Fischer-Tropsch Reactors

Ben Jager

Sasol Process Development Twente (SPDT)
University of Twente: Chemical Technology
PO Box 217
7500 AE Enschede, The Netherlands

Presented at the AIChE Meeting, New Orleans
March 31st to April 4th, 2003

Copyright Sasol, 2003
Fischer-Tropsch technology

- Converts synthesis gas to liquid hydrocarbons
- \[ 2H_2 + CO \rightarrow -CH_2- + H_2O \]
- Product spectrum depends on:
  - temperature, catalyst, pressure, gas composition
- High temperature Fischer-Tropsch
  - 350 °C: gasoline and light olefins
- Low temperature Fischer-Tropsch
  - 250 °C: distillate and waxes
## Fischer-Tropsch product Distribution

Product Distribution for Fe-catalyst  
(per 100 carbon atoms)

<table>
<thead>
<tr>
<th>Product</th>
<th>Low Temperature 220 - 250°C</th>
<th>High Temperature 330 – 350°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>4</td>
<td>7</td>
</tr>
<tr>
<td>C₂-₄ olefins</td>
<td>4</td>
<td>24</td>
</tr>
<tr>
<td>C₂-₄ paraffins</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>Gasoline</td>
<td>18</td>
<td>36</td>
</tr>
<tr>
<td>Distillate</td>
<td>19</td>
<td>12</td>
</tr>
<tr>
<td>Oils and waxes</td>
<td>48</td>
<td>9</td>
</tr>
<tr>
<td>Oxygenates</td>
<td>3</td>
<td>6</td>
</tr>
</tbody>
</table>
Worldwide Interest in Fischer-Tropsch

• **LTFT**
  – Conversion: stranded, remote NG to superior diesel
  – Several projects under consideration
  – Sasol – Qatar Petroleum: Oryx plant for start up in 2006
  – ~ $ 25 000 per daily barrel – total project cost

• **HTFT**
  – Less interest
  – Complex product slate
  – Techno-economic feasibility studies more complex
  – Initial investment higher
  – Provides interesting opportunities
Fischer-Tropsch reactors

High temperature (350°C)
Gasoline & olefins

Low temperature (180-250°C)
Waxes & diesel

Conventional technology

Advanced technology

Synthol

Arge

Advanced Synthol

Slurry
Design Issues

- Catalytic process
- Process conditions
- LTFT - Three phase
  - Multi Tubular Fixed Bed or Slurry Phase Reactors
  - hydrodynamics
  - solid separation
- HTFT – Two phase
- Heat removal – highly exothermal
Multi Tubular Fixed Bed Reactors

- Since 2nd WW used commercially by:
  - Sasol: Arge process (Fe)
  - Shell: SMDS process (Co)
- Heat removal through tube walls
- Gas recycle
  - Enhances heat transfer
  - Conversions: per pass, overall
  - Recompression costs
- Liquid recycle
  - Need for effective distributor
- Pressure drop
Axial and radial temperature profiles
- catalyst activity
- temperature level
- gas & liquid flows
- tube diameters

- Optimise max. ave. and peak temperatures
- Plug flow?
- Cost of reactor
  - Mechanically complex
  - Scale up
  - Catalyst replacement
Slurry Phase Reactor

- Well mixed reactor
- High average temperature and reaction rates
- CSTR behaviour conversion, selectivity
- Easier control
  - virtually isothermal operation
- Higher volumetric conversion rates
- On-line catalyst removal and addition
  - selectivity control
Slurry Phase Reactor (cont.)

- Lower operating cost
  - 70% less catalyst consumption
  - reduced maintenance costs
- Lower capital cost
  - simpler construction
- Solid Separation
  - internal devices
  - crucial development
  - optimisation of catalyst properties
  - effective and relatively cheap
• High reactor capacity
• Good turndown ratio
• Pressure drop reduced 65-85%
• Plug flow behaviour
  – staging in reactors
  – interstage fresh feed
  – series operation with water knock out
LTFT Catalysts

- Cobalt or Iron based
- Oxidized by water
- Co cat has longer life but more expensive
- Fe cat inhibited by water
- Fe cat has water gas shift activity
- Co cat more active at higher conversions
- Recycles or series reactors
- Water gas shift activity for low $\text{H}_2/\text{CO}$ gas
LTFT Catalysts (cont).

- **Cobalt based**
  - conversion proportional to $\text{H}_2/\text{CO}$
  - selectivity($\alpha$) benefits from:
    - low $\text{H}_2/\text{CO}$
    - High partial pressure CO

- **Iron based**
  - conversion proportional to pp ($\text{CO}+\text{H}_2$)
  - selectivity benefits from
    - low $\text{H}_2/\text{CO}$
    - low temperature
Catalysts particle size and activity

Multi tubular fixed bed reactor

- Diameter > 1mm for acceptable pressure drop
- Effectiveness factor below unity
- Selectivity negatively affected by CO and H2 diffusivities
  - higher pressure for Co cat
  - lower temperature for Fe cat
- H$_2$/CO difficult to adjust
- Limited benefit from catalyst activity increases
Catalysts particle size and activity (cont).

Slurry phase reactor

• 20 µm < diameter < 200 µm
  – lower limit due to solid separation
  – upper limit by
    • suspension of particles
    • effectiveness factor
• Effectiveness factor close to unity
• Effective use of increases in catalyst activity
• Benefits selectivity for Co catalyst
Reactor Capacities

• Capacities bbl/day

<table>
<thead>
<tr>
<th></th>
<th>MTFBR</th>
<th>SPR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present</td>
<td>3 000</td>
<td>3 000</td>
</tr>
<tr>
<td>Announced</td>
<td>9 000</td>
<td>17 000</td>
</tr>
<tr>
<td>Potential</td>
<td>10 – 15 000</td>
<td>&gt; 30 000</td>
</tr>
</tbody>
</table>

• Shop fabrication vs. on site assembly
Sasol’s 2 500 bbl/day commercial Slurry Phase Distillate reactor
Multi tubular fixed bed reactor:

- Series reactors: 3 into 1
- Higher capacities due to:
  - better catalyst
  - optimised process conditions
  - optimised reactor
- Size limited by shop fabrication and transport limitations
Reactor Capacities (cont).

**Slurry phase reactors:**
- Higher capacities due to:
  - simpler construction for easier scale up
  - higher activity catalyst can be utilized
  - internal staging – plug flow
  - interstage fresh gas feed – optimal use of reactor volume
  - series reactor configuration with condensing trains
    - reduces recycles
    - higher partial pressures of reagents
  - inter reactor fresh gas feed
- Optimisation of gas loop
- Especially valid for multi reactor plants
- Heat removal becomes limiting
- Early on learning curve
Fischer-Tropsch reactors

High temperature (350°C)
- Gasoline & olefins

Low temperature (180-250°C)
- Waxes & diesel

Synthol
- Conventional technology

Advanced Synthol
- Advanced technology

Arge
- Advanced technology

Slurry
Sasol Advanced Synthol Reactor

- 19 Synthol Circulating Fluidised Bed reactors used during 1955 – 2000
- 16 CFB replaced by SAS reactors:
  - Four 8 m reactors of 11 000bbl/day
  - Four 10 m reactors of 20 000bbl/day
Sasol Advanced Synthol Reactor

(cont).

For the same capacity, the relative reactor sizes are:
Sasol Advanced Synthol Reactor
(cont).

- SAS reactors:
  - simpler structure and support
  - no circulating catalyst
  - all catalyst in use all the time
  - catalyst consumption reduced to 40%
  - easier to operate
  - cheaper – 40%
  - less maintenance - 15%
  - more heat transfer surface
  - greater capacity
Sasol Advanced Synthol Reactor
(cont).

- SAS design geared to replace existing CFB reactors
- Catalyst not used optimally
- Fe cat inhibited by water
- Parallel operations – recycles
- Low conversions per pass
  - Recycle
  - Series reactors
- Interstage removal of water
- Can use higher activity catalyst
- > 20 000bbl/day reactors indicated
In Conclusion

• GTL technology at early stage of development
• Incentive for improved FT technology
• New FT reactors early on learning curve
• Opportunities from
  – better use of more active catalysts
  – series in stead of parallel configurations
  – debottlenecking new limiting mechanisms
    • e.g. heat removal
    • heat management in GTL plants
• Optimal FT reactor design not in isolation
  Part of philosophy of overall plant design
• **Early on learning curve – opportunities**