Fischer-Tropsch fuels and lubricants I:
Germany 1923-1939

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August 22, 2000
Why does the Fischer-Tropsch Process and its history matter?

• High current level of interest
  – High energy prices
  – Limited oil resources
  – Abundant natural gas resources, but difficult to bring to market
  – Specialty products

• Huge volume of literature prior to advent of electronic media
  – “Golden Age” 1920’s to 1950’s
  – Two resurgences
    • 1970’s US energy crisis
    • Mid 1980’s- present
Fischer-Tropsch Process Overview

• Objective:
  – Produce synthetic hydrocarbons from coal (or gas)

\[ n \text{CO} + 2n \text{H}_2 \rightarrow (\text{CH}_2)n + n \text{H}_2\text{O} \]

• Original Driver: Lack of petroleum resources
  – Petroleum had displaced coal as the main source of fuel
  – Germany had abundant coal but lacked petroleum

Franz Fischer
1877-1947
Fischer-Tropsch Process History: “Golden Age” Information Sources

- **Technical literature**
  - Early German concentrated in Brennstoff-Chemie

- **Patent literature**
  - US Patents
  - British Patents
  - Italian Patents
  - Swedish Patents

- **Bibliographies**
Fischer-Tropsch Process History:
Allied Investigation of the German Synthetic Fuels Industry

US Bureau of Mines

Technical Oil Mission (TOM)

British Intelligence Objectives Subcommittee (BIOS)

Field Intelligence Agency Technical (FIAT)

German Synthetic Fuel Industry

TOM Reels 305 microfilm reels

Combined Intelligence Office Subcommittee CIOS Reports

1400 Reports FIAT Reels, BIOS Reports
“Golden Age” Concepts Rediscovered

• Process
  – Reactor-catalyst combinations
    • Cobalt in slurry reactors
  – Synthesis gas (CO and Hydrogen) purification

• Product
  – Totally synthetic
    • Very High Viscosity lubricants
    • Ultrahigh cetane diesel fuel
  – Blending of Synthetic with non-synthetic
    • Fuels
    • Lubricants
Fischer-Tropsch Process Overview

- Generation of Synthesis Gas (CO + H2)
- Preparation of synthetic hydrocarbons (FT Oils and Waxes)
- Product refining
  - Fuels
  - Lubricants
  - Waxes
Fischer-Tropsch Process Overview

- Generation of Synthesis Gas (CO + H2)
- Preparation of synthetic hydrocarbons (FT Oils and Waxes)
- Product refining
  - Fuels
  - Lubricants
  - Waxes
Flow Sheet for FT Process at Ruhrbenzin, Oberhausen-Holten, Ruhr

from Kirk-Othmer, 1951
### German Fischer-Tropsch Plants in order of construction

<table>
<thead>
<tr>
<th>Fischer-Tropsch Plant</th>
<th>Date Operational</th>
<th>1938 tpy C3+</th>
<th>1939 tpy C3+</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ruhrbenzin AG</td>
<td>1937</td>
<td>27.4K</td>
<td>49.4K</td>
</tr>
<tr>
<td>Steinkohlen-Bergwerk Rheinpreussen</td>
<td>1936</td>
<td>28.5K</td>
<td>54.7K</td>
</tr>
<tr>
<td>Gewerkschaft Viktor, Klocknerwerke-Wintershall AG</td>
<td>1936</td>
<td>27.1K</td>
<td>31.2K</td>
</tr>
<tr>
<td>Braunkohle-Benzin AG (Brabag)</td>
<td>1937</td>
<td>103.5K</td>
<td>117.0K</td>
</tr>
<tr>
<td>Mitteldeutche Treibstoff und Öl Werke</td>
<td>1938</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Krupp Treibstoffwerk</td>
<td>1938</td>
<td>-</td>
<td>31.8K</td>
</tr>
<tr>
<td>Chemische Werke Essener Steinkohle AG</td>
<td>1939</td>
<td>-</td>
<td>35.7K</td>
</tr>
<tr>
<td>Hoesch-Benzin GmbH</td>
<td>1939</td>
<td>-</td>
<td>15.6K</td>
</tr>
<tr>
<td>Schaffgotsch Benzin GmbH</td>
<td>1939</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Anthony N. Stranges, Germany’s Synthetic Fuel Industry 1927-45.
Property and Uses of Primary Products: Condensable Gases

- C3 and C4 hydrocarbons
  - 8 Plants
    - Liquified and sold in tank cars and cylinders
- Rheinprussen
  - \( \frac{2}{3} \) Liquified and sold in tank cars and cylinders
  - \( \frac{1}{3} \) converted into alcohols

Property and Uses of Primary Products: Light Oil (25-165 C)

- Base Stock for preparation of motor fuel
  - Typical properties of product from atmospheric plants
    - Sp.Gr. 0.683
    - Vapor Pressure (ats) 0.59
    - % off at 75 C 40
    - FBP, C 165
    - Motor Octane 53
  - Blended to produce 72-78 octane Army motor fuel
    - > 20% benzene
    - 0.02-0.04% Tetra ethyl lead

Property and Uses of Primary Products: Middle Oil (165-230 C)

- Base Stock for high grade oil

<table>
<thead>
<tr>
<th>Property</th>
<th>Synthetic diesel</th>
<th>Mixed diesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sp.Gr.</td>
<td>0.748</td>
<td>0.848-0.880</td>
</tr>
<tr>
<td>Freezing point C</td>
<td>-40</td>
<td>-35 to -26</td>
</tr>
<tr>
<td>Flash point C</td>
<td>45</td>
<td>63</td>
</tr>
<tr>
<td>Cetane Number</td>
<td>78</td>
<td>55 to 48</td>
</tr>
<tr>
<td>Boiling Range C</td>
<td>164 to 238</td>
<td>170 to 280/320</td>
</tr>
</tbody>
</table>

- Blended to produce aviation diesel oil for the Luftwaffe
  - 50% synthetic middle oil
  - 50%petroleum oil

- Rheinprussen
  - 50%synthetic middle oil
  - 50% coal-tar middle oil
  - separation of asphaltic material and remove phenols
  - treated with bleaching earth and filtered

Property and Uses of Primary Products:
Heavy Oil (230-320 C)

- Initial use - entire 170 to 320 C fraction used as diesel oil
- Post 1939 Shortage of soap during the war
  - heavy oil sent to IG Farben
  - Converted into inexpensive detergent “Mersol”

Property and Uses of Primary Products:
Waxes: Soft wax (320-460 C); Hard wax (>460 C)

- Soft wax “Gatsch” sold to Deutche Fettsaure Werke for conversion into fatty acids
- Hard wax sold mainly to blenders and users
- Ruhrchemie had wax refining plant to produce finished grades of wax (data from 1942-43)

<table>
<thead>
<tr>
<th></th>
<th>mp C</th>
<th>Penetration</th>
<th>Mean MW</th>
<th>Mean C No.</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soft wax</td>
<td>44</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>make fatty acids</td>
</tr>
<tr>
<td>Slab wax</td>
<td>53</td>
<td>35.0</td>
<td>380</td>
<td>27</td>
<td>polishes, candles, explosives</td>
</tr>
<tr>
<td>Catalyst wax</td>
<td>ca 30</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Ref. plastic wax</td>
<td>ca85</td>
<td>17.0</td>
<td>500</td>
<td>36</td>
<td>paper, cardboard</td>
</tr>
<tr>
<td>Ref, hard wax</td>
<td>110</td>
<td>4.0</td>
<td>60</td>
<td>43</td>
<td>polishes, candles, explosives</td>
</tr>
</tbody>
</table>

# Fuel Properties from FT Processes

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Wt%</th>
<th>Density</th>
<th>% olefins</th>
<th>av MW</th>
<th>Carbon No</th>
<th>Cloud Point C</th>
<th>Pour Point C</th>
<th>Research Octane</th>
<th>Motor Cetane</th>
<th>Research Cetane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td><strong>Low Pressure</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gasol (C3+C4)</td>
<td>12</td>
<td>-</td>
<td>50</td>
<td>-</td>
<td>C3+C4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Gasoline to 185 C</td>
<td>49</td>
<td>0.689</td>
<td>37</td>
<td>100</td>
<td>C4-C10</td>
<td>-</td>
<td>-</td>
<td>52</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Gasoline to 200 C</td>
<td>54</td>
<td>0.693</td>
<td>34</td>
<td>115</td>
<td>C4-C11</td>
<td>-</td>
<td>-</td>
<td>49</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Diesel Oil, 185-320 C</td>
<td>29</td>
<td>0.760</td>
<td>15</td>
<td>190</td>
<td>C11-C18</td>
<td>-13</td>
<td>-18</td>
<td>-</td>
<td>87</td>
<td>100</td>
</tr>
<tr>
<td>Diesel Oil, 185-320 C</td>
<td>24</td>
<td>0.766</td>
<td>13</td>
<td>205</td>
<td>C12-C19</td>
<td>-7</td>
<td>-9</td>
<td>-</td>
<td>92</td>
<td>105</td>
</tr>
<tr>
<td>Soft wax, 320-450 C</td>
<td>7</td>
<td>0.900</td>
<td>Iodine 2</td>
<td>-</td>
<td>&gt;C18</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Hard wax</td>
<td>3</td>
<td>0.930</td>
<td>Iodine 2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>Medium Pressure</strong></td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gasol (C3+C4)</td>
<td>-</td>
<td>-</td>
<td>30</td>
<td>-</td>
<td>66% C4, 33% C3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Gasoline to 185 C</td>
<td>35</td>
<td>0.685</td>
<td>20</td>
<td>100</td>
<td>C4-C10</td>
<td>-</td>
<td>-</td>
<td>28</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Gasoline to 200 C</td>
<td>40</td>
<td>0.689</td>
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<td>-5</td>
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<td>-</td>
<td>-</td>
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<td>-</td>
<td>-</td>
</tr>
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<td>25</td>
<td>0.900</td>
<td>Iodine 2</td>
<td>-</td>
<td>&gt;C19</td>
<td>-</td>
<td>-</td>
<td>80</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Lubricating Oils Manufacture: Stettin-Politz Plant

FT Wax >80 C mp
Cracking/hydrogenation
Olefins
Polymerization
Separation & Neutralization
Vacuum Distillation

Coal-Tar Wax

Lubricating Oils Properties: Stettin-Politz Plant

<table>
<thead>
<tr>
<th></th>
<th>Lubricating Oil</th>
<th>Diesel Oil</th>
<th>Steam Cylinder Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SS-1103</td>
<td>SS-1106</td>
<td></td>
</tr>
<tr>
<td>Viscosity deg</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Engler at 100 C</td>
<td>3.0</td>
<td>5.5-5.6</td>
<td>6.0</td>
</tr>
<tr>
<td>Viscosity, cSt</td>
<td>24.5</td>
<td>47</td>
<td>52</td>
</tr>
<tr>
<td>Viscosity Index</td>
<td>115-124</td>
<td>108-112</td>
<td>115-116</td>
</tr>
<tr>
<td>Flash Point, C</td>
<td>220 min</td>
<td>248-260</td>
<td>300-310</td>
</tr>
<tr>
<td>Pour Point, C</td>
<td>-30 max</td>
<td>-10.5 max</td>
<td>0±1</td>
</tr>
<tr>
<td>Conradson C</td>
<td>0.2 max</td>
<td>0.2 max</td>
<td>0.4-0.5</td>
</tr>
<tr>
<td>Iodine No.</td>
<td></td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>Cetane No.</td>
<td></td>
<td></td>
<td>72-72</td>
</tr>
<tr>
<td>IBP %</td>
<td></td>
<td></td>
<td>302 min</td>
</tr>
<tr>
<td>Sulfur %</td>
<td></td>
<td></td>
<td>0</td>
</tr>
</tbody>
</table>

Property and Uses of By-Products:

• **Fatty Acids (low amounts)**
  – Formed in F-T water, especially medium pressure
    • about 50% in C11 to C18 range
  – recovered from neutralization of the water
  – Converted into soap
    • e.g., Holten 36 tpy of acids converted

• **Ethyl, Propyl, and Butyl alcohols**
  – produced in medium pressure synthesis
  – at Hoesch-Benzin recovered 1 tpd from condensate water

Property and Uses of By-Products:

- **Tail Gas**
  - Used as fuel for the works
    - organic sulfur purifiers
    - distillation towers
    - power generation
    - coke ovens
    - others

Industrial production of secondary products: Gasoline

- **High Grade Gasoline**
  - Thermal Cracking of high boiling oils
    - Available at all plants
    - TVP or Carburol process
    - Overall quality of final products was poor
  - C3 and C4 olefin polymerization
    - IG Farben or UOP processes
    - Not operated during war years

Industrial production of secondary products: Synthetic Soap

- **Deutsche Fettsaure-Werke**
  - (40,000 tpy)
  - 8 to 20 ton batches
  - Finished product
    - good lathering
    - unpleasant odor
    - for human use, maximum of 30% synthetics in blends

Industrial production of secondary products: Edible fat (margarine)

- Deutsche Fettsaure-Werke
  - (1800 tpy from Witten plant)
  - Esterification of fatty acids produced by oxidation of crude soft wax
  - Approved for human consumption
    - but suppressed university research showed presence of toxic esters of branched chain fatty acids

Industrial production of secondary products: Other uses of fatty acids

- Low-boiling fatty acids
  - preparation of esters
  - preparation of alcohols

- Higher fatty acids
  - emulsifying agents in dyeing
  - lubricating greases

Industrial production of secondary products: Detergent (Mersol)

- IG Farben Process at Leuna plant
  - Product called Mersol D
  - Sent to soap manufacturers for saponification to commercial product called Mersolat
  - 35,000 tpy of FT oil used to produce 50,000 tpy of Mersol products

FT Oil
230-320 C fraction
5-12% olefins

Hydrogenation
200-230 atm hydrogen
Ni-W-S catalyst

Reaction
Cl2 and SO2
UV light
12-16 hours

Stripping
82% sulfonyl chloride form


Conclusions

- Wide variety of products produced from the F-T process materials
  - basic strategies
    - Use pure synthetics where appropriate
    - Blend with non-synthetics to get desired properties
      - Diesel
      - Gasoline
      - Soap
      - Margarine (carotene)
New Internet Site:
www.fischer-tropsch.org

• Purpose:
  – Bring into electronic media documents from the “Golden Age” of the Fischer-Tropsch process
  – Broader exposure for the materials compiled by the German Documents Project at Texas A&M University
  – Service to the GTL industry by Syntroleum Corporation