

An Overview of Fischer-Tropsch Synthesis at the U.S. Bureau of Mines

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In 1925, almost 70% of the world's petroleum was produced by the U.S. However, during the 1940s there was a fear that the US was running out of petroleum and a program to develop a coal-based supply of transportation fuels was undertaken late in 1943. This work involved both direct and indirect processes and was under the direction of H. H. Storch. Bureau personnel were involved in reviewing and translating documents retrieved from Germany following WW II as well as being members of several of the teams that surveyed the German plants and interviewed personnel who worked in the plants. Storch, together with Golumbic and Anderson, published a book that provided comprehensive coverage of work on Fischer-Tropsch and related synthesis; this book was the "standard reference" for many years and is a valuable reference source today. During the late 1940s period, the Bureau was provided funding to construct two pilot plants, one devoted to direct liquefaction and one to indirect liquefaction using the Fischer-Tropsch synthesis. Each plant was allocated five million dollars for construction of the plants at Louisiana, Missouri; in current dollars this would be 50 to 100 million. The indirect liquefaction featured gasification as well as synthesis and product upgrading, although the first two processes were emphasized. Bureau workers concluded that by 1944 most of the basic ideas for the design of FT reactors had been formulated and tested on a pilot-plant scale. Processes were classified on the basis of internal or external cooling. Much of the Bureau work concentrated on synthesis with the catalyst in liquid phase, and most of the emphasis was on the oil recirculation process. Here a combination of gas and oil circulation from bottom to top of the reactor maintained a catalyst suspension. Iron, cobalt and nickel catalysts were utilized in these studies. In addition to pilot-plant work, much effort was expended to understand the composition of the working catalyst, the chemistry involved in catalyst activation and deactivation, and the reaction mechanism. Storch is identified as the driving force behind the "oxygenate mechanism" that became popular during the 1950s. A summary of this work will be provided.

U.S. Bureau of Mines: The Beginning

The US Bureau of Mines was founded by legislation in 1911. While the Bureau was created officially, it did not function as a single unit for some time. In a brief summary of the activities of the first year of its existence, Clement [1] indicated that the chief chemist at each laboratory location functioned independently. From the writing it is not possible to learn whether the author was approving the independence in spite of the joining of the labs under a single umbrella organization or whether he was aghast at the independence of the chief chemists even though they were supposed to be members of

a unit. The Bureau's work is listed and it does not contain synthetic fuels as part of its effort. In fact, the preparation of town gas was the driving force for synthetic fuels at that time. Most cities generated their own town gas on site to be used for illumination, heating and other household uses, and local industry. Thus a fossil fuel, easily transported by rail to the city, was converted to town gas. The high-pressure pipelines needed to transport natural gas to remote distances we far into the future, and gas had to be generated locally.

Fischer-Tropsch: The Beginning

While it is difficult to define the paper that defines the discovery of the Fischer-Tropsch synthesis, it certainly appeared during 1924 _ 2 years. The author has not been able to learn the reason for and timing of the initial work on this topic at the Bureau, interest in the synthesis must have developed shortly after the initial papers by Fischer and Tropsch appeared.

Odell [2] considered the commercial possibilities in the use of synthetic hydrocarbon processes in the gas industry. Odell indicated that it had been known for some time that water gas would react chemically under proper conditions to form methane and that more recent studies of numerous studies here [the U.S.] and abroad had shown that besides methane it was possible to produce higher hydrocarbons. Odell wondered, "...in what manner, if at all, can such processes be incorporated as a part of the gas-making scheme in a city-gas plant?" He also asked, "...To what extent will it be possible to employ a combination system whereby a gas company can produce motor fuel during off-peak periods and meet its own enricher requirements at other times?"

Odell also wrote, "The fact that the reactions are exothermic and occur at the surface of the catalyst makes the problem of temperature control more complicated. How should this be done for large-scale operation? The proper design for a reaction chamber cannot be determined until this question is answered. Must one resort to recirculation of large volumes of gas for the purpose of controlling temperature, or would it be preferable to employ a plurality of reaction chambers containing different catalysts whose activities are progressively greater throughout the series?...To obtain the necessary information experiments should be conducted on a much larger scale than that possible in laboratory glass tubes." His summary listed many questions, many still lacking answers today, and concluded that, "Unless a more satisfactory catalyst is found, one not readily poisoned by sulphur compounds, it may develop that a process employing higher pressures and oxide catalysts will be most satisfactory."

Smith and co-workers at the Bureau initiated research in the FT area because of reports by Fischer and Tropsch [3] and by Elvins and Nash [4]. Smith [5] reported thermodynamic calculations that indicated, among others, that as the temperature is increased the formation of higher, rather than lower, hydrocarbons is favored. However, Tropsch [6] disagreed with this conclusion, indicating that his data did not fit this pattern. Smith considered Tropsch's critical comments and responded, sometimes rather strongly. Smith concluded, emphasizing that he was convinced that his data are currently the most accurate of any literature data dealing with hydrocarbon formation and that **any numerical discrepancies are insignificant** [7] Tropsch [8] responded, indicating that the problem was solved when Smith indicated that at all temperatures hydrocarbons form easier at higher temperatures. Tropsch indicated that thermodynamically feasible reactions depend on the speed of the reactions, which are controlled by the catalyst, etc. In this latter regard, Tropsch completely agreed with Smith.

Smith and co-workers reported that FT synthesis was of greatest practical interest for the gas industry by converting off-peak gas to liquid fuels and/or upgrading the "blue water gas". Liquid fuels would not be the driving force for the work. Fischer described the situation, "In all countries the need for liquid fuels, particularly for light motor fuels, is continually increasing. America is in the fortunate position of having abundant supplies of petroleum and gasoline-containing natural gas, ...Europe, on the

contrary, particularly Middle and Western Europe, is poor in petroleum resources and is therefore forced to import, or to prepare artificial liquid motor fuels.” Thus, an additional driving force for the Bureau work on FT was to develop useful, practical information that would lead to a better understanding of the mechanism of the reactions involved. They concluded that, “... all indications point to the formation of unsaturates (probably of low molecular weight) as the primary reaction. Secondary hydrogenation results in the formation of paraffins, and polymerization results in the appearance of the very heavy hydrocarbons, which may in turn be hydrogenated. They suggested that the primary reaction is the formation on the catalyst surface of CH_2 groups through condensation of which (or of the polymerization products of which) all of the higher hydrocarbons are formed.” They indicated that for the commercial process, the catalyst chamber would have to be designed to carry away the heat of reaction and to maintain rather close temperature control. “This would present some difficulty, but it probably could be accomplished.” They added ethene to the feed and found that this led to an increased oil yield, including also increased water soluble products. They stated that, “it seems that hydrogen and carbon monoxide react to produce substances on the catalyst surface with which ethylene is capable of reacting.” It is likely that they had discovered, but had not recognized, the hydrocarbonylation reaction.

Dr. Henry H. Storch, later to lead the FT work, joined the Bureau in 1928. In 1931 he was persuaded by Dr. A. C. Fieldner to transfer to Pittsburgh, after Smith and co-workers had done their FT work. Dr. Storch had been working on methanol synthesis for Roessler and Hasslacher in New York City and obtained patents in this area as well as publishing in the open literature about work done at the company.

Because of a lack of funds, the FT research was discontinued at the Bureau about 1930 and this area of research was not undertaken again for nearly 12 years [9]. Neither Storch nor Smith did FT work during the 1930s, at least not work that led to publications.

The Golden Years

In 1942 the U.S. Congress appropriated funds to start again the research work on FT synthesis [10]. This work was conducted using six fixed bed reactors and involved both iron and cobalt catalysts. They developed methods of preparation and reactivation of iron catalysts. One iron catalyst was used for three months without loss in activity. The iron catalyst was reported to produce a highly olefinic product and a larger portion of solid paraffins than was obtained with a cobalt catalyst. Their cobalt catalyst at that time was a version of the cobalt-thoria-kieselguhr material that was used in German commercial plants. They found that with periodic scrubbing with hydrogen to remove wax, the catalyst showed only little deterioration in activity over the long-term cycles.

During this period they also utilized the data available on steam-carbon reaction to conclude that hydrogen and carbon monoxide are the primary products and that carbon dioxide is formed as a secondary reaction. They concluded that the rate of gasification is controlled by the rate of reaction of the adsorbed film of steam, and that a steam-saturation pressure exists above which the rate of gasification of a given carbon at constant temperature remains constant with increasing steam pressure.

Two years after re-initiating FT work at the Bureau, Congress passed on April 5, 1944 the Synthetic Liquid Fuels Act. This Act provided \$87 million for a research program on synthetic liquid fuels between 1944 and 1955. This Act was an outgrowth of the stress of wartime on the demands for liquid fuels for the Allies during WW II; the U.S. exported more tons of petroleum than all other products combined during WW II.

The Act represented a response to changing views of petroleum within the U.S. In 1925, Fischer's view that the U.S. was awash in petroleum was widely accepted. However, by 1944 this view was changing. In 1944, domestic production of petroleum was ahead of demand, and about seven percent of the total production was exported. By 1955, U.S. demand had increased by about 70 percent

and production had not increased at the same rate. In 1955, imports accounted for about 20 percent of the total demand. It was concluded that, "Looking ahead, it is believed that the gap between demand and domestic production of petroleum will widen. Therefore, increased reliance must be placed on importation over long sea lanes, or liquid fuels must be supplied from such substances as coal and oil shale." [11]. The 1955 prophecy fell on deaf ears since the administration brought in with the 1952 elections chose to ignore the problems associated with imported oil and terminated the process development work. Only the oil crisis of the 1970s, and the shortages combined with high prices, caused changes in the way of thinking about imports. The result was the U. S. Synthetic Fuels Corporation, established in 1980. The Energy Security Act set a goal of 2 million barrels of oil equivalent production by 1992. There was a vast difference between the reactions to energy supply in 1950 and 1980: in 1950 the Bureau of Mines laboratories and demonstration plants were in the international leadership position but in 1980 industrial companies led both the research and demonstration efforts with the former Bureau of Mines labs largely being ignored. During the period from 1950 to 2000 the function of the Bureau and its predecessors changed from being in the lead by conducting the work to being a flow-through organization for funds that were allocated primarily to industry to do the research and demonstration work. In one respect, the final result was the same: after expending significant funds the synthetic fuels program was terminated. Meanwhile, the problem has grown by more than a factor of five: in 1955 imports were 10% of the total demand and in 2002 they are nearly 60% of a three-fold increase in petroleum usage..

Anderson [12] provided a brief summary of the catalysis research at the Bureau in Pittsburgh and Bruceton. The 1944 Act established the Office of Synthetic Liquid Fuels within the Bureau with Storch assigned as the Chief of its Research and Development Branch. A new laboratory was built at Bruceton, just south of Pittsburgh. In just two years the personnel increased from 30 to 300, including many young people with outstanding abilities. The renewed FT work started with Norma Stern Golumbic preparing catalysts; she soon was to devote most of her time to writing technical reports detailing the documents returned from Germany following WW II and of manuscripts for Storch. She was also a co-author with Anderson and Storch on the book published in 1950 that was to be the "bible" of FT for many years, and is a valuable resource even today. Lary Hofer began studying carbides and published definitive and detailed reports on this topic. Anderson and Sol Weller went to work at the Bruceton site shortly after WW II and subsequently developed separately equations to describe the product distribution of FT products; Anderson continued to work in this area for years and today catalysis scientists usually refer to the distribution as Anderson-Schulz-Flory (ASF) distribution. Dr. R. A. (Gus) Friedel became Chief of the Spectroscopy Section and led the work that provided the carbon number and isomer distributions of the FT products. J. Floyd Shultz and Dr. W. Keith Hall made important contributions in several areas of the scientific work. Hall reported to Bruceton during WW II to work on explosives under the supervision of George Kistiakowsky and Louis Hammett. The latter two individuals were at the Bureau as part of the National Defense Research Committee.

Investigations of the FTS in small pilot plants at Bruceton was initially under the direction of Dr. J. H. Crowell, followed by Homer E. Benson in 1947 and Joseph H. Field in 1958. Benson and Field were also major contributors to the development of the oil circulation and the hot-gas-recycle FTS processes, and the hot carbonate CO₂-scrubbing process. Martin D. Schlesinger studied the FTS in slurry and fluidized-bed reactors.

The Organic Chemistry Section conducted work in FT and related areas. During this period it was headed by D. Milton Orchin until 1953 and then by Dr. Irving Wender. This group emphasized homogeneous catalysis. Their work with cobalt carbonyl catalysts was pioneering and did much to elucidate the mechanism for the hydroformylation reaction [13].

The FT work was extensive, emphasizing a wide range of catalysts, process conditions, and processes. Experimental work was conducted using laboratory, pilot plant and demonstration sized reactors. In addition, they compiled extensive reviews of the FT work done prior to and during WW II, especially work in Germany and Japan.

A bibliography of the Fischer-Tropsch synthesis and related processes was reported in 1954 [14]. Part I contains abstracts for more than 3,780 publications and Part II lists over 4,000 abstracts of patents. The reviews of Japanese work probably is even today the most extensive coverage of the work available in most countries [15-17]. Much of the Japanese work followed the lines of the German processes which they licenced; their work to develop their own processes was not very significant as documented in the Bureau summaries. The German work was covered very extensively and was based on reports of Allied documentation of on-site observations following WW II and translations of many German documents. H. H. Storch and other members of the Bureau were included in many of the visiting technical teams to the European FT plants. The work also included translations of publications of German journals that were not readily available in the U.S. during the period as well as translations of theses and reports of scientific meetings and discussions. An early summary of German work was presented by Lowry and Rose [18] and a number of other summaries followed, usually emphasizing operations at a particular plant.

One of several German scientists and engineers who relocated to the U.S. following WW II was H. Pichler. The U.S. TOM talked to Pichler several times while he was in Germany. He came to the U.S. as a consultant and brought materials on FT synthesis with him. Included in this material was a draft thesis of one of his students, H. Merkel. When he first discussed this for publication by the Bureau, he did not have the complete documents; he planned to draw the figures from his memory and to provide an addendum to express his viewpoint, which differed from that of Merkel. Before publication [19], Merkel had returned to the KWI, revised the thesis and had it accepted at the Technische Hochschule (Aachen) as partial fulfillment for his Ph.D. Pichler though his views were adequately represented in the revised thesis and it was published by the Bureau. The Bureau personnel wanted to publish the thesis since the function of carbide in the FT reaction described in the thesis was considerably more advanced than was the information presented in the older documents found by the TOM teams at the KWI für Kohlenforschung. This study by Pichler and Merkel was at that time the only extensive experimental series of investigations of the changes occurring in the catalyst structure during induction and synthesis. Another major publication described work Pichler and Ziesecke carried out at the KWI for coal research on the isosynthesis reaction. While Pichler came to the U.S. as a consultant, he later joined Hydrocarbon Research Inc. who were constructing the first commercial FT plant in the U.S. at Brownsville, Texas. Years later, Pichler implied that the book by Storch, Golumbic and Anderson was incorrect since it was based upon German work and, of course, the Germans did not tell the Allied representatives everything [20]. While the scientists and engineers may not have divulged all that they know, it appears that the documents removed and later discussions with the Germans involved in FT did transfer much of what was known. In fact, a considerable amount of the German information up to 1940 was transferred to a consortium of six companies that had been members of the old Standard Oil Company. During the 1930s, Jersey sought still other methods for making motor fuels of high quality [21]. For example, Standard Oil (Jersey) was investigating the Fischer-Tropsch hydrocarbon synthesis process, developed by Ruhrchemie, A.G., which converted brown coal into liquid fuel. In 1938 and 1939, patents for this process outside Germany were transferred by Ruhrchemie to Hydrocarbon Synthesis Corporation, in which Standard Oil Development (now Exxon Mobil) took 680 shares, Shell and Kellogg 425 each, and I. G. Farben 170.

On October 1, 1945, the technologic functions of the subcommittees on Liquid Fuels and Lubricants and on Solid Fuels of the Technical Industrial Intelligence Committee were assigned to the Bureau. This transfer included technical files as well as samples of equipment, catalysts, and intermediate and final products. The Foreign Synthetic Liquid Fuels Division was established in the Bureau to handle this work. This effort included microfilming of technical reports by the Field Intelligence Agency - Technical (FIAT) located at Hochst. The quantity of material was staggering and its use gradually declined. With the energy crisis of the 1970s, records were established at Texas A&M University and an assessment/distribution effort was again undertaken. This effort also declined with the disappearance of the oil crisis from the public's mind. Recently, Syntroleum Corp. has revived the program and, working with Prof. Anthony Stranges, is making more and more of this material available to the public through its website (<http://www.fischertropsch.org>).

Reactors

Research Scale Reactors

In the 1940's laboratory reactors were constructed and operated. Eleven fixed bed reactors, 50 cm in length and a 1.25 cm diameter pipe contained in a 6.4 cm outer pipe, would each hold about a 30 cm catalyst bed; another reactor was similar but would have a catalyst bed length of about 90 cm. The reactors were heated by a fluid boiling under constant pressure

Pilot Scale Reactors

The hot-gas recycle pilot plant utilized a reactor that was 30.5 cm in diameter and 122 cm long [22]. A second reactor, when used, was 7.6 cm diameter and 107 cm long. The 30.5 cm diameter reactor was scaled up from results using the 7.6 cm diameter reactor.

A reactor for the oil-circulation process was 8 ft (2.44 m) tall and 3 inch (7.6 cm) diameter and was utilized in a number of process options: gas and liquid concurrent downflow, gas and liquid concurrent upflow (flooding caused problems in this mode) and with the catalyst submersed in oil with gas upflow. A similar barrel/day plant was utilized that had a reactor that was the same height but 8 inches (0.2 m) diameter. Conditions varied over a wide range: $H_2/CO = 0.7$ to 1.3; recycle from 0.5 to 1.0 and conversion in the 70 to 90% range.

Slurry reactors from laboratory to small pilot units were constructed and operated. The reactors had a capacity from 1/4 to 5 gal (0.95 to 19 L) per day. Although they made many successful runs in these reactors, erratic behavior in about half of the runs resulted in poor catalytic activity.

Louisiana, Missouri Demonstration Reactor

Both direct and indirect coal liquefaction demonstration plants were constructed and operated. They were designed to be the minimum size that would provide operating conditions comparable to those expected in full scale commercial plants. The direct liquefaction was built and operated earlier than the FT plant; its design was described in much greater detail than the FT plant was. The FT process included gasification, synthesis and downstream processing capabilities. Pulverized coal was to be gasified using oxygen. Much of the synthesis gas was supplied by a Kerpely coke-gasification unit that was initially intended to be operated as a standby unit. The first gasifier was a Koppers horizontal unit designed to handle one ton of nonslagging coal per hour at atmospheric pressure. Pulverized coal, oxygen and superheated steam were fed into both ends of the horizontal cylinder. A vertical, atmospheric pressure gasifier unit was built to test results obtained at Morgantown, WV in a smaller unit. Pulverized coal was fed by screw feeders and was picked up by the oxygen stream to be fluidized and carried into the gasifier; superheated steam was added near the coal feed. As the coal passed upward and was gasified, molten slag collected on the walls and flowed to the base to be eventually removed through tapping ports. The program was terminated before this all problems associated with the process were solved.

The FT reactor was 30. ft 10 in. (9.14 m) tall and 6 ft. (1.83 m) diameter. The bottom foot (0.3 m) of the reactor space was filled with steel balls to serve as a mixing space for the solvent and feed gas and to support the catalyst. The next 15 ft (4.57 m) of the reactor height was filled with 7 tons (6,356 kg) of iron catalyst. Using this amount of catalyst, the reactor had a capacity of about 50 to 80 bbl/day of products. Synthesis gas was fed at 180,000 ft²/hr (5,100 m³/hr) and the cooling liquid at 900 gal/min. (3,410 liters/min). Mill scale promoted with potassium and magnesium was used as the catalyst. An oil-immersed expanded catalyst bed of 4- to 10-mesh catalyst particles was used. Four runs, ranging from 8 to 39 days in length, were made before the program was terminated and the equipment surplused [23].

The End

The Bureau's work on synthetic fuels became more "academic" at the work developed during the 1950s. Much of this work was devoted to developing understanding of the FT synthesis in small scale reactors.

The Office of Coal Research (ORC) was created by the Interior Department during the early 1960's as the markets for coal continued to decline. The focus of the Office's work was the generation of environmentally clean fuels. Thus, an emphasis was placed on producing pipeline quality synthetic natural gas from coal and the production of low-ash, low-sulfur solid refined coal. ORC had no in-house research so research was contracted with the private sector. A major program was its joint effort with the American Gas Association for various coal gasification projects.

The "oil crisis" caused the synfuels research activities of both the Bureau and ORC to rapidly increase during the 1970's. The two organizations were merged in early 1975 to become a major component of the fossil energy program of the Energy Research and Development Administration (ERDA). The fossil energy program continued to grow as ERDA was incorporated into the Department of Energy in 1977. At the height of the growth the U.S. was headed to energy independence. Congress established the Energy Security Act and it was signed into law on June 30, 1980. This Act created the United States Synthetic Fuels Corporation (SFC) to provide financial assistance to the private sector to stimulate production of synthetic fuels but the only plant that resulted had political overtones.

Viewed from a historical perspective of 2000, the crisis response of the U.S. government to the "oil crisis" was a dramatic failure. Few, if any, technical benefits accrued during this period that are in operation today. No commercial liquefaction plants were built in the United States. Had the U.S. continued to the commercial plant stage for FT synthesis, it is likely that it would be successful today. Sasol committed to large plants that were constructed and brought on-line during the 1980's. While they had government guarantees for some time, today they are a commercial success, allowing Sasol to become a major international company and one of South Africa's leading companies.

While the budget continued to grow for fossil energy during the 1980's, the in-house research did not. Gradually the technical people were assigned more and more as administrators for research conducted in universities and private companies. Thus, the research level of the Bureau in the 1950's, where they were equivalent or ahead of companies, gradually declined to where they enable, but do not lead, in research and development. In spite of this, they still make significant contributions and their lead in slurry phase synthesis of methanol and Fischer-Tropsch synthesis serves to illustrate this.

Note

This manuscript should be considered to be a work in progress. Prior to the AIChE meeting an updated version of the manuscript will be available at <http://www.crtc.caer.uky.edu>.

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