SOx ADDITIVE EFFECTS ON FCC EMISSIONS
İZMİT (1961)
Capacity: 11 million tons
Nelson Complexity: 14.5
Personnel: 1923
Storage: 3.1 million tons

İZMİR (1972)
Capacity: 11 million tons
Nelson Complexity: 7.66
Personnel: 1353
Storage: 2.51 million tons
KIRIKKALE (1986)
Capacity: 5 million tons
Nelson Complexity: 6.32
Personnel: 865
Storage: 1.4 million tons

BATMAN (1955)
Capacity: 1.1 million tons
Nelson Complexity: 1.83
Personnel: 463
Storage: 0.253 million tons
# GENERAL INFORMATION FOR FCC UNITS

<table>
<thead>
<tr>
<th>REFINERY</th>
<th>İZMİT</th>
<th>İZMİR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Licensor</td>
<td>UOP</td>
<td>UOP</td>
</tr>
<tr>
<td>S/U year</td>
<td>1972</td>
<td>1978</td>
</tr>
<tr>
<td>Design Capacity (Sm³/day)</td>
<td>1750</td>
<td>2225</td>
</tr>
<tr>
<td>Maximum Operating Capacity (Sm³/day)</td>
<td>2250</td>
<td>2400</td>
</tr>
<tr>
<td>Feed Properties</td>
<td>HVGO, UCO</td>
<td>HVGO, UCO, DAO, Lube Oil Extracts</td>
</tr>
<tr>
<td></td>
<td>API: Min 19-20</td>
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</tr>
<tr>
<td></td>
<td>IBP=350-380 °C FBP</td>
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</tr>
<tr>
<td></td>
<td>=550-590 °C</td>
<td>=550-590 °C</td>
</tr>
<tr>
<td></td>
<td>Concarbon: 0.6 wt.%</td>
<td>Concarbon: 0.85 wt.%</td>
</tr>
</tbody>
</table>
## REGULATIONS

<table>
<thead>
<tr>
<th>BAT</th>
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<th>BAT</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>SO\textsubscript{x}, mg/Nm\textsuperscript{3} (3% O\textsubscript{2})</td>
<td>NO\textsubscript{x}, mg/Nm\textsuperscript{3} (3% O\textsubscript{2})</td>
</tr>
<tr>
<td>New FCC Units</td>
<td>≤300</td>
<td>&lt;30-100</td>
</tr>
<tr>
<td>Old– Full Burn FCC Units</td>
<td>100-800</td>
<td>&lt;100-300</td>
</tr>
<tr>
<td>Old– Partial Burn FCC Units</td>
<td>100-1200</td>
<td>&lt;100-400</td>
</tr>
</tbody>
</table>

Local regulations?

Refinery bubble concept?

Best available techniques limits?
Options with high operating / investment costs

Crude choices
Feed pretreatment
Scrubbers & crystallisation units

or

ADDITIVES?
Additive performance is unit specific!

- Feed sulfur,
- Good air distribution in regenerator,
- Excess oxygen,
- Regenerator temperatures,
- Catalyst circulation rate,
- Stripper performance,
- Inventory,
- Fresh catalyst addition,
- Lift gas $\text{H}_2\text{S}$ content

affect the performance of the additives.
**SULFUR BALANCE**

Products:
- Light Gas: $\text{H}_2\text{S}$ (20-60%)
- Gasoline: 2-10%
- LCO: 10-25%
- Bottoms: 5-35%
- $\sim$ 90 - 98%

Flue gas
- SOx: 2-10%

S (in coke) 2-10%

$\text{SO}_2 + \frac{1}{2} \text{O}_2 \leftrightarrow \text{SO}_3$
- (90%) (10%)

Air

Feedstock
- Sulphur: 0.3-3.0 wt%

Figure by: Grace
SULFUR SPECIES IN REGENERATOR

Partial Burn
- COS, CS₂
- H₂S
- SO₂
- SO₃

Full Burn
- SO₂
- SO₃

Oxidizing environment around air grid will form oxidized species.

Figure by: Grace
M is mixed Mg/Al oxide.

Cerium is effective in the formation of $\text{SO}_3$.

Vanadates form $\text{H}_2\text{S}$ from $\text{S}$ and release in the reactor.
Check CO to CO$_2$ ratio in regenerator. Additives must have minimum effect on CO:CO$_2$ balance.
Consider using CO promoters, Pt – Pd based or preblended catalysts?

Figure by: Intercat (1) & UOP (2)
ADDITIVE LOADERS

Single Addition System

Multi-Compartment System (left)

Figure by: Intercat
ADDITIVE LOADERS

Figure by: Grace
LOADING OF SOx ADDITIVES

FULL BURN UNITS

Baselading for SOx trial

Additive concentration at workable level

Calculated SOx additive concentration (wt%)

Baselading for 7 days
LOADING OF SOx ADDITIVES

PARTIAL BURN UNITS
Flue gas elemental sulfur (kg/day) = -14.241 + 0.107 * Fresh Feed Elemental Sulfur Mass (kg/day)

\[
\text{FG SO}_x \ (\text{mg/Nm}^3) = \frac{\text{Flue gas elemental sulfur (kg/day)}}{\text{Air Rate (kNm}^3/\text{h})/24*1000*2}
\]
FULL BURN TRIAL RESULTS

11 days of base loading at 100 kg/day, loading rate decreased to 40 kg/day after the base loading

10 days of base loading at 500 kg/day, loading rate decreased to 95 kg/day after the base loading
FULL BURN TRIAL RESULTS

SUPPLIER-1

SUPPLIER-2
FULL BURN TRIAL RESULTS

SUPPLIER-1

Additive amount in the inventory
Estimated pick up factor
Real pick up factor

SUPPLIER-2

Additive amount in the inventory
Estimated pick up factor
Real pick up factor
SOx VARIATION IN PARTIAL BURN UNITS

<table>
<thead>
<tr>
<th>Flue Gas Analysis (mol/h)</th>
<th>CO Boiler Inlet</th>
<th>CO Boiler Outlet</th>
<th>% S Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total SOx</td>
<td>x</td>
<td>3.1 x</td>
<td>32%</td>
</tr>
</tbody>
</table>

SOx Reduction in Stack: \( \frac{(10 - \text{CO})}{\text{CO}} \times 100 \)
PARTIAL BURN TRIAL RESULTS

CO: CO₂ ratio kept constant during the trial

12 days of loading at 45 kg/day to observe CO: CO₂ ratio, loading rate increased to 100 kg/day after the base loading

50 -60 % reduction in SOx emissions
IMPORTANT POINTS IN ADDITIVE SELECTION

- Low consumption rates,
- High PUF,
- High SOx reduction,
- Effectiveness in short duration,
- Interaction with the catalyst,
- Low percentage in the inventory to aid the use of other additives without sacrificing from the general yield structure