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BUREAU OF MINES
JAMES BOYD, DIRECTOR

REPORT OF INVESTIGATIONS

EFFECT OF OPERATING VARIABLES UPON THE FISCHER-TROPSCH SYNTHESIS

BY

SOL WELLER

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By Sol Weller[2]

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INTRODUCTION

The Fischer-Tropsch synthesis consists of the formation of long-chain hydrocarbons by passage of carbon monoxide-hydrogen mixtures over metal catalysts, usually based on iron, cobalt, nickel, or ruthenium, at temperatures in the range 180°-300° C., and at pressures of 1-15 atmospheres. Although the reaction has been known and studied for more than 20 years, the mechanism by which it occurs is still poorly understood. One approach to understanding is to consider the effect upon the course of the synthesis of variations in each of the important operating variables. Consideration of the experimental data pertaining to these variables may suggest an over-all picture describing the synthesis - a picture which, in turn, would have to be consistent with all the known facts. The first part of this paper will be concerned with such a consideration of operating variables; the second portion will discuss recent work pertaining to the role of metal carbides as intermediates in the synthesis.

1/ The Bureau of Mines will welcome reprinting of this paper, provided the following footnote acknowledgment is used: "Reprinted from Bureau of Mines Report of Investigations 4405."

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EFFECT OF OPERATING VARIABLES UPON THE SYNTHESIS

General

Aside from the catalyst composition itself, which will not be treated here, probably the most important variables influencing the synthesis are contact time, temperature, pressure, and gas composition. Very few quantitative data have been published to date on the newer methods of conducting the synthesis (fluidized bed, hot-gas recycle, internally cooled converter); as a result, illustrations of the dependence of the synthesis on these variables will be based upon experiments with a fixed bed, once through process.

Space Velocity

The contact time[3], θ, is related to the pressure, P, the temperature, T, and the space velocity, S, by equation (1):

$$(1)\quad \theta = \frac{1}{S} \frac{P}{P_{std.}} \frac{T_{std.}}{T}$$

(Pressure and temperature are included because space velocity is usually expressed as volumes of gas under standard conditions ($P_{std.}$ and $T_{std.}$) flowing through unit catalyst volume in unit time.) The contact time is short at high space velocities and long at low space velocities.

The effect of space velocity (or contact time) upon the synthesis is illustrated in figures 1 and 2. In figure 1, which is based upon the data of Pichler and Buffleb[4] for a ruthenium catalyst at 230° C. and 100 atmospheres pressure, we note that the yield of total hydrocarbons per liter of catalyst per hour (the "space-time yield" of total hydrocarbons) increases from zero at zero space velocity to a limiting maximum value at very high space velocity (curve 1). The yield of total hydrocarbons per cubic meter of synthesis gas, on the other hand, is greatest at very low space velocity and decreases asymptotically to zero at high space velocity (curve 2). The yields of liquid and solid hydrocarbons behave similarly, except that the space-time yield of liquids and solids decreases at very high space velocities after reaching a maximum (curve 3), and the yield based upon gas volume decreases at very low space velocities after reaching a maximum. This last point is not apparent in figure 1 but is illustrated by figure 2, which is based upon data of Murata, Ishikawa, and Tsuneoka[5] with a Ni-Co catalyst at 190° C. and atmospheric pressure.

3/ For purposes of this discussion, the apparent contact time, defined by equation (1), will be used instead of the true contact time, which is the time required for a given volume element of gas to pass from the entrance to the exit of the reactor. The two are not equivalent because of the volume change accompanying the synthesis.

4/ Pichler, H., and Buffleb, H., Behaviour of Ruthenium Catalysts in Synthesis of Paraffin Hydrocarbons of High Molecular Weight: Brennstoff Chem., vol. 21, 1940, pp. 273-280.

5/ Murata, Y., Tsuneoka, S., and Ishikawa, S., Benzine Synthesis from Carbon Monoxide and Hydrogen at Ordinary Pressure. XXXI. The Influence of Current Velocity: Jour. Soc. Chem. Ind., Japan, vol. 39, 1936, (suppl. binding), pp. 325-333.

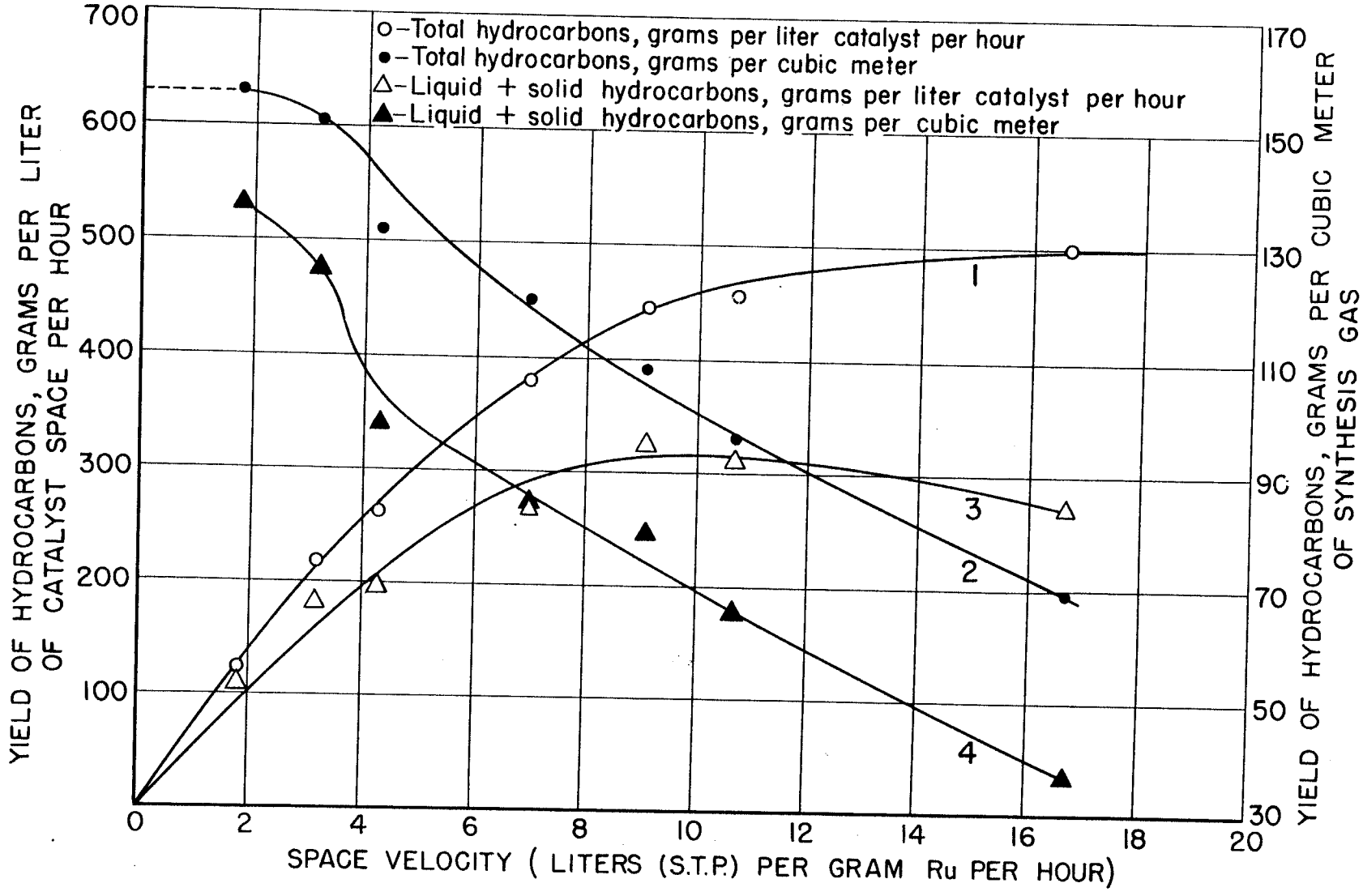

Figure 1. - Effect of space velocity. Pichler and Buffleb, Brenn. Chem. 21, 273 (1940).

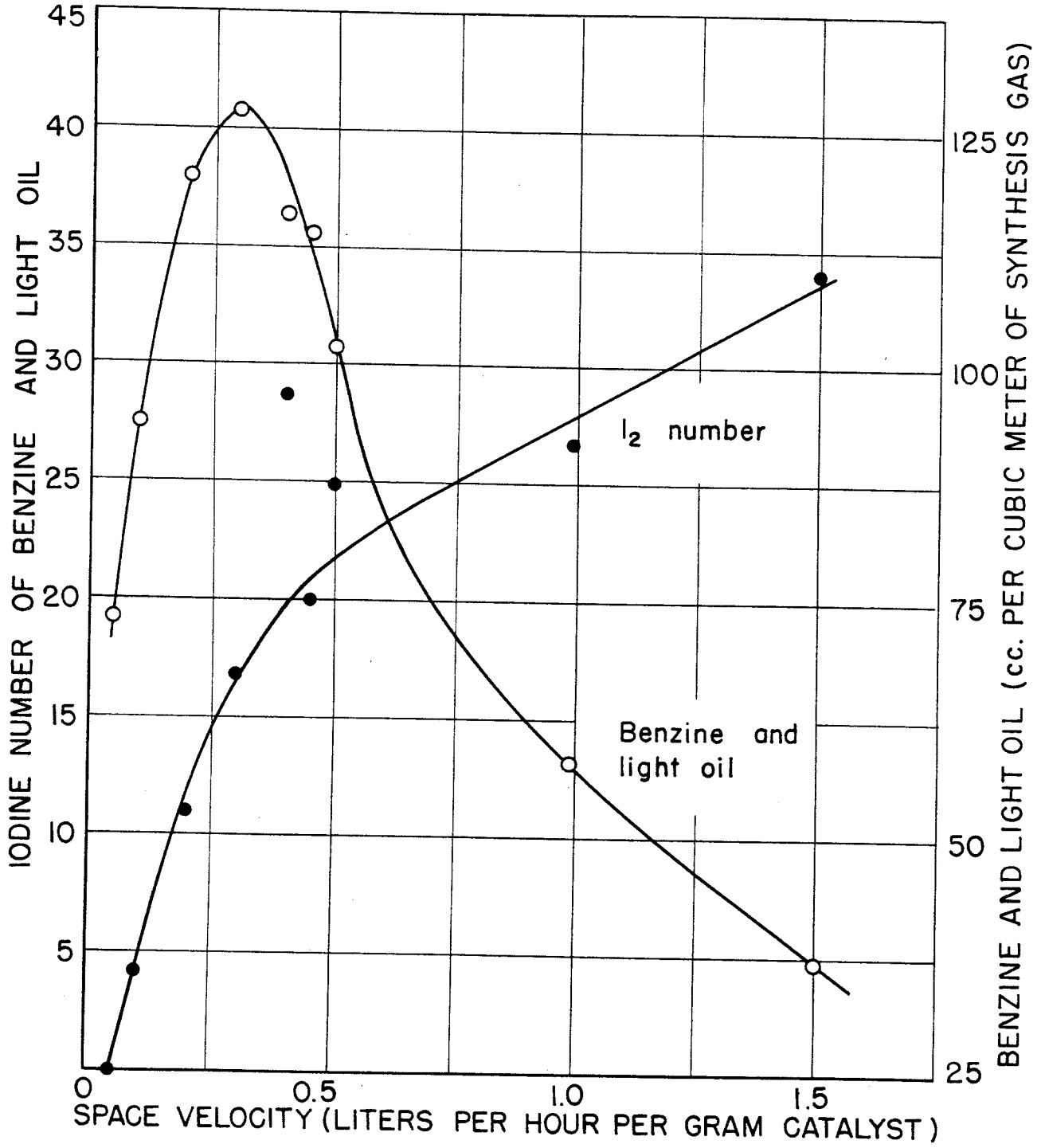

Figure 2. - Effect of space velocity. Murata, Ishikawa, and Tsuneoka, J. Soc. Chem. Ind. Jap., S.B. 39, 329 (1936).

Similar behavior at low space velocities has been recently observed by Craxford.6/ Also to be noted in figure 2 is the fact that the greater the space velocity, the more unsaturated the synthesis products become (as measured, for example, by the iodine number).

It is apparent from figure 1 that the phrase "maximum efficiency of the synthesis" can have two meanings: Maximum utilization of reactor space and catalyst is achieved at high space velocities, where the space-time yield is greatest; most efficient utilization of synthesis gas occurs at low space velocities, where the greatest fractional conversion of carbon monoxide is obtained. Decision as to the "most efficient" space velocity to employ in the synthesis obviously depends on such economic factors as relative costs of synthesis gas, catalyst, reactors, and power (if multistage or recycle operation is considered).

Temperature

Increase in temperature results in an increase in over-all synthesis rate. Recent work by the Bureau of Mines7,8/ indicates that for cobalt catalysts the activation energy for the over-all synthesis is 25-26 kcal./mole, corresponding to a coefficient of about 1.8 per 10° C. If the temperature becomes too high, however, the catalyst activity may decrease because of increased carbon deposition and sintering.

There is a shift in synthesis-product distribution toward lower molecular weights and, in particular, an increase in methane production as the temperature is increased. It is possible, in fact, to obtain methane almost exclusively by employing an appropriately high temperature. Accompanying this trend to shorter-chain products is an increase in unsaturation of the products as the temperature is increased. These effects of temperature are illustrated by the data of Tsuneoka9/ on an Ni-Co catalyst (table 1).

TABLE 1. - Effect of temperature upon synthesis products

Temperature, °C.	C_nH_{2n+2} in tail-gas, percent	Benzine/light oil	I_2 number of benzine
180	4.4	0.73	20.6
190	12.5	.76	19.9
200	24.4	1.10	25.6
205	-	1.21	30.5

6/ Craxford, S. R., Mechanism of the Fischer-Tropsch Reaction: Trans., Faraday Soc., vol. 42, 1946, pp. 576-580.

7/ 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.

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

9/ Tsuneoka, S., Synthesis of Benzine: Jour., Soc. Chem. Ind., Japan, vol. 37, 1934 (suppl. binding), pp. 738-744.

As the temperature is increased from 180° to 205° C., the iodine number, which measures the unsaturation, of the light product increases from 20 to 30, the benzine:light-oil ratio increases by 70 percent, and there is a striking increase in gaseous hydrocarbons (chiefly methane) in the tail-gas from 4 percent to at least 24 percent.

As a practical matter, if the synthesis is run primarily for gasoline production, high temperature is desirable because of increased rate and increase in unsaturation of products; these effects, however, have to be balanced against the increase in methane production and increased carbon deposition on the catalyst at high temperature.

Pressure

At pressures below 1 atmosphere, the space-time yield with a cobalt catalyst increases approximately as the square root of the synthesis-gas pressure,[10] provided that the concentration of synthesis products is kept at a very low value. When the synthesis products are not removed, Fischer and Pichler[11] found the fractional gas conversion on a cobalt catalyst to be almost independent of pressure between 1/3 and 1 atmosphere, provided the contact time was kept constant; the space-time yield, however, was here linear with pressure. Some of their data are given in table 2.

TABLE 2. - Effect of pressure upon synthesis rate

(Temp., 210° C; flow, 4 l.(S.T.P.)/hr.; contraction, 50 percent[1])

P, atm.	Weight catalyst, g.	Tail gas	
		CO, percent	H_2, percent
1/3	15	16.4	39.6
1	5	18.2	36.6

1/ The contraction is the percentage decrease in volume as the gas proceeds through the catalyst bed.

Information on the effect of pressure above 1 atmosphere at constant temperature and contact time is not available. At constant temperature and constant space velocity, increasing the pressure from 1 to 10 atmospheres with a cobalt catalyst is reported by Dr. C. C. Hall of the British Fuel Research Board to result in a 5- to 10-percent increase in product yield and an increase in proportion of wax from 10 to 30 or 40 percent. Work at the Bureau of Mines on cobalt catalysts indicates an even smaller effect upon increasing the pressure from 1 atmosphere to 100 p.s.i.[12]; almost no change was observed in the contraction or the yield of liquid and solid hydrocarbons.

10/ Work cited in footnote 8.

11/ Fischer, F., and Pichler, H., The Influence of Pressure Upon Several Conversions of Water Gas: Brennstoff Chem., vol. 12, 1931, pp. 365-372.

12/ Storch, H. H., Anderson, R. B., Hofer, L. J. E., Hawk, C. O., Golumbic, N., Synthetic Liquid Fuels from Hydrogenation of Carbon Monoxide. Part I. Review of Literature: Bureau of Mines Tech. Paper 709 (in press).

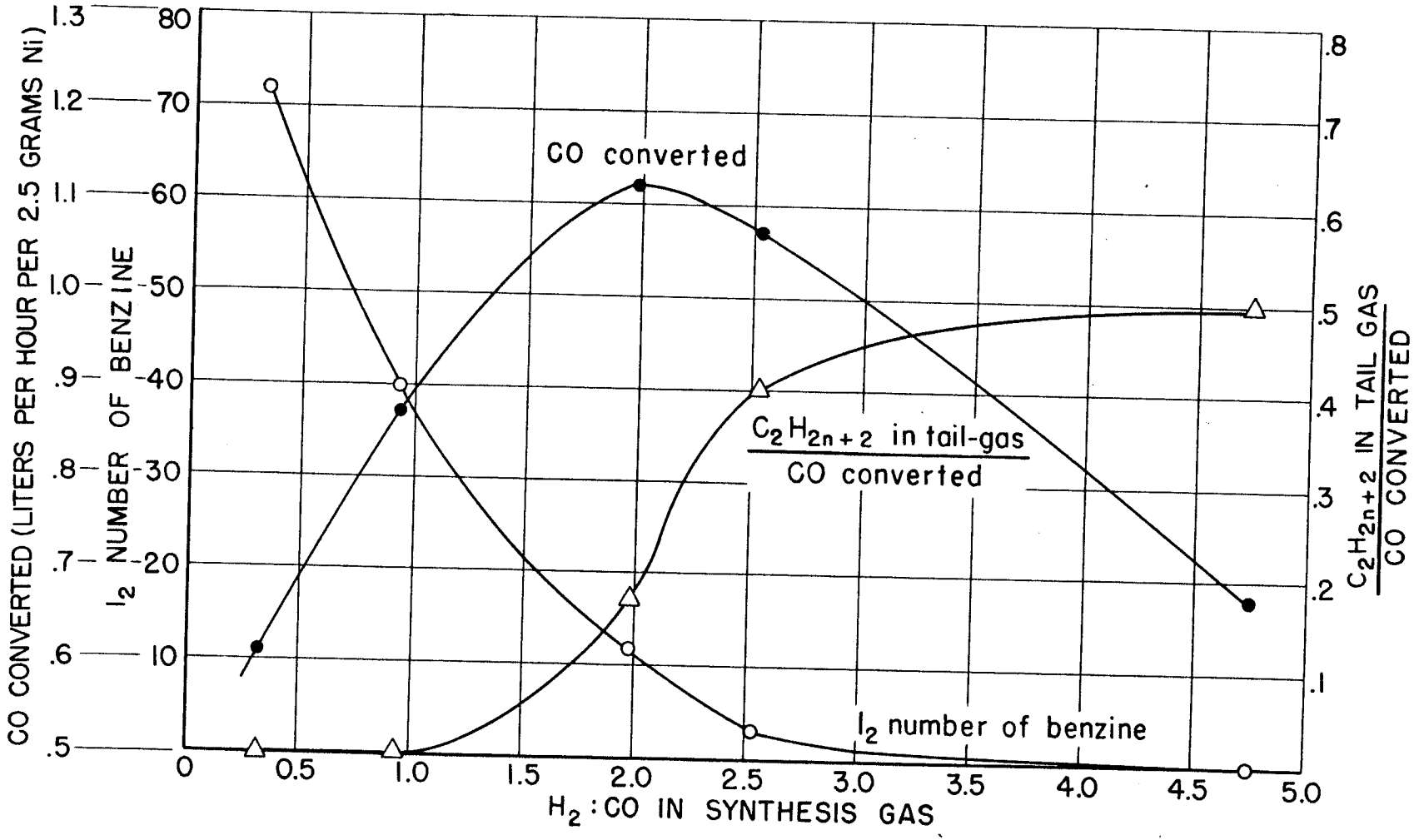

Figure 3. - Effect of synthesis gas composition. Tsuneoka, J. Soc. Chem. Ind. Jap. S.B. 37, 711 (1934).

At very high pressures, where the formation of volatile metal carbonyls is favored, the catalyst activity is known to fall off.

Synthesis-Gas Composition

If the flow and pressure of synthesis gas are held constant, as the H_2:CO ratio of the entrant gas is increased, the over-all synthesis rate increases to a maximum and then fails. In fact, to the extent that the dependence of the synthesis rate on the H_2 and CO partial pressures can be expressed in the form

$$(2) \quad \text{Rate} = k\, p_{H_2}{}^{a}\, p_{CO}{}^{b},$$

The rate should exhibit a maximum for a H_2:CO ratio equal to a:b (at constant pressure). The data of Tsuneoka[13] on an Ni-Mn-Al_2O_3-kieselguhr catalyst at 200° C. and 1 atmosphere (fig. 3) show this maximum, which for cobalt catalysts occurs at an H_2:CO ratio of about 2. Similar Bureau of Mines data[14] on a Co-ThO_2-MgO-kieselguhr catalyst at 170° C. and 1 atmosphere are listed in table 3.

TABLE 3. - Effect of gas composition upon synthesis rate

H_2:CO in in-gas	Synthesis rate[1]
3.09	23.6
2.46	24.7
.93	17.7

1/ cc. (S.T.P.) of synthesis gas converted per hour per gram of unreduced catalyst.

In figure 3 may also be noted the fact that as the H_2:CO ratio decreases, the extent of unsaturation of the product increases and a shift in product distribution to higher molecular weight occurs (as evidenced, for example, by the decrease in fraction of CO converted to gaseous hydrocarbons).

Description of the Synthesis

The experimental facts presented above may be correlated in terms of the following assumed picture of the processes occurring during the synthesis. Many of the ideas to be presented are not original with the author but have been assembled from the literature. The synthesis is certainly more complicated than is represented here, and many details of the reaction are not discussed, but it is hoped that the postulated picture will serve to unify the experimental data and perhaps to serve as a basis for predicting new effects.

13/ Tsuneoka, S., Benzine Synthesis from Carbon Monoxide and Hydrogen at Ordinary Pressure. XXI. Relations of the Gas Composition to the Working Temperature and to the Degree of Saturation of the Benzine, Respectively: Jour., Soc. Chem. Ind., Japan, vol. 37, 1934 (suppl. binding), pp. 711-716.

14/ Work cited in footnote 12.

The formation of hydrocarbons during the synthesis takes place on the catalyst surface. In order to have reaction, the CO and H_2 must be adsorbed on the surface, and the greater the concentration of adsorbed CO and H_2, the greater the rate of reaction. The increase in rate which is therefore expected as the gas pressure is increased may, however, be minimized if synthesis products are not removed, since adsorption of the products reduces the amount of catalyst surface that is available to the reactants.

The synthesis of long-chain hydrocarbons may proceed in a stepwise fashion by the successive addition, in some way, of CH_2 groups to the molecule. In this case, lower molecular-weight hydrocarbons precede higher ones in the course of the synthesis. At any stage in the synthesis, a given CH_2 polymer, represented as $(CH_2)_n$, can either (1) stay on the catalyst surface and increase in length by further addition of CH_2 groups to form $(CH_2)_{n+1}$, $(CH_2)_{n+2}$, etc., (2) be desorbed as the olefin, $(CH_2)_n$, or (3) react with hydrogen and be desorbed as the saturated hydrocarbon, C_nH_{2n+2}. The relative probability of (1) will be increased by any factor that increases the surface concentrations of the reactants or decreases the rate of product desorption; high pressures, for example, will result in an increased proportion of high molecular hydrocarbons in the product. The relative probability of (3) will be especially favored by an increase in the surface concentration of hydrogen; a high H_2:CO ratio will therefore result in increased proportions of saturated and low molecular weight products.

Both saturated and unsaturated hydrocarbon products in the gas phase can react further. The saturated hydrocarbons formed in one portion of the catalyst bed can be cracked, as they pass through the rest of the bed, to form lower molecular-weight products, and the already unsaturated products formed in one portion of the bed can either be cracked as they pass through the bed or react with hydrogen to form saturated products.

At very low space velocities, the available catalyst surface is able to handle all of the synthesis gas passing through, and a constant, maximum conversion is observed per unit volume of synthesis gas. As the space velocity increases, the residence time of the synthesis gas in contact with the catalyst becomes too short, and conversion is no longer complete. At very high space velocities a situation is approached where all of the catalyst surface may be considered to be busy all of the time; here the space-time yield reaches a maximum value independent of space velocity, whereas the over-all yield per unit volume of synthesis gas falls off asymptotically to zero.

As we have assumed that short-chain molecules precede long ones in the synthesis, increasing space velocity (decreasing contact time) will result in a shift toward lower molecular weight products. Furthermore, at high space velocity, olefinic products in the gas phase will not have time enough to be hydrogenated before passing out of the reactor, and an increasing proportion of unsaturated hydrocarbons in the synthesis products will result. Similarly, as the space velocity decreases, there will be a shift toward higher molecular-weight, more saturated, synthesis products. At space velocities that are too low, however, most of the carbon monoxide and hydrogen will have reacted in passing through the catalyst bed, whereas hydrocarbons already

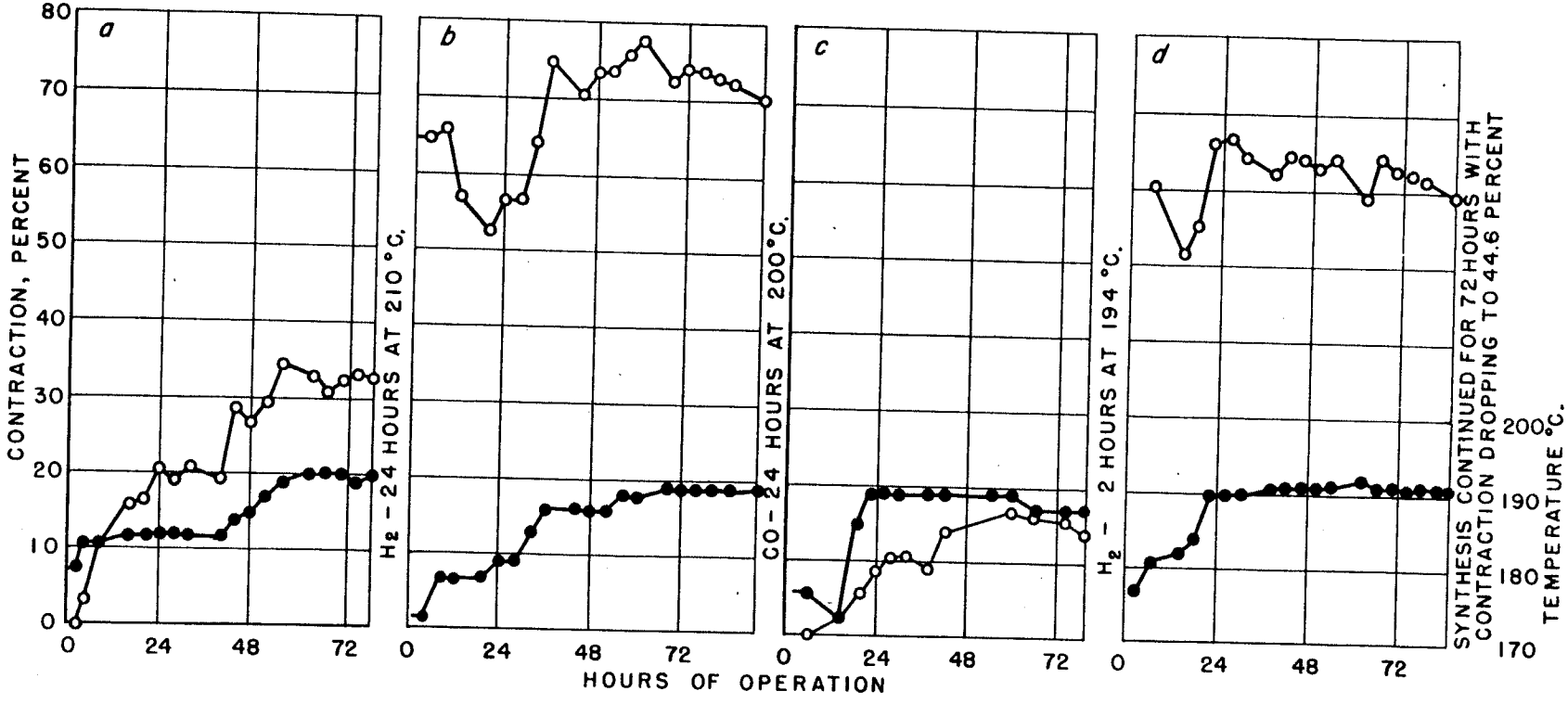

Figure 4. - Apparent contraction o and temperature of operation ● versus time for test 73 with cobalt catalyst 108 B at atmospheric pressure. Catalyst was reduced in hydrogen at 360° C. and carbided with carbon monoxide at 200° C. for 24 hours prior to testing.

formed will be cracked on going through the last portions of the bed; a decrease in higher molecular-weight (liquid and solid) products and an increase in gas will therefore be observed at very low space velocities.

As the temperature is raised, the over-all reaction rate increases, as the number of molecules with enough energy for reaction increases very rapidly with temperature. As the amount of adsorption of CO and H_2 decreases, however, with increasing temperature, at higher temperatures reactant molecules are, on the average, in actual contact with the catalyst surface for a shorter time than they are at lower temperatures (for fixed average time of passage through the reactor). If the relative rates of the different hydrocarbon-producing reactions do not change greatly with temperature, this will result in the production of less saturated and lower molecular-weight hydrocarbons as the temperature increases.

COBALT CARBIDE AS AN INTERMEDIATE IN THE SYNTHESIS

The hypothesis that the synthesis proceeds through the intermediate formation of a metal carbide has been popular ever since it was first suggested by Fischer and Tropsch in 1926.15/ Distinction has rarely been made, however, between bulk carbide and some sort of "surface" carbide as a possible intermediate; the latter is an elusive entity, as it is very difficult to distinguish between a "surface" carbide and, say, adsorbed carbon monoxide. Very little is known yet about the role of "surface" carbide with cobalt catalysts, but recent work16/ has shown it very likely that bulk carbide is neither an intermediate nor an active catalyst for the synthesis.

The presence of extensive amounts of bulk cobalt carbide severely inhibits the synthesis; complete carbiding at 200° C. results in almost complete loss of catalyst activity. The loss of activity can persist even when synthesis is continued for several days; this behavior is illustrated in figure 4. A sample of Co-ThO_2-kieselguhr catalyst which had been approximately 70 percent carbided (based on Co_2C) originally showed no catalytic activity in flowing synthesis gas at 182° C. (figure 1a). During operation for 1 day at 182° C., the contraction (fractional decrease in gas volume) rose to 20 percent but did not increase further during another 18 hours of sysnthesis. Increasing the temperature to 190° C. increased the contraction only to 33 percent, even after a day. Subsequent hydrogenation at 210° C., which removes carbide but not free carbon, and re-exposure to synthesis gas resulted in a (normal) contraction greater than 70 percent (figure 1b). Recarbiding the active catalyst again reduced the activity to the low value observed after the first carbiding (figure 1c), and rehydrogenation of the carbided sample again restored the normal activity (figure 1d).

15/ Fischer, F., and Tropsch, H., The Synthesis of Petroleum at Atmospheric Pressures from Gasification Products of Coal: Brennstoff Chem., vol. 7, 1926, pp. 97-104.

16/ Weller, S., Hofer, L. J. E., and Anderson, R. B., The Role of Bulk Cobalt Carbide in the Fischer-Tropsch Synthesis: Jour., Am. Chem. Soc., vol. 70, 1948, pp. 799-801.

It was also found[17] by X-ray analysis that if cobalt catalyst samples were partly carbided before synthesis and then used in synthesis, carbide was still present in the samples even after several days of synthesis. On the other hand, if the samples were used in the synthesis without precarbiding, no carbide was found at the conclusion of the synthesis. The indication is that bulk carbide is neither formed nor destroyed as part of the synthesis process.

Furthermore, it was observed[17] that although the cubic cobalt present in catalysts reduced at 360°-400° C. is converted to hexagonal cobalt by carbiding the reduced sample and subsequent hydrogenation (both at 200° C.), all samples of not-precarbided catalysts examined after use in the synthesis gave X-ray diffraction patterns identical with that of the freshly reduced catalyst. If any appreciable quantity of the cobalt had been through the cycle of carbiding and hydrogenation at any time during the synthesis, it would have appeared as hexagonal, not cubic, cobalt in the used catalyst sample. As this did not occur, it appears that, within the limits of the X-ray method, the cobalt was not converted to bulk carbide and subsequently hydrogenated during the synthesis; that is, bulk cobalt carbide is not an intermediate in the synthesis.

17/ Work cited in footnote 16.