TC9027</td>
<td>321°C</td>
<td>321°C</td>
<td>316°C</td>
<td>362°C</td>
<td>MV is ON</td>
</tr>
</tbody>
</table>

### Monitored points:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Aktuell</th>
<th>Vorausberechnet</th>
<th>Min.</th>
<th>Max.</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure Feed–control valve FC9011</td>
<td>1 bar</td>
<td>1 bar</td>
<td>1 bar</td>
<td>6 bar</td>
<td>GOOD</td>
</tr>
<tr>
<td>Max. Skintemperature O-901</td>
<td>402°C</td>
<td>403°C</td>
<td>0°C</td>
<td>460°C</td>
<td>GOOD</td>
</tr>
<tr>
<td>Max. combustion chamber temperature O-901</td>
<td>643°C</td>
<td>644°C</td>
<td>0°C</td>
<td>700°C</td>
<td>GOOD</td>
</tr>
<tr>
<td>Opening control valve fuelgas to O-901</td>
<td>71%</td>
<td>71%</td>
<td>10%</td>
<td>95%</td>
<td>GOOD</td>
</tr>
<tr>
<td>Max. Reactortemperature</td>
<td>365°C</td>
<td>364°C</td>
<td>0°C</td>
<td>380°C</td>
<td>GOOD</td>
</tr>
<tr>
<td>Ampere V-901</td>
<td>1057 A</td>
<td>1059 A</td>
<td>0 A</td>
<td>1230 A</td>
<td>GOOD</td>
</tr>
<tr>
<td>Raffinate sulfur</td>
<td>6.81 ppm</td>
<td>7.20 ppm</td>
<td>0.00 ppm</td>
<td>7.20 ppm</td>
<td>GOOD</td>
</tr>
</tbody>
</table>

### Comparison measurement/calculated:

- **Sulfur analyzed:** 6.82 ppm
- **Sulfur calculated (corr.):** 6.81 ppm
- **Sulfur calculated (uncorr.):** 6.37 ppm
DK 4 Advanced Control (RMPCT)

Figure 24

Sulfur content of raffinate, ppm

Set points

actual data

Feb.02  Mrz.02  Apr.02  Jun.02  Jul.02  Aug.02  Okt.02  Nov.02
Changeover fuel quality from 50 to < 10 ppm Sulfur

Figure 25

Supply 9 ppm

Supply 4 ppm

Sulfur content, ppm

days

0 20 40 60 80 100 120
DK 4 Sulfur content of raffinate


on line ppm

Lab ppm

1000
100
10
1

Figure 26
ULSD Hydrotreater DK 4 unit

![Graph showing WABT in °C vs. catalyst life (t feed/m³ catalyst)]

- WABT in °C
- Catalyst life (t feed/m³ catalyst)

Start to 10 ppm S
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
## FCC Features at the Beginning and Today

<table>
<thead>
<tr>
<th>early days of catalytic cracking</th>
<th>today</th>
</tr>
</thead>
<tbody>
<tr>
<td>• synthetic catalyst era</td>
<td>• zeolitic catalyst era</td>
</tr>
<tr>
<td>• catalysts highly temperature sensitive → Reg.-temp. limited to 600 °C</td>
<td>• stable up to 800 °C</td>
</tr>
<tr>
<td>⇒ residence time in regen. 10 -15 min</td>
<td>⇒ residence time in regen. 3 - 4 min</td>
</tr>
<tr>
<td>⇒ 0.6 % carbon on regenerated cat</td>
<td>⇒ &lt; 0.05 % carbon on regen. cat</td>
</tr>
<tr>
<td>⇒ CO₂/CO ratio ~ 1</td>
<td>⇒ complete combustion</td>
</tr>
<tr>
<td>⇒ runaway afterburning</td>
<td>⇒ no afterburning</td>
</tr>
<tr>
<td>→ 1000 °C</td>
<td></td>
</tr>
<tr>
<td>• catalysts rel. low activity</td>
<td>• high activity</td>
</tr>
<tr>
<td>→ high recycle</td>
<td>⇒ no recycle</td>
</tr>
<tr>
<td>→ high coke yield</td>
<td>⇒ coke yield</td>
</tr>
</tbody>
</table>
## FCC Features at the Beginning and Today

<table>
<thead>
<tr>
<th>early days of catalytic cracking</th>
<th>today</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Fluidized bed cracking</td>
<td>• Riser cracking</td>
</tr>
<tr>
<td>- catalyst residence time 30 -120 sec</td>
<td>- cat residence time 5 - 15 sec</td>
</tr>
<tr>
<td>- vapor residence time 10 - 60 sec</td>
<td>- vapor residence time 1 - 5 sec</td>
</tr>
<tr>
<td>- Temperatur 500 °C</td>
<td>- 540 °C</td>
</tr>
</tbody>
</table>

⇒ Progress in Technology

- Equipment
- Catalyst

Figure 33
## FCC History

### FCC Performance at the Beginning and Today

<table>
<thead>
<tr>
<th>PCLA* No 1 May 1942</th>
<th>Today</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feedstock Boiling range, °C 265 - 400</td>
<td>360 - 560</td>
</tr>
<tr>
<td>Catalyst natural day</td>
<td>Zeolite Re-H-Y ZSM 5</td>
</tr>
<tr>
<td>Cat/Oil</td>
<td>3.5</td>
</tr>
<tr>
<td>Cat losses kg/t</td>
<td>1.5</td>
</tr>
<tr>
<td>Reactor Temp. °C</td>
<td>490</td>
</tr>
<tr>
<td>Conversion wt.-%</td>
<td>55</td>
</tr>
<tr>
<td>C₃/C₄ wt.-%</td>
<td>10</td>
</tr>
<tr>
<td>Gasoline wt.-%</td>
<td>38</td>
</tr>
</tbody>
</table>

* Powdered Catalyst Louisiana No.1

---

**Figure 34**
... there have been so many changes in the ... FCC unit that its forefathers wouldn‘t recognize their offspring.
Cracking of VGO by FCC

Figure 36

Air

Vacuum Gasoil

Flue gas

Cracked products to Distillation

Light Naphtha
Heavy Naphtha
Light Cycle Oil
Slurry

Regenerator
Reactor
FCC Catalyst Additives

- for low sulfur gasoline
- for light olefines
Possible Gasoline Sulphur Reduction Mechanisms

A) Removal of S from gasoline precursors

\[
\text{S-H} \xrightarrow{\text{Crack}} \text{Hydrocarbon + H}_2\text{S}
\]

B) Removal of S from gasoline range molecules

\[
\text{HT} \quad \text{R} \xrightarrow{\text{Crack}} \text{Hydrocarbon + H}_2\text{S}
\]

C) Conversion of heavy S species to coke

\[
\text{Condensation} \quad \text{Coke} \xrightarrow{Q, \Delta \text{FCCU Regenerator}} \text{SO}_x \text{Emissions}
\]
FCC Catalyst Additives

- for low sulfur gasoline

- for light olefines
World Propylene Demand by Region

(source: G. McElhiney Grace)

- 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 intermediates 10%

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

- world wide -

~ 2.5 Billion $/yr

growth rate 75 Million$/yr
Capacities of catalytic units in Germany (Millions t/yr)

<table>
<thead>
<tr>
<th>Process</th>
<th>Capacity (Millions t/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluid Catalytic Cracking</td>
<td>18</td>
</tr>
<tr>
<td>Hydrocracking</td>
<td>9</td>
</tr>
<tr>
<td>Catalytic Reforming</td>
<td>17</td>
</tr>
<tr>
<td>Alkylation</td>
<td>1</td>
</tr>
<tr>
<td>Isomerization</td>
<td>4</td>
</tr>
<tr>
<td>Ether</td>
<td>0.5</td>
</tr>
<tr>
<td>Hydrotreating</td>
<td>87</td>
</tr>
<tr>
<td>(Naphtha 27/Kero 5/MD 43/VGO 12)</td>
<td></td>
</tr>
</tbody>
</table>

Total: 136.5

⇒ ≈ 120 % of crude capacity
## Catalysts in the Schwedt Refinery

<table>
<thead>
<tr>
<th>Process</th>
<th>Inventory Kilograms</th>
<th>Annual Consumption kgs/yr</th>
</tr>
</thead>
<tbody>
<tr>
<td>FCC</td>
<td>200 000</td>
<td>1 000 000</td>
</tr>
<tr>
<td>Hydrotreater</td>
<td>1 700 000</td>
<td>400 000</td>
</tr>
<tr>
<td>Mild Hydrocracker</td>
<td>65 000</td>
<td>30 000</td>
</tr>
<tr>
<td>Isomerization</td>
<td>90 000</td>
<td>10 000</td>
</tr>
<tr>
<td>Cat Reformer</td>
<td>105 000</td>
<td>10 000</td>
</tr>
<tr>
<td>Ether (ETBE)</td>
<td>60 000</td>
<td>10 000</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>2 220 000</strong></td>
<td><strong>1 460 000</strong></td>
</tr>
</tbody>
</table>
rule of thumb

added value by only 10 %

performance improvement

is much more than the
total catalyst cost
**Potentials for Improvement**

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

\[ \text{FCC Overcracking} \]

\[ \rightarrow \text{Reduction of gasoline acc. market} \]
\[ \rightarrow \text{Manufacturing of boosters (export)} \]
\[ \rightarrow \text{Increase of propylene yield} \]
\[ \rightarrow \text{Increase of biofuels (etherification of tertiary } C_4^-/C_5^-\text{-Olefines)} \]
**FCC Yields (wt.-% on feed)**

<table>
<thead>
<tr>
<th></th>
<th>Base Y-Zeolith + ZSM5</th>
<th>Overcracking (enhanced Catalyst)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propylene</td>
<td>7.0</td>
<td>13.0</td>
</tr>
<tr>
<td>Isobutane</td>
<td>4.7</td>
<td>8.8</td>
</tr>
<tr>
<td>n-Butanes</td>
<td>5.2</td>
<td>9.3</td>
</tr>
<tr>
<td>Isobutene</td>
<td>2.1</td>
<td>3.9</td>
</tr>
<tr>
<td>Isoamylenes (tert.)</td>
<td>1.7</td>
<td>3.1</td>
</tr>
<tr>
<td>Naphtha</td>
<td>45.7</td>
<td>26.9</td>
</tr>
</tbody>
</table>
Closing Comments

• Needs both Teamplayers & Individuals

• Is of interest to both Academe + Industry

• R&D in catalysis will remain challenging and rewarding
Thank you for your attention