

## Conditions for Practical Operation

Synthesis at high temperatures increases the yield of gasoline and light hydrocarbon gases. It would be desirable to learn how to control the relative production of gasoline and these gases in order to make the process as versatile as possible. During periods of small demand for heating gas, production of gasoline could then be increased at the expense of gas, and vice versa. Further work on catalyst and operating variables may result in a more flexible process.

The oil-circulation process has been shown to operate satisfactorily up to 270° C. Above that temperature deposition of carbon and oxidation of the catalyst were accelerated, and the active surface of lathe turnings was lost in a relatively short time. These problems, and the effects of additives, catalyst pretreatment, and partial pressures of water vapor and carbon dioxide on rate of oxidation and carbon deposition need further study. To perform experiments of this nature a small reactor, designed to permit high recycle rates of end gas, would be advantageous.

The oil-slurry process requires only about one-tenth as much catalyst as the oil-circulation process. The main problems with the slurry system have been agglomeration and settling of finely divided catalyst; at times, the catalyst adheres to the walls of the reactor. With nitrided iron catalyst agglomeration did not occur during several months of experimentation, probably because of the presence of alcohols in the oil. Favorable results have been obtained also by addition of high-boiling alcohols to a slurry containing reduced iron catalyst. The factors affecting agglomeration are being studied further.

A recently completed pilot plant will be employed to investigate the hot-gas-recycle process, operated at relatively high temperature, with the newly developed lathe-turning catalysts. With this form of catalyst the pressure drop through the catalyst bed was reduced to only about two percent of that through a bed of 6- to 20-mesh granules. The rate of carbon deposition, reported to be high in fluidized-bed Fischer-Tropsch reactors, must be determined. However, the true catalyst temperature in hot-gas-recycle operation is expected to be considerably lower than in fluidized beds at the same nominal temperature, and thus less deposition of carbon should be expected.

Literature Cited

- ANDERSON, R. B. Iron Nitrides as Fischer-Tropsch Catalysts. *Advances in Catalysis*, vol. 5, Academic Press, Inc., New York, N. Y., 1953, pp. 355-384.
- ANDERSON, R. B., KRIEG, A., SELIGMAN, B., AND O'NEILL, W. E. Fischer-Tropsch Synthesis. Tests of Cobalt Catalysts at Atmospheric Pressure. *Ind. Eng. Chem.*, vol. 39, No. 12, December 1947, pp. 1548-1554.
- ANDERSON, R. B., McCARTNEY, J. T., HALL, W. K., AND HOFER, L. J. E. Kieselguhrs - Suitability as Carriers in Catalysts. *Ind. Eng. Chem.*, vol. 39, No. 12, December 1947, pp. 1618-1628.
- ANDERSON, R. B., SELIGMAN, B., SHULTZ, J. F., KELLY, R., AND ELLIOTT, M. A. Fischer-Tropsch Synthesis. Some Important Variables of the Synthesis on Iron Catalysts. *Ind. Eng. Chem.*, vol. 44, No. 2, February 1952, pp. 391-397.
- ANDERSON, R. B., AND SHULTZ, J. F. Iron Nitride Catalysts in Carbon Oxide Hydrogenations. U. S. Patent 2,629,728, Feb. 24, 1953.
- ANDERSON, R. B., SHULTZ, J. F., SELIGMAN, B., HALL, W. K., AND STORCH, H. H. Studies of the Fischer-Tropsch Synthesis. VII. Nitrides of Iron as Catalysts. *Jour. Am. Chem. Soc.*, vol. 72, No. 8, Aug. 1950, pp. 3502-3508.
- BADISCHE ANILIN- UND SODA-FABRIK. (Process for Producing Hydrocarbons and Their Derivatives.) German Patent 295,202, Nov. 8, 1916.
- BAHR, H. A., AND BAHR, T. (Decomposition of Carbon Monoxide on Nickel.) *Ber. deut. chem. Gesell.*, vol. 61B, 1928, pp. 2177-2183.
- BAHR, H. A., AND JESSEN, V. (Decomposition of Carbon Monoxide on Iron Oxide and Iron.) *Ber. deut. chem. Gesell.*, vol. 66B, 1933, pp. 1238-1247.
- BUREAU OF MINES. Synthetic Liquid Fuels - Annual Report of the Secretary of the Interior for 1953. Part I. - Oil From Coal. Rept. of Investigations 5043, 1954, 66 pp.
- CHEMICAL ENGINEERING. Progress in Synthetic Liquid Fuels. *Chem. Eng.*, vol. 62, August 1955, pp. 120-122.
- CRAXFORD, S. R., AND RIDEAL, E. K. The Mechanism of the Synthesis of Hydrocarbons From Water Gas. *Jour. Chem. Soc.*, 1939, pp. 1604-1614.
- DENT, F. J., MOIGNARD, L. A., EASTWOOD, A. H., BLACKBURN, W. H., AND HEBDEN, D. An Investigation Into the Catalytic Synthesis of Methane for Town Gas Manufacture. 49th Report of Joint Research Committee of Gas Research Board and University of Leeds. Communication GRB 20, November 1945, 104 pp.

14. DUFTSCHMID, F., LINCKH, E., AND WINKLER, F. (I. G. Farbenindustrie A. G.). Catalytic Production of Hydrocarbons and Oxygen Derivatives From Carbon Monoxide and Hydrogen. U. S. Patent 2,159,077, May 23, 1939; Catalytic Hydrogenation of Carbon Monoxide to Form Hydrocarbons. U. S. Patent 2,207,581, July 9, 1940.

---

15. \_\_\_\_\_ (Standard Catalytic Co.). Hydrocarbon Synthesis From Hydrogen and Carbon Monoxide. U. S. Patent 2,287,092, June 23, 1942; Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen. U. S. Patent 2,318,602, May 11, 1943.
16. ELVINS, O. C., AND NASH, A. W. The Reduction of Carbon Monoxide. *Nature*, vol. 118, No. 2961, July 31, 1926, p. 154.
17. FIELD INFORMATION AGENCY, TECHNICAL. Design of Catalyst Chamber. FIAT Reel K22, Frames 1,177-84.
18. \_\_\_\_\_. Gasoline Synthesis in Liquid Phase. FIAT Reel X-115, Frames 1,388-447; 1,593-672.
19. FISCHER, F. (The Synthesis of Fuels (Kogasin) and Lubricants From Carbon Monoxide and Hydrogen at Ordinary Pressure.) *Brennstoff-Chem.*, vol. 16, 1935, pp. 1-11.
20. FISCHER, F., AND KOCH, H. (New Developments in the Adaptation of Cobalt Catalysts to the Benzine Synthesis.) *Brennstoff-Chem.*, vol. 13, 1932, pp. 61-68.
21. FISCHER, F., AND MEYER, K. (The Applicability of Nickel Catalysts to the Benzine Synthesis.) *Brennstoff-Chem.*, vol. 12, 1931, pp. 225-232.
22. FISCHER, F., AND PICHLER, H. (Studien- und Verwertungs-G.m.b.H.). (Process for the Production of Solid, Liquid, and Easily Liquefied Aliphatic Hydrocarbons From Carbon Monoxide and Hydrogen.) German Patent Appl. St. 56,470, IV d/120, July 30, 1937.
23. \_\_\_\_\_. (The Synthesis of Paraffin From Carbon Monoxide and Hydrogen Upon Cobalt Catalysts (Medium-Pressure Synthesis).) *Brennstoff-Chem.*, vol. 20, 1939, pp. 41-48.
24. FISCHER, F., AND TROPSCH, H. (Preparation of Synthetic Oil Mixtures (Synthol) From Carbon Monoxide and Hydrogen.) *Brennstoff-Chem.*, vol. 4, 1923, pp. 276-285. (Preparation of Synthetic Oil (Synthol) From Carbon Monoxide and Hydrogen.) *Brennstoff-Chem.*, vol. 5, 1924, pp. 201-208, 217-227.
25. \_\_\_\_\_. (Synthesis of Petroleum at Atmospheric Pressures From Gasification Products of Coal.) *Brennstoff-Chem.*, vol. 7, 1926, pp. 97-104.

6. FRIEDEL, R. A., AND ANDERSON, R. B. Composition of Synthetic Liquid Fuels. I. Product Distribution and Analysis of C<sub>5</sub>-C<sub>8</sub> Paraffin Isomers From Cobalt Catalyst. Jour. Am. Chem. Soc., vol. 72, No. 3, March 1950, pp. 1212-1215, and No. 5, May 1950, p. 2307.
7. FUEL RESEARCH BOARD. Reports for the years ending March 31, 1936, p. 148; March 31, 1937, p. 141; March 31, 1938, p. 186; March 31, 1939, p. 151. H. M. Sta. Office, London.
8. GREYSON, M., DEMETER, J. J., SCHLESINGER, M. D., JOHNSON, G. E., JONAKIN, J., AND MYERS, J. W. Synthesis of Methane. Bureau of Mines Rept. of Investigations 5137, 1955, 50 pp.
9. HÄGG, G. (Powder Photographs of a New Iron Carbide.) Ztschr. Krist., vol. 89, 1934, pp. 92-94.
10. HALL, C. C., AND CRAXFORD, S. R. Additional Information Concerning the Fischer-Tropsch Process and Its Products. PB 93,498, July 1946, 203 pp.; BIOS Final Rept. 1722, Item 22, 1946, 178 pp.
11. HALL, C. C., CRAXFORD, S. R., AND GALL, D. Interrogation of Dr. Otto Roelen of Ruhrchemie A.-G. PB 77,705, May 1946, 67 pp.; BIOS Final Rept. 447, Item 30, 1945, 50 pp.
12. HALL, C. C., GALL, D., AND SMITH, S. L. A Comparison of the Fixed-Bed Liquid-Phase ("Slurry"), and Fluidized-Bed Techniques in the Fischer-Tropsch Synthesis. Jour. Inst. Petrol., vol. 38, No. 346, October 1952, pp. 845-876.
13. HALL, W. K., DIETER, W. E., HOFER, L. J. E., AND ANDERSON, R. B. Preparation and Reactions of Carbonitrides on Iron. Jour. Am. Chem. Soc., vol. 75, No. 6, Mar. 20, 1953, pp. 1442-1447.
14. HERINGTON, E. F. G. The Fischer-Tropsch Synthesis Considered as a Polymerization Reaction. Chem. & Ind., vol. 65, No. 38, Sept. 1946, pp. 346-347.
15. HOFER, L. J. E., ANDERSON, R. B., PEEBLES, W. C., AND STEIN, K. Chloride Poisoning of Iron Copper Fischer-Tropsch Catalysts. Jour. Phys. and Colloid Chem., vol. 55, 1951, pp. 1201-1206.
16. HOFER, L. J. E., AND COHN, E. M. Synthesis of Cementite. Jour. Chem. Phys., vol. 18, 1950, pp. 766-767.
17. I. G. FARBENINDUSTRIE. Report 317 on Hydrocarbon Synthesis Experiments. Leuna, Feb. 13, 1939; TOM Reel 134, sec. 1a, Item 8.
18. JACOBSON, B., AND WESTGREN, A. (Nickel Carbide and Its Relation to the Other Carbides of the Series of Elements Scandium-Nickel.) Ztschr. physik. Chem., vol. B20, 1933, pp. 361-367.

39. KASTENS, M. L., HIRST, L. L., AND DRESSLER, R. G. An American Fischer-Tropsch Plant. *Ind. Eng. Chem.*, vol. 44, No. 3, March 1952, pp. 450-466.
40. KÖLBEL, H., AND ACKERMANN, P. (Rheinpreussen Aktiengesell. für Bergbau u. Chemie). *Catalytic Hydrogenation of Carbon Monoxide in Liquid Suspensions of Catalyst*. U. S. Patent 2,671,103, Mar. 2, 1954.
41. KRIEG, A., DUDASH, A. P., AND ANDERSON, R. B. Improved Caustic Scrubber. *Ind. Eng. Chem.*, vol. 41, No. 7, July 1949, p. 1508.
42. KUMMER, J. T., DEWITT, T. W., AND EMMETT, P. H. Some Mechanism Studies on the Fischer-Tropsch Synthesis Using C<sup>14</sup>. *Jour. Am. Chem. Soc.*, vol. 70, No. 11, November 1948, pp. 3632-3643.
43. KUMMER, J. T., AND EMMETT, P. H. Fischer-Tropsch Synthesis Mechanism Studies. The Addition of Radioactive Alcohols to the Synthesis Gas. *Jour. Am. Chem. Soc.*, vol. 75, No. 21, November 1953, pp. 5177-5183.
44. KUMMER, J. T., PODGURSKI, H. H., SPENCER, W. B., AND EMMETT, P. H. Mechanism Studies of the Fischer-Tropsch Synthesis. The Addition of Radioactive Alcohol. *Jour. Am. Chem. Soc.*, vol. 73, No. 2, February 1951, pp. 564-569.
45. LE CLERC, G., AND LEFEBVRE, H. (Comparison of Catalytic Activity of Allotropic Varieties of Nickel.) *Compt. rend.*, vol. 208, 1939, pp. 1650-1651.
46. LE CLERC, G., AND MICHEL, A. (Hexagonal Nickel.) *Compt. rend.*, vol. 208, 1939, pp. 1583-1585.
47. LEFEBVRE, H., AND LE CLERC, G. (Iron Catalysts in the Synthesis of Motor Spirit by Hydrogenation of Carbon Monoxide.) *Cong. chim. ind.*, *Compt. rend. 18<sup>me</sup> Cong.*, Nancy, September-October 1938, pp. 725-730.
48. LEVA, M. Translations of German Documents on the Development of Iron Catalysts for the Fischer-Tropsch Synthesis. Part I. Bureau of Mines, Pittsburgh, Research and Development Division, Rept. 2774-Q:18, September 1946, 168 pp.
49. MEYER, G., AND SCHEFFER, F. E. C. (Formation of Carbides in the Systems Metal-Carbon-Hydrogen and Metal-Carbon-Oxygen.) *Rec. trav. chim.*, vol. 46, 1927, pp. 359-368.
50. \_\_\_\_\_. (The Dissociation of Carbon Monoxide.) *Rec. trav. chim.*, vol. 46, 1927, pp. 754-762.
51. \_\_\_\_\_. (Formation of Carbides in the Systems: Metal-Carbon-Oxygen.) *Rec. trav. chim.*, vol. 47, 1928, pp. 401-405.
52. \_\_\_\_\_. The Properties of Nickel Carbide. *Jour. Am. Chem. Soc.*, vol. 75, No. 2, Jan. 29, 1953, p. 486.

53. MINISTRY OF FUEL AND POWER. Report on the Petroleum and Synthetic Oil Industry of Germany. BIOS Overall Rept. 1, H. M. Sta. Office, London, 1947, 134 pp.; Fischer-Tropsch Process, pp. 82-103.
54. MITTASCH, A. Early Studies of Multicomponent Catalysts. *Advances in Catalysis*, vol. 2, Academic Press, Inc., New York, N. Y., 1950, pp. 81-104.
55. MITTASCH, A., AND SCHNEIDER, C. (Badische Anilin- u. Soda-Fabrik). (Production of Hydrocarbons and Their Derivatives.) German Patent 293,787, Aug. 23, 1916. (Process for Producing Hydrocarbons and Their Derivatives.) German Patent 295,203, Nov. 8, 1916.
56. PERRIN, M. Recherches sur les synthèses d'hydrocarbures aliphatiques a l'aide des mélange d'oxide de carbons et d'hydrogène. Doctoral dissertation under Prof. M. Prettre, University of Lyon, 1948.
57. PICHLER, H. Twenty-Five Years of Synthesis of Gasoline by Catalytic Conversion of Carbon Monoxide and Hydrogen. *Advances in Catalysis*, vol. 4, Academic Press, Inc., New York, N. Y., 1952, pp. 271-341.
58. PICHLER, H., AND BUFFLEB, H. (Synthesis of Paraffin (Wax) on Ruthenium Catalysts at Pressures up to 1,000 Atmospheres.) *Brennstoff-Chem.*, vol. 21, 1940, pp. 257-264. (Behavior of Ruthenium Catalysts in Synthesis of Paraffin Hydrocarbons of High Molecular Weight), pp. 273-280. (Properties of Some Solid Paraffins Produced From Carbon Monoxide and Hydrogen at High Pressures on Ruthenium Catalysts, With Special Reference to the Previously Unknown Highest Melting Constituents), pp. 285-288.
59. PICHLER, H., AND MERKEL, H. (Chemical and Magnetochemical Investigations of Iron Catalysts Used in Fischer-Tropsch Syntheses. I.) *Brennstoff-Chem.*, vol. 31, 1950, pp. 1-9. (II. Magnetochemical Investigations.), pp. 33-42. Chemical and Thermomagnetic Studies on Iron Catalysts for Synthesis of Hydrocarbons (trans. by R. Brinkley), Bureau of Mines Tech. Paper 718, 1949, 108 pp.
60. PICHLER, H., AND ZIESECKE, K. H. The Isosynthesis. TOM Reel 279, item 13, frames 789-931; trans. by R. Brinkley, pub. in Bureau of Mines Bull. 488, 1950, 39 pp.
61. PIER, M., MICHAEL, W., AND JAECKH, W. (I. G. Farbenindustrie A. G.). Hydrocarbon Production From Carbon Monoxide and Hydrogen. U. S. Patent 2,167,004, July 25, 1939.
62. ROELEN, O. (Oxo Process.) German Patent Application R 103,362, R 402, Sept. 19, 1938; Production of Oxygenated Carbon Compounds. U. S. Patent 2,327,066, Aug. 17, 1943.
63. \_\_\_\_\_. (Oxo Process.) TOM Reel 14, bag 3,043, item 4, frames 478-858; TOM Reel 55, bag 2,523, documents 69-85, 88-93; TOM Reel 134, sec. VII.
64. SABATIER, P., AND SENDERENS, J. B. (New Synthesis of Methane.) *Compt. rend.*, vol. 134, 1902, pp. 514-516; *Jour. Chem. Soc.*, vol. 82, I, 1902, p. 333.

65. SCHLESINGER, M. D., AND BENSON, H. E. Upgrading Fischer-Tropsch Products. *Ind. Eng. Chem.*, vol. 47, No. 10, October 1955, pp. 2104-2108.
66. SCHLESINGER, M. D., BENSON, H. E., MURPHY, E. M., AND STORCH, H. H. Chemicals From The Fischer-Tropsch Synthesis. *Ind. Eng. Chem.*, vol. 46, No. 6, June 1954, pp. 1322-1326.
67. SCHMIDT, J. (The Nonexistence of a Higher Nickel Carbide.) *Ztschr. anorg. allgem. Chem.*, vol. 216, 1933, pp. 85-98.
68. SHULTZ, J. F., HALL, W. K., DUBS, T. A., AND ANDERSON, R. B. Studies of the Fischer-Tropsch Synthesis. XV. Cementite as Catalyst. *Jour. Am. Chem. Soc.*, vol. 78, No. 2, Jan. 20, 1956, pp. 282-285.
69. SHULTZ, J. F., HALL, W. K., SELIGMAN, B., AND ANDERSON, R. B. Studies of the Fischer-Tropsch Synthesis. XIV. Hagg Iron Carbide as Catalysts. *Jour. Am. Chem. Soc.*, vol. 77, No. 1, January 1955, pp. 213-221.
70. SHULTZ, J. F., SELIGMAN, B., SHAW, L., AND ANDERSON, R. B. Fischer-Tropsch Synthesis. Effect of Nitriding on Three Types of Iron Catalysts. *Ind. Eng. Chem.*, vol. 44, No. 2, February 1952, pp. 397-401.
71. SMITH, D. F., HAWK, C. O., AND GOLDEN, P. L. Mechanism of the Formation of Higher Hydrocarbons From Water Gas. *Jour. Am. Chem. Soc.*, vol. 52, 1930, pp. 3221-3232.
72. STORCH, H. H., GOLUBIC, N., AND ANDERSON, R. B. The Fischer-Tropsch and Related Syntheses, Including a Summary of Theoretical and Applied Contact Catalysis. John Wiley and Sons, Inc., New York, N. Y., 1951, 610 pp.
73. SWAMINATHAN, V. S. Oil From Coal - Full Scale. *Petrol. Proc.*, vol. 10, No. 7, July 1955, pp. 985-988.
74. TECHNICAL OIL MISSION. (Oil Circulation Process.) TOM Reel 134, Item Ia, No. 8; Item Ib, Nos. 11, 12, 13.
75. \_\_\_\_\_. (Official Test of Six Iron Catalysts. Schwarzheide Tests.) TOM Reel 33, bag 3440, item 29.
76. WELLER, S., AND FRIEDEL, R. A. Isomer Distribution in Hydrocarbons From the Fischer-Tropsch Process. *Jour. Chem. Phys.*, vol. 17, September 1949, pp. 801-803.
77. WENDER, I., AND ORCHIN, M. Critical Review of Chemistry of Oxo Synthesis for Production of Alcohols From Olefins, Carbon Monoxide, and Hydrogen, With Discussion of Reaction Mechanism for Oxo and Related Syntheses. Bureau of Mines Rept. of Investigations 4270, 1948, 26 pp.
78. WENDER, I., ORCHIN, M., AND STORCH, H. H. Mechanism of the Oxo and Related Reactions. III. Evidence for Homogeneous Hydrogenation. *Jour. Am. Chem. Soc.*, vol. 72, No. 10, October 1950, pp. 4842-4843.
79. ZORN, H. The Carbon Monoxide-Hydrogen Synthesis at I. G. Farbenindustrie A. G. Trans. published as FIAT Final Rept. 1267, Apr. 14, 1949, 173 pp.; PB 97,368, October 1947, 182 pp.