

KINETICS OF THE FISCHER-TROPSCH SYNTHESIS

To study the kinetics of a flowing system in which measurements are desired at moderate to high conversions, it is usually preferable to vary the flow of feed gas at constant temperature and pressure to obtain a wide range of conversions of $H_2 + CO$, x . The differential reaction rate, $r = dx/d(1/S)$, where S is the space velocity, can then be related to the exit-gas composition at the space velocity at which r is determined. Rate equations, either fundamental or empirical, may be tested by graphical differentiation of rate data or by integrating the rate equation. Integration is usually difficult for reactions as complex as the Fischer-Tropsch synthesis. Simple, reliable tests of the overall dependence of rate on temperature or pressure may be made by maintaining the conversion of $H_2 + CO$ constant

and varying flow, as required, when temperature or pressure is changed. The space-time yield, xS , is then a reliable measure of rate that can be used to determine the effects of temperature or pressure.

IRON CATALYSTS

Hall²⁸ and workers of the Federal Bureau of Mines²⁹ have shown that the overall rate of synthesis increases linearly with pressure up to at least 45 atmospheres for experiments at approximately constant conversions, as figure 5

²⁸ 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, 1952, pp. 845-876.

²⁹ Anderson, R. B., Seligman, B., Shultz, J. F., Kelly, R., and Elliott, M. A., Studies of the Fischer-Tropsch Synthesis. X. Some Important Variables in the Synthesis of Iron Catalysts: Ind. Eng. Chem., vol. 44, 1952, pp. 391-397.

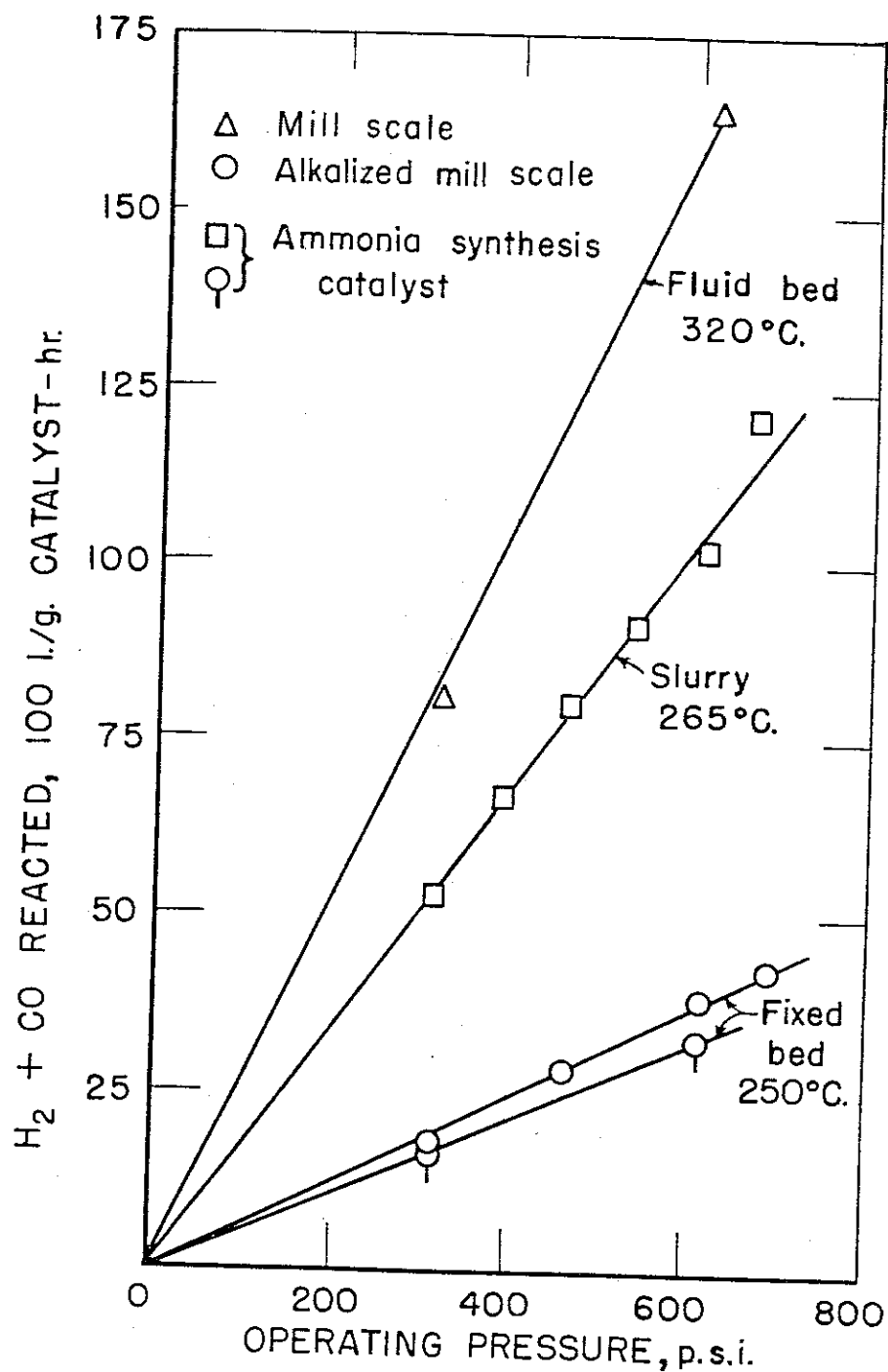


FIGURE 5.—Variation of Reaction Rate With Operating Pressure on Iron Catalysts for Three Types of Reactors Using $2\text{H}_2 + 1\text{CO}$ Gas.

shows. Data of Kölbel^{30 31} indicate that this relationship is also valid for synthesis with H_2O+CO gas. In other experiments with $1H_2+1CO$ gas in which temperature was varied, overall apparent activation energies of 18 to 21 kcal. per mole have been obtained.

On iron catalysts the differential reaction rate decreases rapidly with increasing conversion (x), as figure 6 shows. The empirical equation,

$$-\log(1-x) = (AP/S) \exp(-E/RT), \quad (1)$$

where P is the operating pressure and E overall activation energy, usually fits the rate data to within the experimental error between about 0- and 50-percent conversion. This equation has been useful in correlating activities of catalysts used in the Bureau of Mines testing

³⁰ Kölbel, H., and Engelhardt, F., [Reaction Mechanism of the Fischer-Tropsch Synthesis. VI. The Function of Water Vapor in the Carbon Monoxide Hydrogenation]; *Erdöl u. Kohle*, vol. 3, 1950, pp. 529-533.

³¹ Titles in brackets are translations from the language in which the item was originally published.

program. For example, it was employed in computing activities reported in figure 2 (p. 7).

On fused iron catalysts at constant temperature, the rate of synthesis expressed as conversion of H_2+CO increased slowly with increasing $H_2:CO$ ratio in the feed gas, passed through a relatively flat maximum for a volume ratio of $H_2:CO$ near 1.5, and then decreased. The usage ratio, $H_2:CO$, increased with increasing $H_2:CO$ ratio of the feed gas. For a given feed gas, the usage ratio varied widely with conversion but was usually independent of temperature, when compared at constant conversion.

Integral and differential usage ratios (expressed as H_2 converted: (H_2+CO) converted) are shown as functions of conversion in figure 7. The integral curve decreases rapidly with increasing conversion, passing through a minimum and increasing. The differential curve has a similar shape,³² but the minimum occurs at

³² Tramm, H. [Technology of Carbon Monoxide Hydrogenation]; *Brennstoff-Chem.*, vol. 33, 1932, pp. 21-30.

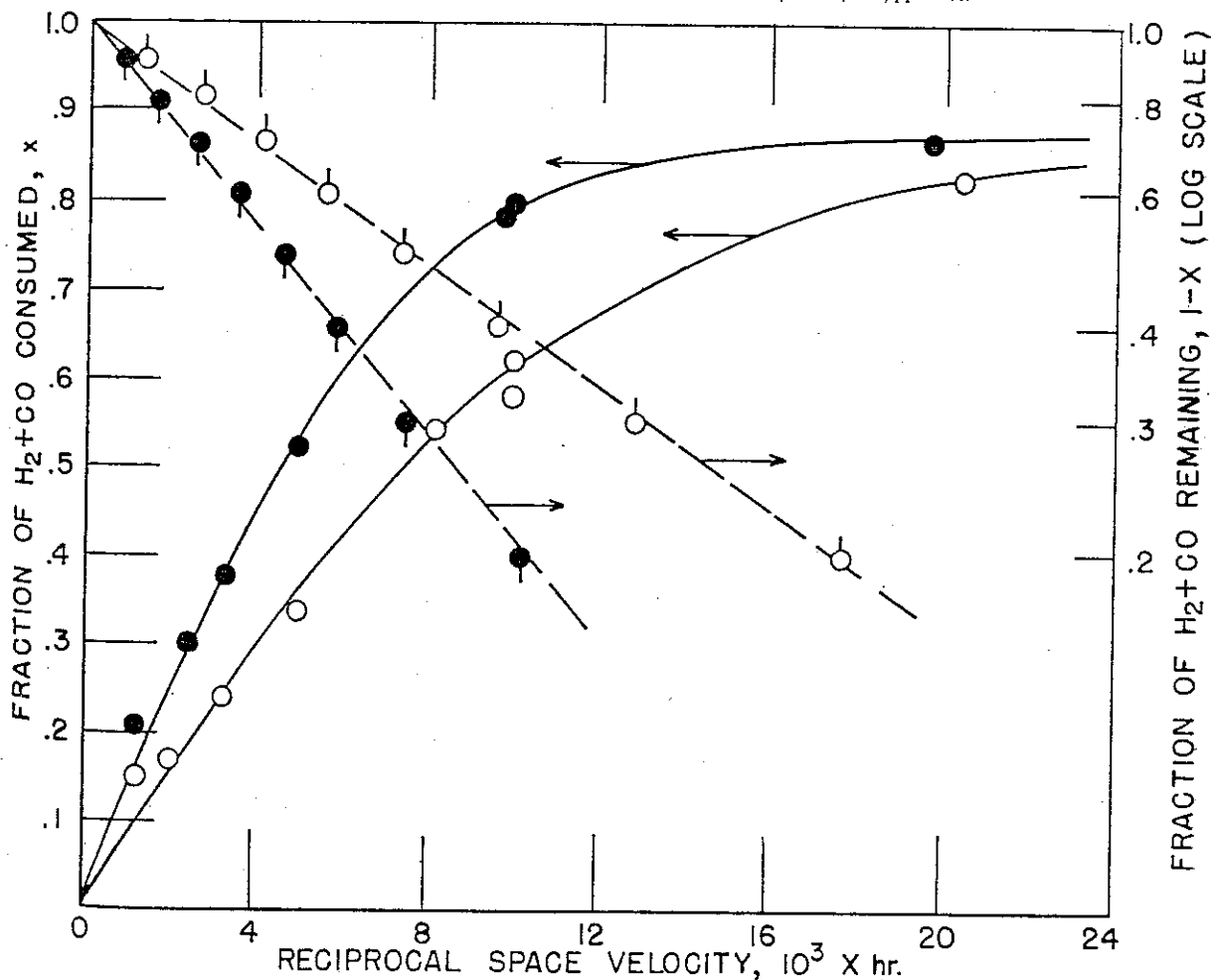


FIGURE 6.—Variation of Conversion With Space Velocity. Fused $Fe_2O_3-MgO-K_2O$ Catalyst. $1H_2:1CO$, 7.8 Atm., ○ 249°C., ● 261°C.

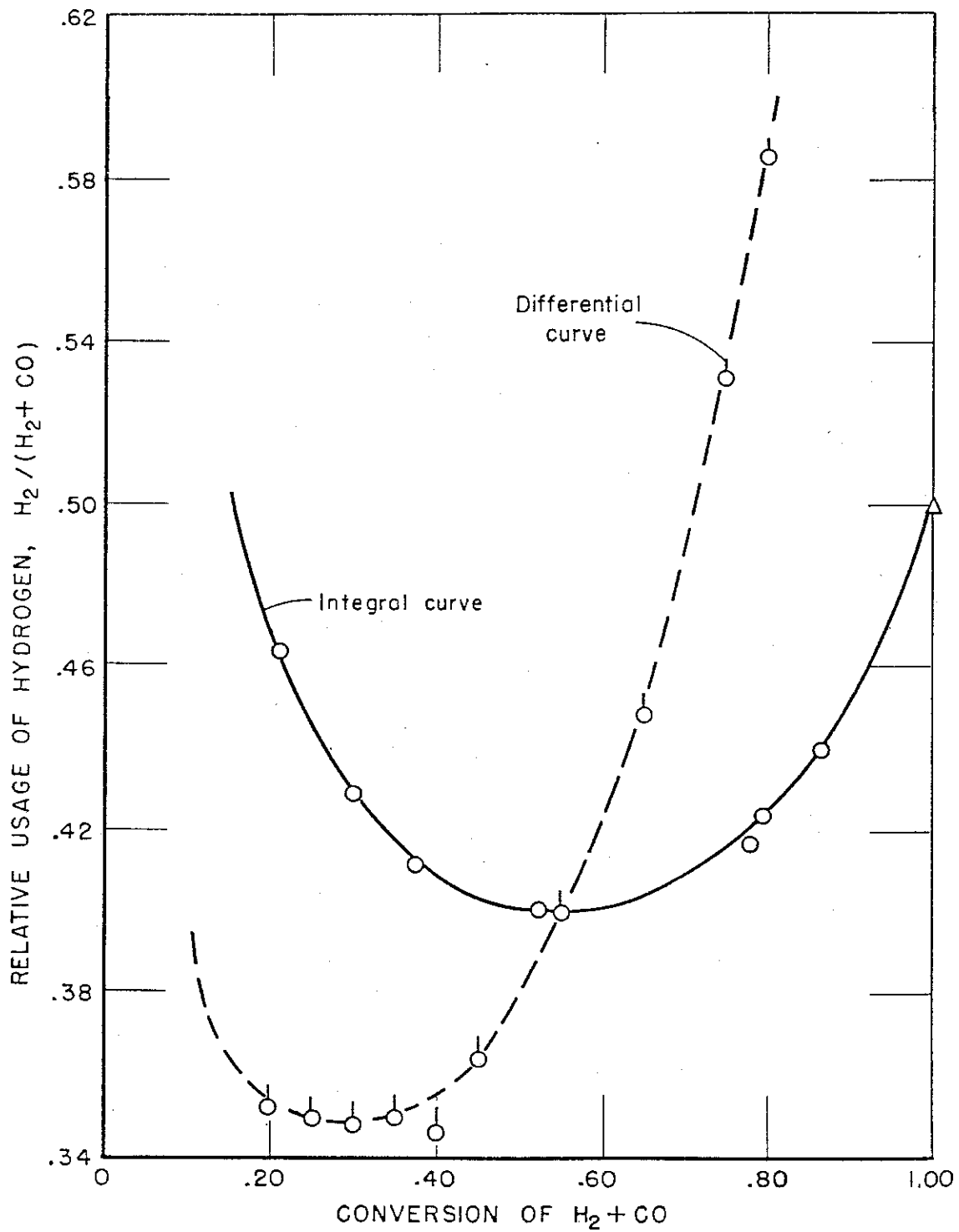


FIGURE 7.—Integral and Differential Usage of Hydrogen on Fused Iron Catalyst With $1H_2+1CO$ Gas at 7.8 Atm. and $249^\circ C$.

lower conversions. At low conversions the usage ratio is high, approaching $2\text{H}_2:1\text{CO}$.

With increasing conversion the partial pressure of water increases, and the water-gas shift sharply decreases the usage ratio.³²⁻³⁵ As conversion increases, the $\text{H}_2:\text{CO}$ ratio of the gas remaining increases sharply. This factor tends to increase the usage ratio and produces the minimum in the integral curve. Variations that decrease the partial pressure of water vapor in the gas stream, such as cold-gas recycle, increase the usage ratio. Apparently

the relative rates of the primary synthesis reaction and the secondary water-gas reaction vary in the same manner as pressure and temperature are varied.

Studies of reduced fused catalysts having different particle size indicate that the activity increases with decreasing particle size to a high limiting value for small particles.³⁶ A simple approximate treatment of these data suggests that only a thin layer of catalyst (about 0.1 mm. in thickness from the external surface) is effective in the synthesis. These and other data lead to the qualitative picture of the mass transport in a catalyst pore, as shown in figure 8.

³² See footnote 29, p. 11.

³⁴ See footnote 30, p. 13.

³⁵ Köbel, H., Ackermann, P., Ruschenburg, E., Langheim, R., and Engelhardt, F. [The Fischer-Tropsch Synthesis With Iron Catalysts. I.] Chem.-Ing.-Tech., vol. 23, 1951, pp. 153-157.

³⁶ See footnote 29, p. 11.

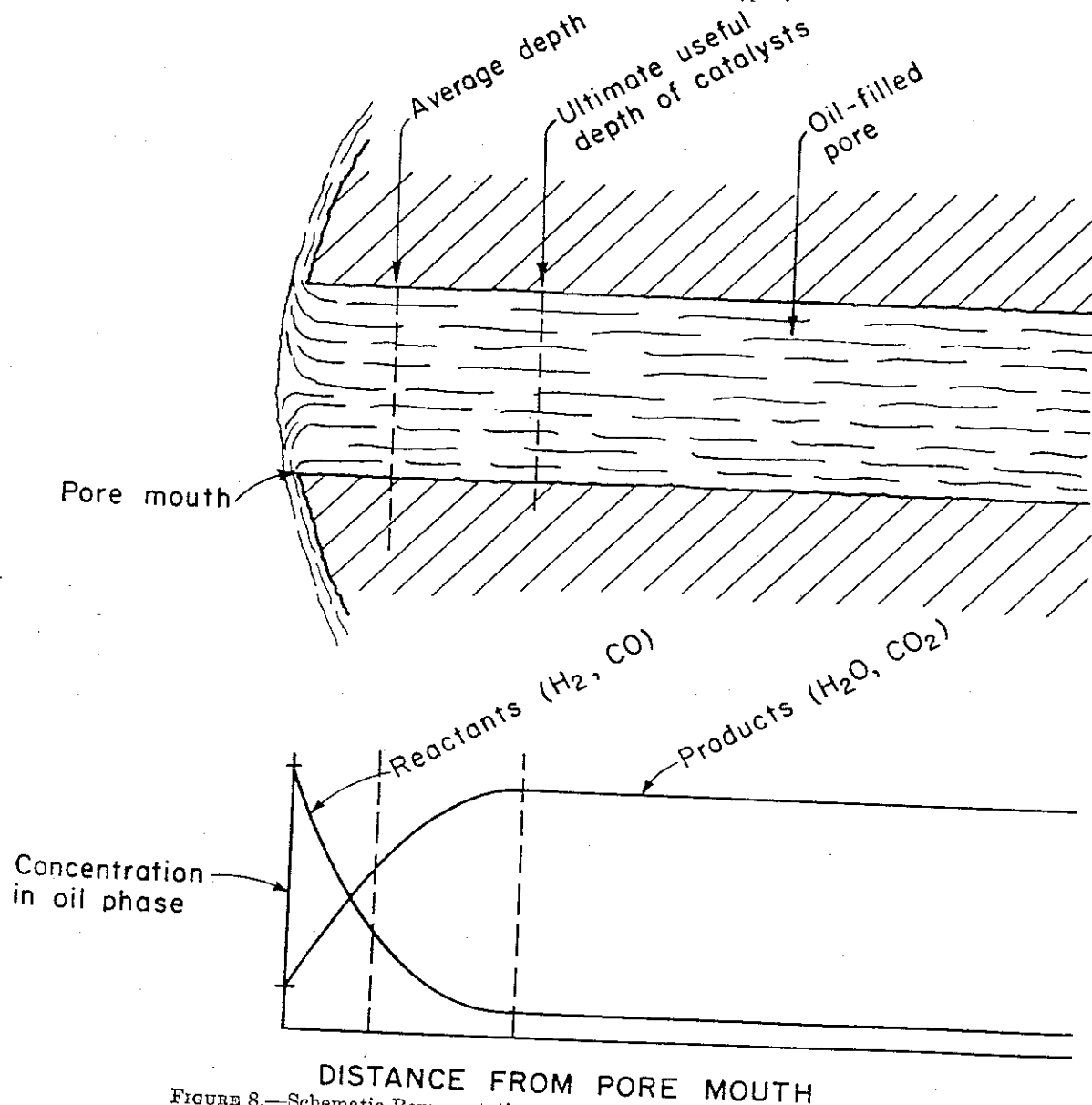


FIGURE 8.—Schematic Representation of a Pore in a Fischer-Tropsch Catalyst.

At synthesis temperatures less than 280° or 290° C. the pores of the catalyst are filled with liquid hydrocarbons, and H₂ and CO dissolve in the liquid and diffuse into the pores. As reaction at the catalyst surface produces the concentration gradients for the diffusion, the two processes are intimately connected. Figure 8 shows only one curve each for concentrations of reactants (H₂, CO) and products (H₂O, CO₂). The concentration of reactants falls sharply with distance from the pore mouth to a very low value at a short distance (of the order of 0.1 mm.). The concentrations of products vary in an inverse manner, increasing to a high constant value at approximately the effective depth. Thus, the interior of the particle affords ideal conditions for oxidation of iron (large H₂O:H₂ and CO₂:CO ratios) and the external portions ideal conditions for reduction of iron oxide and carbon deposition.

The following changes in depth of the active layer may be predicted: (1) As temperature is increased, the depth will decrease because the reaction rate at the surface increases more rapidly than the rate of diffusion; (2) the depth should be relatively independent of operating pressure as the solubility and diffusion of reactants and products in the oil-filled pores, as well as the reaction rate at the surface, are directly proportional to pressure. These hypotheses are consistent with virtually all information available about synthesis on iron catalysts. Diffusional difficulties of this magnitude complicate the kinetics, and no simple fundamental rate equation has been found.

COBALT AND NICKEL CATALYSTS

In synthesis with cobalt catalysts supported on kieselguhr, the rate is independent of pressure in the range from 0.2 to 15 atmospheres for tests in which the pressure is increased.³⁷ When pressure is decreased during the experiment, the rate decreases with decreasing pressure.³⁸ Atmospheric- and medium-pressure (5 to 25 atmospheres) syntheses appear to be basically different. At pressures near atmospheric most of the hydrocarbon product is vaporized, and high-molecular-weight wax is selectively adsorbed on the catalyst. The activity is largely independent of particle size and density, and the rate remains constant until the particle becomes filled with heavy wax.

In the medium-pressure synthesis most of the hydrocarbons are condensed and flow as liquid through the catalyst bed. Thus, the particle is quickly filled with hydrocarbons, and the composition of this material is the same as that of the synthesis product. As in

the medium-pressure synthesis with iron, the activity remains essentially constant for long operating periods. In figure 9 the composition of wax on the catalyst is compared with the composition of wax in the product from data of Hall and Smith³⁹ for synthesis at 1 and 11 atmospheres.

In atmospheric synthesis plots of conversion as a function of reciprocal space velocity show long linear portions;⁴⁰ however, in the medium-pressure range, equation (1) may fit the data.⁴¹ Apparent overall activation energies of about 25 kcal. per mole were observed in the atmospheric synthesis^{42 43} and 20 kcal. per mole in the medium-pressure range. At atmospheric pressure maximum synthesis rates are observed for 2H₂ + 1CO gas, and the catalyst appears to be poisoned by carbon monoxide-rich gas; however, in medium-pressure synthesis the activity is not adversely influenced by a carbon monoxide-rich gas such as 1.5H₂ + 1CO. Broetz and Spengler⁴⁴ considered mass-transfer problems in cobalt catalysts and suggested that surface as well as bulk diffusion were important.

Rate data are available for nickel catalysts only at atmospheric pressure, and the data suggest that the kinetics of synthesis is similar to that on cobalt catalysts at this pressure.

Water appears to be the principal oxygenated product of synthesis on cobalt and nickel catalysts, and carbon dioxide is largely produced by subsequent water-gas shift. Kölbel and Engelhardt⁴⁵ demonstrated that the water-gas reaction at about 220° C. is equally rapid on cobalt and iron catalysts. The large production of carbon dioxide in synthesis with iron and small yields in synthesis with cobalt must result from the fact that the rate of the primary reaction on cobalt is much greater than that on iron; for example, cobalt catalysts usually convert synthesis gas to hydrocarbons as rapidly at 185° to 195° C. as iron catalysts do at 225° to 250° C.

³⁷ See footnote 8, p. 3.

³⁸ Anderson, R. B., Hall, W. K., Krieg, A., and Seligman, B., Studies of the Fischer-Tropsch Synthesis. V. Activities and Surface Areas of Reduced and Carburized Cobalt Catalysts: *Jour. Am. Chem. Soc.*, vol. 71, 1949, pp. 183-188.

³⁹ Hall, C. C., and Smith, S. L., Hydrocarbon Synthesis in the Presence of Cobalt Catalysts at Medium Pressures: *Jour. Inst. Petrol.*, vol. 33, 1947, pp. 439-459.

⁴⁰ Anderson, R. B., Krieg, A., Friedel, R. A., and Mason, L. S., Fischer-Tropsch Synthesis. VI. Differential Reaction Rate Studies With Cobalt Catalysts: *Ind. Eng. Chem.*, vol. 41, 1949, pp. 2189-2197.

⁴¹ Gibson, E. J., and Hall, C. C., Fischer-Tropsch Synthesis with Cobalt Catalysts. II. The Effect of Nitrogen, Carbon Dioxide, and Methane in the Synthesis Gas: *Jour. Appl. Chem.*, vol. 4, 1954, pp. 464-468.

⁴² Anderson, R. B., Krieg, A., Seligman, B., and O'Neill, W. E., Fischer-Tropsch Synthesis. I. Tests of Cobalt Catalysts at Atmospheric Pressure: *Ind. Eng. Chem.*, vol. 39, 1947, pp. 1548-1554.

⁴³ Weller, S., Kinetics of Carbiding and Hydrocarbon Synthesis With Cobalt Fischer-Tropsch Catalysts: *Jour. Am. Chem. Soc.*, vol. 69, 1947, pp. 2432-2436.

⁴⁴ Broetz, W., and Spengler, H. [Physicochemical Behavior of Fischer-Tropsch Catalysts]: *Brennstoff-Chem.*, vol. 31, 1950, pp. 97-102.

⁴⁵ Kölbel, H., and Engelhardt, F. [Reaction Mechanism of the Fischer-Tropsch Synthesis. I.]: *Erdöl u. Kohle*, vol. 2, 1949, pp. 52-59.

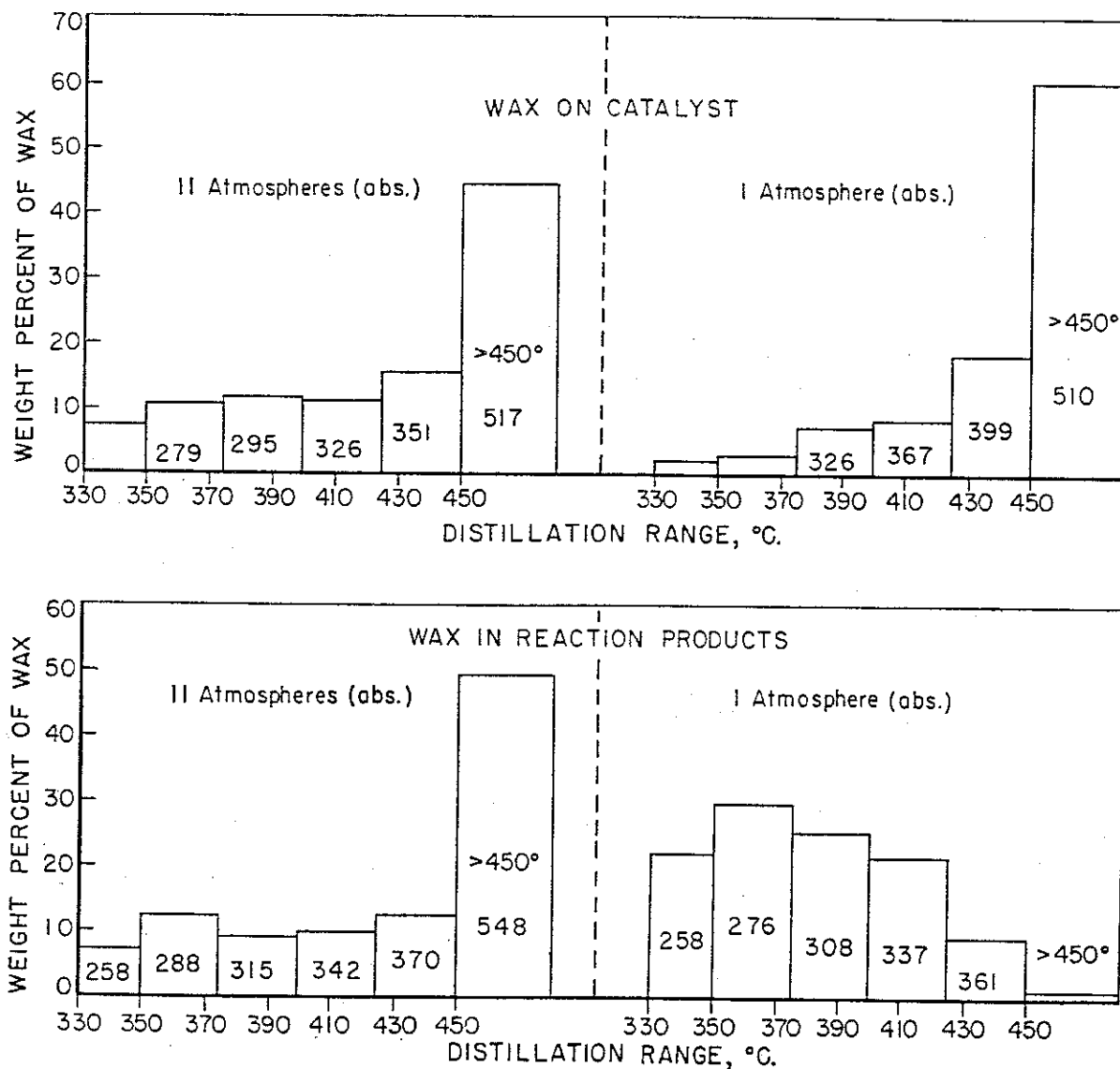


FIGURE 9.—Comparison of Catalyst Wax With Wax in Synthesis Products.
(Numbers in blocks are the average molecular weights.)