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

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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

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Fischer-Tropsch Process Overview

Franz Fischer
1877-1947

- **Objective:**
  - Produce synthetic hydrocarbons from coal (or gas)

  $nCO + 2nH_2 \longrightarrow (CH2)n + nH_2O$
- **Original Driver: Lack of petroleum resources**
  - Petroleum had displaced coal as the main source of fuel
  - Germany had abundant coal but lacked petroleum

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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**
  - **US Bureau of Mines "Bibliography of the Fischer-Tropsch Synthesis and Related Processes (In Two Parts), by H. C. Anderson, J. L. Wiley, and A. Newell, 1955**

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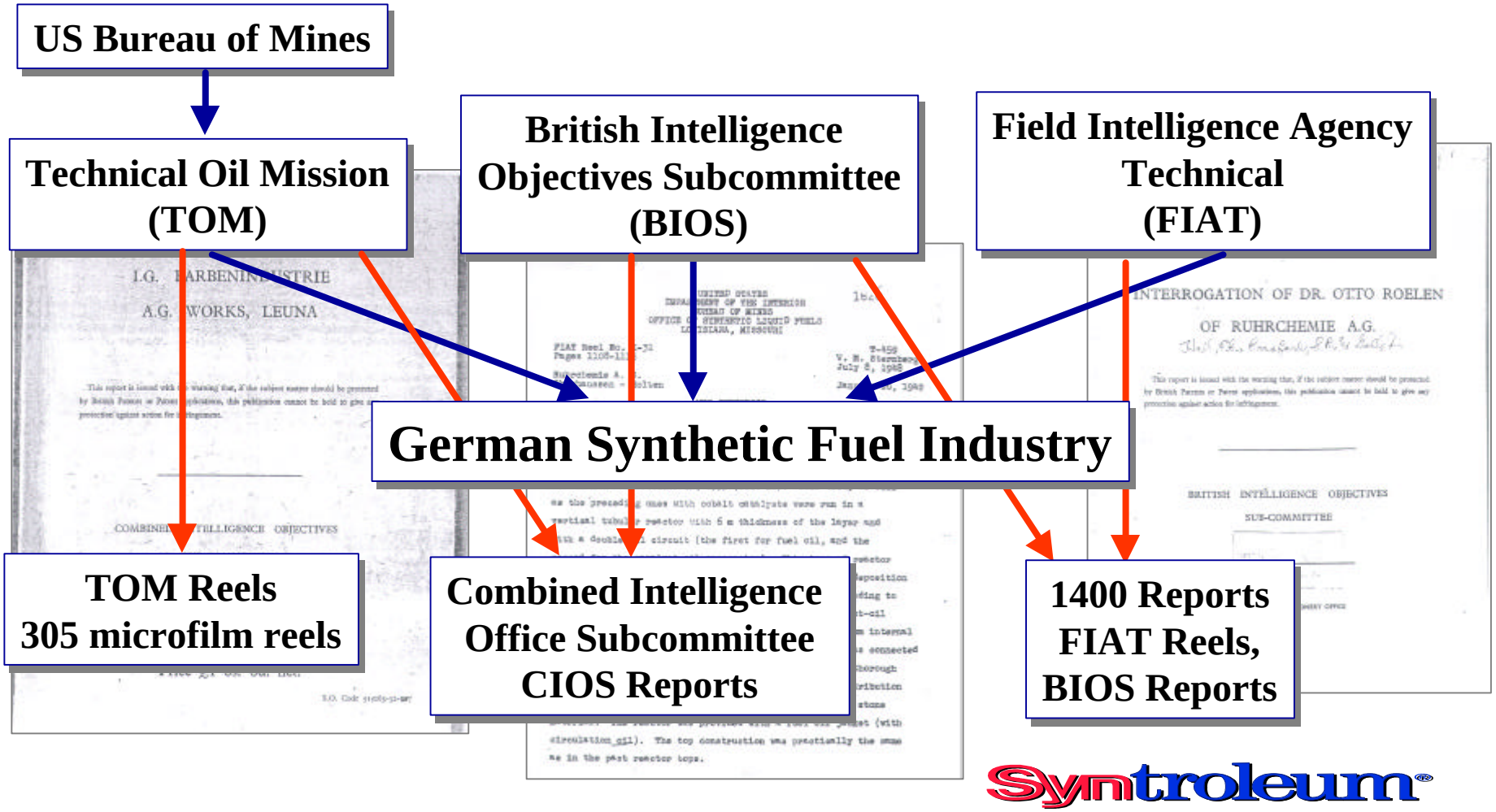
Fischer-Tropsch Process History:
Allied Investigation of the German Synthetic Fuels Industry



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“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**

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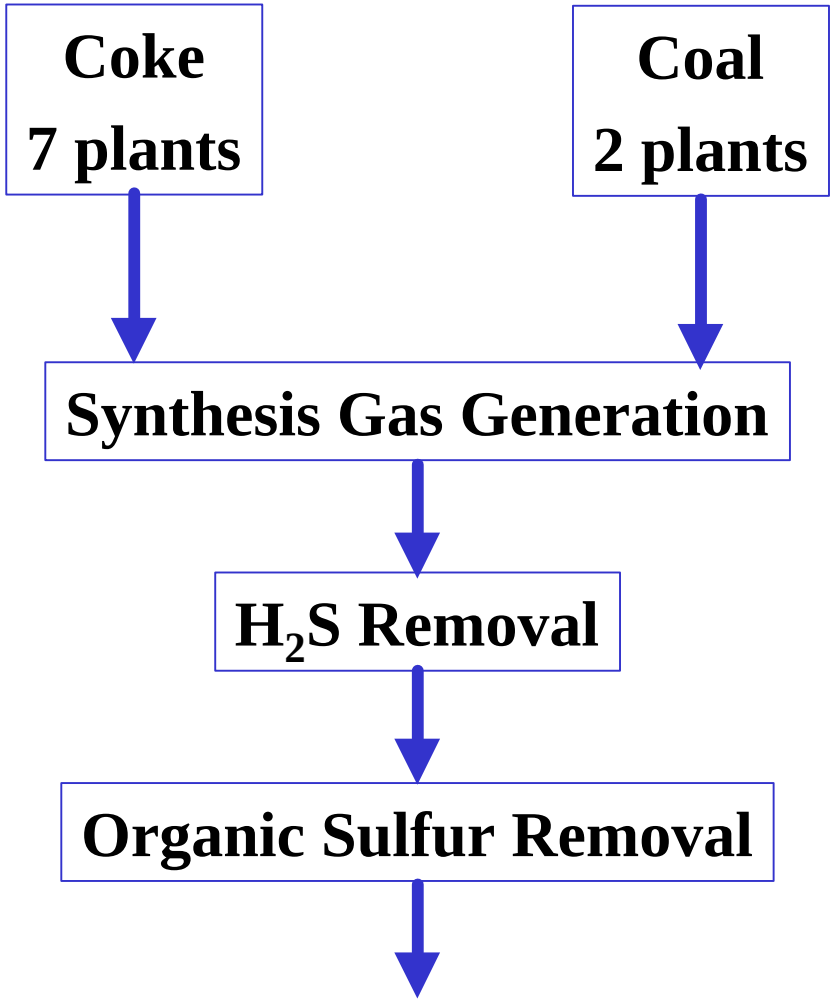
Fischer-Tropsch Process Overview



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

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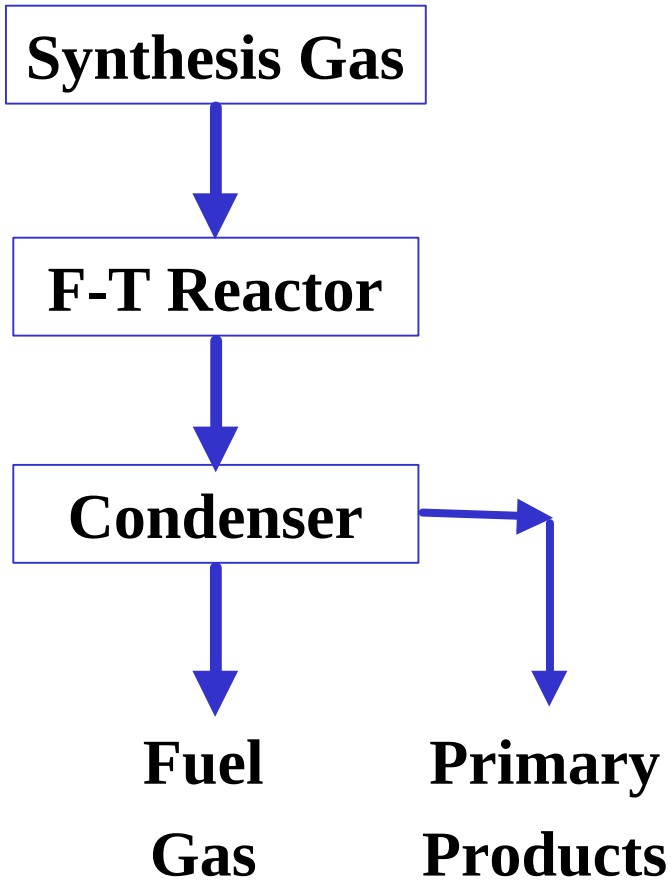
Fischer-Tropsch Process Overview



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

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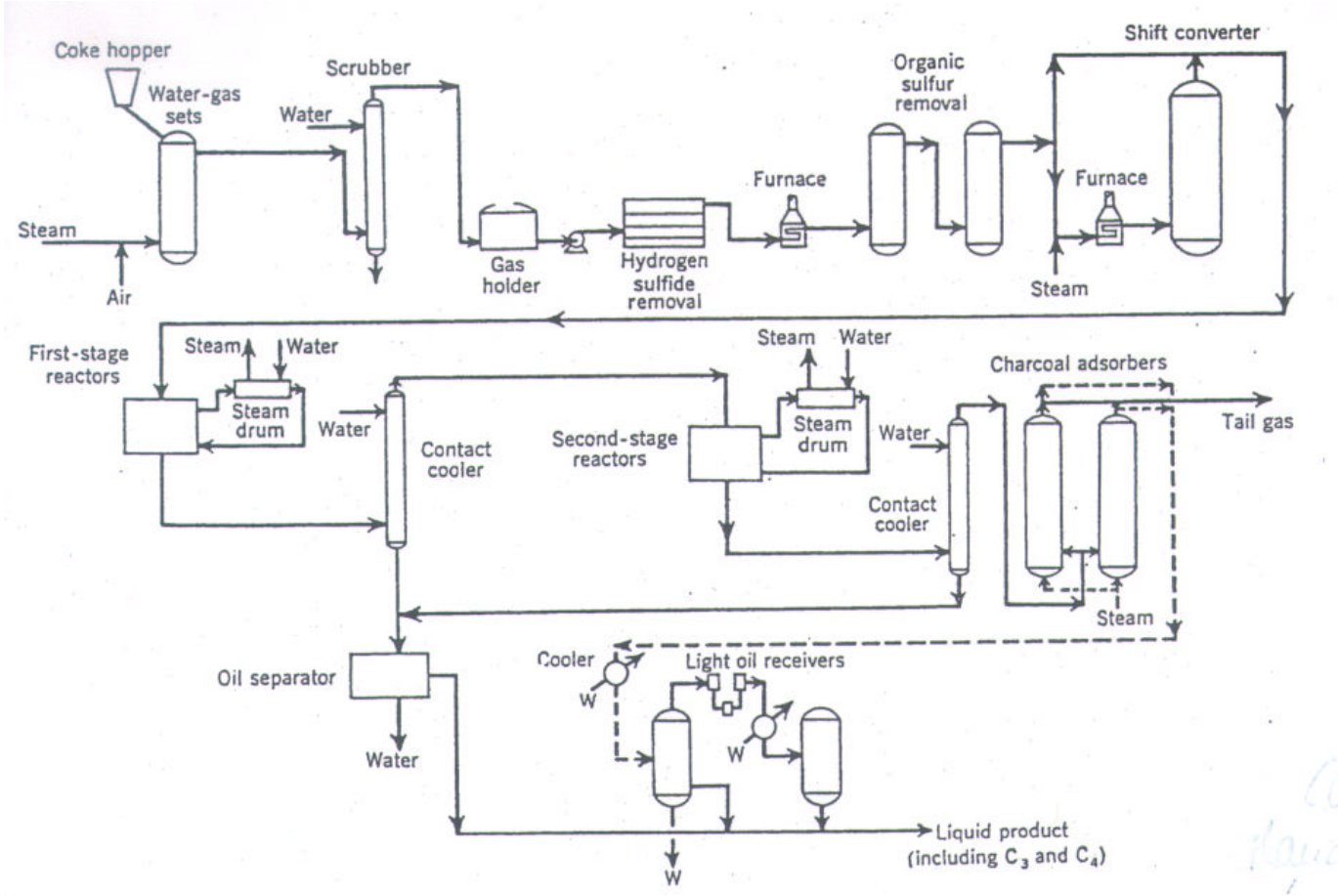
Flow Sheet for FT Process at Ruhrbenzin, Oberhausen-Holten, Ruhr



from Kirk-Othmer, 1951

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German Fischer-Tropsch Plants
in order of construction

Fischer-Tropsch Plant	Date Operational	1938 tpy C3+	1939 tpy C3+
Ruhrbenzin AG	1937	27.4K	49.4K
Steinkohlen-Bergwerk Rheinpreussen	1936	28.5K	54.7K
Gewerkschaft Viktor, Klocknerwerke-Wintershall AG	1936	27.1K	31.2K
Braunkkohle-Benzin AG (Brabag)	1937	103.5K	117.0K
Mitteldeutche Treibstoff und Ol Werke	1938	-	-
Krupp Treibstoffwerk	1938	-	31.8K
Chemische Werke Essener Steinkohle AG	1939	-	35.7K
Hoesch-Benzin GmbH	1939	-	15.6K
Schaffgotsch Benzin GmbH	1939	-	-

Anthony N. Stranges, Germany's Synthetic Fuel Industry 1927-45.

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Property and Uses of Primary Products: Condensable Gases

- **C3 and C4 hydrocarbons**
  - **8 Plants**
    - **Liquified and sold in tank cars and cylinders**
- **Rheinprussen**
  - **$^{2}/_{3}$ Liquified and sold in tank cars and cylinders**
  - **$^{1}/_{3}$ converted into alcohols**

Report on the Petroleum and Synthetic Oil Industry of Germany, Ministry of Fuel and Power, London, His Majesty's Stationery Office, 1947, pg 87**.**

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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**

Report on the Petroleum and Synthetic Oil Industry of Germany, Ministry of Fuel and Power, London, His Majesty's Stationery Office, 1947, pg 87.

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

- **Base Stock for high grade oil**

Property	Synthetic diesel	Mixed diesel
• Sp.Gr.	0.748	0.848-0.880
• Freezing point C	- 40	- 35 to - 26
• Flash point C	45	63
• Cetane Number	78	55 to 48
• Boiling Range C	164 to 238	170 to 280/320

  - **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**

Report on the Petroleum and Synthetic Oil Industry of Germany, Ministry of Fuel and Power, London, His Majesty's Stationery Office, 1947, pg 87.

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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”**

Report on the Petroleum and Synthetic Oil Industry of Germany, Ministry of Fuel and Power, London, His Majesty’s Stationery Office, 1947, pg 87.

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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)**

	mp C	Pene-tration	Mean MW	Mean C No.	Uses
Soft wax	44	-	-	-	make fatty acids
Slab wax	53	35.0	380	27	polishes, candles, explosives
Catalyst wax -	ca 30	-	-		
Ref. plastic wax	ca85	17.0	500	36	paper, cardboard
Ref, hard wax	110	4.0	60	43	polishes, candles, explosives

Report on the Petroleum and Synthetic Oil Industry of Germany, Ministry of Fuel and Power, London, His Majesty's Stationery Office, 1947, pg 87-88.

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Fuel Properties from FT Processes

Constituent	Wt%	Density	% olefins	av MW	Carbon No	Cloud Point C	Pour Point C	Research Octane	Motor Cetane	Research Cetane
Low Pressure										
Gasol (C3+C4)	12	-	50	-	C3+C4	-	-	-	-	-
Gasoline to 185 C	49	0.689	37	100	C4-C10	-	-	52	-	-
Gasoline to 200 C	54	0.693	34	115	C4-C11	-	-	49	-	-
Diesel Oil, 185-320 C	29	0.760	15	190	C11-C18	-13	-18	-	87	100
Diesel Oil, 185-320 C	24	0.766	13	205	C12-C19	-5	-9	-	92	105
Soft wax, 320-450 C	7	0.900	Iodine 2	-	>C18	-	-	-	-	-
Hard wax	3	0.930	Iodine 2	-	-	-	-	-	-	-
Medium Pressure										
Gasol (C3+C4)	-	-	30	-	66% C4, 33% C3	-	-	-	-	-
Gasoline to 185 C	35	0.685	20	100	C4-C10	-	-	28	-	-
Gasoline to 200 C	40	0.689	18	115	C4-C11	-	-	25	-	-
Diesel Oil, 185-320 C	35	0.760	10	190	C11-C18	-7	-11	-	87	100
Diesel Oil, 185-320 C	35	0.766	8	205	C12-C19	-2	-5	-	92	105
Soft wax, >320 C	30	0.900	Iodine 2	-	>C18	-	80	-	-	-
Soft wax, >330 C	25	0.900	Iodine 2	-	>C19	-	80	-	-	-

from Kirk-Othmer, 1951, citing: Pichler, H. “Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen,” Technical Oil Mission Report, Reel 259, Frames 467-654 (1957)

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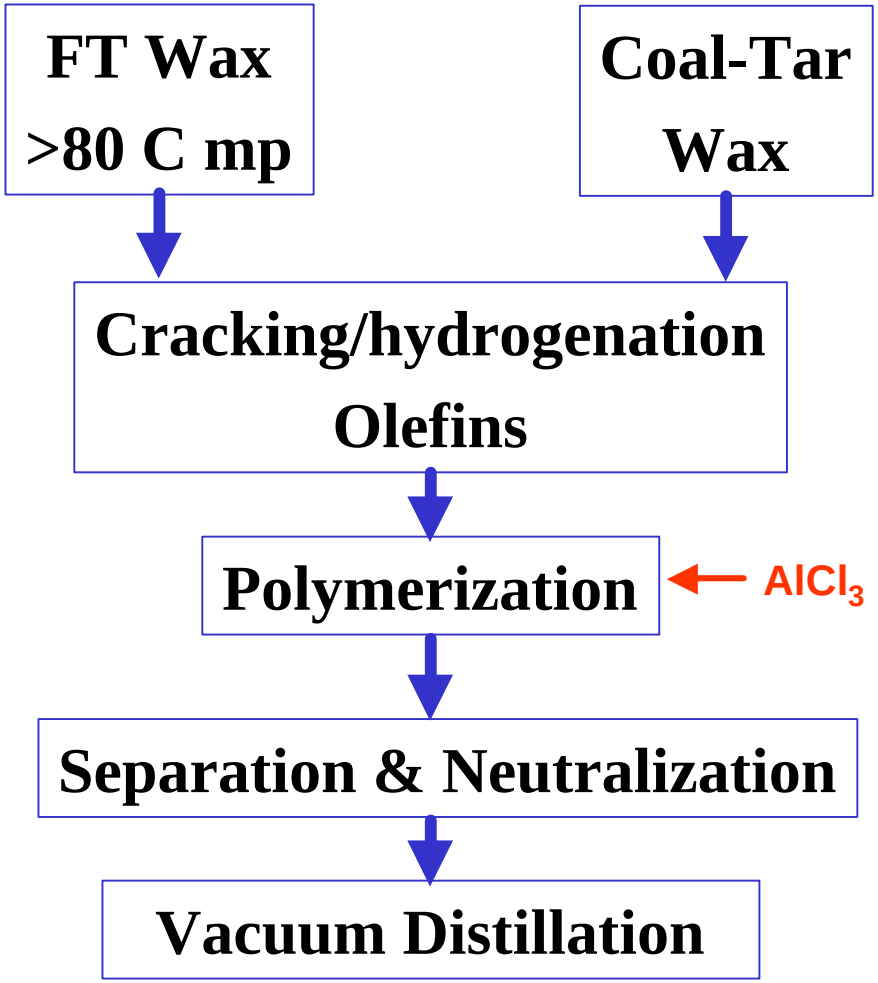
Lubricating Oils Manufacture: Stettin-Politz Plant



Report on Investigations by Fuels and Lubricants Teams at the I.G. Farbenindustrie A.G. Works at Leuna, ed. R. Holroyd, CIOS Target No. 30/4.02, Fuels and Lubricants, Item No. 30, File No. XXXII-107Combined Intelligence Objectives Sub-Committee, pg 81-84.

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Lubricating Oils Properties: Stettin-Politz Plant

	Lubricating Oil		Diesel	Steam Cylinder
	SS-1103	SS-1106	Oil	Oil
Viscosity deg				
Engler at 100 C	3.0	5.5-5.6	-	6.0
Viscosity, cSt	24.5	47	-	52
Viscosity Index	115-124	108-112	-	115-116
Flash Point, C	220 min	248-260	-	300-310
Pour Point, C	-30 max	- 10.5 max	0±1	-15.5
Conradson C	0.2 max	0.2 max	-	0.4-0.5
Iodine No.				20
Cetane No.			72-72	
IBP %			302 min	
Sulfur %			0	

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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**

Report on the Petroleum and Synthetic Oil Industry of Germany, Ministry of Fuel and Power, London, His Majesty's Stationery Office, 1947, pg 87-88.

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Property and Uses of By-Products:

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

Report on the Petroleum and Synthetic Oil Industry of Germany, Ministry of Fuel and Power, London, His Majesty's Stationery Office, 1947, pg 88.

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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**

Report on the Petroleum and Synthetic Oil Industry of Germany, Ministry of Fuel and Power, London, His Majesty's Stationery Office, 1947, pg 93-94.

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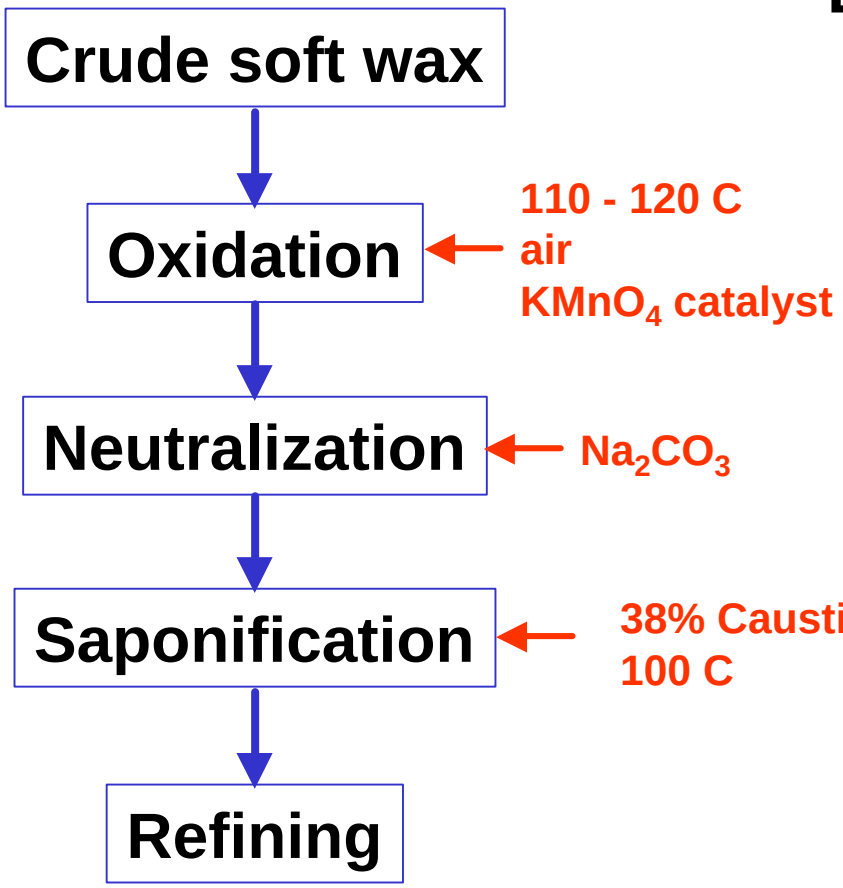
Industrial production of secondary products: Synthetic Soap



- **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

Report on the Petroleum and Synthetic Oil Industry of Germany, Ministry of Fuel and Power, London, His Majesty's Stationery Office, 1947, pg 94.

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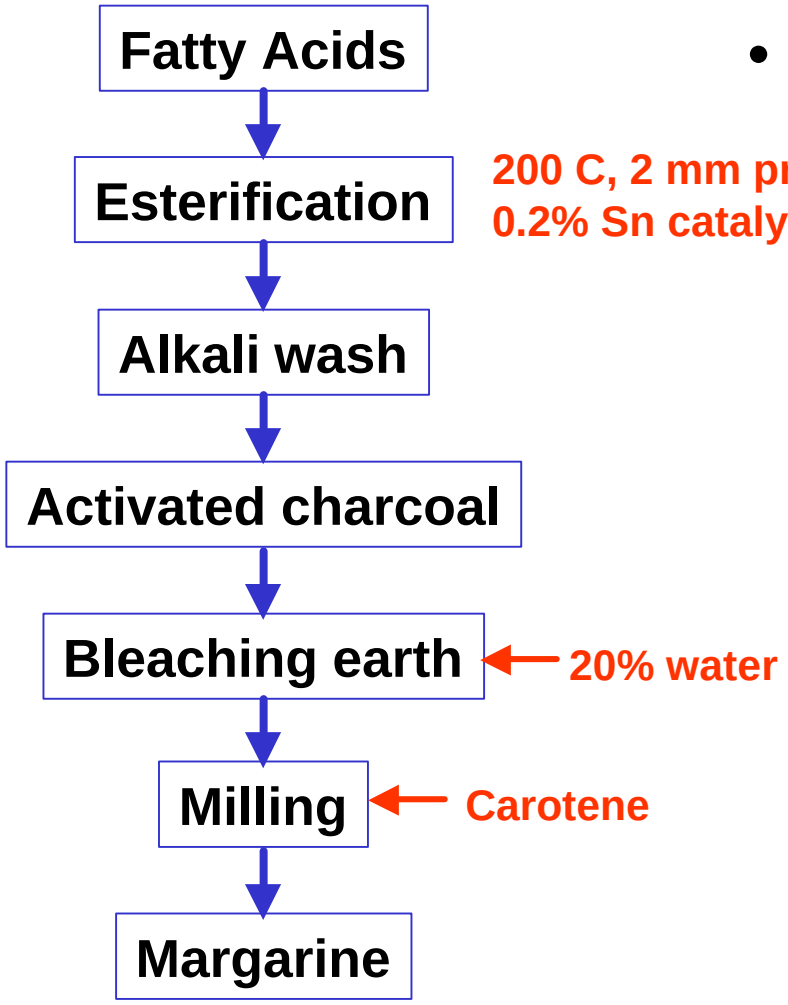
Industrial production of secondary products: Edible fat (margarine)



- **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**

Report on the Petroleum and Synthetic Oil Industry of Germany, Ministry of Fuel and Power, London, His Majesty's Stationery Office, 1947, pg 94.

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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**

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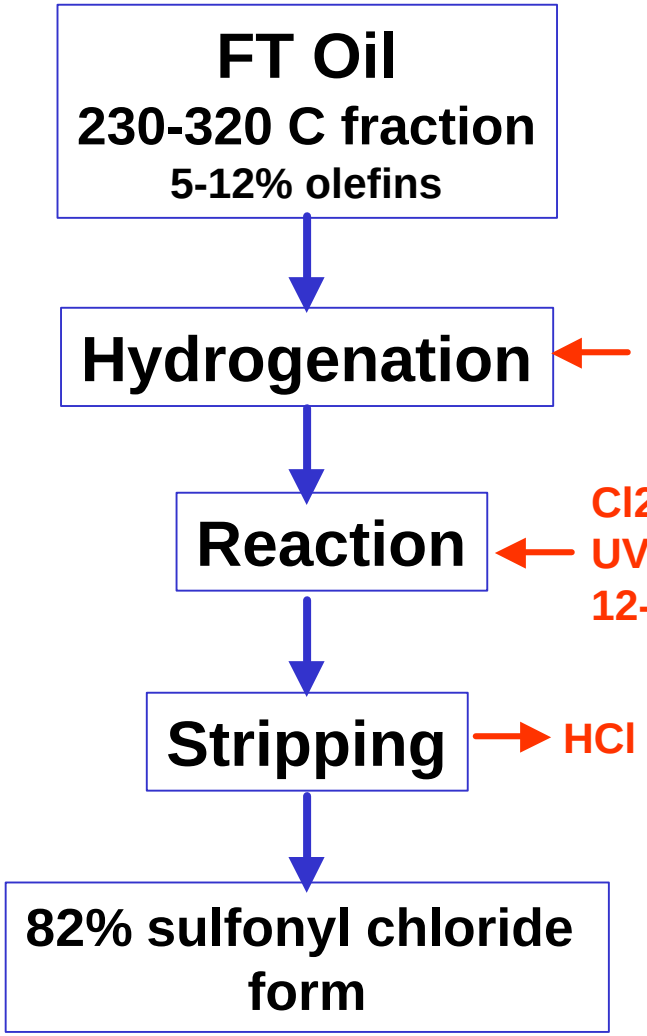
Industrial production of secondary products: Detergent (Mersol)



- **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

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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)

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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**

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