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Upgrading F-T Products From Germany to the 1950’s

German Hydrocarbon Needs 1939-1945

- **Limited natural liquid hydrocarbon sources[1]**
- **Significant coal resources**
- **War increased demand for**
  - **Fuel**
  - **Lubricants**
  - **Chemicals**
  - **Personal Care Products**
  - **Food**
- **All could be partially supplied from F-T plants[1,2]**

F-T Reaction and Products

- CO and H2 combine to produce linear and slightly branched products[1]
  - Paraffins—Predominantly Linear
  - Olefins—both terminal and internal
  - Alcohols—Mostly to completely terminal
  - Aldehydes
  - Acids
- Product distribution varies with catalyst and conditions

German Fuel Situation prior to WWII

- Germany has limited domestic oil production, but has significant coal reserves[1]
- WWI demonstrated need for alternative sources for liquid fuels[1,2]
- Romania, Poland, Russia and Austria supplied some crude oil, but supply was not consistent
- Domestic production of fuels and lubricants needed for energy security

Coal Liquefaction and Shale Oil[4]

- **Low Temperature Carbonization of Lignite**
  - **Produced 3% of oil containing 20% creosote**
  - **Octane varied from 38 to 48**
- **Hydrogenation of coal, coal tar, and lignite**
  - **Good Diesel Fuel**
- **High Temperature Carbonization**
  - **Further processed or mixed to produce fuel**
- **Distillation of Shale Oil**
  - **Handled similar to Coal Tar**

Coal Hydrogenation Product Properties[4]

Property	Typical Value	Conventional D2
Gravity	0.85 to 0.885	0.83
Aniline Point	31 to 53°C	
Aromatics and Unsaturates	38 to 49%	20-25%
Boiling Index	255 to 265	
Cetane Rating	30 to 45	41
Pour Point	-35 to -70°C	-5 to -20°C
Viscosity—Engler@20°C	1.45 to 1.81	

Shale Oil Properties[3]

Property	Typical
Gravity	0.916
Cetane Rating	35
Neutralization Index	0
Ash	0.02%
Water	0.09%
Sulphur	4.4%
Saponification No.	4.4%
Conradson Carbon	0.15%
Asphalt	0.06%

Synthetic Diesel Fuels

- Low Temperature-Low Pressure Carbonization of Coal[17]
  - Coal Tar not suitable as fuel
- High Temperature Hydrogenization of Coal[17]
  - Acceptable diesel fuel
- FT Fuel Known as “Kogasin II”[17]
  - Not Suitable as diesel fuel for then-current engines
    - Exceptional ignitability, however
      - 5% Higher Fuel Consumption
      - 25% Higher Exhaust Gas Temperature
  - Excellent Blend Component with Coal-derived products[17,18]

FT Diesel Typical Properties[1]

	Summer	Winter
Diesel Fuel Dist Range	150-320°C	150-250°C
Cloud Point	-6°C	-26 °C
Pour Point	-12 °C	-34 °C

German Diesel Fuel Specifications[4,17]

Property	Wehrmacht Diesel Kraftstoff	Sonder Diesel Kraftstoff	Luftwaffe K1	Mineral Oil; FT Synthesis; Hydrogenation	Lignite Oil
Clearance	The Fuel must be clear, free from all solid matter				
Gravity@15oC	0.810 to 0.865			0.88 Max	0.90Max
				For U-Boat	0.84-0.87
Viscosity,Engler@ 20°C	1.1° to 2°			1.2° to 2.6°	
Pour Point	Winter:	-30°C Max	-45°C Max	Must flow freely without separation	
	Summer:	-10°C Max			
Flash Point, PM	55°C	21°C	50°C	55°C	
Neutralization No.	0.4 mg Max		1% Max	1.50%	
Water	0.5% Max			0.5% Max	
Ash	0.05% Max				
Sulphur	1% Max			1% Max	1.3% Max
Conradson Carbon	0.05% Max		1% Max	0.8% Max	1% Max
Lower Heat Value	9900 Kcal/kg. Min			9900 Kcal/kg Min	
Ignitability	45 Cetane Min		50 Cetane Min	No Specification	
				(In practice 50-55)	
Volatility	80% Min Distilled at 360°C			60% Min Distilled @ 350°C	
Compatibility	All Diesel fuels must mix together without precipitation			All Diesel fuels must mix together without precipitation	

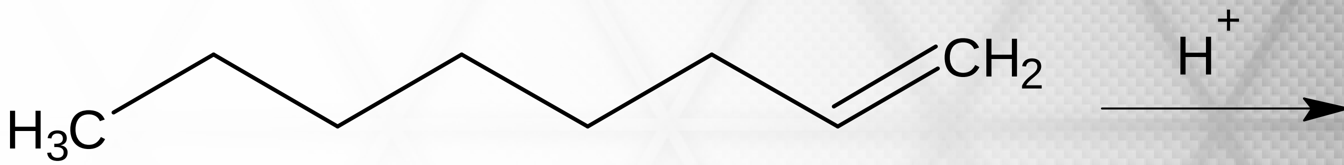
Diesel Blend Example

- FT Diesel Fraction of 100 Cetane blended with tar oils to give desired Cetane Product
  - For a 30 Cetane Blend—10%
  - For an 83 Cetane Blend—60%
- Medium Pressure FT process was preferred over Low Pressure Process

Other Products from F-T Process

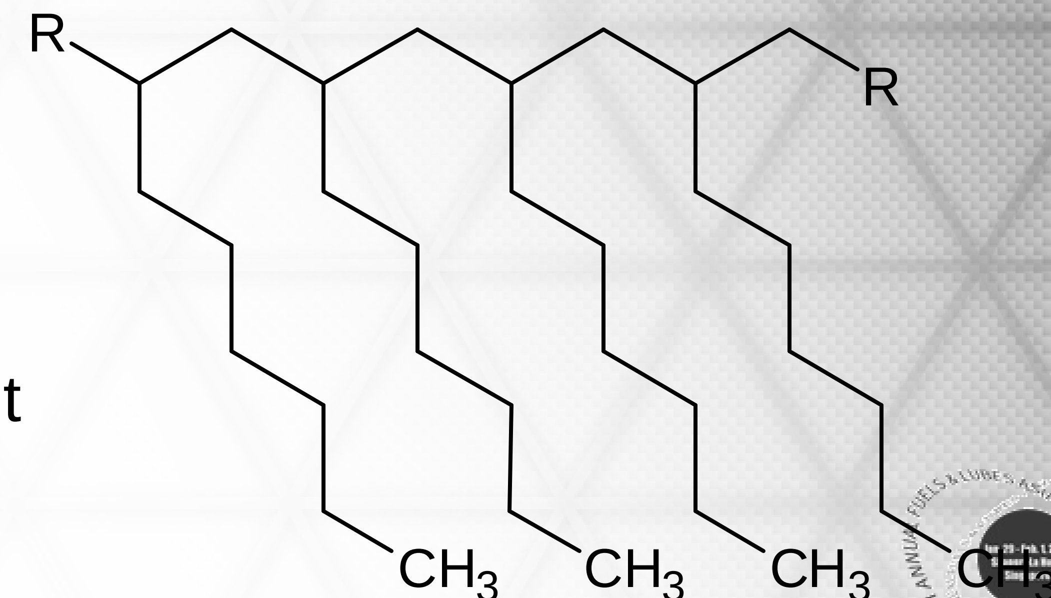
- **Olefins used as feedstocks for other products**
  - **Synthetic base oil**[17,21]
    - **10% of overall base oil production**
    - **45% of aircraft lubricants**
  - **Higher carbon number alcohols via Oxo (hydroformylation) Process**
  - **Same carbon number alcohols via hydration**
  - **Alcohols and acids from F-T water extraction**[30]

Synthetic Base Oil Production[7,21]



110 V.I.

-40°C Pour Point



Synthetic Base Oil Research[7,21]

- Polymerization of olefins[7,21,24,25]
- Alkylation of Aromatics with F-T olefins[21,25]
- Chlorination and direct polymerization
- Chlorination/de hydrochlorination followed by polymerization[24]
- Polymerization of ethylene followed by thermal cracking.[7,21,25]
- Oxidation of cyclohexane and formation of diesters with alcohols from OXO process[25]
- Alkylation of mineral oils with FT olefins[25]
- Cannizzaro Reaction of aldehydes followed by esterification with fatty acids[25]

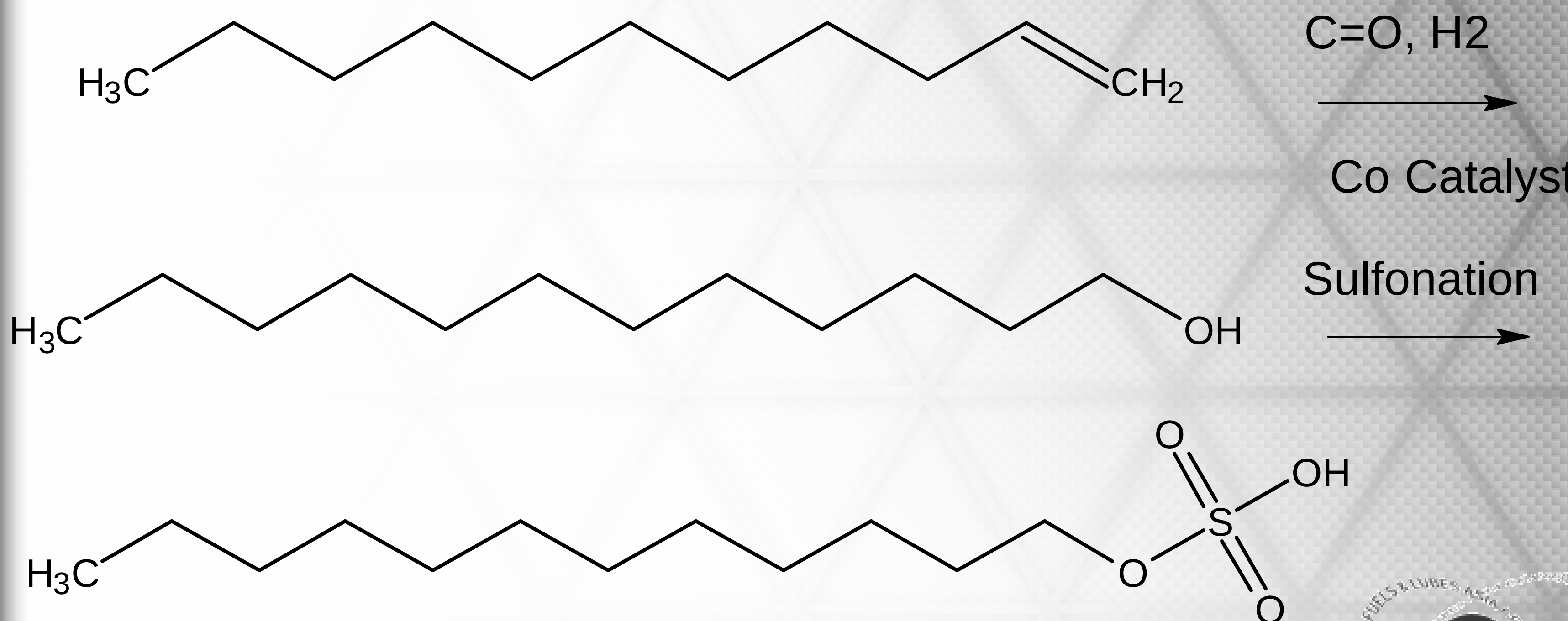
Current Commercial Products Derived from German Work

- Poly alpha Olefin (PAO) fluids[7]
- Synthetic Ester Fluids
  - Especially diesters
- Synthetic Alkyl Aromatics
- Ethylene-Propylene Co-Polymer Oils

F-T Derived Olefins

- Isolated from F-T Light Oil
- Produced by Cracking F-T Wax[7]
- Used as feed for several processes
  - Base oil[7]
  - Synthetic detergent alcohols via two processes[30]
    - OXO Synthesis[7]
    - Hydration
  - Other detergents[30]
    - Alkyl sulfates
    - Aromatic sulfates

Detergents from F-T Wax/Olefins[7]



Synthetic Detergents

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- **Alkyl sulfates produced by Mersol Process**[7,30]
  - **Reaction with SO_2 and Cl_2**
- **Aryl Sulfates from alkylation of Toluene and sulfonation**
- **Alkylsulfonates are superior to alkylsulfates derived directly from olefins**
- **All were used to supplant natural soaps to some extent.**

Alcohols from F-T Reaction

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- Isolated from LT and HT Raw F-T Products[6]
- Recovered from F-T Water
- Produced via OXO process[34]
- Produced directly via Synol Process[7,30]
  - Low H_2/CO ratio
  - High Temperature
- Used for detergent, plasticizer and base oil production[30,]

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F-T Wax Uses[30]

- **At least 5 grades of wax produced**
- **Uses**
  - **Coatings**
  - **Water-Proofing**
  - **Filler for Rubber Products**
- **Small Volume compared to fuel uses**

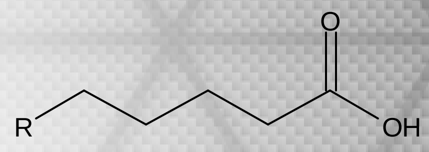
Typical Wax Production from a MP F-T Plant

Wax Description	Melting Point, °C	Production, kg/day	Disposition
Soft Wax (Gatch)	35-45	22359	Fatty Acid Synthesis
Block Paraffin	50-52	2200	Olefins for Synthetic Oils
Plastic Wax	70-75	2688	Cardboard, Candles, Paints
Catalyst Wax	80-90	6360	
R.B Hard Wax	90-95	8976	Paper, Wood Barrels, Polish

Fatty Acid Synthesis[30]

Air, Aqueous $KMnO_4$

C_{20}-C_{40} Wax ——→



C8-C10	**16%**
C10-C20	**45%**
C21-C28	**10%**
Residue	**9%**
Unconverted Wax	**20%**

3 Plants Converted 80,000 tons/yr into Fatty Acids

Fatty Soaps

- 3 Plants alone converted 80,000 tons/yr of wax into Fatty Acids
- Significant source of soap for cosmetic use
- Some fraction had significant odor which limited use to 30% in natural soap
- Odor attributed to branched chain soaps
- Acids also used for:
  - Lubricants, lube additives and grease thickeners
  - Preservatives
  - Converted to alcohols and used as plasticizers
  - Mineral floatation

Fatty Esters

- Esterification with Glycerol produced fatty esters
  - Margarine Substitute
  - Contains even and odd carbon number compared to only even numbers for natural fats
  - Physiological testing indicated no harm
    - Animal and human testing
    - Concern by some researchers about long term toxicology

Post-War Oil Industry

- Perceived Shortage of Crude Oil
- Perceived Need for Additional Hydrocarbon Resources
  - Coal
  - Natural Gas
- Knowledge that Germany Possessed Significant Technology

Post War Upgrading of F-T Products Information Sources

- British and US interrogation of German scientists
  – US Navy Technical Mission in Europe
  – British Intelligence Objective Sub-Committee
  – Combined Intelligence Objectives Sub-Committee
  – Bureau of Mines Information Circular
  – Technical Oil Mission Microfilm Reels

Post War F-T Upgrading Most Significant Effort

- **Shell Conversion of F-T Product**[51,52,53,54]
  - **Solid Paraffin wax converted into liquid products with essentially no change in molecular weight**
  - **Products are branched chain paraffins where the branches "consist substantially exclusively of methyl groups" USP 2,475,358**
  - **Initial conversions accomplished with $AlCl_3$ and cracking suppressor**

Subsequent Upgrading Efforts

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- Shell improved $AlCl_3$ process[53,54]
  - Continuous Vapor Phase Conversion
  - Continuous Liquid Phase Conversion
- Others further improved process
  - New Catalysts
  - New Conditions
  - Same Products
- Outcome is our modern hydroisomerization/hydrocracking technology
- Mechanism now well understood and support observation that branching is mostly methyl groups

Conclusions

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- Germans successfully produced many useful products utilizing F-T process technology
- Successfully developed foundation for many current products
  - Synthetic base oils and fuels
  - Chemical feed stocks
  - Chemical processes
- Post War Efforts led to many current catalytic hydrocarbon conversion processes

References

- Complete References from the written paper are included in the following slides.
- Reference numbers in the preceding slides refer to the same reference numbers used in the written paper

References 1-8

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3. British Intelligence Objectives Sub-Committee Final Report No. 1697 (Interrogation No. 667), Item 30, Synthetic Oil Production in Germany—Interrogation of Dr. Bütefisch, January 1946, page 2.
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7. U.S Department of the Interior, Bureau of Mines Information Circular 7370, Report on the Investigation by Fuels and Lubricants Teams at the I.G. Farbenindustrie A.G. Leuna Works, Nerseburg, Germany, July 1946, pp 52-57 & 59.
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11. See Ref 7, page 55.

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26. See Ref. 7, pages 81-83.

27. See Ref. 7, page 69.

28. See Ref. 21, pages 28-30.

29. See Ref.5, page 42.

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34. British Intelligence Objective Sub-Committee Interrogation Report No. 736, Interrogation of Dr. Roelen, 20-21 October, 1945.

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41. *See Ref. 30, pages 26-27.*
42. *See Ref. 30, page 27.*
43. *See Ref. 30, pages 22-23.*
44. *See Ref. 30, page 26*
45. *See Ref. 6, page 148*
46. *See Ref. 6, pages 144-145.*
47. *See Ref. 6, pages 144-149*
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49. *See Ref. 6, page 162.*
50. *See Ref. 6, page 166*

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