Fischer Tropsch Synthesis

- History
- Process schemes
- Catalysts
- Reactions
- Industrial realization

Historical development

1902 Sabatier and Sendersen report that methane is formed from CO and hydrogen over Ni and Co catalysts.

1908 Orlov finds ethene from synthesis gas over NiPd catalysts.

1913 BASF patent for "Preparation of a liquid oil from synthesis gas", Co and Os catalysts.

1924 Fischer and Tropsch report about the preparation of hydrocarbons over an Fe catalyst, the catalyst deactivates rapidly.

1936 The first 4 plants are commissioned (200,000 t/year capacity), Pichler finds that by increasing the pressure to 15 bar, the lifetime of the catalyst increases.

1944 9 plants and a total of 700,000 t/year; Co catalyst (Co, ThO₂, MgO, Kieselguhr)

1955 Sasol I starts (combination of fixed and fluid bed reactors)

1994 Shell starts operating plant in Malaysia (SMDS process)

2005 - Several large GTL processes under construction
Process basics

- Developed during WW II in order to satisfy the demand for fuel with the abundant coal supply.
- High pressure hydrogenation of CO over metal or transition metal carbide catalysts.
- The process leads to oligomer like large saturated and mostly unbranched alkanes, as well as some oxygenates.
- Fe, Co and Ru are the most widely use catalysts.
- Alkali metal oxide promoters seem essential for good catalytic performance.
- The two main catalytic functions are
  - CO bond activation and dissociation
  - Formation of C-C and C-H bonds

Reactions during FT synthesis

<table>
<thead>
<tr>
<th>Main reactions</th>
<th>Product</th>
<th>Reactions</th>
<th>( \text{H}_2/\text{CO usage ratio} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkanes</td>
<td>( C_n \text{H}_{2n+2} )</td>
<td>( n \text{CO} + (2n+1) \text{H}<em>2 \rightarrow C_n \text{H}</em>{2n+2} + n \text{H}_2\text{O} )</td>
<td></td>
</tr>
<tr>
<td>Alkenes</td>
<td>( C_3\text{H}_6 )</td>
<td>( n \text{CO} + 2n \text{H}_2 \rightarrow C_3\text{H}_6 + n \text{H}_2\text{O} )</td>
<td></td>
</tr>
<tr>
<td>Water-gas shift</td>
<td>( \text{CO}_2 + \text{H}_2 )</td>
<td>( \text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 )</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Side reactions</th>
<th>Product</th>
<th>Reactions</th>
<th>( \text{H}_2/\text{CO usage ratio} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alcohols</td>
<td>( \text{H}(-\text{CH}_2^\text{)}_n\text{OH} + (n-1) \text{H}_2\text{O} )</td>
<td>( n \text{CO} + 2n \text{H}_2 \rightarrow \text{H}(-\text{CH}_2^\text{)}_n\text{OH} + (n-1) \text{H}_2\text{O} )</td>
<td></td>
</tr>
<tr>
<td>Boudouard reaction</td>
<td>( \text{C} + \text{CO}_2 )</td>
<td>( 2 \text{CO} \rightarrow \text{C} + \text{CO}_2 )</td>
<td></td>
</tr>
</tbody>
</table>

- Catalysts that facilitate the dissociation of CO produce less alcohols (and aldehydes/ketones) than catalysts that favor CO hydrogenation.
Sasol II & III flow scheme

Sasol-Qatar Petroleum Oryx plant
Fixed bed reactor

- Removal of the heat of reaction and achieving constant temperature over the entire catalyst bed are challenging.
- Catalyst is placed in tubes with small diameter.
- High space velocity (250 h⁻¹) and high recycle result in SV of 500 h⁻¹ for new feed.
- T = 493-523 K, p = 2.7 MPa, lifetime up to 350 days.
- High wax production
- Improving the isothermicity by
  - high recycle ratio (up to 20/1)
  - large empty reactor volume
  - tube wall reactors

Slurry reactors

- Gas is passed through suspension of small catalyst particles in a liquid with low vapor pressure (high boiling waxes)
- Low reaction temperature
- High wax selectivity
- Most flexible design
Fluidized bed reactors

• Fixed fluidized bed reactors
  - T = 593 K, p = 2.7 MPa
  - high gas velocity, LHSV = 2000-3000
  - 1.5 recycle ratio
  - High yields, high throughput, good temperature control

• Moving fluidized bed
  - T = 593 - 633 K, p = 2.7 MPa
  - Kellog and Sasol Synthol design
  - Catalyst lasts about 40 days and is replaced.

Comparison of reactors

Activity

Using standard catalysts (size typical for the process) the sequence in the space time yields is

slurry < fixed bed < fluidized bed reactor

using identical catalysts

slurry < fluidized bed < fixed bed reactor

Selectivity

High yields in

Waxes isothermal fixed bed and slurry reactors
Gasoline fluidized bed and slurry reactors
Light products fluidized bed reactors
Comparison of reactors

<table>
<thead>
<tr>
<th>Case</th>
<th>Bed type</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Fixed</td>
<td>Slurry</td>
<td>Fluidized</td>
<td>Slurry</td>
</tr>
<tr>
<td>Catalyst type*</td>
<td>Precipitated</td>
<td>Fused</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Particle size</td>
<td>en. 2.5 mm</td>
<td>40–150 μm</td>
<td>&lt;70 μm</td>
<td>&lt;40 μm</td>
<td></td>
</tr>
<tr>
<td>Catalyst load/kg Fe</td>
<td>2.7</td>
<td>0.8</td>
<td>4.2</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Catalyst bed height/m</td>
<td>3.8</td>
<td>3.8</td>
<td>2.0</td>
<td>3.8</td>
<td></td>
</tr>
<tr>
<td>Bed Inlet Temp./K</td>
<td>496</td>
<td>509</td>
<td>593</td>
<td>593</td>
<td></td>
</tr>
<tr>
<td>Bed Outlet Temp./K</td>
<td>509</td>
<td>511</td>
<td>598</td>
<td>601</td>
<td></td>
</tr>
<tr>
<td>H2O Exit Pressure/MPa</td>
<td>1.9</td>
<td>1.9</td>
<td>2.0</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>Recycle to Fresh Feed ratio</td>
<td>46</td>
<td>49</td>
<td>93</td>
<td>79</td>
<td></td>
</tr>
<tr>
<td>Total Gas Linear Velocity/cm sec⁻¹</td>
<td>36</td>
<td>36</td>
<td>45</td>
<td>45</td>
<td></td>
</tr>
</tbody>
</table>

FT Product distribution in various reactors

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Multi-tubular fixed-bed reactor</th>
<th>Riser reactor</th>
<th>Slurry reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet T (K)</td>
<td>496</td>
<td>593</td>
<td>533</td>
</tr>
<tr>
<td>Outlet T (K)</td>
<td>509</td>
<td>598</td>
<td>538</td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>25</td>
<td>43</td>
<td>42</td>
</tr>
<tr>
<td>H2/CO feed ratio</td>
<td>1.7</td>
<td>2.54</td>
<td>0.68</td>
</tr>
<tr>
<td>Conversion (%)</td>
<td>60 – 66</td>
<td>85</td>
<td>87</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Products (wt%)</th>
<th>Multi-tubular fixed-bed reactor</th>
<th>Riser reactor</th>
<th>Slurry reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH4</td>
<td>2.0</td>
<td>10.0</td>
<td>6.8</td>
</tr>
<tr>
<td>C2H4</td>
<td>0.1</td>
<td>4.0</td>
<td>1.6</td>
</tr>
<tr>
<td>C2H6</td>
<td>1.8</td>
<td>4.0</td>
<td>2.8</td>
</tr>
<tr>
<td>C3H6</td>
<td>2.7</td>
<td>12.0</td>
<td>7.5</td>
</tr>
<tr>
<td>C3H8</td>
<td>1.7</td>
<td>1.7</td>
<td>1.8</td>
</tr>
<tr>
<td>C4H8</td>
<td>2.8</td>
<td>9.4</td>
<td>6.2</td>
</tr>
<tr>
<td>C5H10</td>
<td>1.7</td>
<td>1.9</td>
<td>1.8</td>
</tr>
<tr>
<td>C5 – C11 (gasoline)</td>
<td>18.0</td>
<td>40.0</td>
<td>18.6</td>
</tr>
<tr>
<td>C12 – C18 (diesel)</td>
<td>14.0</td>
<td>7.0</td>
<td>14.3</td>
</tr>
<tr>
<td>C19+ (waxes)</td>
<td>52.0</td>
<td>4.0</td>
<td>37.6</td>
</tr>
<tr>
<td>Oxygenates</td>
<td>3.2</td>
<td>6.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>
### Catalysts

#### Possible catalyst cost basis

<table>
<thead>
<tr>
<th>Catalyst Type</th>
<th>Cost Basis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe based</td>
<td>1</td>
</tr>
<tr>
<td>Ni based</td>
<td>250</td>
</tr>
<tr>
<td>Co based</td>
<td>1000</td>
</tr>
<tr>
<td>Ru based</td>
<td>48000</td>
</tr>
</tbody>
</table>

*Precipitated catalyst*  
*Fused catalyst*
Influence of promoters and support on precipitated Fe catalysts

- For Fe, promoters (alkali metal) are essential to obtain high basicity and to stabilize high specific metal surface areas.
- Highly electronegative anions decrease the activity (Br\(^-\), Cl\(^-\), SO\(_4^{2-}\), S\(^2-\))
- The effect of alkali metals on the activity of an Fe-Cu-SiO\(_2\) catalyst decreases in the sequence 
  \[ \text{K} > \text{Rb} > \text{Na} > \text{Li} \quad (100, 90, 90, 40) \]
- The wax selectivity increases in the sequence 
  \[ \text{Li} < \text{Na} < \text{K} < \text{Rb} \]
  - The relatively low activity of Rb promoted samples is due to the high wax selectivity (diffusion problems).
- The higher the alkali level the higher the shift to longer chains.
- Addition of Cu enhances the reducibility and increases the activity for a given degree of reduction.
- SiO\(_2\) is the best support.

Fused iron catalysts

- Iron oxide should contain small impurities of SiO\(_2\), TiO\(_2\), MgO and Al\(_2\)O\(_3\); mill scale from steel works is used, electrically fused with the desired amount of promoters, particles are crushed and fractionated
- Before loading the catalyst is reduced in H\(_2\) (FFB reactor)
- Microscopic investigation of the particles reveals that only the very outside skin is Fe\(_2\)O\(_3\)
- Small occlusions of alkali silicates are present; their size increases towards the center of the particle.
- Little of the structural promoter is present in the silicate inclusions, most of it is in solid solution with the magnetite phase.

Strong heterogeneity of the catalyst - redistribution of Fe during reduction
Promoters and physical properties of fused Fe catalysts

• After reduction, metallic Fe is finely dispersed between promoter particles. The metal surface area increases with the concentration of the promoter.
• H₂O has a strong inhibiting effect. Insignificant reduction in the presence of 20% water

\[
4 \text{H}_2 + \text{Fe}_3\text{O} \rightarrow 3 \text{Fe} + 4 \text{H}_2\text{O}
\]
• The higher the charge/radius ratio of the metal cation is the higher the resulting specific surface area.
  - \(\text{Al}_2\text{O}_3, \text{TiO}_2, \text{Cr}_2\text{O}_3\) increase spec. surface area strongly
  - \(\text{MnO, Li}_2\text{O, CaO}\) little influence
  - \(\text{Na}_2\text{O, K}_2\text{O}\) negative effect
• The catalyst becomes more basic as the alkali content increases. Pre-reduction of fused Fe to obtain reasonable surface areas, the reduction temperature is between 623 - 723 K with H₂ as reducing agent
• Increase of the hydrogen space velocity increases the rate of reduction corresponding to a higher final spec. surface area.
• Pores smaller than 5 nm do not exist, the average pore size is 30 nm.

Co based catalysts

• Promoted with small amounts of noble metals
  – Decrease reduction temperature
  – Increase activity
• Transition metal oxides are added to improve wax selectivity
• Catalyst are able to operate at lower pressure (1 – 10 bar)
• Yield less olefins and oxygenated products.
• Catalytic activity is directly proportional to concentration of Co available.
**Ruthenium based catalysts**

- Activity at lower temperatures better than with conventional FT catalysts.
- At high temperatures excellent methanation catalyst.
- At low temperatures & high pressures large amounts of very high molecular mass waxes (low in oxygen)
- Most active when pure, promoters do not have positive effects.
- However, even under conditions of high wax yields – high methanation activity (~10 %)
- Supported catalysts contain approximately 5 % Ru
- At low conversions → Ru produces light hydrocarbons (high olefin and alcohol content)

**Alternative catalysts**

**Ni based catalysts**
- Good methanation catalysts
- Catalysts have too high hydrogenolysis activity.

**Activity of other (supported) metal catalysts**
- Maximum of activity is observed at moderate heats of adsorption of CO
Catalyst aging and poisoning

Activity loss
- Conversion of the active phase  
  \[ \text{e.g., metal } \rightarrow \text{oxide} \]
- Loss of active specific surface area  
  crystalline growth
- Deposition of carbonaceous residues  
  fouling
- Chemical poisoning  
  \[ \text{e.g., sulfur sorption, sulfide formation} \]

Conversion of the active phase
- Ease of reducibility  \( \text{Fe} < \text{Co} < \text{Ni} < \text{Ru} \), the oxidizability has, therefore, the reverse order.
  \( \text{Fe}_3\text{O}_4 \) is always present under reaction conditions
  \[ \text{If metallic Fe is present after reaction } \rightarrow \text{Fe was not accessible during reaction.} \]
- Active catalyst contains mixture of Fe carbides and oxides (strong dependence on conversion)

Carbon deposition

\[ \text{CO} + \text{CO} \rightleftharpoons \text{C} + \text{CO}_2 \]
\[ \text{CO} + \text{H}_2 \rightleftharpoons \text{C} + \text{H}_2\text{O} \]

- Formation at  \( T > 573 \text{ K} \), particles disintegrate  
  (catalyst volume of FB reactors increases, fixed bed reactors can plug).
- First carbides formed, after saturation; carbon nuclei begin to grow
- Sensitive to temperature. \( E_a \) is higher (113 kJ/mol) than for FT reaction.
  - 50 % higher C deposition when bed temperature increases by 10 K.
Factors influencing carbon deposition

- H₂O, C₂H₅OH, CH₃COOH increase the rate of formation.
- Hydrocarbons have no effect.
- Al₂O₃ increases the overall rate
- K₂O, Na₂O increase the intrinsic rate.

**Product composition and mechanism**
Product selectivity - thermodynamic considerations

• Thermodynamics imply for a H₂ / CO ratio of 2 at 0.1 MPa that CH₄, CO₂ and graphite are the main products, while negligible amounts of higher hydrocarbons are formed.

• As pressure is increased to 6 MPa HC increase 100 fold, but are still negligible compared to CH₄.

Product distribution

• Oxygenated compounds are also found in excess.

• Oxygenates interact among themselves (restricted equilibrium)

  \[
  C₂H₅OH \rightleftharpoons CH₃CHO + H₂ \\
  CH₃CHO + H₂O \rightleftharpoons CH₃COOH + H₂ \\
  (CH₃)₂CO + H₂ \rightleftharpoons (CH₃)₂CHOH
  \]

Reactions far from equilibrium

• FT reaction
• - H₂ / + H₂ reactions
• Elimination reactions of ROH
Chain growth probability

Initiation

CO + H₂ → CH₃

Propagation

CH₃ → C₂H₅ → C₃H₇ → ... → CₙH₂ₙ+₁ → CH₄

Product probability

1 - α

1 - α

α(1 - α)

αⁿ⁻¹(1 - α)

Interrelation between product carbon numbers

A scheme for calculating the carbon-number product distribution. In the example given, the probability of chain growth is 0.4 and thus the probability of chain termination is 0.6.
Interrelation between product carbon numbers

If selectivity to one particular carbon number is altered – the selectivity of all other species will shift by a predictable amount.

Synthesis temperature: 453 - 658 K, p=1-7.5 MPa, fresh gases mixtures (CO, H2 & CO2) and feed / recycle ratio varied over a wide range.

Interrelation between product carbon numbers

With the exception of C2 simple models such as assuming a fixed probability of chain growth are suitable.

$$\log \frac{W_n}{n} = n \log \alpha + \log \left( \frac{(1-\alpha)^2}{\alpha} \right)$$

$W_n$ mass fraction

$n$ carbon number

$\alpha$ probability of chain growth

Similar results with Anderson-Schulz-Flory distribution

$$F_n = n \cdot (1-\alpha)^2 \cdot \alpha^{n-1}$$
Mechanisms of FT synthesis

Key aspects of the three FT mechanisms

1. Polymerization of CHₙ units and hydrogenation of polymerized carbon chains

   Cannot explain the low percentage of branched HC and the formation of oxygenated products.

2. Partial hydrogenation CO leading to alcohol like units at the surface.

   Alcohols are able to initiate the reaction, but are unable to contribute to the chain growth (olefins can also initiate chain growth)

3. Repeated CO insertion into Me-H or Me-R bond
Potential unifying mechanism

**Initiation**

**Propagation**

C₂ “active initiator” species

Overall FT mechanism with Co catalysts