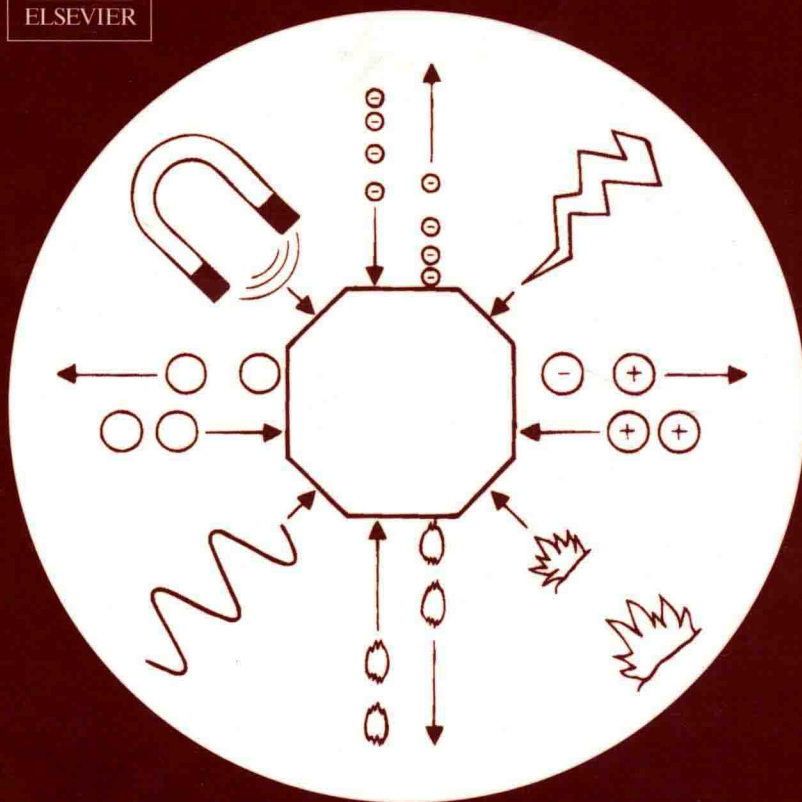


studies in surface science and catalysis



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FISCHER-TROPSCH SYNTHESIS, CATALYSTS AND CATALYSIS

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FISCHER-TROPSCH SYNTHESIS, CATALYSTS AND CATALYSIS

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Studies in Surface Science and Catalysis 163

FISCHER-TROPSCH SYNTHESIS, CATALYSTS AND CATALYSIS

Foreword

In general, there are two approaches to the production of substitutes for crude petroleum. In one of these, the organic material is heated at high temperatures under a high pressure of hydrogen. In the other approach, the organic material is converted to a mixture of hydrogen and carbon monoxide (syngas) and this syngas is converted to hydrocarbons by conversion over suitable catalysts. The papers included in the present volume are concerned with the indirect liquefaction approach.

The introduction of the catalytic synthesis of ammonia was widely recognized. The Nobel Prize in 1918 for chemistry was awarded to Fritz Haber for his developments that led to the synthesis of ammonia from the elements. The development of the very high pressure ammonia synthesis and its commercial success gave Germany a decided leadership position in high pressure process during the early part of the twentieth century. Rapidly following the ammonia synthesis, the commercial production of methanol from synthesis gas was a commercial success. After much work, Bergius finally was able to show that heating coal at high temperatures under high pressures of hydrogen led to the production of liquid products. Fritz Fischer, director of the coal research laboratory, worked to develop a coal conversion process that could compete with the direct process developed by Bergius. During the 1920s, the work by Fischer and coworkers led to what is now known as the Fischer-Tropsch process. The advances in high pressure process technology led to the Nobel Prize being awarded in 1932 to Bergius and Carl Bosch; however, the Fischer-Tropsch scientific advances were not afforded this honor. The Fischer-Tropsch process also lost out to the direct coal liquefaction process in the production of synfuels in Germany during the 1935-1945 period, for both technological and political reasons.

During the energy crisis of the 1970s the direct and indirect coal liquefaction processes received much attention. During this period the direct coal liquefaction process received more attention in the U.S., with four large scale demonstration plants being operated. At that time, the major goal of producing synfuels was to provide a source of gasoline and the direct liquefaction process provided high octane gasoline due to its high aromatics content. Today the direct coal liquefaction process is out of favor, primarily because of the high aromatics content and the reduction of the high heteroatom content which greatly exceed today's environmental requirements. This, plus the advances in Fischer-Tropsch technology during the intervening thirty years, leads to the concentration of the effort to produce commercial quantities of synfuels upon the Fischer-Tropsch technology. In addition to the fifty year efforts by Sasol that now produces about 150,000 bbl/day, Shell Oil (15,000 bbl/d) and PetroSA (formerly Moss gas; 40,000 bbl/d) became commercial producers in the early 1990s. Sasol has brought on line a 35,000 bbl/d plant in Qatar in mid-2006.

The present book addresses four major areas of interest in Fischer-Tropsch synthesis (FTS). The first three contributions address the development of FTS during the early years in Germany and Japan and more recently by BP. The next section includes eight contributions that relate to the development of catalysts for FTS, their structure and changes that occur during use. The third section contains six contributions that relate to impact of various process conditions upon the productivity and selectivity of the FTS operation. The final section consists of six contributions relating to the FTS process and the conversion of the primary products to useful fuels. Most of these contributions are based on presentations at the 2005 Spring National Meeting of the American Chemical Society, held in San Diego in 2005.

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A History of the Fischer-Tropsch Synthesis in Germany 1926-45

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1. Introduction: twentieth-century synthetic fuels overview

The twentieth-century coal-to-petroleum, or synthetic fuel, industry evolved in three stages: (1) invention and early development of the Bergius coal liquefaction (hydrogenation) and Fischer-Tropsch (F-T) synthesis from 1910 to 1926; (2) Germany's industrialization of the Bergius and F-T processes from 1927 to 1945; and (3) global transfer of the German technology to Britain, France, Japan, Canada, the United States, South Africa, and other nations from the 1930s to the 1990s.

Petroleum had become essential to the economies of industrialized nations by the 1920s. The mass production of automobiles, the introduction of airplanes and petroleum-powered ships, and the recognition of petroleum's high energy content compared to wood and coal, required a shift from solid to liquid fuels as a major energy source. Industrialized nations responded in different ways. Germany, Britain, Canada, France, Japan, Italy, and other nations having little or no domestic petroleum continued to import petroleum. Germany, Japan, and Italy also acquired by force the petroleum resources of other nations during their 1930s-40s World War II occupations in Europe and the Far East. In addition to sources of naturally-occurring petroleum, Germany, Britain, France, and Canada in the 1920s-40s synthesized petroleum from their domestic coal or bitumen resources, and during the 1930s-40s war years Germany and Japan synthesized petroleum from the coal resources they seized from occupied nations. A much more favorable energy situation existed in the United States, and it experienced few problems in making an energy shift from solid to liquid fuels because it possessed large resources of both petroleum and coal.

Germany was the first of the industrialized nations to synthesize petroleum when Friedrich Bergius (1884-1949) in Rheinau-Mannheim in 1913 and Franz Fischer (1877-1947) and Hans Tropsch (1889-1935) at the Kaiser Wilhelm Institute for Coal Research (KWI) in Mülheim, Ruhr, in 1926 invented processes for converting coal to petroleum. Their pioneering researches enabled IG Farben, Ruhrchemie, and other German chemical companies to develop a technologically-successful synthetic fuel industry that grew from a single commercial-size coal liquefaction plant in 1927 to twelve coal liquefaction and nine F-T commercial-size plants that in 1944 reached a peak production of 23 million barrels of synthetic fuel.

Britain's synthetic fuel program evolved from post-World War I laboratory and pilot-plant studies that began at the University of Birmingham in 1920 on the F-T synthesis and in 1923 on coal liquefaction. The Fuel Research Station in East Greenwich also began research on coal liquefaction in 1923, and the program reached its zenith in 1935 when Imperial Chemical Industries (ICI) constructed a coal liquefaction plant at Billingham that had the capacity to synthesize annually 1.28 million barrels of petroleum. British research and development matched

Germany's, but because of liquefaction's high cost and the government's decision to rely on petroleum imports rather than price supports for an expanded domestic industry, Billingham remained the only British commercial-size synthetic fuel plant. F-T synthesis in the 1930s-40s never advanced beyond the construction of four small experimental plants: Birmingham, the Fuel Research Station's two plants that operated from 1935 to 1939, and Synthetic Oils Ltd. near Glasgow [1].

Britain and Germany had the most successful synthetic fuel programs. The others were either smaller-scale operations, such as France's three demonstration plants (two coal liquefaction and one F-T), Canada's bitumen liquefaction pilot plants, and Italy's two crude petroleum hydrogenating (refining) plants, or technological failures as were Japan's five commercial-size plants (two coal liquefaction and three F-T) that produced only about 360,000 barrels of liquid fuel during the World War II years [2].

The US Bureau of Mines had begun small-scale research on the F-T synthesis in 1927 and coal liquefaction in 1936, but did no serious work on them until the government expressed considerable concern about the country's rapidly increasing petroleum consumption in the immediate post-World War II years. At that time the Bureau began a demonstration program, and from 1949 to 1953 when government funding ended, it operated a small 200-300 barrel per day coal liquefaction plant and a smaller fifty barrel per day F-T plant at Louisiana, Missouri. In addition to the Bureau's program, American industrialists constructed four synthetic fuel plants in the late 1940s and mid-1950s, none of which achieved full capacity before shutdown in the 1950s for economic and technical reasons. Three were F-T plants located in Garden City, Kansas; Brownsville, Texas; and Liberty, Pennsylvania. The fourth plant was a coal liquefaction plant in Institute, West Virginia [3].

Following the plant shutdowns in the United States and until the global energy crises of 1973-74 and 1979-81, all major synthetic fuel research and development ceased except for the construction in 1955 of the South African Coal, Oil, and Gas Corporation's (SASOL) F-T plant in Sasolburg, south of Johannesburg. South Africa's desire for energy independence and the low quality of its coal dictated the choice of F-T synthesis rather than coal liquefaction. Its Johannesburg plant remained the only operational commercial-size synthetic fuel plant until the 1970s energy crises and South Africa's concern about hostile world reaction to its apartheid policy prompted SASOL to construct two more F-T plants in 1973 and 1976 in Secunda.

The 1970s energy crises also revitalized synthetic fuel research and development in the United States and Germany and led to joint government-industry programs that quickly disappeared once the crises had passed. Gulf Oil, Atlantic Richfield, and Exxon in the United States, Saarbergwerke AG in Saarbrücken, Ruhrkohle AG in Essen, and Veba Chemie in Gelsenkirchen, Germany, constructed F-T and coal liquefaction pilot plants in the 1970s and early 1980s only to end their operation with the collapse of petroleum prices a few years later [4].

In the mid-1990s two developments triggered another synthetic fuel revival in the United States: (1) petroleum imports again reached 50 percent of total consumption, or what they were during the 1973-1974 Arab petroleum embargo, and (2) an abundance of natural gas, equivalent to 800,000,000,000 barrels of petroleum, but largely inaccessible by pipeline, existed. Syntroleum in Tulsa, Oklahoma; Exxon in Baytown, Texas; and Atlantic Richfield in Plano, Texas, developed modified F-T syntheses that produced liquid fuels from natural gas and thereby offered a way of reducing the United States's dependence on petroleum imports. The Department of Energy (DOE) at its Pittsburgh Energy Technology Center through the 1980s-90s also continued small-scale research on improved versions of coal liquefaction. DOE pointed out

that global coal reserves greatly exceeded petroleum reserves, anywhere from five to twenty-four times, and that it expected petroleum reserves to decline significantly in 2010-2030. Syntroleum, Shell in Malaysia, and SASOL and Chevron in Qatar have continued F-T research, whereas DOE switched its coal liquefaction research to *standby*. The only ongoing coal liquefaction research is a pilot plant study by Hydrocarbon Technologies Incorporated in Lawrenceville, New Jersey, now Headwaters Incorporated in Draper, Utah.

A combination of four factors, therefore, has led industrialized nations at various times during the twentieth century to conclude that synthetic fuel could contribute to their growing liquid fuel requirements: (1) the shift from solid to liquid fuel as a major energy source, (2) the invention of the Bergius and F-T coal-to-petroleum conversion or synthetic fuel processes, (3) recognition that global petroleum reserves were finite and much less than global coal reserves and that petroleum's days as a plentiful energy source were limited, and (4) the desire for energy independence.

With the exception of South Africa's three F-T plants the synthetic fuel industry, like most alternative energies, has endured a series of fits and starts that has plagued its history. The historical record has demonstrated that after nearly 90 years of research and development synthetic liquid fuel has not emerged as an important alternative energy source. Despite the technological success of synthesizing petroleum from coal, its lack of progress and cyclical history are the result of government and industry uninterest in making a firm and a long-term commitment to synthetic fuel research and development. The synthetic fuel industry experienced intermittent periods of intense activity internationally in times of crises, only to face quick dismissal as unnecessary or uneconomical upon disappearance of the crises. Even its argument that synthetic liquid fuels are much cleaner burning than coal, and if substituted for coal they would reduce the emissions that have contributed to acid rain formation, greenhouse effect, and to an overall deterioration of air quality has failed to silence its critics. The hope of transforming its accomplishments at the demonstration stage into commercial-size production has not yet materialized.

The history of the synthetic fuel industry's fits and starts remains only partially written, with much of the historical interest having focused on Germany's coal hydrogenation process because it was the more advanced and contributed much more significantly to Germany's liquid fuel supply than the F-T synthesis. Coal hydrogenation produced high quality aviation and motor gasoline, whereas the F-T synthesis gave high quality diesel and lubricating oil, waxes and some lower quality motor gasoline. The two processes actually were complementary rather than competitive, but because only coal hydrogenation produced high quality gasoline it experienced much greater expansion in the late 1930s and war years than the F-T synthesis, which hardly grew at all. F-T products were mainly the raw materials for further chemical syntheses with little upgrading of its low quality gasoline by cracking because of unfavorable economics. Hydrogenation also experienced greater development because brown coal (lignite), the only coal available in many parts of Germany, underwent hydrogenation more readily than a F-T synthesis. In addition, the more mature and better developed hydrogenation process had the support of IG Farben, Germany's chemical leader, which successfully industrialized coal hydrogenation beginning in 1927 [5].

Despite its smaller size and lower production, the 9 F-T plants contributed 455,000-576,000 metric tons of coal-derived oil per year during the war years 12-15 percent of Germany's total liquid fuel requirement. The historical analysis that follows examines the F-T's invention and industrial development during several decades of German social, political, and economic unrest and complements the historical literature on Germany's coal hydrogenation process. The

historical examination of the two processes provides a more complete history of Germany's synthetic fuel industry.

2. Early development of the F-T synthesis: catalysts, conditions, and converters

Germany has virtually no petroleum deposits. Prior to the twentieth century this was not a serious problem because Germany possessed abundant coal reserves. Coal provided for commercial and home heating; it also fulfilled the needs of industry and the military, particularly the navy. In the opening decade of the twentieth century, Germany's fuel requirements began to change. Two reasons were especially important. First, Germany became increasingly dependent on gasoline and diesel oil engines. The appearance of automobiles, trucks, and then airplanes made a plentiful supply of gasoline essential. Moreover, ocean-going ships increasingly used diesel oil rather than coal as their energy source. Second, Germany's continuing industrialization and urbanization led to the replacement of coal with smokeless liquid fuels that not only had a higher energy content but were cleaner burning and more convenient to handle.

Petroleum was clearly the fuel of the future, and to insure that Germany would never lack a plentiful supply, German scientists and engineers invented and developed two processes that enabled them to synthesize petroleum from their country's abundant coal supplies and to establish the world's first technologically successful synthetic liquid fuel industry [6]. Bergius in Rheinau-Mannheim began the German drive for energy independence with his invention and early development of high-pressure coal hydrogenation in the years 1910-25. Bergius crushed and dissolved a coal containing less than 85 percent carbon in a heavy oil to form a paste. He reacted the coal-oil paste with hydrogen gas at high pressure ($P = 200$ atmospheres = 202.6×10^2 kPa) and high temperature ($T = 400^\circ\text{Celsius}$) and obtained petroleum-like liquids. Bergius sold his patents to BASF in July 1925, and from 1925 to 1930 Matthias Pier (1882-1965) at BASF (IG Farben in December 1925) made major advancements that significantly improved product yield and quality. Pier developed sulfur-resistant catalysts, such as tungsten sulfide (WS_2), and separated the conversion into two stages, a liquid stage and a vapor stage [7].



Figure 1. Friedrich Bergius

A decade after Bergius began his work Fischer and Tropsch at the Kaiser-Wilhelm Institute invented a second process for the synthesis of liquid fuel from coal. Fischer and Tropsch reacted coal with steam to give a gaseous mixture of carbon monoxide and hydrogen and then converted the mixture at low pressure ($P = 1\text{--}10$ atmospheres $= 1.013\text{--}10.013 \times 10^2$ kPa) and a temperature ($T = 180\text{--}200^\circ$ Celsius) to petroleum-like liquids. Fischer and his co-workers in the 1920s-30s developed the cobalt catalysts that were critical to the F-T's success, and in 1934 Ruhrchemie acquired the patent rights to the synthesis.

Fischer had received the PhD at Giessen in 1899, where he studied under Karl Elbs (1858-1933) and his research focused on the electrochemistry of the lead storage battery. He continued his electrochemical studies spending a semester with Henri Moissan (1852-1907) in Paris, the years 1901-2 in Freiburg's chemical industry and 1902-4 at the University of Freiburg's physiochemical institute. Upon leaving Freiburg Fischer conducted additional research from 1904 to 1911 in the institutes of Wilhelm Ostwald (1853-1932) in Leipzig and Emil Fischer in Berlin and from 1911 to 1914 at the Technische Hochschule in Berlin-Charlottenburg.

Emil Fischer (1852-1919) had an interest in Fischer's electrochemical work, and as a leading figure in establishing the KWIs beginning in 1912 he invited Fischer to direct the new institute for coal research planned for Mülheim in the Ruhr valley. The institute, which opened on 27 July 1914 was the first KWI located outside of Berlin-Dahlem, and like the others the Imperial Ministry of Education provided funding for the operating and administration costs whereas private industrial firms paid for the building and equipment. The Ruhr industries, particularly Hugo Stinnes, supported the Mülheim institute.



Figure 2. Franz Fischer



Figure 3. Hans Tropsch

Fischer had planned to study a coal-to-electricity direct path conversion, but with the institute's opening four days before World War I began and Germany's lack of petroleum quickly becoming apparent, the institute's program shifted from basic research on coal to methods of converting coal to petroleum. This wartime work was the institute's first comprehensive research program. It involved the decomposition of coal and the production of tar from the low-temperature carbonization (LTC) of different coals, giving yields of 1-25 percent, and the extraction (solution) of a coal with different organic solvents such as alcohols, pyridine, benzene, and petroleum ether at various temperatures and pressures. The extraction studies showed that

decreasing the coal's particle size by grinding increased tar yields. With benzene as the solvent at 270°C and 55 atm Fischer and W. Gluud in 1916 obtained tar yields many times the low yields obtained at atmospheric pressure. These early studies on coal also led Fischer and Hans Schroder in 1919 to propose their controversial lignin theory of coal's origin in which during the peat-bog stage of coal's formation the cellulose material in the original plant material decomposed leaving only the more resistant lignin that then changed into humus coal.

With the wartime coal investigations well underway, Fischer's interest shifted to a different hydrocarbon reaction. In 1913 Badische Anilin-und Soda-Fabrik (BASF) in Ludwigshafen patented a process for the catalytic hydrogenation (reduction) of carbon monoxide to give hydrocarbons other than methane, alcohols, ketones, and acids. According to the patent, hydrocarbon synthesis occurred best with an excess of carbon monoxide (2:1 carbon monoxide, hydrogen volume mixture) at 300-400°C, 120 atm, and the metals cerium, cobalt, or molybdenum, or their alkali-containing (sodium hydroxide) metallic oxides as catalysts. Because of World War I and priority given to industrializing the ammonia and methanol syntheses, BASF never continued its hydrocarbon synthesis [8]. Upon learning of BASF's patent Fischer decided to test its claims. Working with Tropsch he began investigating the catalytic reduction of carbon monoxide at various temperatures and pressures but using excess hydrogen gas, a 2:1 hydrogen: carbon monoxide volume mixture they called synthesis gas. This avoided carbon monoxide decomposition ($2\text{CO} \rightarrow \text{C} + \text{CO}_2$) which deposited carbon (soot) on the catalyst and rendered it ineffective.

The experiments with synthesis gas continued into the 1920s, and in 1923 Fischer and Tropsch showed that reacting the gas in a tubular, electrically-heated converter at high temperature and pressure, 400-450°C and 100-150 atm, and with alkali-iron instead of metallic oxide catalysts, gave a mixture of oxygen-containing organic compounds, such as higher alcohols, aldehydes, ketones, and fatty acids, that they called synthol. The reaction produced no hydrocarbons [9]. Additional studies in 1925-1926 using small glass combustion tubes 495 millimeters (mm) long, a gas-heated horizontal aluminum block furnace, and different reaction conditions, cobalt-iron catalysts at 250-300°C and 1 atm eliminated completely the oxygenated compounds. The product contained only hydrocarbon gases (ethane, propane, butane) and liquids (octane, nonane, isononene) with a boiling point range of 60-185°C [10].

Fischer continued his investigations into the 1930s, constructing a small pilot plant in Mülheim in 1932. The plant contained a series of converters five meters (m) high, 1.2 m wide, 12 mm thick walls, immersed in an oil bath for cooling and operated at the same conditions he had used earlier (2:1 hydrogen : carbon monoxide volume mixture, 190-210°C, 1 atm) but with a catalyst having the weight ratio 100 nickel-25 manganese oxide-10 aluminum oxide-100 kieselguhr. The catalyst, containing previously untested nickel, which differed in atomic number from iron and cobalt only by one and two units, had a short four to six week lifetime because of sulfur poisoning. The total yield per cubic meter (m^3) of synthesis gas consumed was only 70 grams (g) of a 58-octane number gasoline and a diesel oil boiling above 220°C [11].

Two years later Fischer's decade-long research moved to the next level with the construction in 1934 of the first large pilot plant in which he planned to solve the synthesis' three main problems and synthesize hydrocarbons from carbon monoxide and hydrogen. Ruhrchemie AG, a company Ruhr coal industrialists founded, envisioned the F-T synthesis as an outlet for its surplus coke, and upon acquiring the patent rights to the synthesis in 1934, constructed the pilot plant in Oberhausen-Holten (Sterkrade-Holten), near Essen. The plant operated at the conditions used in Fischer's small pilot plant and had an annual capacity of 1,000 metric tons (7,240 barrels) of motor gasoline, diesel oil, and lubricating oil.

Although the larger pilot plant demonstrated the overall success of the F-T synthesis, its three main problems, removing the large amount of heat released in the gas stream during the reaction, the nickel catalyst's short lifetime, and the significant loss of catalytic metals (nickel, manganese, aluminum) during their recovery (regeneration) for reuse, persisted during the operation. The nickel catalyst's poor performance forced Fischer and Ruhrchemie to abandon its use for commercial development. At this time research resumed with the more active but expensive cobalt catalysts. Oberhausen-Holten subsequently became the production center for a standardized cobalt catalyst used in all the F-T plants constructed later in the 1930s, for all the development work on synthetic motor fuel and lubricating oil, and for the oxo process [12].

The successful pilot plant research and development at Oberhausen-Holten was the major turning point in the F-T synthesis. By November 1935, less than three years after Germany's Nazi government came to power and initiated the push for petroleum independence, four commercial-size Ruhrchemie licensed F-T plants were under construction. Their total annual capacity was 100,000-120,000 metric tons (724,000-868,000 barrels) of motor gasoline, diesel oil, lubricating oil, and other petroleum chemicals. The motor vehicle products comprised 72 percent of the total capacity. Petroleum chemicals made up the remaining 28 percent and included alcohols, aldehydes, soft waxes which when oxidized gave the fatty acids used to produce synthetic soap and edible fat (margarine), and heavy oil for conversion to the inexpensive detergent *Mersol*.

All the plants were atmospheric pressure (1 atm) or medium pressure (5-15 atm) syntheses at 180-200°C. They produced synthesis gas by reacting coke with steam in a water gas reaction and adjusting the proportions of carbon monoxide and hydrogen, and used a cobalt catalyst (100 Co-5 ThO₂-8 MgO-200 kieselguhr) that Ruhrchemie chemist Otto Roelen (1897-1993) developed from 1933 to 1938. Roelen's catalyst became the standard F-T catalyst because of its greater activity and lower reaction temperature, but its preparation was expensive, costing RM 3.92 per kg of cobalt. For this reason Ruhrchemie recovered the cobalt and thorium from the spent (used) catalyst by treatment with nitric acid and hydrogen gas at a cost of RM 2.97 per kg of cobalt, and re-used them in preparing fresh catalysts[13]. This gave a total catalyst cost of RM 6.89 per kg of cobalt or nearly 30 percent of the total F-T production cost. By 1937-38 the combined annual capacity of the four F-T plants increased to 300,000 metric tons (2.17 million barrels) and with the completion of five additional plants, total capacity rose to 740,000 metric tons (5.4 million barrels) at the outbreak of World War II in September 1939. Production at the nine F-T plants peaked at 576,000 metric tons (4.1 million barrels) in 1944 [14].



Figure 4. Otto Roelen

The older F-T plants operated at 1 atm whereas three of the five newer plants were medium pressure 5-15 atm syntheses. Converter design differed depending on the reaction pressure, but all the plants had inefficient externally cooled converters that dissipated the high heat of reaction (600 kilocalories per m^3 of synthesis gas consumed) and controlled the reaction temperature by arranging the cobalt catalyst pellets in a fixed bed within the converter and circulating pressurized water through the converter. Synthesis gas entered at the converter's top at the rate of 650-700 m^3 per hour per converter and flowed down through the catalyst bed, hydrocarbon products passed out the bottom. The medium pressure synthesis gave a slightly higher yield and extended the catalyst's life from 4-7 months to 6-9 months.

For the 1 atm synthesis the converter (tube and plate design) was a rectangular sheet-steel box 5 m long, 2.5 m high, 1.5 m wide, containing about 600 horizontal water cooling tubes interlaced at right angles with 555 vertical steel plates or sheets. The complicated grid-like arrangement over which the synthesis gas flowed from top to bottom eliminated any localized heat buildup in the converter. Each steel plate was 1.6 mm thick, a space of 7.4 mm separated adjacent plates. The cooling tubes were 40 mm in diameter, 40 mm apart, and led to a boiler (steam drum) for recovery of the heat released in the synthesis. One boiler recovered the heat released from two converters. An empty converter weighed 50 metric tons. The catalyst pellets, which filled the space between the tubes and plates and occupied a volume of 12 m^3 , weighed 3 metric tons of which 900 kg were cobalt.

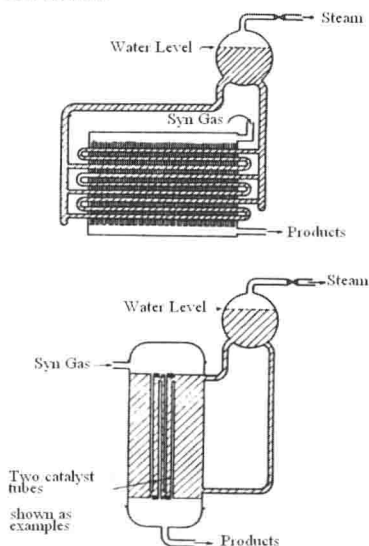


Figure 5. Tube and plate 1 atm converter (upper), concentric double tube medium pressure converter (lower).

The medium pressure converter (concentric double tube) had a simpler design. It consisted of a 50-metric ton vertical cylindrical steel shell 6.9 m high, 2.7 m internal diameter, 31 mm thick walls, and contained 2,100 vertical cooling tubes. Each cooling tube was 4.5 m long and double in construction, consisting of an outer tube of 44-48 mm diameter fitted with a concentric inner tube of 22-24 mm diameter. A top and bottom weld (T-connections) between the converter's horizontal face and an outer tube connected an inner tube with a boiler that allowed cooling water to circulate from the boiler to the main space in the shell around the outer

tubes and through the inner tube. One boiler recovered the heat released from four converters. The catalyst pellets filled the annular space between the concentric tubes and occupied a volume of 10 m^3 .

In the 1 atm synthesis, water sprays in packed towers directly cooled the hot hydrocarbon vapors and gases (primary products or primary oils) leaving the bottom of the converter. The vapors condensed to give light oil ($\text{C}_5\text{-C}_{12}$, boiling point range $25\text{-}165^\circ\text{C}$), middle oil ($\text{C}_{10}\text{-C}_{14}$, boiling point range $165\text{-}230^\circ\text{C}$), heavy oil ($\text{C}_{20}\text{-C}_{70}$, boiling point range $230\text{-}320^\circ\text{C}$), and hard and soft wax ($\text{C}_{20}\text{-C}_{30}$, boiling point range $320\text{-}460^\circ\text{C}$ and above).

The cooled gases (propane, butane) passed to an absorber for their removal and recovery with activated charcoal and subsequent liquefaction. In the medium pressure synthesis about 35 percent of the primary products left the converter as hydrocarbon liquids. Passage through a tubular-type steel alloy condenser liquefied the hydrocarbon vapors. The remaining hydrocarbon gases, after expansion to atmospheric pressure, underwent recovery and removal with activated charcoal in an absorber.

The biggest converter used in German F-T plants had a production capacity of only 2.5 metric tons per day (18 barrels per day) so that a small, 70 metric ton per day (500 barrels per day) plant had 25 or more converters, requiring considerable amounts of material and manpower for its construction and operation. All the plants operated their converters in stages. The 1 atm plants had two stages, operating two-thirds of the converters in the first stage and one-third in the second. Some of the plants placed the condensers and absorbers between the stages, others placed only condensers. All the plants had absorbers after the second stage converters and condensers. During the last two years of the war the medium pressure plants switched from two stages to three stages, successively operating one-half, one-third, and one-sixth of their converters. They had condensers between each stage and absorbers after the final stage converters and condensers.

Average plant yield for the 1 atm synthesis was $130\text{-}165 \text{ g}$ of liquid hydrocarbons per m^3 of synthesis gas, or about 80 percent of the theoretical maximum yield. Annual production per converter was $500\text{-}720$ metric tons. For the middle pressure synthesis the corresponding yields were $145\text{-}160 \text{ g}$ per m^3 and $600\text{-}750$ metric tons. The medium pressure synthesis also extended the catalyst's life from four-seven months to six-nine months.

Product refining, especially by fractional distillation, was the same for both syntheses. Low-grade gasoline which made up the light oil fraction, had a 45-53 octane number, which after blending with 20 percent benzol and adding 0.02-0.04 percent lead tetraethyl, increased to 70-78 and provided the German army with motor gasoline. High-grade diesel oil with a 78 cetane number (middle oil fraction) and some of the heavy oil fraction, after blending with 50 percent petroleum oil, served as aviation fuel for the German air force. Further treatment of most of the heavy oil at IG Farben's Leuna plant after its opening in 1927 gave the inexpensive synthetic detergent *Mersol*; cracking and polymerizing the remaining heavy oil and some of the soft wax gave good quality lubricating oil. Oxidizing the rest of the soft wax produced fatty acids for conversion to soap and small quantities of edible fat. The German wax industry used most of the hard wax for electrical insulation, the manufacture of polishes, and as a paper filler [15].

The most efficient F-T plants recovered only 30 percent of the total heat energy input as primary products and another 25 percent as steam and residual gas. The net heat energy required for the production of one metric ton of primary products was equivalent to 4.5 metric tons of coal (1 lb coal = 12,600 BTU) [16].